Supported transition metal complexes for ethylene polymerization

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Abstract

This paper describes the preparation of some active organometallic species derived from nickel, titanium and zirconium fixed on the surface of different supports and their behaviour for the catalytic polymerization of ethylene. In the case of nickel, the transition metal species were attached to crosslinked polystyrene resins through a carbon atom of the P/O chelate ligand. The formation of high molecular weight linear polyethylene is discussed in comparison to homogeneous analogs giving oligomeric products under the same conditions. Titanium containing species on the $MgCl_2$ surface are obtained by coprecipitating the metals from solution of their alcoholates or carboxylates. These species are shown to be sensitive to the presence of carboxylate ligands which affect the catalytic process. Finally biscyclopentadienyl dichloro or dimethyl zirconium have been supported on modified HY zeolite to give catalysts showing the same activity as the homogeneous analogs but higher stability during the polymerization reactions. General aspects deriving from these results are discussed with reference to the possibility of improving the design of well defined physically heterogeneous catalysts.

Keywords: Ethylene; Metallocenes; $MgCl_2$; Nickel; Polymerization; Polystyrene supports; Supported catalysts; Titanium; Ylide complexes; Zeolite; Zirconium complexes

1. Introduction

Catalysis is characterized by the continuous and productive competition between homogeneous and heterogeneous systems. While these concepts were in the past simply associated with soluble and insoluble systems, respectively, nowadays multiphase systems can be also considered as homogeneous catalysts provided activity is due to monosite species. This concept becomes even broader in catalyzed oligomerization and polymerization as even monosite systems can yield products consisting of chain where all monomeric units have the same chemical structure but with different molecular weight due to the occurrence of chain transfer reactions. Attachment of metal complexes to a support [1] is one of the most efficient routes to chemically homogeneous but physically heterogeneous catalysts.

In this general context the present paper deals with our recent approaches to prepare supported polymerization catalysts with controlled structure of the active sites. Both organic (crosslinked polystyrene) and inorganic ($MgCl_2$ and zeolite) supports have been used with nickel, titanium and zirconium as transition metal species. The refer-

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[1] This paper is at the same time coauthored by Prof. Giuseppe Braca (deceased 5 August 1994) and dedicated in fond memory.

ence reaction used in this study is the polymerization of ethylene [2].

The anchoring of alkyl or hydride nickel complexes to polystyrene resin through a carbon atom of the chelate P/O ligand gave catalysts producing linear polyethylene having the same morphology as the polymeric support beads [3]. The formation of high molecular weight macromolecules instead of oligomers obtained in solution with the same complexes was attributed to the bidentate firm coordination of nickel to the polymer. The role of P/O chelate ligand and resins as well as of the type and amount of ancillary ligand around the nickel are discussed with reference to the mechanism of the catalytic reaction.

The catalytic polymerization of ethylene and copolymerization with α-olefins were also investigated in the presence of both Group IV transition metal complexes supported on $MgCl_2$ and metallocene complexes supported on silica or zeolite Y. In the former case it has been shown that the supported transition metal species can be modulated in their catalytic activity by the coordination of organic ligands. Thus addition of carboxylic acids modifies catalytic performances due to the coordination on the transition metal atoms.

Better defined catalytic species supported on the inorganic surface are obtained in case of metallocene complexes. In order to avoid destructive reactions between the biscyclopentadienyl dichloro or dimethyl zirconium complex and the Brønsted acid species on the surface of the inorganic support, this last was pretreated with $Al(CH_3)_3$ or $ClSi(CH_3)_3$. In this way substantially unmodified zirconocene complexes were supported on the surface or entrapped within the pores of the zeolite. These complexes can be activated with aluminum alkyls or methylalumoxane, this last giving a larger activity. The catalysts behave as monosite heterogeneous systems for monoalkene polymerization.

The main results concerning the above systems are described in this paper by discussing separately non Ziegler–Natta nickel catalyst supported on crosslinked polystyrene and titanium carboxylate or zirconocene supported respectively on

$MgCl_2$ and HY zeolite and activated with aluminum cocatalysts (Ziegler–Natta catalysts).

