New Crystalline Complex Chlorides Containing Transition Metal Chlorides or Oxychlorides as Components of Coordination Catalysts

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Synopsis

Novel complex chlorides have been obtained by reacting $TiCl_4$, $VOCl_3$, $MoOCl_4$, $WOCl_4$, or $AlCl_3$ with Be, Mg, Ca, or Sr chlorides in the presence of electron donors such as $POCl_3$ (L) or $C_6H_5POCl_2$ (L'). The resulting products, obtained with good yield, show defined stoichiometry, ionic character, and crystalline structure, and may be considered reference systems for high-yield catalysts in the low-pressure polymerization of ethylene (HDPE). Complexes $(TiCl_6)MgL_6$, $(TiCl_5L')_2MgL'_6$, and $(Ti_2Cl_{10})MgL_6$ associated with $(i\text{-}C_4H_9)_3Al$ were found very active in HDPE synthesis, but completely unable to polymerize propylene. This result and other evidence suggest that part of the catalytic activity of these systems is displayed by soluble species. The role played by the Mg ion in high-yield catalysts is discussed in the light of the peculiar behavior shown by the complex chlorides containing this earth-alkali metal.

INTRODUCTION

In previous articles,[1,2] we have tackled the study of high-yield polyethylene catalysts by preparing mixed chlorides of $TiCl_3$ with different metal halides as components of systems catalytically more active, in general, than the most efficient unsupported $TiCl_3$-based systems. The interest in these catalysts stems from the crystalline structure, identified by x-ray investigations, of the solid solutions obtained so that these catalysts may be considered reference systems displaying peculiar performances.

Pursuing our effort of preparing crystalline compounds containing the transition metal in different and defined arrangements, we succeeded in obtaining new ionic complex chlorides and oxychlorides containing, usually, the transition metal in the highest valency state. These salts, in particular those containing the Ti(IV) species, have been associated with aluminum trialkyls and found to yield very active catalysts for the low-pressure polymerization of ethylene. The incorporation of the Mg ion in the binary chlorides described in this work, was found to be of crucial importance for preparing highly efficient catalyst systems, in agreement with our previous work[2] and those of several other authors.[3-19]

Despite the huge number of patents claiming the unspecified role of Mg derivatives in realizing high-yield catalyst systems for the polymerization of α-olefins,[3-5] a relatively scarce number of articles have reported fundamental investigations on this broad topic.[1,4,6-19]

Our present work was promoted by the fact that several systems described in the literature postulate the formation of binary halides, e.g., Mg chlorotitanates when $MgCl_2$ and $TiCl_4$ are mixed to yield the solid component of some catalyst

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systems.[3] However, defined mixed chlorides were claimed to be formed only in the presence of electron donor molecules,[20,21] but their nature remained undisclosed. Therefore, the first aim of our work has been the preparation and structural characterization of complex chlorides not yet described and containing the transition metal moiety associated with a metal belonging to the IIA group of the Periodic Table and possibly an electron-donor molecule.

The second aim has been the study of the catalytic behavior of the systems resulting from the association of AlR_3 with these new complex salts during the polymerization of ethylene in order to relate the catalytic peculiarities observed to the structural arrangement in which the transition metal exists.

EXPERIMENTAL

Materials

$TiCl_4$, $FeCl_3$ (C. Erba), $BeCl_2$, $VOCl_3$, $C_6H_5POCl_2$ (Alpha-Inorganic Chemical Co.) were pure-grade reagents used as received. $POCl_3$ was distilled and $AlCl_3$ was sublimed under dry nitrogen atmosphere. $BaCl_2$, $CaCl_2$, and $SrCl_2$ were dried with $SOCl_2$.[22] $MgCl_2$ was dried at 350°C in a stream of anhydrous HCl for 24 hr. $TiCl_3$ was a Stauffer Chemical Co. product (H-type, i.e., H_2 reduced) used without any preliminary treatment. $MoOCl_4$ and $WOCl_4$ were synthesized as described elsewhere.[23,24] Hydrocarbon solvents, ethylene, and alkyl-aluminum derivatives were the same products reported previously.[1]

$(CH_3)_2Hg$ was prepared according to the methods used by Gilman and Brown.[25] A polystyrenic resin (XAD2-type produced by Rohm and Haas) was used as a catalyst carrier after grinding in a ball mill. Its surface area had a value of 330 m^2/g, specific volume = 0.69 cm^3/g, pore diam = 90 μm. Before use, the powdered resin was washed with CH_3OH and dried *in vacuo* in the presence of P_2O_5. The complex salt was supported on the carrier by means of a solvent (CH_2Cl_2).

Procedure

Synthesis of Complex Salts

Two procedures were adopted, depending on the solubility of some reagent in the excess of the electron donor compound, i.e., $POCl_3$ or $C_6H_5POCl_2$, and on its volatility. Both the methods, as well as the handling of reagents and products, were carried out under inert atmosphere.

Direct procedure. The chosen quantities (cf. Tables I and II) of earth-alkali metal chloride, transition-metal chloride, and $C_6H_5POCl_2$ (or $POCl_3$) were introduced in a 250-cm^3 three-necked, round-bottom flask equipped with a magnetic stirrer, condenser, and inlet tube for N_2. The temperature of the reaction mixture was subsequently increased by means of a heating bath until gentle reflux, or maintained at 140°C (in the case of $C_6H_5POCl_2$) for the time reported in Tables I and II. After cooling at room temperature and resting for 20 hr, a crystalline product separated from the reaction solution. The yield is reported in Tables I and II.

