Catalytic systems supported on $MgCl_2$ doped with $ZnCl_2$ for olefin polymerization

Daniele Fregonese, Silvano Bresadola *

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica dell'Università di Padova and Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione-CNR, Via Marzolo 1, I-35131 Padova, Italy

Abstract

Ziegler–Natta type catalysts for α-olefin polymerization supported on $MgCl_2$–$ZnCl_2$ mixtures were prepared and the effect of Zn doping on the catalyst performance was investigated. The supports were obtained by reacting a blend of powdered metallic magnesium and zinc with an excess of 1-Cl-*n*-butane under UV-visible radiations. Their treatment with $TiCl_4$ yielded procatalysts, which were fully characterized and tested in propylene and ethylene polymeriza-tion. The effects of $ZnCl_2$ as doping salt in $MgCl_2$ supports were also investigated in dependence on the zinc concentration. In particular, in the propylene polymerization carried out at 70°C and 2 atm, the catalyst increased its activity on increasing the $ZnCl_2$ content in the procatalyst up to 0.73 wt.% expressed as zinc. Going to a higher $ZnCl_2$ content, it was found that the activity decreases. The isotactic index of polypropylene produced increases only slightly on increasing the zinc content up to a weight percentage of 0.73, but going to a higher zinc chloride content, the isotacticity decreases. In comparison with a reference commercial catalyst, the polydispersity was found to be very little affected, at least in the range of $ZnCl_2$ content that we had investigated. The $ZnCl_2$ doping was shown to cause a notable effect on the activity of the catalyst also in the ethylene polymerization ($T = 70$°C, $P = 2$ atm). In fact, in ethylene polymerization, a catalyst based on a support containing a doping amount of 0.73 wt.% of zinc exhibited an activity 2.5 times greater than that shown by the reference catalyst. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ziegler–Natta catalysis; Supported catalysis; Magnesium chloride; Zinc chloride; Propylene; Ethylene; Polymerization: powder XRD

1. Introduction

The discovery that active magnesium chloride, i.e., δ-$MgCl_2$, behaves as an ideal support material to fix titanium tetrachloride or its derivatives opened a new era in the field of Ziegler–Natta catalysis, from both academic and industrial viewpoint. The researches on supported catalysts for α-olefin polymerization started in the early 60s and led to the development of catalysts based on activated $MgCl_2$ [1], active for both ethylene and propylene polymerizations. Afterwards, the investigations were directed to improve the performance of these catalysts, and catalysts of third and fourth generations were so obtained by using several combinations of internal and external electron donors. In the 90s, catalysts of the fifth genera-

---

* Corresponding author. E-mail:
bresadola@chim02.chin.unipd.it

tion were discovered [2], in which a new type of electron donors, i.e., 1,3-diethers, was used. If these were employed as internal donors, they led to catalysts characterized by high activity and high sterospecificity without the need of any external electron donor.

While the influence of the electron donors on the catalyst performance have been extensively investigated, the effect of changes in the composition of the supporting material have been scarcely taken into consideration. In fact, only one paper was recently published [3], in which the effect of the presence of $MnCl_2$ in $MgCl_2$ support material was investigated. The results reported show that the activity of the catalysts and the molecular weight distribution of the polymers obtained are remarkably affected by doping the support material with $MnCl_2$. In particular, the activity of the catalysts at first increases, but on further increase of the $MnCl_2$ concentration (> 10 mol%) causes an almost linear drop of efficiency. In this paper, we report an investigation on α-olefin polymerization catalyzed by titanium supported on mixtures of δ-$MgCl_2$ doped with $ZnCl_2$. The $ZnCl_2$ salt was chosen as doping agent because its X-ray diffraction pattern resembles that of $MgCl_2$, supporting that these salts reasonably give homogeneous mixtures on a molecular level. Supports containing different amounts of $ZnCl_2$ were so prepared, which, by treatment with $TiCl_4$, yielded the corresponding procatalysts. Supports and procatalysts were fully characterized by elemental analysis and by XRD technique. The procatalysts were activated by treatment with the cocatalyst $AlEt_3$ and tested in propylene and ethylene polymerization carried out under slurry conditions.