2. Polystyrene supported nickel catalysts

Homogeneous nickel catalysts have been extensively studied in the oligomerization and polymerization of olefins without cocatalysts (non Ziegler–Natta catalysts) by many authors: particularly chelate nickel complexes resulted very active in ethylene oligomerization to give predominantly linear products [4–9].

In the last five years our attempts in this field were devoted to heterogenize these complexes by the anchoring to crosslinked polystyrene resins through a carbon atom of the chelate ligand, yielding structures of the type I.


(I)
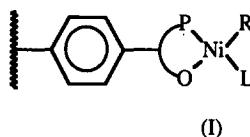
The heterogenization of the complexes caused a very drastic change of the catalytic process, as ethylene polymerization instead of oligomerization was observed [3]. To better elucidate the role played by the nature of the polymeric chelating group and of the ancillary ligand new heterogenized nickel catalysts were synthesized by reaction of functionalized polystyrenes with a suitable nickel precursor. In this way the ylidic systems (II) were obtained, where L can be a phosphine, a phosphite, a nitrogen base and so on [3,10].

(II)
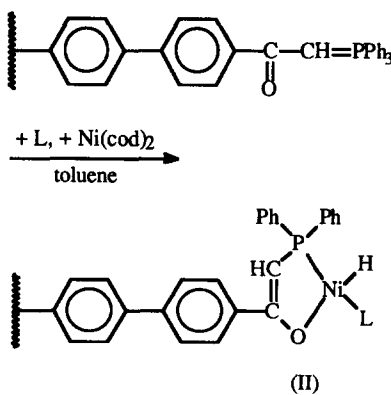
Also phosphino-carboxylate systems (III) [11]:

(III)
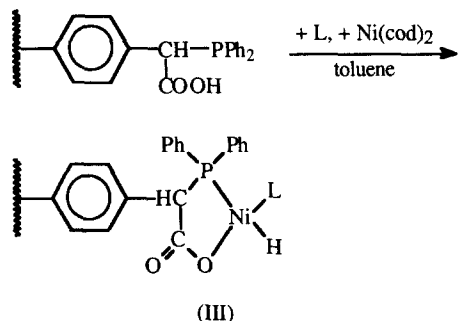
and non chelate phosphino-carboxylate systems (IV and V):

(IV)

(V)
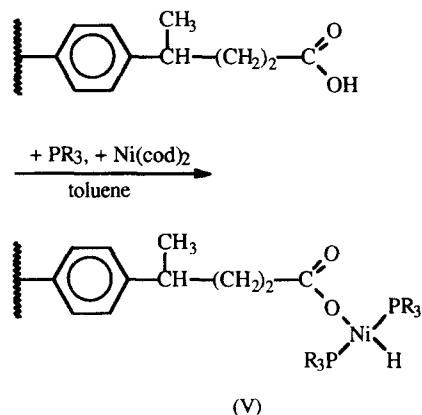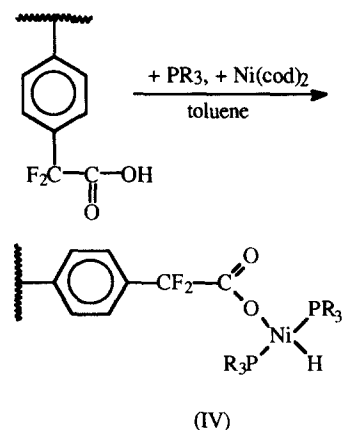
were prepared by a similar route [12].

Heterogenized nickel ylidic catalysts (II) were always active in ethylene polymerization to give

Table 1
Ethylene polymerization with nickel ylidic catalysts (II) [a]

Ancillary ligand (L)	pKa	L/Ni	T.N. [b]
none	–	–	1
PPh$_3$	2.73	1	135
PPh$_3$	2.73	10	4
PPh$_3$ [c]	2.73	1	153
P(PhNMe$_2$)$_3$	8.65	1	4
P(OBu)$_3$	3.31	1	3
PCy$_3$	9.65	1	47

[a] Reaction conditions: functionalized matrix: 200 mg (functional groups: 0.2 mequiv./g); Ni(cod)$_2$: 30 mg; P C$_2$H$_4$: 5 MPa; toluene: 20 ml; T: 50°C; time: 3 h.
[b] kg PE/g atom Ni·h.
[c] Preactivated with H$_2$ (0.5 MPa) for 15 min.

high crystallinity (>80%) and high density (0.95–0.96 g/ml) polyethylene having the same morphology of the polymeric support matrix (Table 1).