Extraction procedure. This method was usually adopted when $POCl_3$, which has a bp lower than $C_6H_5POCl_2$, and $TiCl_3$ or $MgCl_2$ were used. Very pure

TABLE I

Synthesis of Complex Chlorides Containing Cations of Elements of the IIA Group of the Periodic Table Solvated by Phosphorus Oxychlorides and Anions Based on Ti Chlorides

Complex	Ligand Type	Ligand (cm³)	Ti chloride Type	Ti chloride mmol	Earth-alkali metal Type	Earth-alkali metal mmol	Reaction time, hr	Formula of the obtained complex[a]	Yield[b] g	Yield[b] %	Aspect of crystals[c]	Mp[d], °C	IR data[e] cm⁻¹	Structural parameter space unit cell Group	Const.[f]	Z[g]
(I)	$POCl_3$	25	$TiCl_4$	23.0	$BeCl_2$	21.0	0.1	$(Ti_2Cl_{10})^{2-} \cdot (BL_4)^{2+} \cdot 2L$	5.2	15	(A)	126–7	1160	n.d.	n.d.	n.d.
(II)	$POCl_3$	50	$TiCl_4$	10.0	$MgCl_2$	2.0	4.0	$(Ti_2Cl_{10})^{2-} \cdot (MgL_6)^{2+} \cdot 2L$	2.4	70	(B)	170 (decomp.)	1270	$P2_1/c$	(A)	2
(III)[h]	$POCl_3$	45	$TiCl_4$	21.5	$CaCl_2$	10.0	4.0	$(TiCl_6)^{2-} \cdot (CaL_8)^{2+}$	n.d.	n.d.	(B)	150 (decomp.)	1275	$I4_1/a$	(B)	8
(IV)[h]	$POCl_3$	100	$TiCl_4$	45.0	$SrCl_2$	2.5	4.0	$(TiCl_6)^{2-} \cdot (SrL_8)^{2+}$	4.2	100	(B)	155–60	1275	$I4_1/a$	(C)	8
(V)[h]	$POCl_3$	50	$TiCl_3$	1.25	$MgCl_2$	8.5	0.25	$(TiCl_6)^{2-} \cdot (MgL_6)^{2+}$	n.d.	low	(C)	n.d.	n.d.	Pbca	(D)	4
(VI)	$(C_6H_5)\text{-}POCl_2$	35	$TiCl_4$	22.7	$MgCl_2$	10.6	0.5	$(TiCl_5L)_2^{-} \cdot (MgL_6)^{2+}$	15.2	70	(B)	124–5	1250 1225[i]	P-1	(E)	2

[a] Based on elemental analysis and x-ray investigations. Only the formula of complex (I) was based on the elemental analysis simply: Ti = 6.4% (calcd. 6.9); P = 11.5 (13.5), Cl = 71.5 (72.0); L = $POCl_3$ or $(C_6H_5)POCl_2$.

[b] Based on the chloride used in minor amount, n.d. = not determined.

[c] (A) = golden-yellow lamellae; (B) = golden-yellow prisms; (C) = golden-yellow cubes.

[d] Uncorrected values.

[e] Main absorption band due to $^\nu P{=}O$; $^\nu Cl = 698$ cm⁻¹ in the case of complex (I).

[f] (A) $a = 12.515$; $b = 11.417$; $c = 20.852$ Å; $\beta = 113.9°$; (B) $a = 17.230$; $c = 33.917$; (D) $a = 16.211$, $b = 16.250$, $c = 16.263$; (E) $a = 13.085$; $b = 19.552$; $c = 17.981$ Å; $\alpha = 99.9$; $\beta = 68.9$; $\gamma = 109.7°$. (C) $a = 17.077$; $c = 33.651$;

[g] Number of molecules per unit cell.

[h] Prepared with the extraction method (see Experimental section).

[i] $^\nu MgL$ and $^\nu TiL$, respectively.

TABLE II

Synthesis of Complex Chlorides Containing Cations of Elements of the IIA Group of the Periodic Table Solvated by POCl$_3$ and Anions Based on Some Transition Elements or Al

Complex,[a] n°	POCl$_3$, cm^3	Transition metal Type	mmol	Earth-alkali metal Type	mmol	Reaction time hr	Formula of the obtained complex[b]	Yield[c] g	%	Aspect of crystals[d]	Mp[e] °C	IR data[f] cm^{-1}	X-ray data[g]
(VII)	50	VOCl$_3$	2.5	MgCl$_2$	8.0	1.0	$(VCl_6)^{2-}(MgL_6)^{2+}$	1.8	60	(A)	140 (decomp.)	(A)	n.d.
(VIII)	50	VOCl$_3$	2.5	CaCl$_2$	8.0	4.0	$(VCl_6)^{2-}(CaL_8)^{2+}$	1.0	25	(A)	140–50 (decomp.)	(A)	n.d.
(IX)	60	MoOCl$_4$	15.0	BeCl$_2$	18.0	1.5	$(Mo_2O_2Cl_8)^{2-}(BeL_4)^{2+}\cdot 2L$	3.5	15	(B)	n.d.	(B)	n.d.
(X)	50	MoOCl$_4$	1.0	MgCl$_2$	7.5	0.2	$(Mo_2O_2Cl_8)^{2-}(MgL_6)^{2+}\cdot 2L$	0.5	20	(C)	90–5	(C)	(A)
(XI)	50	MoOCl$_4$	5.0	MgCl$_2$	7.5	2.0	$(Mo_2O_2Cl_8)^{2-}(MgL_6)^{2+}\cdot 2L$	—[h]		(D)	205–7	(C)	(B)
(XII)	35	MoOCl$_4$	6.0	CaCl$_2$	40.0	2.0	$(Mo_2O_2Cl_8)^{2-}(CaL_8)^{2+}$	4.0	20	(B)	105–16 (decomp.)	(C)	n.d.
(XIII)	40	WOCl$_4$	9.0	MgCl$_2$	15.0	1.5	$(WOCl_5)_2^-(MgL_6)^{2+}\cdot 2L$	4.2	25	(E)	230–3	(D)	n.d.
(XIV)	25	FeCl$_3$	20.0	BeCl$_2$	8.8	1.0	$(FeCl_4)_2^-(BeL_4)^{2+}\cdot 2L$	3.0	30	(F)	200 (decomp.)	(E)	n.d.
(XV)	40	FeCl$_3$	12.5	MgCl$_2$	11.0	2.0	$(FeCl_4)_2^-(MgL_6)^{2+}$	4.5	30	(F)	230–5	(A)	n.d.
(XVI)	45	AlCl$_3$	20.0	MgCl$_2$	10.0	2.0	$(AlCl_4)_2^-(MgL_6)^{2-}$	10.5	60	(G)	n.d.	(A)	n.d.

[a] Prepared with the extraction method (see Experimental section) except complexes (IX) and (XIV).

[b] Based on elemental analyses reported in Table III, and also on x-ray structural determinations in the case of complexes (X) and (XI).

[c] Based on the chloride used in minor amount.

[d] (A) = black; (B) = green needles; (C) = brown yellow; (D) = emerald green; (E) = red prisms; (F) pale-yellow lamellae; (G) = colorless needles.

[e] Uncorrected values; n.d. = not determined.

