

Novel Binary Chlorides Containing TiCl_3 as Components of Coordination Catalysts for Ethylene Polymerization. I. Synthesis and Characterization of the Solid Solutions Obtained*

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Synopsis

New binary chlorides have been obtained by reacting TiCl_4 with $\text{V}(\text{CO})_6$, $\text{Cr}(\text{CO})_6$, $\text{Mn}_2(\text{CO})_{10}$, $\text{Mn}(\text{CO})_5\text{Cl}$, $\text{Ni}(\text{CO})_4$, $\text{Co}_2(\text{CO})_8$, $\text{Fe}(\text{CO})_5$, or $\text{Mo}(\text{CO})_6$. The reactions yield quantitatively mixed chlorides having the general formula $\text{MCl}_n \cdot n\text{TiCl}_3$, where $n = 2$ or 3 and M is a divalent or trivalent transition metal cation. MCl_n is generally isomorphous with the α - or γ -modification of TiCl_3 . X-Ray and spectroscopic investigations indicate that the mixed chlorides obtained are solid solutions. High surface area values are associated with the adducts displaying lower crystallinity. Catalyst efficiencies two or three times higher than that of $\text{AlCl}_3 \cdot 3\text{TiCl}_3$ were observed in the low-pressure polymerization of ethylene (HDPE) when some binary chloride was associated with $\text{Al}(i\text{-C}_4\text{H}_9)_3$. These results allow treating the obtained solid solutions as reference systems of high-yield catalysts for HDPE synthesis.

INTRODUCTION

The great importance of TiCl_3 in Ziegler-Natta catalyst systems used for synthesizing poly- α -olefins, in particular high-density polyethylene (HDPE) and isotactic polypropylene,¹ stems from its essential role in producing the active polymerization sites which are believed to be Ti-carbon bonds originated by the presence of an alkylating agent (cocatalyst).²

Much work has been undertaken in the last years to increase the efficiency of these systems and to improve their stereospecificity, so that new types of catalysts have been prepared recently.³ On the basis of this work, it has appeared that the performance of TiCl_3 -based catalysts depends not only on the crystalline form of TiCl_3 (four modifications, denoted as α -, β -, γ -, and δ -type, are known⁴), but also on the morphology of its solid phase which can assume different surface area value, and different volume and diameter of pores; and hence different distributions of the active centers can result.

The control of TiCl_3 morphology can be achieved more easily by distributing TiCl_3 on a carrier which may display different degrees of interaction with Ti chlorides. This fact avoids coalescence phenomena and maintains the initial morphology resulting from the specific method of preparation of TiCl_3 . However, these benefits for TiCl_3 performance are not always met when some metal halide is associated with TiCl_3 . This is certainly the case of AlCl_3 , which can

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be easily incorporated by TiCl_3 during the reduction of TiCl_4 with Al^5 or alkylaluminum derivatives.⁶ But the presence of AlCl_3 in TiCl_3 reduces somewhat the stereospecificity of the resulting catalyst even though it improves markedly the efficiency in the case of polypropylene synthesis.⁶ By contrast, the use of $\text{AlCl}_3\cdot 3\text{TiCl}_3$ solid solution does not attain high yield in the low-pressure polymerization of ethylene (Table V).

Magnesium compounds, which have been claimed to be excellent carriers of Ti chlorides and have been found to enhance by some two orders of magnitude the efficiency of conventional catalysts for the synthesis of HDPE³ present a different case. The role played by Mg-based carriers has not yet been well elucidated since attempts of explanation so far published were based on difficult kinetic experiments which, however, suggest that a relatively great amount of the Ti atoms present in the initial catalyst is involved in originating the active centers.⁷⁻¹¹ Conventional Ziegler-Natta catalysts are known to originate a number of active centers corresponding only to a few percent or less of all the Ti atoms.^{12,13}

As far as supported catalysts for ethylene polymerization are concerned, very little is known about (a) the stabilization of the active sites by the carrier; (b) the interaction of the carrier with the alkylating agent; (c) the modification of the original morphology of TiCl_3 during the polymerization and the influence on the catalyst efficiency; (d) the influence of the polymer molecular weight regulator on the catalyst performance; and (e) the dependence of the proportion of "working" titanium ions and TiCl_3 morphology on the conditions of catalyst preparation. A contribution for tackling some of these problems could be expected to come from the study of mixed chlorides of TiCl_3 with different metal halides, both from the structural point of view and as components of catalysts displaying peculiar performances. They can be considered, in fact, as reference systems of the most active supported catalysts because, in general, they have been found more active than unsupported TiCl_3 -based systems (Table V).