The catalytic systems are found to be active also in the absence of ancillary ligands, but their presence stabilized the catalytic complex preventing the decomposition to metal.

An excess of ancillary ligand is detrimental to the catalytic activity, probably due to the formation of inactive phosphinated nickel species (Table 1).

Strongly basic phosphines depressed the activity as observed for homogeneous ylidic systems, while an increase of the steric hindrance had a positive role.

Preactivation with hydrogen reduced the induction period, favoring the formation of the active nickel hydride.

In addition, the catalyst heterogenized by anchoring the phosphino acetate moiety to a polystyrene matrix (III) was found to be active in the polymerization of ethylene to HDPE with replication of the support morphology. In fact when the polymeric support was a powdered resin polyethylene was obtained as a powder whilst using a microspherical resin as support, polyethylene spheres ($\phi \cong 5$ mm) were formed. Also in this case the polyethylene characteristics were quite analogous to those observed with ylidic heterogeneous systems: in every case polydispersity

Table 2
Ethylene oligomerization/polymerization with nickel phosphinocarboxylate chelate (III) and non-chelate (IV and V) heterogenized catalysts

Catalyst	Polymeric matrix	L	L/Ni	Polyethylene(g)	Oligomers(g)	T.N. [a]
III [b]	micropheres	PPh$_3$	1	18.7 spheres	–	11.5
III [b]	micropheres	–	–	15.9 spheres	–	9.4
III [b,c]	micropheres	PPh$_3$	1	7.9 spheres	–	4.7
III [b]	powder	PPh$_3$	1	6.9 powder	–	4.1
IV [d]	micropheres	PCy$_3$	2	–	1.4	0.5
V [d]	micropheres	PCy$_3$	2	–	0.8	0.4

[a] kg PE/g atom Ni·h.
[b] Reaction conditions: P C$_2$H$_4$: 5 MPa; T: 75°C; toluene: 20 ml; time: 3 h.
[c] Preactivated with hydrogen (0.5 MPa) for 15 min.
[d] Reaction conditions: P C$_2$H$_4$: 4MPa; T: 90°C; toluene: 15 ml; time: 8 h.

indexes ($30 < M_w/M_n < 50$) were very high, suggesting the presence of different populations of active centers with very dissimilar activities. The origin of this behaviour is not clear at present; both metal species with different environment and access to the substrate can play a certain role.

The catalytic activity observed for heterogenized phosphinoacetate systems was lower than that for the ylidic ones (Table 2) similarly to the respective homogeneous systems in ethylene oligomerization [5].

For these chelate catalysts the presence of added phosphine ligand seemed unnecessary: no decomposition is observed in the runs carried out without any ligand, and only lowering of the activity was ascertained. Moreover the preactivation step under hydrogen appeared detrimental, causing a partial reduction to Ni(0).

To gain better insight into the effect played by the rigid chelating ligand in the previously described heterogenized systems, the heterogenized non-chelate phosphino carboxylate nickel catalysts (IV and V) were tested (Table 2) [12]. Rather surprisingly these last systems were always active in ethylene oligomerization. They also appeared less stable than the chelate complexes. A decomposition mechanism involving the phosphine ligand dissociation was ascertained, which could be prevented by preparing the catalyst under ethylene atmosphere.

The results reported up to now allow a better clarification of the respective roles of the chelate part and of the ancillary ligand in the proposed catalytic mechanism of the heterogenized system depicted in Scheme 1. The polymeric nature of the chelate ligand blocks the bidentate coordination to the nickel centre and makes the chelation rigid and probably irreversible. This bidentate firm coordination greatly favours the polymerization over oligomerization which requires a vacant coordination site for β-extraction of the hydrogen (step C) [13]. In contrast, when the phosphine and the carboxylic moieties are bonded in a non-chelate arrangement, the coordination of the phosphino group becomes reversible and oligomers are formed.