[f] Main absorption bands; (A) $\nu_{P=O}$ = 1270; (B) $\nu_{P=O}$ = 1267, $\nu_{Mo=O}$ = 1000, ν_{Cl} = 1185; (C) $\nu_{P=O}$ = 1265, $\nu_{Mo=O}$ = 995; (D) $\nu_{P=O}$ = 1270, $\nu_{W=O}$ = 995; (E) $\nu_{P=O}$ = 1220, ν_{Cl} = 730 cm^{-1}.

[g] (A) Space group = Triclinic, P-1; unit-cell constant: a = 12.643, b = 11.830, c = 11.142 Å; α = 118.0, β = 90.2, γ = 111.1°; Z = 1; (B) space group = monoclinic $P2_1/c$; unit-cell constants a = 12.666, b = 11.239, c = 20.890 Å; β = 114.2°; Z = 4.

[h] Obtained from complex (X) by heating.

products were obtained since commercial $MgCl_2$ contains insoluble undisclosed material. A Kumagawa extractor was equipped with a porous glass (G3-type) thimble in which the desired amounts of earth-alkali metal chloride and the transition metal chloride (or $AlCl_3$) were introduced.

An excess of $POCl_3$ was charged in the extractor flask, whose gentle reflux allowed the reaction between the salts by dissolving them. When the thimble did not contain any more soluble material (at this point the extracting liquid was colorless in the case of $VOCl_3$), the extraction was stopped and the reaction solution was cooled at room temperature. In both procedures, the crystalline product was collected by filtration, washed twice with 5-ml portions of $POCl_3$ or $C_6H_5POCl_2$ and twice with dry n-heptane, and then dried under reduced pressure. An excess of the transition metal chloride is without influence on the purity of the resulting complex salt since its adduct with $POCl_3$ or $C_6H_5POCl_2$ is much more soluble in the excess of the phosphorous derivative than the complex salt.

All the complex salts listed in Tables I and II are practically insoluble in apolar organic solvents, e.g., aliphatic or aromatic hydrocarbons, except. berillium chlorotitanates, berillium oxychloromolibdate, and magnesium titanate (VI). All of them can be recrystallized unaltered from chlorobenzene. Magnesium chlorotitanates and oxychloromolibdates are soluble in CH_2Cl_2, but they are prone to decomposition on standing in this solvent. Other solvents are pyridine, organic esters, and cyclic ethers, but the complex salts recovered from them are altered. Therefore, the best solvent for the purification of the products listed in Tables I and II is the ligand itself.

Polymerization

The equipment, some reagents, and the procedure adopted were described previously.[1]

Analyses

The elemental analysis of the complex salts was carried out according to ASTM methods.[26] Ti, V, and Fe were determined photometrically (Optika II instrument) according to the method employing H_2O_2, sodium tungstate, and o-phenathroline, respectively. Mg, Ca, and Sr were evaluated through atomic absorption spectroscopy (Perkin–Elmer model 503 instrument).

Mo, W, and P contents were obtained gravimetrically as oxides after precipitation with α-benzoyloxime, cinchonine, and alkalimetrically, respectively, after the precipitation of ammonium phosphomolibdate. Al and Cl were determined as reported previously.[1] Melting points were measured in glass capillaries sealed under N_2. IR spectra were recorded with a Perkin–Elmer model 157 instrument from powders in nujol.

^{1}H-NMR investigations were performed on CH_2Cl_2 (at 35°C) or C_6H_5Cl (at 90°C) solutions of complex (VI) and $(CH_3)_2Hg$ with a Varian instrument, model HA 100. The values of chemical shift were calculated from the signal of protons of $(CH_3)_2Hg$. ESR investigations were carried out with a Varian 4502-11 spectrometer at a field modulation of 100 KHz and at the liquid nitrogen temperature. The resonance frequencies were derived by standardization with DPPM.

RESULTS AND DISCUSSION

Synthesis of Complex Chlorides Containing Transition Metals or Al and Metals of the IIA Group

The affinity of transition metal salts with salts of IIA group metals have been recently calculated on the basis of calorimetric data,[27] but the formation of the corresponding complex salts has not yet been verified. On the basis of our work (described later in this article), it is doubtful that the binary chlorides previously mentioned can be synthesized in the absence of electron donors which seem to display a stabilizing role in the complex molecule. Furthermore, we have observed that the conditions adopted to obtain crystalline binary chlorides of Ti(IV) with bivalent metals of the IIA group are not suitable to prepare the corresponding complex salts of Zr(IV). Similarly, the chlorides of the IIA group metals cannot be replaced by other bivalent metal chlorides, e.g., $MnCl_2$, $NiCl_2$, or $ZnCl_2$, even though the ionic radius of the corresponding elements is between 0.74 and 0.80 Å of the value of Mg and Ca ions (0.65 and 0.99 Å, respectively). Conversely, alkali metals (mainly K and Cs) enter cations associated with anions containing Ti(IV)[28,29] or Ti(III).[30]

Therefore, there is scarce knowledge of the conditions presiding at the formation of complex salts involving transition metal halides to predict their existence and stability with sufficient certainty.

We have found that $TiCl_4$, $VOCl_3$, $MoOCl_4$, $WOCl_4$, and $AlCl_3$ react with Be, Mg, Ca, or Sr chlorides in the presence of electron donors such as $POCl_3$ or $C_6H_5POCl_2$. Mixed salts having defined stoichiometry and structure were obtained with good yields (cf. Tables I–III). On the contrary, no complex salt was observed to form when the previously mentioned interactions were carried out in the absence of any electron donor molecule.

The ligand ability of $POCl_3$ with $TiCl_4$ was known, since two complexes, having a well-characterized structure, were previously prepared,[31] i.e., $TiCl_4 \cdot POCl_3$ and $Ti_2Cl_8 \cdot 2POCl_3$. We used a large excess of the electron donor (cf. Experimental section) in which both the transition metal and the earth-alkali metal derivative progressively dissolved at the boiling temperature of the "solvent" as the reaction went on.