However, there are some difficulties in preparing mixed chlorides of TiCl_3 ,^{14,15} since the mechanical incorporation of two powders may give inhomogeneous mixtures, even though they are isomorphous. Furthermore, crystalline solids furnish final powders which show low surface area values even after prolonged milling. Finally, some contamination of the resulting mixture may occur during the grinding process.

Despite these difficulties, interesting results have been achieved by extensive dry-ball milling of TiCl_3 and AlCl_3 .¹⁴⁻¹⁶ On the other hand, the reaction of TiCl_4 with several metals, e.g., Mg, Ni, Fe, Mn, etc., requires polar solvents or high temperatures, sometime above that of TiCl_3 decomposition (ca. 500°C), so that the reduction of TiCl_4 occurs with poor yield (ca. 5%–10%).^{17,30}

The preparation of $\text{AlCl}_3\cdot 3\text{TiCl}_3$ can be carried out at 250°C when powdered Al is employed to reduce TiCl_4 , but the raw material shows poor catalytic efficiency and needs further activation treatment.¹⁸ Organometallic compounds can reduce TiCl_4 to TiCl_3 , but this approach is not always feasible (e.g., in the case of transition metals).

In part I of this work, we describe a new method to reduce selectively TiCl_4 to TiCl_3 by means of transition metal carbonyls having low valency states. Binary chlorides of TiCl_3 displaying definite stoichiometry and, usually, high surface area values have been obtained under mild conditions. They have been

characterized mainly through x-ray investigations and showed interesting performances during the low-pressure polymerization of ethylene (cf. part II).

RESULTS AND DISCUSSION

Reduction of TiCl_4 with Transition Metal Carbonyls

The reaction of transition metal carbonyls having low valency states with liquid TiCl_4 yields, under moderate conditions, a precipitate which is an intimate association of TiCl_3 with the chloride of the element used as carbonyl. Transition metal carbonyls are usually soluble in organic solvents and also in TiCl_4 , where some of them give colored solutions which are stable for many hours. The dissolution process of metal carbonyls in TiCl_4 may be favored by a complexation process between the Lewis acid and the base (carbonyl), as observed between AlCl_3 and $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$.¹⁹

Very likely, this complexation is the preliminary step occurring before metal carbonyl decomposition initiates. However, the evolution of carbon monoxide takes place speedily at the boiling temperature of TiCl_4 (140°C), but sometimes it can be observed also at temperatures lower than the ambient value. According to the general reaction scheme



the reaction products are in part volatile and hence easily separated from the reaction mixture, while the transition metal may be assumed to react in the atomic state after the decomposition of the carbonyl. In fact, the formation of the adduct of TiCl_3 with MCl_n is observed to occur as soon as the evolution of CO begins.

The stoichiometry of the resulting association is usually defined rather well and is regulated by the oxidation of the transition metal to a definite valency state, while TiCl_4 is always reduced to Ti(III). The complexation of some TiCl_4 molecules per each carbonyl molecule through CO ligands and the reaction of discrete and constant amounts of metal (as soon as it is formed from the decomposition of the carbonyl) with the TiCl_4 molecules to which it is associated can explain the cocrystallization of binary chlorides with constant stoichiometry.

TABLE I
Grinding of Equimolar Amounts of TiCl_3^a and MnCl_2^b and Catalytic Activity of Resulting Mixture in Ethylene Polymerization

Time of grinding, ^c hr	Surface area, m^2/g	Average catalyst polymerization rate ^d
48	—	850
100	—	1040
130	38	910
Reference ^e	157	2800

^a TiCl_3 -H type (Stauffer Co.).

^b Prepared according to ref. 31.

^c Carried out in a rotating stainless mill (see experimental section).

^d Calculated as $\text{g polymer}/(\text{g Ti} \times \text{atm C}_2\text{H}_4 \times \text{hr})$. Conditions: *n*-hexane; $T = 85^\circ\text{C}$; $t = 2$ hr; $[\text{Al}(i\text{-C}_4\text{H}_9)_3] = 8.0$ mmole/l; $[\text{TiCl}_3] = 0.11\text{--}0.14$ mmole/l; $P_{\text{C}_2\text{H}_4} = 5$ atm; $P_{\text{H}_2} = 5$ atm.