The ancillary ligand L is not always necessary for the activation of the heterogeneous chelate complexes (II) and (III) and is involved only in the formation of the active hydride species from the precursor (step A). Once displaced by ethylene from the nickel centre (step B), the ancillary ligands become ineffective for the process selectivity.

These results are quite different from those observed for analogous homogeneous complexes, where the ancillary ligand coordination appears to be reversible and the chelating ligand is involved in a reversible opening–closing equilibrium which
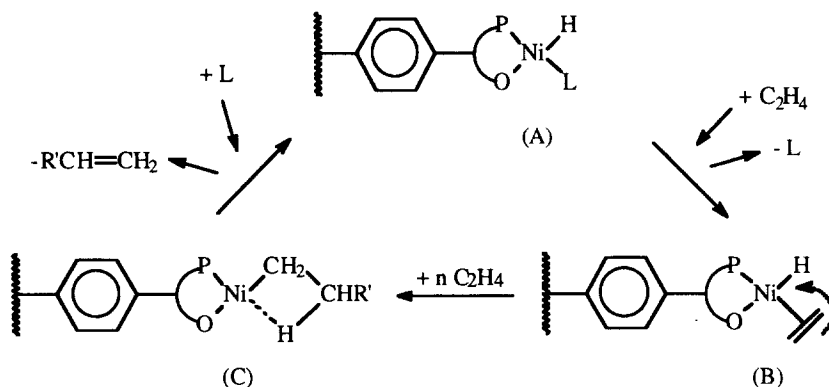
Scheme 1.

causes the formation of a coordination vacant site and therefore the production of oligomers.

2.1. Ziegler–Natta catalysts on inorganic support

As mentioned in the Introduction the original objective of the heterogenization of homogeneous catalysts was to fix on an insoluble support well defined catalytic species, that is, complexes having the same chemical structure as the starting soluble system [1]. More than 25 years of investigation in this field have demonstrated that this was very difficult and was achieved only rarely, whereas in many cases supported catalysts not only had different physical properties but also a different chemical structure. Therefore at present the heterogenization of organometallic catalyst is a way for preparing new catalysts with controlled structure and behaviour rather than a simple way to physical heterogenization. This aspect is particularly true when the organometallic species are derived from the conventional Ziegler–Natta catalyst preparation, while they can be approached more properly starting with metallocene systems.

In the early work by Ziegler [14] and Natta [15], these systems have been considered as heterogeneous catalysts. Accordingly Natta [15] was able to show the importance of crystalline $TiCl_3$ with active organometallic species based on alkyl-titanium species on the surface, for determining both catalytic activity and isotactic stereospecificity in case of monosubstituted ethylene monomers.

In the present work results from our laboratory will be reviewed in the frame of the relevant literature in order to provide some insight into the possibility of obtaining active sites on inorganic supports where the catalytic activity can be influenced by ligands around the transition metal atom.

Indeed, previous work concerning $MgCl_2$ supported Ti/Hf catalysts activated with trialkylaluminum had shown that addition of carboxylic acids narrows the molecular weight distribution (MWD) due to selective complexation of active sites producing low molecular weight chains [16]. In order to confirm the presence on the active sites of the carboxylate ligand, optically active carboxylic acids such as $(+)(R)$-3,7-dimethyl-6-octenoic acid (C4) and $(+)(S)$-2-phenylbutanoic acid (PB) were used for the catalyst preparation. The catalyst was prepared by treatment with aluminum alkylchlorides of Ti-carboxylates solutions with analogous Mg-derivatives giving coprecipitation of Ti and Mg chlorinated products. FT-IR analysis indicated the presence of carboxylate in the catalyst, mainly bound to titanium as a bidentate ligand [17]. A molar ratio carboxylic acid/Ti = 1 was detected by chemical analysis.