TABLE III
Elemental Analyses of the Complex Salts Reported in Table II

Complex No.	Results[a]
(VII)	V = 4.2 (4.2), Mg = 1.8 (2.0), P = 15.8 (15.4), Cl = 69.5 (70.4)
(VIII)	V = 4.2 (4.5), Ca = 3.4 (3.3), P = 15.0 (15.2), Cl n.d. (69.5)
(IX)	Mo = 12.7 (13.4), Be n.d. (0.6), P = 12.6 (12.9), Cl = 64.2 (63.6)
(XI)[b]	Mo = 10.8 (10.9), Mg = 1.4 (1.4), P = 15.0 (14.1), Cl = 64.0 (64.5)
(XII)	Mo = 11.0 (10.8), Ca = 2.6 (2.3), P = 14.0 (14.0), Cl n.d. (64.0)
(XIII)	W = 17.5 (18.3), Mg = 1.2 (1.2), P n.d. (12.0), Cl = 59.9 (60.3)
(XIV)	Fe = 8.6 (9.6), Be n.d. (0.8), P = 12.8 (13.2), Cl = 66.8 (69.6)
(XV)	Fe = 7.9 (8.3), Mg = 1.4 (1.8), P = 14.8 (13.8), Cl = 68.8 (68.8)
(XVI)	Al = 4.1 (4.2), Mg = 1.5 (1.6), P = 15.4 (15.6), Cl = 69.9 (71.4)

[a] The calculated values from the formulae of Table II are given in parentheses; n.d. = not determined.

[b] Complex (X) is isomeric of complex (XI) (cf. Fig. 2).

Table I shows the results obtained when $TiCl_4$ or $TiCl_3$ were allowed to react with $BeCl_2$, $MgCl_2$, $CaCl_2$, or $SrCl_2$. It is worth noting that attempts carried out with $BaCl_2$ were unsuccessful perhaps because of the relatively low charge density, depending in turn on the large size of the ionic radius of Ba (1.35 Å) which may hinder the hexaco-ordination of ligands. The results obtained by using transition metal chlorides or oxychlorides different from Ti derivatives are reported in Table II. X-ray investigations[32] performed on the crystalline products containing the Ti atom have shown that the transition metal enters one of the three arrangements described by the schemes represented in Figure 1. Interestingly, the structural features of the crystalline complex salts described in this article, which will be fully discussed in another work,[32] indicate that they have to be considered chlorotitanates of different electropositive metals, displaying an ionic character.

The hexaco-ordination of the Ti(IV) ion in the complex salts synthesized by us is the same existing in the violet crystalline forms of $TiCl_3$. It is worth noting that the octaedric ion $(TiCl_6)^{2-}$, typical of arrangement B (Fig. 1), is isolated in an NaCl-like cubic crystalline matrix of the complex salt. Therefore, it is of interest to study the catalytic behavior of the systems based on chlorotitanates
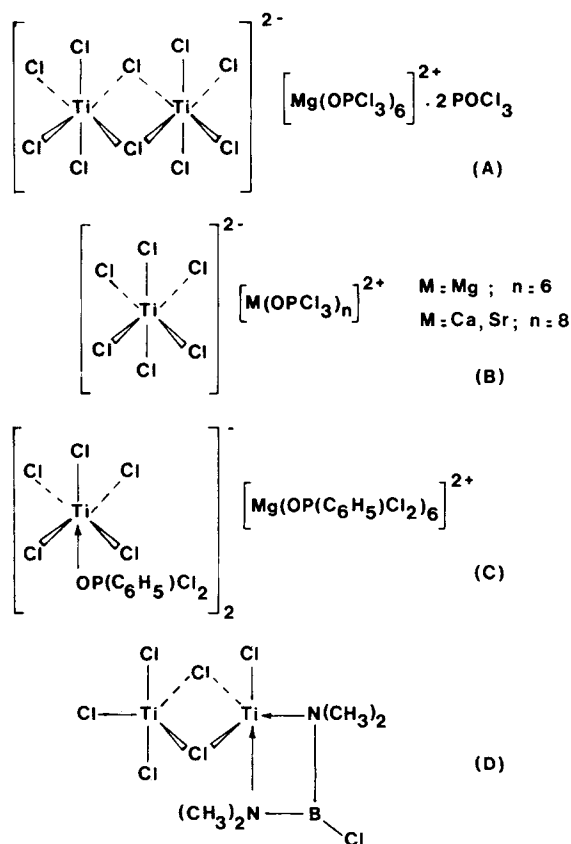

Fig. 1. X-ray structures of some chlorotitanates described in this work.[32] (A) found for complex (II); (B) found for complexes (III), (IV), and (V), respectively; (C) found for complex (VI), (D) from ref. 33.

of different earth-alkali metals by comparing them with catalysts containing supported Ti halides[6-19] or solid solutions of $TiCl_3$.[1,2]

Figure 1 shows that only the weaker electron donor, i.e., $C_6H_5POCl_2$, can be a ligand of the Ti anion, while each cation is coordinatively saturated by a number of electron donor molecules which depend on the ionic radius of the earth-alkali metal. Structure B of Figure 1, containing the isolated ion $(TiCl_6)^{2-}$, was previously found in the complex salts, already mentioned, containing K, Rb, or Cs cation,[28-30] while dimeric structure A was ascertained to exist through x-ray investigations in salt $(PCl_4)_2^+(Ti_2Cl_{10})^{2-}$ (ref. 34). Conversely, structure C, containing an electron-donor ligand on the Ti ion, is rather unusual and shows some analogy with structure D which contains bisdimethylamide borochloride as bidentate ligand.[33] Product (V) (see Table I), displaying structure B, has been prepared from $TiCl_3$. Therefore, a chlorination action exerted by $POCl_3$ and accompanied by oxidation of Ti(III) to Ti(IV) has to be postulated. A similar chlorination has been observed during the synthesis of product $(VCl_6)^{2-}$ $[Mg(POCl_3)_6]^{2+}$ [(VII); see Table II] obtained from both VCl_3 or $VOCl_3$. However, in the latter case, the chlorination is accompanied by the reduction of V(V) to V(IV). Product (VII) did not show any IR absorption in the region between 780 and 1000 cm^{-1}, where V=O and V—O—V groups exhibit typical bands. In the literature,[35] it is reported that chlorinating agents are able to replace the oxygen of chlorovanadyl salts with chlorine atoms, e.g.,

$$M_2VOCl_4 + SOCl_2 \rightarrow M_2VCl_6 + SO_2 \qquad (1)$$

Conversely, no chlorination process was observed when $MoOCl_4$ and different earth-alkali metal chlorides were allowed to react in the presence of $POCl_3$ [cf. products (IX)–(XII) in Table II]. An analogous result was obtained by reacting $WOCl_4$ and $MgCl_2$ [product (XIII)]. However, the salts obtained from $MoOCl_4$ contained the transition metal in the pentavalent form, whereas the valency state of W in its corresponding complex salt remained unchanged. The reduction of Mo(VI) to Mo(V), both thermally and in the presence of ligands, is an easy process when the transition metal is in the form of oxychloride.[24] A similar situation is observed for $VOCl_3$ (see above) since the more stable valency state is not the highest but the intermediate one.