^e MnTiCl_5 , prepared as described in this work and employed without preliminary grinding.

TABLE II
Properties of Binary Chlorides Containing TiCl_3

Compound no.	Composition	Elemental analysis ^a			Color	Electronic spectrum absorptions nm	Type of Crystall. Phase	Degree of crystall. ^b	Ionic Radius of M^h	Q^c	Surface area, m^2/g
		Ti	M	Cl							
Ref.	$\text{AlTi}_3\text{Cl}_{12}$	24.1 (24.1)	4.3 (4.5)	71.6 (71.4)	red-violet	520 (vb) 372 (sh)	+++	0.53	1.26	20	
I	$\text{CrTi}_3\text{Cl}_{12}$	24.4 (23.1)	8.7 (8.3)	67.1 (68.5)	violet	535 (vb) 470 (sh) 372	+++	0.62	1.08	18	
I ^d	$\text{CrTi}_3\text{Cl}_{12}$	24.4 (23.1)	8.7 (8.3)	67.1 (68.5)	violet	n.d.	+	0.62	1.08	8	
II	$\text{MoTi}_3\text{Cl}_{12}$	23.3 (21.6)	15.7 (14.4)	63.0 (64.0)	brown	n.d.	+++	0.67	1.00	n.d.	
III	FeTi_2Cl_8	21.7 (22.0)	12.7 (12.8)	66.9 (65.2)	red-brown	no definite absorption	++	0.78	0.86	113	
III ^e	FeTi_2Cl_8	21.7 (22.0)	12.7 (12.8)	66.9 (65.2)	red-brown	n.d.	+	0.78	0.86	163	
III ^f	FeTi_2Cl_8	21.7 (22.0)	12.7 (12.8)	66.9 (65.2)	red-brown	n.d.	+++ β ++ γ	0.78	0.86	115	

IV	MnTi ₂ Cl ₈	21.8 (22.0)	12.7 (12.8)	65.5 (65.2)	red-violet	525 (vb)	γ	++	0.82	0.82	57
V	NiTi ₂ Cl ₈	22.3 (21.9)	13.3 (13.4)	63.8 (64.7)	black	350 (vb) n.d.	γ	++++	0.70	0.96	3
VI	MnTiCl ₅	19.3 (17.1)	20.2 (19.6)	60.2 (63.3)	red-violet	510 (vb)	γ	+	0.82	0.82	157
VII	VTi _{1,1} Cl _{6,7}	15.4	16.4	68.3	violet	350 (vb)	δ	++	0.64	1.05	39
VIII	CoTi _{1,6} Cl _{6,8}	20.9	15.9	63.2	brown	n.d.	γ	n.d.	0.74	0.91	n.d.

^a Data in parentheses are calculated values for the composition given.

^b Determined by evaluating the broadness of x-ray pattern: (+) low crystallization, (+++++) high crystallization.

^c Ratio of the ionic radius of Ti(III) referred to that of the metal ion Mⁿ⁺.

^d After dry grinding for 60 hr in a ball mill.

^e Obtained at -40°C and annealed at 140°C for 1 hr.

^f Obtained at -40°C and annealed at 80°C for 2 hr.

^g β-Phase practically coincident with β-TiCl₃.

^h Reference 20.

TABLE III
X-Ray Powder Data for Some Binary Chlorides Described in this Work

$\text{CrCl}_3 \cdot 3\text{TiCl}_3$		α -Phase		γ '-Phase		$\text{MoCl}_3 \cdot 3\text{TiCl}_3$		β '-Phase		γ -Phase		
I_0	d_0	hkl	d_c	hkl	d_c	hkl	I_0	d_0	hkl	d_c	hkl	d_c
vs	5.868	003	5.859				m	5.887			003	5.883
w	5.285			100	5.296		s	5.405	100	5.395		
w	5.046			101	5.069		vw	2.988			101	3.00
vw	4.524			102	4.533		s	2.743	111	2.746		
w	3.018			111	3.012		w	2.550	102	2.561		
mw	2.917						mw	2.498			104	2.506
s	2.703	113	2.707				s	2.122	112	2.127		
ms	2.511			114	2.508		w	2.037	210	2.039		
w	2.110						w	1.976	202	1.978		
vw	1.946						mw	1.797	300	1.798		
s	1.762	300	1.762				mw	1.756			110	1.758
mw	1.689	033	1.688	033	1.690		w	1.678				
vw	1.646	119	1.645				w	1.499				
vw	1.509	036	1.510				vw	1.455	004	1.455		
vw	1.477	223	1.477				vw	1.441			024	1.439
w	1.461			0012	1.461		vw	1.406	104	1.405		
vw	1.444			224	1.443		vw	1.375	222	1.373		
							w	1.1309	304	1.1312		
							vw	1.1138			214	1.1137