2. Experimental

2.1. Reagents

Powdered metallic magnesium and zinc (50 mesh), 1-chlorobutane, hexane, heptane and ti-

tanium tetrachloride were Aldrich Reagent Grade. Propylene and ethylene (polymerization grade), triethylaluminium (reagent grade) and reference catalyst were supplied by Montell. The reagents were purified by standard methods in order to obtain reproducible polymerization tests. Propylene and ethylene were treated with molecular sieves 4A and BASF catalyst R 11-3, in order to remove oxygen and water. Titanium tetrachloride and triethylaluminium were used without further purification.

2.2. Instrumentation

The synthesis of the supports was carried out in a four-necked glass reactor equipped with a graduated funnel, a reflux condenser, a valve and a quartz UV lamp. The light source unit is a low-pressure 150 W UV–Vis lamp that is characterized by a spectrum in the range 250–450 nm in accordance with the bond energy of C–H (kJ/mol = 416, $\lambda = 287$ nm), C–Cl (kJ/mol = 328, $\lambda = 364$ nm) and C–C (kJ/mol = 356, $\lambda = 336$ nm). The lamp is provided with a quartz water-cooled jacket.

The XRD spectra were scanned by transmission technique, using a GD-2000 diffractometer (Ital Structures, Riva Del Garda, Italy) operating in the Seemann–Bohlin geometry and equipped with a quartz-curved crystal monochromator of the Johansson type aligned on the primary beam. The spectra were recorded by using the $CuK_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å), at $0.1°$ (2θ) steps of 10 s. The diffraction measurements were carried out under a strictly inert atmosphere on samples prepared in a Braun MB-150 I/II dry-box. The molecular weight distribution of the polymers was measured by gel permeation chromatography (Waters mod-200) using four spherosil columns (10^3–10^7 Å, 37–75 μm) and 1,2-dichlorobenzene as solvent at 135°C and equipped with a refractive index detector.

The melting point (T_m) and crystallinity index (X_c) of the polymers were determined by DSC using a Perkin Elmer mod. DSC-4 instrument following the ASTM method [4].

Carbon was quantitatively determined by an Elemental Analyser CHN Mod. 1106 Carlo Erba, while magnesium, zinc and titanium were measured by atomic absorption spectrometry with a Perkin–Elmer 1100B instrument.

2.3. Preparation of doped supports

The $MgCl_2/ZnCl_2$ mixed supports were prepared by reacting a blend of powdered metallic magnesium and zinc with a large excess of 1-Cl-*n*-butane. Unlike magnesium, zinc reacts hardly with chloroalkane so that the reaction needs to be activated with UV-Visible radiations. Thus, magnesium–zinc blends (ca. 3 g) having different composition were treated with 1-Cl-*n*-butane (80 ml) under strictly inert atmosphere and heated for 8 h under rapid stirring. A thick white-gray solid was formed. After standing for 1 h, the surnatant liquid was removed at room temperature by settling. The solid residue was washed four times with hexane and then heated at 120°C for 8 h under vacuum. The materials so obtained were characterized by

Table 1
Chemical composition of supports and procatalysts (wt.%)

Zn added (wt.%)	Support			Procatalyst		
	Zn	Mg	C	Zn	Ti	C
0	0	23.8	6.4	0	1.22	1.82
2	1.0	22.0	4.2	0.55	0.93	1.30
5	1.3	21.5	5.0	0.73	1.12	3.22
10	3.6	21.0	4.6	1.98	1.09	1.74

XRD spectra (Fig. 1a–c) and by elemental analysis (Table 1).