Two isomers were obtained from $MoOCl_4$ and $MgCl_2$, i.e., yellow-brown salt (X) and green salt (XI) (see Table II). The former, obtainable after 0.2 hr of reaction, was transformable by heating (80–100°C) into product (XI); the latter resulted after the usual reaction time (2 hr). The structure of isomer (XI) was determined by x-ray diffraction analysis[32] and is drawn in Figure 2. Isomers (X) (cis) and (XI) (trans) contain the oxygen atoms in different situations, but not in the bridge position, since the absorptions typical of this arrangement[36] are lacking in their IR spectra.

All the products listed in Tables I and II are indefinitely stable at room temperature under inert atmosphere, except the complex salts containing W and Al, i.e., products (XIII) and (XVI) in Table II, since they show the tendency to lose $POCl_3$.

Several bromoaluminates of IIA group metals, i.e., $M^{2+}(AlBr_4)_2^-$, were prepared by melting Mg, Ca, Zn, or Cd bromide (or chloride) with $AlBr_3$.[37] When $AlCl_3$ was used[38] only derivative $Ba^{2+}(Al_2Cl_8)^{2-}$ was obtained. Very likely, these salts possess a good stability even when electron donors are not present in the complex molecule, but this does not occur in the case of Mg chloroaluminate.
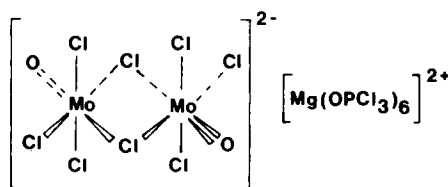
(E)
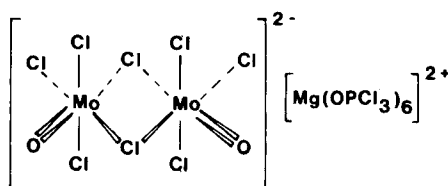
(F)

Fig. 2. X-ray structures of two isomers of Mg oxychloromolibdate; (E) = complex (XI) and (F) = complex (X) in Table II.

Polymerization of Ethylene

The complex salts described in the previous section are able to polymerize ethylene or to copolymerize it with α-olefins when they are associated with $Al(i\text{-}C_4H_9)_3$. Conversely, these systems are unable to polymerize propylene. However, the overall catalytic efficiency can reach high values of up to 400 kg of HDPE/g Ti, when Mg chlorotitanates are used. These results refer to polymerization experiments carried out for 6 hr in the presence of H_2, used as chain-transfer agent in different concentration, and with overall pressure $p\text{-}C_2H_4$ + $p\text{-}H_2$ = 13 atm.

The average polymerization rates observed for chlorotitanate containing four different metals of the IIA group are shown in Figure 3. The same figure shows the MFI values of the resulting polymers which are related to $\overline{M}_n$ through the Queckebans equation.[39]

HDPE polydispersity has been evaluated by shear sensitivity measurements,[2] and in the samples of polymer prepared with chlorotitanate-based systems it was found to be constantly rather low, $\overline{M}_w/\overline{M}_n$ = 3.5–5. These results differ greatly from the polydispersity indexes evaluated for classical heterogeneous Ziegler–Natta systems which are in the range 3–20. Conversely, soluble (at least in great part) catalysts yield HDPE having $\overline{M}_w/\overline{M}_n$ = 2.[13]

Figure 4 shows the same parameters as those of Figure 3 obtained with Mg chlorotitanates having structures A, B, and C of Figure 1, respectively. Higher catalytic efficiency and MFI value were displayed by systems containing isolated Ti(IV) ion, i.e., arrangements B and C.

The average polymerization rates obtained with catalysts based on chlorovanadates are about one order of magnitude lower than those exhibited by chlorotitanates, but at the same time, chlorovanadate-based systems are more sensitive to the MW regulating action of H_2.
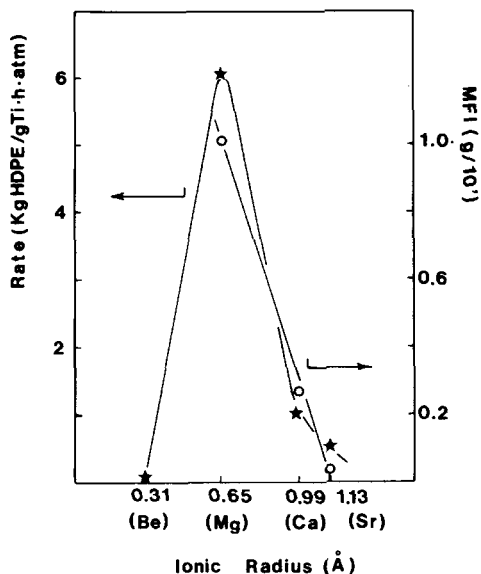
Fig. 3. Average polymerization rate and MFI of HDPE obtained with chlorotitanates of different earth-alkali metals having structure B of Fig. 1 (except the Be derivative) vs. their ionic radius. Conditions: complex salt = 25–100 mg/l.; Al $(i\text{-}C_4H_9)_3$ = 8 mmol/l.; n-heptane = 1 l.; T = 85°C; $p\text{-}C_2H_4$ = 10 atm; $p\text{-}H_2$ = 3 atm; time = 5 hr.