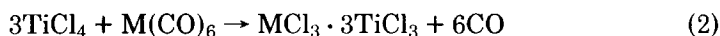
NiCl ₂ ·2TiCl ₃			γ-phase		
I ₀	d ₀	h k l	I ₀	d ₀	h k l
s	5.848	0 0 3		5.864	
mw	2.998	1 0 1		2.998	
w	2.926	0 0 6		2.932	
mw	2.867	0 1 2		2.875	
vs	2.502	1 0 4		2.502	
nw	2.298	0 1 5		2.301	
mw	1.937	1 0 7		1.938	
mw	1.783	0 1 8		1.782	
s	1.754	1 1 0		1.756	
mw	1.684	1 1 3		1.683	
w	1.509	0 2 1		1.515	
w	1.464	0 0 12		1.466	
mw	1.438	0 2 4		1.438	
vw	1.416	0 1 11		1.416	
w	1.252	2 0 8		1.251	
vw	1.1733	0 0 15		1.1727	
mw	1.1252	1 1 12		1.1255	
mw	1.1133	2 1 4		1.1125	
mw	1.0465	2 1 7		1.0456	
vw	1.0333	1 0 16		1.0340	

FeCl ₂ ·2TiCl ₃			γ-phase		
I ₀	d ₀	h k l	I ₀	d ₀	h k l
s	5.877	0 0 3		5.869	
w	3.018	1 0 1		3.030	
w	2.885	0 1 2		2.903	
s	2.519	1 0 4		2.521	
s	1.775	1 1 0		1.776	
w	1.703	1 1 3		1.700	

MnCl ₂ ·2TiCl ₃			γ-phase		
I ₀	d ₀	h k l	I ₀	d ₀	h k l
s	5.95			5.95	
vw	3.08			3.08	
vw	2.94			2.94	
vw	2.62			2.62	
w	1.824			1.824	
mw	1.791			1.791	

It is worth noting that the mixed chlorides described in this paper, which are exempt from organic material, cannot be obtained satisfactorily through other ways since, for instance, grinding of mixtures of single halides yields associations which show lower surface area values and lower catalytic activity toward the low-pressure polymerization of ethylene (cf. Table I). Metal carbonyls belonging to the first transition period, i.e., $V(CO)_6$, $Cr(CO)_6$, $Mn_2(CO)_{10}$, $Mn(CO)_5Cl$, $Ni(CO)_4$, $Co_2(CO)_8$, and $Fe(CO)_5$, but also carbonyls of the second period, e.g., $Mo(CO)_6$, can be used in reaction (1). Perhaps, also transition metal nitrosyl may be utilized to prepare binary chlorides containing $TiCl_3$.

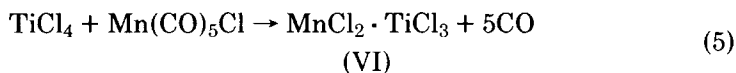
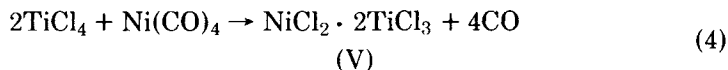
Actually, the following products I through VI have been obtained with quantitative yield through reactions (2) through (5):



where $M = Cr$ (I) and Mo (II),



where $n = 5$ and $M = Fe$ (III) or Mn (IV),



When $V(CO)_6$ and $Co_2(CO)_8$ were employed, the resulting mixed chlorides had the following composition: $VTi_{1.1}Cl_{6.7}$ (VII) and $CoTi_{1.6}Cl_{6.6}$ (VIII). The lack of a well-defined stoichiometry could be due to the partial solubility of V and Co carbonyls in the reaction medium and also to their thermal sensitivity (T_{dec} ca. $50^\circ C$), so that incompleteness of reaction resulted. In reality, as will be shown in the next section, x-ray investigations have allowed to conclude that solid solutions are always formed, even when the stoichiometry of the mixed chlorides is not well defined.