2.4. Preparation of procatalysts

Hexane, 60 ml, was added to 3 g of the supporting material, prepared as reported above, put into a glass reactor equipped with condenser, magnetic stirrer and an ice-cooling system. Titanium tetrachloride, 60 ml, was then added drop by drop under inert atmosphere at 65°C. The obtained mixture was heated at reflux temperature for 2 h. Finally, the suspension so formed was cooled and the solvent was re-
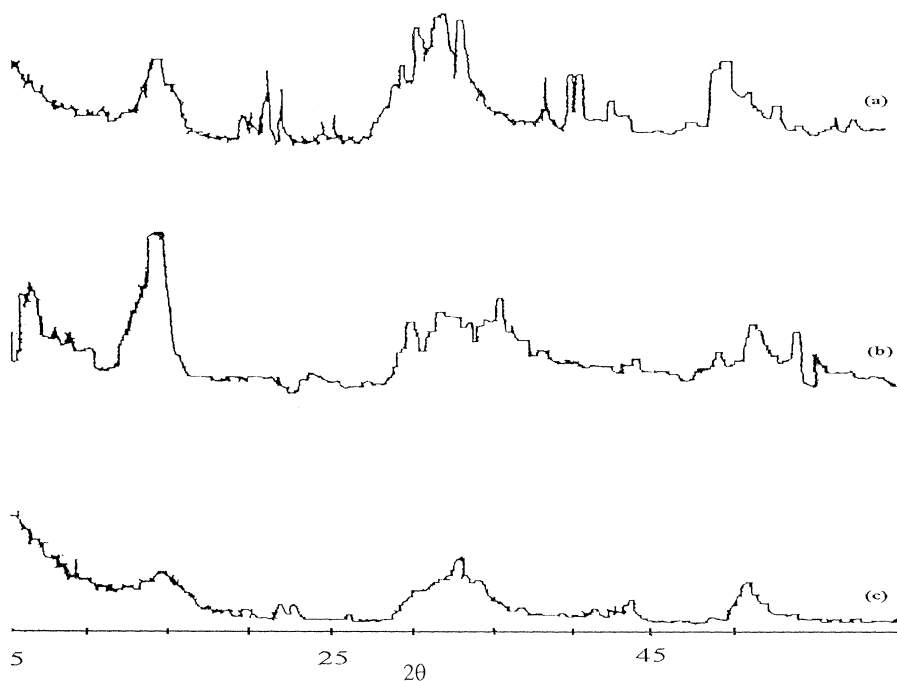

Fig. 1. Powder X-ray diffraction patterns of $MgCl_2/ZnCl_2$ supports: wt.% Zn = 1.0 (a); 1.3 (b); 3.6 (c).

moved under reduced pressure. The solid residue was washed four times with 40 ml of hexane and kept to room temperature and reduced pressure (10^{-2} atm) for 8 h. The procatalysts so obtained showed titanium and zinc contents in the ranges 0.93–1.22 and 0.55–1.98 wt.%, respectively.

2.5. Polymerization tests

The slurry polymerizations of ethylene and propylene were carried out at constant pressure ($P = 2$ atm) in a BUCHI 2l stainless steel reactor equipped with a thermostatic system and a turbine stirrer. Heptane was used as solvent of the monomer. Before use, the reactor was heated at 105°C for 12 h under reduced pressure and then in turn filled with nitrogen and evacuated several times. The reactor was charged with 1.2 l of heptane. A weighted amount of procatalyst (0.05–0.1 g) suspended in mineral oil was injected into the reactor ($P_{olefin} = 1.2$ atm). Afterwards, the pressure and the temperature were raised up to the selected reaction values (2 atm and 70°C) and the polymerization started when the cocatalyst (triethylaluminium) was added. The cocatalyst was added in an adequate amount to achieve anyhow Al/Ti molar ratio of 50. The temperature of the reactor and the pressure were maintained constant within ± 0.5°C and ± 0.02 atm, respectively. The stirring speed was 1200 rpm in order to avoid effects due to monomer diffusion through the gas–liquid interface. The polymerization rate was determined by measuring the monomer consumption rate using a mass flow-meter. After 2 h, the polymerization reaction was stopped by rapidly decreasing the temperature and pressure. With this procedure, the entire polymerization reaction course could be monitored. The catalytic activity was expressed as grams of polymer produced per gram of titanium per hour and per gram of catalyst per hour.

The isotacticity index (I.I.) was expressed as weight percentage of the insoluble polypropylene in boiling heptane. The total weight of produced polymer was calculated by taking into account also the fractions soluble in heptane (low isotactic and atactic polymers).