The catalyst prepared from the optically active acid induces the formation of optically active polymers due to the preferential (stereo-elective) [18] polymerization of the R enantiomer of racemic α-olefins having the asymmetric carbon in the

Table 3

Polymerization of $(R)(S)$-4-methyl-1-hexene (4MH) and of $(R)(S)$-3,7-dimethyl-1-octene (DMO) in the presence of $MgCl_2$ supported titanium catalysts containing optically active carboxylic acids [a]

Olefin	Acid	Molar ratio Olefin/Ti	Temp. (°C)	Duration (h)	Conv. [b] (%)	$[\alpha]_D^{25}$ rec. mon. [c]	$[\alpha]_D^{25}$ polymer [d]
4MH	C4	300	20	8	27.7	− 0.004	+ 0.35
4MH	PB4	200	20	7	35.6	− 0.015	− 1.10
4MH	PB4	200	0	6	7.8	− 0.008	− 3.19
4MH	PB4	200	− 30	8	0.6	− 0.001	− 6.81
DMO	PB4	200	20	7	6.6	+ 0.023	− 1.66

[a] In n-heptane, molar ratio $Al/Ti = 30$.
[b] Evaluated as (polymer weight/olefin weight) · 100.
[c] Neat.
[d] In cyclohexane ($c = 0.5$ g/dl).

Table 4

Characterization of the fraction of poly(4MH) samples obtained in the presence of $MgCl_2$ supported titanium catalysts containing optically active carboxylic acids

Fraction extracted with:	Acid C4			Acid PB		
	%	$[\alpha]_D^{25}$ [a]	$\bar{M}_v$ [b]	%	$[\alpha]_D^{25}$ [a]	$\bar{M}_v$ [b]
acetone	14	+ 0.05	n.d.	7	+ 0.04	n.d.
ethyl acetate	29	+ 0.31	35,000	28	− 1.23	32,000
diethyl ether	27	+ 0.49	133,000	23	− 1.54	158,000
cyclohexane	30	+ 0.38	372,000	42	− 0.96	455,000

[a] In cyclohexane ($c = 0.5$ g/dl).
[b] Evaluated from viscosity values in tetraline at 120°C.

α- (3,7-dimethyl-1-octene, DMO) or β-position (4-methyl-1-hexene, 4MH) to the double bond (Table 3). PB gives better results than C4 thus suggesting the importance of the distance of the chiral carbon atom from the carboxylic group and then from titanium. This would be clearly effective if either the acid is attached (or complexed) to the active sites or promotes the formation of inherently chiral sites during catalyst coprecipi-

tation. The effect is larger for DMO than for 4MH, and increases with decreasing the temperature from 20 to − 30°C (Table 3).

Fractionation with boiling solvents of the polymers obtained at 20°C by polymerizing 4MH indicates that the stereo-electivity is connected to the stereospecific centers giving high molecular weight macromolecules (Table 4). The lower optical rotation, in absolute values, of the cyclohexane extracted fraction with respect to the diethyl ether extracted fraction is connected to the higher stereoselectivity of more isotactic specific active centers.

These data confirm the presence of carboxylate ligands around the titanium in the active sites. Therefore starting with selected Ti-complexes it is possible to support better defined species on $MgCl_2$ by coprecipitation [2,16]. Indeed even if a precise structure cannot be determined these results strongly support the attachment of titanium species bearing bidentate carboxylate ligands, to a $MgCl_2$ support, which are successively con-
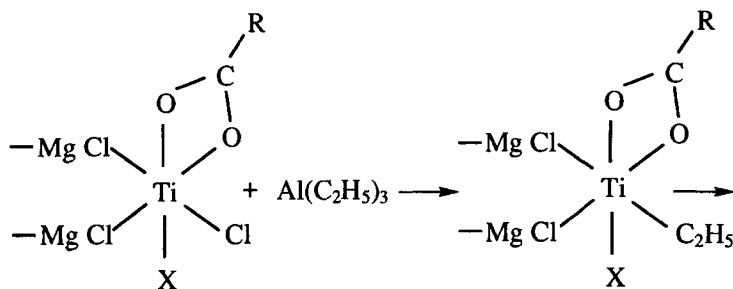
Scheme 2.