The binary chlorides obtained have been characterized by elemental analysis, electronic spectra in diffuse reflectance, x-ray analysis of the powders, and surface area measurements. The results obtained are collected in Table II and are compared with those resulting from $AlCl_3 \cdot 3TiCl_3$ study. The latter mixed chloride has been extensively studied.^{6,14,15} It shows the crystalline phase of δ - $TiCl_3$, and can be described as a solid solution of the two chlorides.

X-Ray Characterization of the Binary Chlorides Obtained

X-Ray analysis of the powders of the binary chlorides obtained showed that all the prepared compounds crystallize in one of the violet structural modifications of $TiCl_3$, viz., α -, γ -, and δ -phase, with the presence, in a few cases, of the brown-black β -type phase. Different sizes and perfection of the crystals were evident from the different line broadening of the x-ray patterns. A qualitative estimation of these features is reported in Table II. For the more crystalline binary chlorides based on $CrCl_3$, $MoCl_3$, $FeCl_2$, and $NiCl_2$, x-ray data were suitable for an accurate determination of the unit cell parameters by least-squares fit of the observed interplanar spacings of the single reflections; the results are

reported in Tables III and IV. The x-ray patterns obtained from the adducts IV, VI, VII, and VIII, although appropriate for defining the type of phase, were too diffuse for a correct determination of the lattice parameters.

In this work we indicate as γ' the phase corresponding to that described by Natta et al.²¹ for the γ modification of TiCl_3 , with an ordered location of metal ions sandwiched by two chlorine layers ($P3_112$ space group), while γ indicated the modification related to the structure of CdI_2 , which fits a reduced unit cell and the $R\bar{3}m$ space group. It is worth noting that a quantitative evaluation of the intensities of the diffraction pattern of $\text{NiCl}_2 \cdot 2\text{TiCl}_3$, the most crystallized compound, suggests that the γ -phase is affected by some disorder on the stacking of the chlorine layers, but in a form (the study of which is in progress) which differs notably from that assigned to $\delta\text{-TiCl}_3$.²¹ Even for the γ -phase of the other compounds, a similar stacking fault could be present.

Inspection of Table IV shows that the unit cell constants of the synthesized binary chlorides differ for several times their standard deviation values from the constants of the single-constituent chlorides. In particular, it is evident that the a parameter pertaining to Ni, Fe, and Cr mixed chlorides takes intermediate values between the TiCl_3 and NiCl_2 , FeCl_2 , and CrCl_3 parameters. For the γ -phases, the trend of c is not well defined, primarily because the lower precision for the measurement of this parameter. However, the extrapolated value for TiCl_3 composition is closer to the more accurate c value given²² for $\alpha\text{-TiCl}_3$ (17.623 Å) rather than to the probably underestimated value of 17.40 Å given²¹ for $\gamma\text{-TiCl}_3$. The parameters calculated for the β -type phase of $\text{MoCl}_3 \cdot 3\text{TiCl}_3$, as well for the α -type phase of $\text{CrCl}_3 \cdot 3\text{TiCl}_3$, are clearly shifted from those of the corresponding phases of TiCl_3 . Similarly, for the two Mn binary chlorides the trend toward lattice parameters greater than those of $\gamma\text{-TiCl}_3$ is revealed from the change in the angular position of the broad peaks.

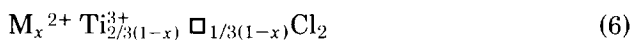
TABLE IV
Lattice Parameters of the Binary Chlorides and Single Chlorides Constituting Them