3. Results and discussion

We have prepared four supports and the corresponding procatalysts following the procedure above described. The composition of the obtained supports and procatalysts are listed in Table 1. It is interesting to note the large differ-
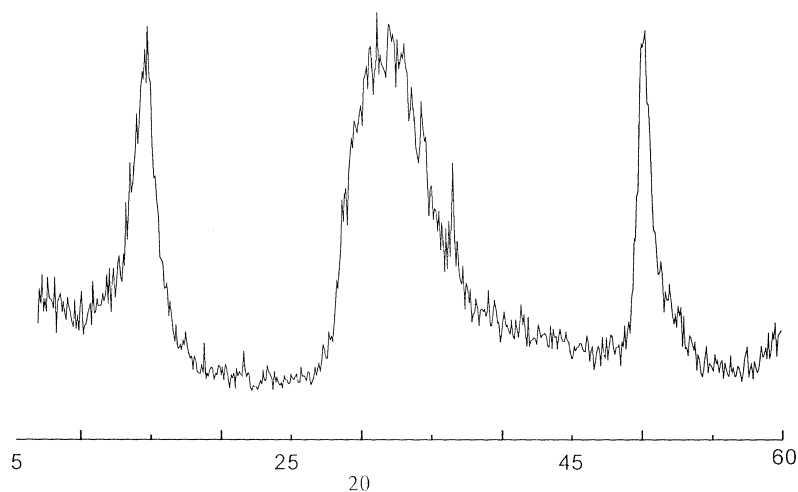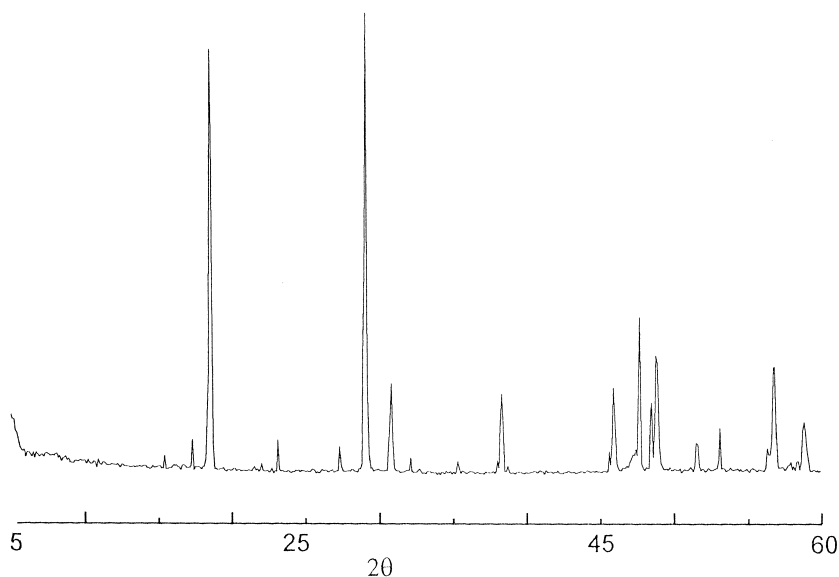

Fig. 2. Powder X-ray diffraction pattern of δ-MgCl$_2$.

Fig. 3. Powder X-ray diffraction pattern of $ZnCl_2$.

ence in the zinc content occurring between supports and procatalysts. The zinc decrease observed (ca. 50%) is probably due to the presence in the support of zincalkil derivatives which are removed in the course of the procatalyst synthesis.

X-ray diffraction patterns (Fig. 1a–c) have been taken from all the support batches to test the influence on the spectral shape of the increasing $ZnCl_2$ doping concentration. As an example, Figs. 2 and 3 show the powder XRD spectra of δ-$MgCl_2$ and $ZnCl_2$, respectively. All the spectra of the $MgCl_2$ doped supports exhibit broad bands centered at $2\theta \cong 15$, 32 and 50.5°, which correspond to those exhibited by the structurally disordered δ-$MgCl_2$ [5]. However, in comparison with δ-$MgCl_2$ (Fig. 2), the Zn doped $MgCl_2$ exhibit the broad band centered at $2\theta \cong 32°$ remarkably modified. Such a behavior might be ascribed both to the presence of alkyl metal derivatives and to structures in which magnesium is partially replaced by zinc, on considering that their ionic radii are very alike ($Zn^{2+} = 0.88$ Å; $Mg^{2+} = 0.86$ Å). The XRD patterns allowed us to determine the crystallite size by using the Scherrer equation [6]. The results reported in Table 2 are an evidence

of an increase in the crystallite thickness along the (110) face with the increase of zinc content.

The procatalysts were tested in the propylene polymerization carried out under slurry conditions and their performance were compared with that exhibited by the reference catalyst (Ti = 2.45 wt.%) as well as by a catalyst supported on pure δ-$MgCl_2$. The polymerization results are reported in Table 3.