The polymerization rates exhibited by systems based on Mg chlorotitanates reach maximum values within the first and the second hour of polymerization (Fig. 5), because the used complex salts were in the form of relatively large crystals (sizes of up to 1–2 mm) and they needed some time to be grinded or dissolved during the early polymerization time. In fact, when the crystals were grinded in a ball mill or were supported upon an inert carrier, no induction time
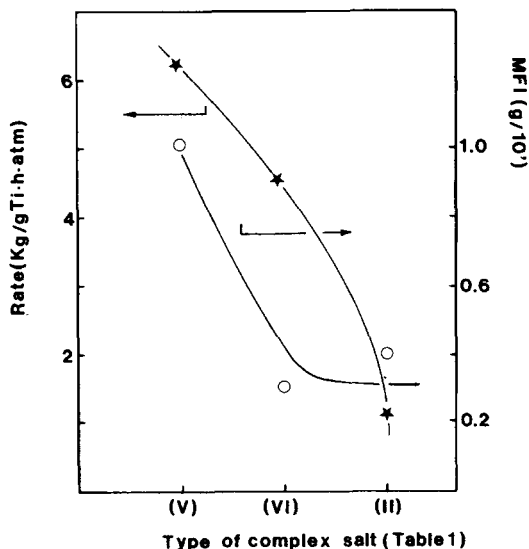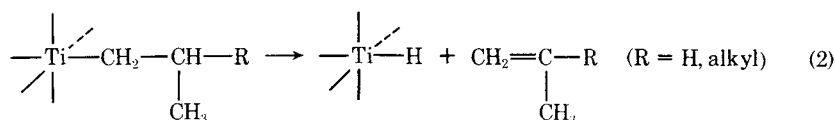

Fig. 4. Average polymerization rate and MFI of HDPE obtained with Mg chlorotitanates having structures B, C, and A, respectively, of Fig. 1. Complex salt = 25–40 mg/l.; other conditions as in Fig. 3.

was observed (Fig. 6).   However, the size and the morphological aspects of chlorotitanates have no influence on the overall catalytic activity, provided that long enough polymerization times, e.g., 6 hr, were adopted.

This means that occlusion phenomena affecting the active sites are of scarce importance in these systems.   Certainly, the first amount of HDPE is formed on a heterogeneous catalyst since the cubic lattice of the chlorotitanates is replicated in the cubic shape of part of the polymer particles, at least in the case of complex (V) (Fig. 7).   However, the diffusion of the monomer and co-catalyst through the shell of the early formed polymer involves, probably, a solubilization process of the Ti ions constituting the bulk of crystals of Mg chlorotitanate.   Such a process has to be invoked to account for the high activity of the catalyst system based on complex (VI).   Conversely, a grinding process, which is usually postulated in the case of HDPE synthesis with heterogeneous systems,[15] would destroy the apparent morphology of the polymer shown in Figure 7.   Polymerization experiments with conjugated dienes indicate that homogeneous solutions were formed in the particular cases where Mg chlorotitanates-based systems were used.   The lack of propylene polymerization might support the solubilization of Ti atoms since the presence of a heterogeneous catalyst greatly favors the synthesis of polypropylene.[4]   More likely, the high electron affinity of Ti in $(TiCl_6)^{2-}$ ion, which carries typical acceptor ligands, induces favorably β-hydrogen elimination,[41] i.e., hydrogen transfer

$$-\overset{|}{\underset{/}{Ti}}{-}CH_2{-}\underset{\underset{CH_3}{|}}{CH}{-}R \longrightarrow -\overset{|}{\underset{/}{Ti}}{-}H + CH_2{=}\underset{\underset{CH_3}{|}}{C}{-}R \quad (R = H, alkyl) \quad (2)$$

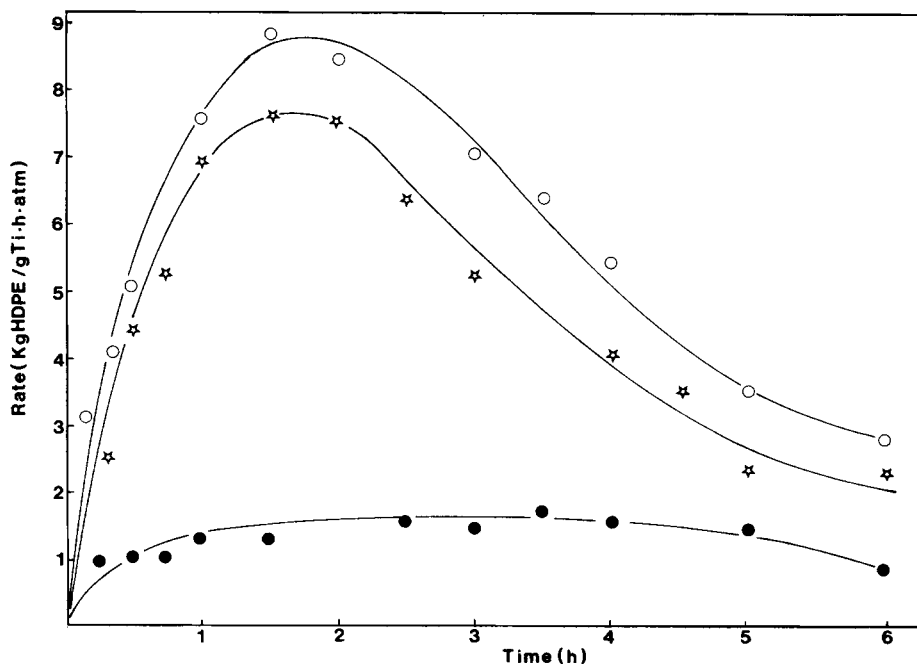so that the chain growth process is practically impossible.

Fig. 5.   Instantaneous polymerization rate of ethylene with: ($\bigcirc$) = complex (V), Ti = 1.0 mg/l.; ($\star$) = complex (VI), Ti = 1.25 mg/l; ($\bullet$) = complex (III), Ti = 3.54 mg/l.   Other conditions as in Fig. 3.
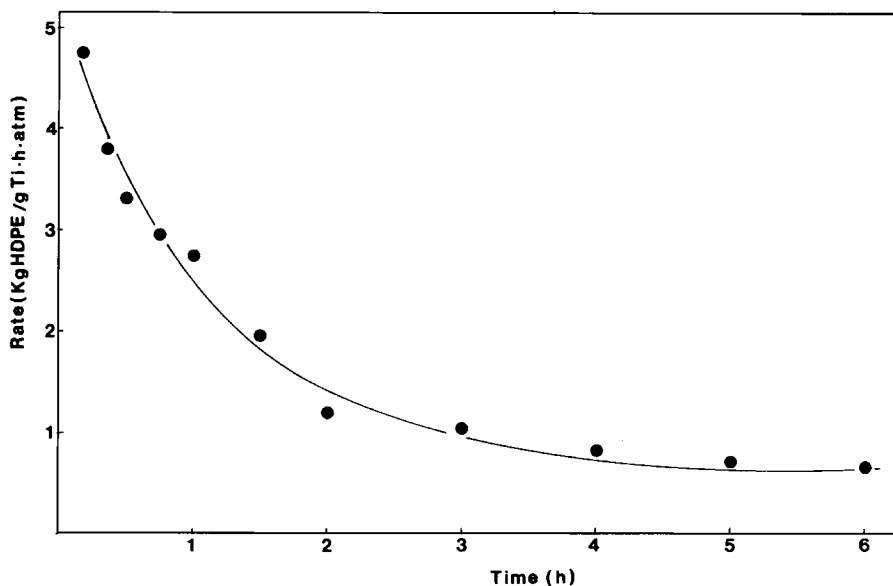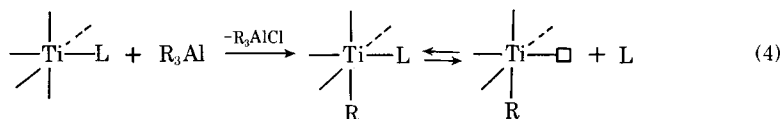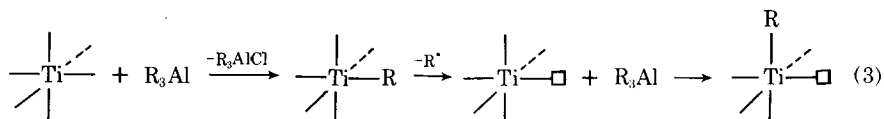
Fig. 6. Instantaneous polymerization rate of ethylene with complex (II) supported on a polystyrene resin (1% of Mg; see Experimental section). Ti = 3.94 mg/l.; other conditions as in Fig. 3.