Binary chloride		Individual chloride		Notes
Type	Lattice parameters ^a	Type	Lattice parameters ^a	
$\text{NiCl}_2 \cdot 2\text{TiCl}_3$	$\gamma a = 3.513(2) \text{ \AA}$ $c = 17.591(9)$	NiCl_2	$\gamma a = 3.478(1)$ $c = 17.41 (2)$	ref. 23
		TiCl_3	$\gamma a = 3.54$ $c = 17.40$	ref. 21
$\text{FeCl}_2 \cdot 2\text{TiCl}_3$	$\gamma a = 3.551(5)$ $c = 17.61(17)$	FeCl_2	$\gamma a = 3.579$ $c = 17.536$	ref. 24
$\text{MoCl}_3 \cdot 3\text{TiCl}_3$	$\gamma a = 3.516(4)$ $c = 17.65(19)$ $\beta a = 6.230(4)$ $c = 5.820(3)$	TiCl_3	$\beta a = 6.251(2)$ $c = 5.817(2)$	^b
		TiCl_3	$\gamma' a = 6.14$ $c = 17.40$	ref. 21
$\text{CrCl}_3 \cdot 3\text{TiCl}_3$	$\gamma' a = 6.115(2)$ $c = 17.530(7)$ $\alpha a = 6.105(2)$ $c = 17.577(12)$	TiCl_3	$\alpha a = 6.1573(3)$ $c = 17.623(3)$	ref. 22
		CrCl_3	$\gamma a = 5.953$ $c = 17.44$	ref. 25

^a γ and γ' refer, respectively, to the structures adopting $R\bar{3}m$ (or $R\bar{3}$) and $P3_112$ space group.

^b Values calculated in the present work using the data obtained from an original sample of $\beta\text{-TiCl}_3$.

All the crystallographic evidence so far discussed for Cr, Ni, Fe, Mo, and Mn derivatives and the presence of a unique phase observed for Co and V derivatives, together with compositional data and electronic spectra, show that the synthesized compounds are solid solutions of the two-constituent chlorides. For layer-type structures of the α -, γ -, and δ -type, considering the vacant octahedral cationic sites (symbol \square), pertinent formulas could be written as



the x value varying between 0 and 1. For $x = 1/4$, they correspond to the stoichiometry given by the $MCl_n \cdot nTiCl_3$ formula when n is 2 or 3. When $x = 2/5$, formula (6) corresponds to $M^{2+}TiCl_5$ as found actually for product VI.

Formulas (6) and (7) are, however, very suitable for expressing fractional composition of solid solutions. In fact, when $x = 0.3$, formula (5) is equivalent to $M^{2+}Ti_{1.54}Cl_{6.6}$ as found for derivative VIII ($CoTi_{1.6}Cl_{6.6}$); and when $x = 0.44$, formula (7) yields $M^{3+}Ti_{1.22}Cl_{6.7}$, which is very close to the analytic composition found for product VII ($VTi_{1.1}Cl_{6.7}$).

It is of interest to consider the role played by the isomorphism in stabilizing the oxidation number of the metals associated to Ti^{3+} . In fact, Ni, Fe, Co, and Mn give rise to phases with an oxidation number of 2+, according to the strict isomorphism of the corresponding dichloride. In the case of Cr and V, the oxidation number 3+ is in line with the structural similarity of their trichlorides with the layer structures of $TiCl_3$. The lack of informations on the Mo chloride structures prevents definite conclusions. However, it is remarkable that binary chloride (II) is the unique case presenting a consistent formation of the β -type phase.

The specific surface area (SA) values of the products, obtained under comparable conditions, are in line with the broadening of the x-ray diffraction patterns which originates both in disorder and crystal size, the former effect being very probably the cause more important than the latter. In turn, even if not so clear, the disorder of crystal structure and thus surface area values seems related to the ionic radius of the metals with respect to that of Ti^{3+} . In this view it is remarkable that by far the largest specific surfaces were found for Fe and Mn derivatives (cf. Table II, products III and VI).

The thermal history is less important for determining the SA values, at least in the range of temperatures explored ($T \leq 150^\circ C$). For instance, product III showed SA data ranging between 100 and 150 m^2/g depending on the reaction conditions. As expected, when the reaction temperature was maintained lower than the transition temperature from the β - to the γ - $TiCl_3$ modification, the former crystalline phase was evident in product III prepared at $80^\circ C$, whereas only the latter form was observed in the same binary chloride prepared at $140^\circ C$. Mechanical operations, i.e., grinding in a ball mill, reduced the SA value of the adduct (cf. the case of I in Table II), while the initial crystalline modification ($\alpha + \gamma$) changed to the more disordered δ -phase, as observed in the case of pure $TiCl_3$.⁶