Table 5
Activity of zeolite supported Cp_2ZrCl_2 for polymerization of ethylene [a]

Cocatalyst	[Al]/[Mt]	Surface treatment	S.A. [b]
AlMe₃	10	–	3
AlMe₃	50	HY–AlMe₃	37
AlEt₃	12	–	3
MAO	1500	–	195
MAO [c,d]	1500	HY–AlMe₃	2800
MAO [c,e]	1500	HY–AlMe₃	2280

[a] P ethylene = 1 bar, T = 25°C.
[b] kg PE/g atom Zr·h.
[c] Carried out in a Büchi 2 l glass reactor.
[d] P ethylene = 3 bar.
[e] P ethylene = 1 bar, P propene = 2 bar.

verted into active polymerization sites by alkylation with aluminium alkyls as presented tentatively in Scheme 2.

Previous studies using silica as support for different titanium and zirconium complexes active as homogeneous catalysts for ethylene polymerization [19] did not give clear results. Indeed in some cases removal of the metallocene ligand was observed [20], and the activity was dependent on preparation conditions [21,22], thus confirming the formation of non definite species on the surface of the inorganic support.
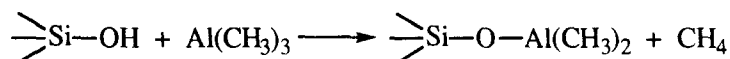
In this context HY-zeolite appeared to be a more suitable support because of the well characterized structure and the possibility of entrapping in the pores organometallic complexes. In this connection the catalyst preparation was performed starting with biscyclopentadienyl zirconium complexes and HY zeolite.

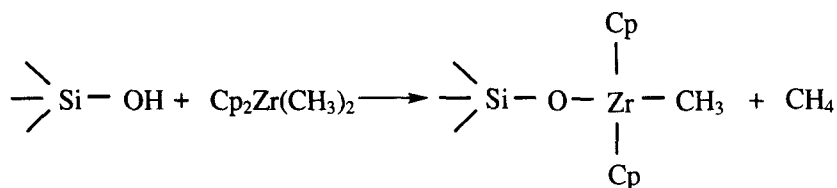Cp_2ZrCl_2 supported on merely thermally treated HY-zeolite displays (Table 5) rather modest activity with aluminum trialkyls, which is substantially improved by using MAO, even if remaining below the value obtained in solution under similar conditions. As this result could be in some way connected to a modification of Zr-complex through reaction with the silanol functionalities, the zeolite was pretreated with $AlMe_3$ [20]. This reaction occurs with methane evolution and conversion of all –OH groups into Si–O–Al oxane species [23] as indicated in the Scheme 3.

On this modified support the catalyst shows improved activity (one order of magnitude) both with $AlMe_3$ and with MAO; in the last case the productivity (S.A. = 2,800 kg/mol Zr·h with Al/Zr = 1500 molar ratio) was comparable to that expected for the analogous complex in solution. Also good activity was obtained in the ethylene/propene copolymerization, with about 20% mol of α-olefin in the copolymer. In toluene solution Cp_2ZrCl_2 with MAO (Al/Zr = 1500) gave S.A. = 2,200 kg/mol Zr·h with 20% mol propene in the final product (Table 5).

To confirm the possibility of supporting the unmodified metallocene, Cp_2ZrMe_2 and more thoroughly purified HY-zeolite were used because even the dealuminated zeolite contains extraframework aluminum. Biscyclopentadienyl dimethyl zirconium is in some way a simplified derivative as it eliminates the presence of chlorine. Moreover it is a probable intermediate product during catalyst preparation starting with Cp_2ZrCl_2 as the latter can be methylated by methylalumoxane in the activation step. Also, its interaction with silanol groups still present on the support could

$$\text{Si—OH} + \text{Al(CH}_3)_3 \longrightarrow \text{Si—O—Al(CH}_3)_2 + \text{CH}_4$$

Scheme 3.

$$\text{Si—OH} + \text{Cp}_2\text{Zr(CH}_3)_2 \longrightarrow \text{Si—O—Zr—CH}_3 + \text{CH}_4$$
$$\text{(Cp, Cp)}$$

Scheme 4.

be easily shown by methane evolution (Scheme 4).