While the active centers formed initially through the alkylation of the surface of chlorotitanate crystals are mainly based on Ti(IV) ions, dissolved $(TiCl_6)^{2-}$ or $(TiCl_5L)^-$ ions need the removal of two Cl ligands or one Cl ligand, respectively, to give rise to active sites:

$$—Ti— + R_3Al \xrightarrow{-R_3AlCl} —Ti—R \xrightarrow{-R^\cdot} —Ti—\Box + R_3Al \longrightarrow —Ti—\Box \quad (3)$$

$$—Ti—L + R_3Al \xrightarrow{-R_3AlCl} —Ti—L \leftrightarrows —Ti—\Box + L \quad (4)$$

In other words, in the absence of olefinic ligands the Ti atom of $(TiCl_6)^{-2}$ and of $(TiCl_5L)^-$ is reduced to Ti(III) by alkylating agents. In fact, yellow solutions of complex (VI) turned to green when an excess of $(CH_3)_2Hg$ was added. $(CH_3)_2Hg$ was used since it is unreactive toward $POCl_3$. ESR measurements indicated that unidentified paramagnetic species were formed during the interaction of complex (VI) and $(CH_3)_2Hg$, while ^1H–NMR investigations showed that CH_3HgCl concentration was progressively increasing (signal at 0.48 and 0.80 ppm, respectively, at 35 and 90°C). At the same time, a weak signal at 2.50 and 2.72 ppm (at 35 and 90°C, respectively) suggested that a thermolabile alkylated species of Ti was present in the reaction solution. However, from the catalytic point of view, the distinction between Ti(IV) and Ti(III) species is difficult to achieve and seems of scarce importance in HDPE synthesis since the chemical facts involved in alkylation, coordination, and polymerization steps are mainly governed by factors different from the Ti valency.

Quite surprising and obscure is the almost negligible catalytic activity of Be chlorotitanate (Fig. 3). Unfortunately, we have not yet obtained the definition of the structure of this crystalline product, so we cannot correlate its catalytic inefficiency with possible unusual structural features. Apparently, both chemical and structural factors are involved in the catalytic behavior of chlorotitanates of the IIA group metals.

The results of Figure 4 show directly that more than one structural arrangement of the Ti ion can generate active centers and confirm previous findings concerning the multiplicity of active species in Ziegler–Natta systems. However, the MWD of HDPE, obtained with Mg chlorotitanate-based systems, is constantly rather narrow, and this result might suggest that a limited number of types of active species originates from each chlorotitanate used. But also the pseudo-homogeneous way of working of this kind of catalyst might account for the MWD data. According to our work, Mg chlorotitanates containing isolated Ti(IV) ions can be obtained by using an appropriate ligand and a low atomic ratio Mg:Ti, i.e., ≤ 1. Contrarily, heterogeneous catalyst systems containing a Ti halide on carrier need high values of the Mg:Ti ratio, i.e., $\gg 1$, to attain the highest efficiency which can be reached in the most favorable conditions, $3–10.10^3$ kg polymer/g Ti.[7,15]

In some supported catalysts, the Ti ions appear substantially decoupled by ESR measurements,[4,40] i.e., in the form of isolated, octaedrally coordinated ions, as observed in structure B of Figure 1.[32]

Such a situation is very likely a general condition for obtaining a high catalytic efficiency and, hence, a high utilization of the Ti atoms in forming the active centers. In the case of heterogeneous systems, the dilution of Ti ions in the solid matrix has to be accompanied by a very small size of the carrier particles. Evidently, this condition is not necessary in the case of soluble systems, as Mg chlorotitanate-based catalysts seem to be. However, it is worth noting that an excess of Mg compound with respect to the Ti halide is of crucial importance for
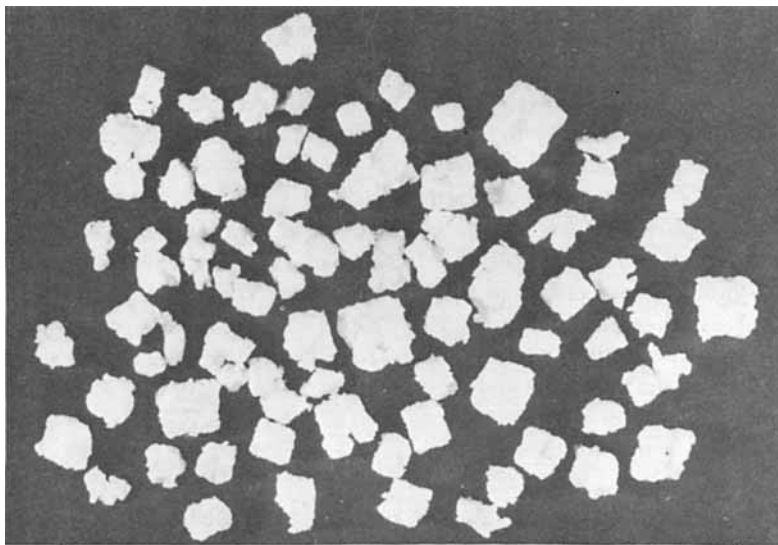

Fig. 7. Aspect of HDPE synthesized with the catalyst system based on complex (VI).
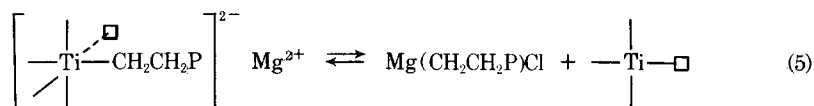
reaching the highest efficiencies, which are about an order of magnitude higher than that of the best Mg chlorotitanate-based system.