The doped catalysts showed an increasing activity on increasing the $ZnCl_2$ amount up to 0.73 wt.% expressed as zinc. Going to higher doping concentrations, there is a drastic drop in the activity. However, if g PP/g Ti h units are used, the activity found is almost two times higher than that showed by the reference catalyst even with a $ZnCl_2$ doping concentration of

Table 2
Crystallite size of $ZnCl_2$ /$MgCl_2$ supports

Wt.% Zn in support	$\varepsilon(110)$ (Å)
0	51
1.0	57
1.3	73
3.6	74

Table 3
Activity of reference and $ZnCl_2$ doped catalysts in the propylene polymerization

Procatalyst Zn content (wt.%)	Activity (g PP/g Ti h)	Yield (g PP/g of catal. h)
Reference procatalyst	7000	171
0	9000	110
0.55	15400	143
0.73	24800	278
1.98	13600	150

$T = 70°C$.
$P = 2$ atm.
Time: 2 h.
$AlEt_3$ as cocatalyst, Al/Ti molar ratio = 50.

1.98 wt.% expressed as zinc (see Table 3). The polymers obtained were fully characterized and the results are listed in Table 4, which collects molecular weights (M_w, M_n), polydispersity (M_w/M_n), isotacticity index (I.I.), percentage of atactic polypropylene, melting point and percentage of crystalline polymer (X_c) in the isotactic fraction.

Finally, the most active procatalyst (Zn = 0.73 wt.%) was tested even in the ethylene polymerization working at 70°C, 2 atm with $AlEt_3$ as cocatalyst (Al/Ti molar ratio = 50). The results of this test were compared with those obtained by using the reference catalyst. Even in the ethylene polymerization, the doped catalyst showed an activity higher than that exhibited by the undoped reference catalyst (84.5 vs. 34.6 kg PE/g Ti h).

These results show that the doped supports affect both the activity of the derived catalysts and the properties of the polymers obtained (Tables 3 and 4). This could be due to structural modification of the supporting materials. It should be noticed that unlike the α-$MgCl_2$ form, the structurally disordered δ-$MgCl_2$ form is a useful supporting material for the preparation of active catalysts. Moreover, a catalyst more active can be obtained using a δ-$MgCl_2$ support prepared by reacting metallic magnesium with 1-Cl-*n*-alkane. In this case, the supporting material contains small amounts of alkyl radicals which can induce a still greater structural disorder (see XRD patterns in Fig. 2). Likewise, the increased activity shown by the catalyst supported on $MgCl_2$ doped with $ZnCl_2$ could be due to the formation of structural defects in the supporting material (Fig. 1a–c). Moreover, it should be remarked that these doped catalysts produce polymers characterized by a polydispersity similar to that found using the undoped catalysts. These results lead to the following conclusions: (1) the doped and undoped catalysts contain active sites which are basically of the same types, so justifying the trifling differences found in polymer polydispersity; (2) the higher activity showed by the doped catalysts can be due to a higher structural disorder, which makes the catalytic sites kinetically more active.

Work is now in progress with the aim of verifying whether the higher activity showed by the doped catalysts might be also due to an influence on the oxidation state distribution of titanium in the activated catalysts.

Table 4
Characterization of polypropylene obtained

Procatalyst wt.% Zn content	M_w	M_n	M_w/M_n	I.I.[a]	X_c	T_m (°C)	atactic PP wt.%[b]
Reference procatalyst	357000	44400	8.0	96.6	25	160.9	56.0
0	306000	32500	9.4	84.5	24.8	159.0	45.2
0.55	402000	36800	10.9	86	26.5	157.5	48.0
0.73	504000	53600	9.4	88.6	28.0	158.4	40.0
1.98	373000	35400	10.5	77.1	25.0	159.0	44.0

[a] I.I. of the insoluble boiling heptane polymer fraction.
[b] wt.% referred to the total product.

References

[1] P.C. Barbé, G. Cecchin, L. Noristi, Adv. Polym. Sci. 1 (1987) 81.

[2] U.S. Patent, 4971937 to Himont, 1990.

[3] T. Garoff, T. Leinonen, J. Mol. Catal. A Chem. 104 (1996) 205.

[4] Annual book of ASTM Standards, 1982, D 3417-82.

[5] V. Di Noto, S. Bresadola, Makr. Chem. Phys. 197 (1996) 3827.

[6] H.P. Klug, L.E. Alexander, in: X-Ray Diffraction Procedures, Wiley, New York, 1974, cap. 9.