The resulting μ-oxo zirconium species are inactive for polymerization; therefore the above reaction would be accompanied by a decrease of productivity.

Extraframework aluminum can be removed by exhaustive extraction at 50°C with a solution of acetylacetone in ethanol [24]. After this treatment the ^{27}Al-NMR (MAS) spectrum shows a single resonance at 57.45 ppm of the tetrahedral Al, whereas resonances at 0 and 30–50 ppm of the extraframework Al are completely lacking. However silanol groups are still present and treatment with Cp_2ZrMe_2 is accompanied by CH_4 evolution associated with cleavage of the Zr–carbon bond. The zeolite was then treated with a 2 M solution of $AlMe_3$ in toluene and successively washed with dry toluene until the test for aluminum was negative; the resulting support in the ^{27}Al-NMR (MAS) spectrum shows three resonances at 60.4, 33.1 and 2.2 ppm, suggesting that two different species of aluminum, associated with absorbed $AlMe_3$ and the reaction product of $AlMe_3$ with silanol groups, are now present.

The addition of Cp_2ZrMe_2 to the modified zeolite does not evolve any CH_4, and the ^{27}Al-NMR (MAS) spectrum shows the same resonances as before the addition of zirconocene. Also, in the ^{29}Si-NMR (MAS) spectrum only the resonance of the Si(OAl) species at -107 ppm can be observed, indicating that no change occurred for Si after addition of the zirconocene to the zeolite pretreated with $AlMe_3$. Therefore it is likely that the zirconocene maintains its original structure when supported on this modified HY-zeolite (HY**).

This catalyst with MAO as cocatalyst gave comparable activity to that in solution and needed comparable amounts of MAO, as expected by the fixation on surface and inside the channels of the zeolite [25] of unmodified species. Replacement of $AlMe_3$ with Me_3SiCl for HY** pretreatment gave a support without free silanol groups and extraframework aluminum. With this last support no activity was detected for Cp_2ZrMe_2 in the presence of $AlMe_3$ cocatalyst, whereas with MAO analogous productivity was achieved as with the HY**–$AlMe_3$ support, indicating the similar structure of the supported species without any involvement of aluminum species on the surface.

Interesting differences exist between time dependence of polymerization rate with soluble and zeolite-supported species in the case of Cp_2ZrMe_2. The soluble system is initially more active than the supported one, but shows a typical decay profile of polymerization rate (R_p) vs. time. By contrast R_p of the zeolite supported system remains almost constant in the first 60 min and already after 20 min is higher than that for the soluble catalyst. The comparable productivity of the zeolite supported catalysts with respect to the corresponding systems in solution, despite the lower initial activity, is therefore a consequence of the better stability of the active sites in the former systems [22].

These preliminary results show that the use of properly treated zeolite supports allow us to obtain heterogenized zirconocene species showing appreciable activity with constant R_p, indicating that entrapment in the zeolite channels prevents deactivation reactions and allows the modulation of catalytic activity by molecular modification of the support without preventing activation by MAO.

3. Concluding remarks

As anticipated in the Introduction the main objective of the work described in the present paper was to indicate the possibility of obtaining well defined and structurally homogeneous metal complexes catalysts fixed on a solid support, consisting of either an organic resin or inorganic materials.

The data reported indicate that crosslinked polystyrene appears to be suitable to be functionalized with chemical species which can act as ligands for fixation of transition metals to give structurally uniform catalytic species. The inorganic matrices can present different sites due to the solid structure

and characteristics of the surface. Chemical treatment with specific reagents can give some improvement of selected properties, depending on the nature of inorganic surface and type of organometallic species. In this case the inorganic supports can also offer the possibility of fixing the unaltered organometallic complex through weak bonding or absorption.

This area needs more work both on the structure and surface properties of supports and on the suitable processes to obtain controlled fixation. However it is mature enough to show the validity of the idea of hybrid catalysts developed by the series of SHHC conferences looking at systems which join chemical homogeneity to physical heterogeneity.

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