This result is to be ascribed to the role played by Mg ions which appears, on the basis of our work and previous investigations,[4-19] to be at least fourfold.

(1) Ti ions are diluted by Mg ions by entering the crystalline matrix of complex salts (case of chlorotitanates) and of solid solutions ($MgCl_2$ and $TiCl_3$ are isomorphous), or by anchoring Ti species on the surface of the carrier. In the last case, the Mg ion is not essential and the carrier can be formed by compounds which do not contain Mg at all, e.g., aluminum silicate,[8,9] SiO_2[4,40] or Al_2O_3.[4] In each case, this distribution effect influences the number of active centers[9,11,13] which tend to be isolated, as discussed previously. Their amount is at least an order of magnitude higher than in classical coordination catalysts.

(2) The active centers formed by alkylation of Ti halides, i.e., the Ti—C bonds where the polymer chains grow, are stabilized by the presence of Mg ions. The effect depends, in turn, on the type of ligand of Mg ion as proved directly in this work and previous kinetic investigations,[7,9,11,13] which showed a marked influence on the propagation rate constant by the type of carrier. In this respect, the Mg ions play a specific role which is not common to other IIA group metals or carriers not containing Mg ions. The presence of an excess of Mg compound with respect to Ti halide implies usually the heterogeneity of the catalyst. Such a situation apparently increases the stability of the active centers as indicated by kinetic determinations,[13] because the deactivation processes of active sites are reduced with respect to soluble systems (cf. also the subsequent point).

(3) Chain transfer processes are enhanced by the presence of Mg ions since $\overline{M}_n$ of HDPE decreases when the Mg:Ti ratio increases, both in partly homogeneous systems (Fig. 3) and supposed heterogeneous systems.[17] This peculiar effect of Mg ions might be accounted for by an alkyl exchange between the Ti ligands and the Mg ion,

$$\left[\begin{array}{c} | \quad \square \\ -\overset{|}{\underset{/}{Ti}}{-}CH_2CH_2P \\ | \end{array} \right]^{2-} Mg^{2+} \;\rightleftharpoons\; Mg(CH_2CH_2P)Cl \;+\; -\overset{|}{\underset{|}{Ti}}{-}\square \qquad (5)$$

which is practically a chain-breaking reaction when the equilibrium is shifted to the right. At the same time, reduced and probably inactive Ti species are formed. However, in the presence of an excess of AlR_3 and $MgCl_2$ (this in the case of several heterogeneous high-yield catalysts), some amount of RMgCl might be formed and the equilibrium (5) would not be shifted to the right, thus the degeneration of active species would be limited.

(4) Despite the numerous, possible structural arrangements of the Ti ions which can give rise to active sites, the presence of Mg ions favors the homogeneity of the polymerization centers as it can be inferred from MWD data (see Table IV and ref. 9). Very likely, only those Ti ions which are able to accommodate Mg ions in their proximity benefit from the stabilizing effect induced by this peculiar earth-alkali metal.

CONCLUSIONS

The present work has demonstrated that it is possible to synthesize complex salts of transition metal chlorides with chlorides of elements belonging to the

TABLE IV

Properties of HDPE Obtained with the Catalyst System Based on Complex (VI)

Run No.	p-H_2,[a] atm.	Catalyst efficiency, Kg pol/H/g Ti	Ashes in the polymers, ppm			MFI, g/10 min	Shear sensitivity[b]	Density, g/cm^3	Impact resistance, J/m	Flexural modulus, MPa	Yield strength, MPa	Tensile at break, MPa	Elongation at break, %	ESC, hr	$\dot{\gamma}_c$, sec^{-1}	Corrosivity
			Ti	Cl	P											
1	3	230	4.6	29	4.7	0.37	30	0.9654	721	1500	28	39	1106	82	130	0–1
2	4	210	4.8	30	4.7	0.57	34	0.9660	498	1260	29	37	1183	64	315	0–1
3	5	200	5.0	33	3.3	0.92	30	0.9677	319	1236	29	35	1248	54	420	0–1

[a] Other conditions: Ti = 0.03 mmole/l.; $(i\text{-}C_4H_9)_3Al$ = 4.0 mmole/l.; n-heptane 1 l.; T = 85°C; time = 4 hr; p-C_2H_4 = 10 atm.

[b] $(MFI)_{21.6}/(MFI)_{2.16}$.

[c] Ratings 0–1 classed as noncorrosive.

IIA group of the Periodic Table. They display peculiar structural features shown by x-ray investigations. In particular, complex salts of $TiCl_4$ and $MgCl_2$ can exist in three different structural arrangements, provided that a donor molecule such as $POCl_3$ enters the complex molecules. One of these structures (B in Fig. 1) is of particular catalytic interest since it contains isolated octaedral$(TiCl_6)^{2-}$ ions, similar to the arrangement postulated for the Ti ions in several high-yield catalysts for HDPE synthesis. Interestingly, Mg chlorotitanate having structure B realizes the separation of Ti ions with ratio Mg:Ti = 1, whereas Ti halide-based catalysts supported on Mg compounds need Mg:Ti ratios much higher to attain the separation of Ti ions, and, hence, the best efficiency.

However, Mg chlorotitanate-based systems exhibit catalytic efficiency which is about an order of magnitude lower than that of typical heterogeneous high-yield catalysts. Furthermore, they are unable to polymerize propylene. The formation of soluble catalytic species is believed to be responsible for the results obtained. In particular, some degeneration of active sites may explain the lower catalytic activity compared with that of heterogeneous systems. Tentatively, the degeneration process has been attributed to scrambling of ligands between Ti and Mg ions, which implies some chain breaking and the formation of low-valency Ti species assumed to be scarcely active, if any. The interpretation is supported by the influence exerted by the Mg ions on $\overline{M}_n$ of HDPE produced, as well as on the number of active centers and their stabilization.

The last feature is of overwhelming importance in explaining the behavior of several high-yield catalysts and appears a peculiar property of Mg not shared by other earth-alkali metals.

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