HDPE Synthesis with Catalyst Systems Based on Binary Chlorides

As will be discussed in detail in part II, the binary chlorides reported in Table II promote efficiently the low-pressure polymerization of ethylene to HDPE. Here, it can be sufficient to compare the overall catalyst efficiency of the systems based on adducts I through VIII with that of the $\text{AlCl}_3 \cdot 3\text{TiCl}_3$ -based system (Table V) and to observe that products III, IV, and VI are 2 to 3 times more efficient than the reference binary chloride. However, the reasons of these different behaviors are not easy to understand. In fact, the overall catalyst efficiency is independent of the surface area (SA) of the binary chloride and hence of the exposition of the active centers originating on the catalyst surface. For instance, III shows an SA value which is three times higher than that of IV (Table II), while the efficiency is almost the same (Table V).

These experimental data suggest that only a more detailed analysis of the polymerization process can elucidate the action mechanism of different binary chlorides and possibly of supported catalysts. The results of our efforts along this line will be the arguments of part II.

EXPERIMENTAL

Reagents

TiCl_4 was a commercial product (BDH) and was distilled under reduced pressure before use. $\text{AlCl}_3 \cdot 3\text{TiCl}_3$, $\text{Fe}(\text{CO})_5$, $\text{Co}_2(\text{CO})_8$, $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{Ni}(\text{CO})_4$ were Schuchardt products used as received. $\text{Mn}_2(\text{CO})_{10}$ and $\text{Mn}(\text{CO})_5\text{Cl}$ were prepared as described.^{26,27} $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ was a C. Erba product dehydrated according to reference 31. Ethylene was a Phillips product (polymerization grade) used without preliminary purification. Solvents (n -hexane or n -pentane, Shell products) were purified by fractional distillation under nitrogen. $\text{Al}(i\text{-C}_4\text{H}_9)$ was a Schuchardt product used as received.

TABLE V
Catalytic Activity of Systems Based on Binary Chlorides Containing TiCl_3

Type	Binary chloride		Overall catalyst ^a efficiency, kg polymer/g Ti	Specific activity ^b
	Type	Composition		
I		$\text{CrCl}_3 \cdot 3\text{TiCl}_3$	9.0	0.82
II		$\text{MoCl}_3 \cdot 3\text{TiCl}_3$	1.0	0.09
III		$\text{FeCl}_2 \cdot 2\text{TiCl}_3$	24.0	2.18
IV		$\text{MnCl}_2 \cdot 2\text{TiCl}_3$	22.6	2.05
V		$\text{NiCl}_2 \cdot 2\text{TiCl}_3$	4.2	0.38
VI		$\text{MnCl}_2 \cdot \text{TiCl}_3$	28.1	2.55
VII		$\text{VTi}_{1.1}\text{Cl}_{6.7}$	24.1	2.65
VIII		$\text{CoTi}_{1.6}\text{Cl}_{6.6}$	19.1	1.74
Ref.		$\text{AlCl}_3 \cdot 3\text{TiCl}_3$	11.0	1.00

^a Experimental conditions: n -hexane = 1000 cm^3 ; $[(i\text{-C}_4\text{H}_9)_3\text{Al}] = 4.0$ mmole/l; $[\text{Ti}] = 0.5\text{--}2$ matom/l; $T = 85^\circ\text{C}$; $\text{C}_2\text{H}_4 = 5$ atm; $\text{H}_2 = 5$ atm; time = 2 hr.

^b Referred to the overall catalyst efficiency of the $\text{AlCl}_3 \cdot 3\text{TiCl}_3$ -based system.

Procedure

All products were handled and reactions carried out under an atmosphere of dry nitrogen. The syntheses of binary halides were performed in dry glassware equipment by using an excess of TiCl_4 . A typical preparation is reported here for MnTi_2Cl_8 : 20 cm^3 (182 mmole) TiCl_4 is introduced in a two-necked round-bottom flask fitted with a magnetic stirrer and a reflux condenser. Successively, 1 g $\text{Mn}_2(\text{CO})_{10}$ (3 mmole) was added to TiCl_4 and the resulting solution was heated at 140°C . Within 4 hr the evolution of CO was complete and red-violet powder separated. It was transferred on a porous glass filter (G 4 type) to separate the excess TiCl_4 and to wash several times the solid with anhydrous *n*-pentane. The final product was dried under vacuum; it weighed 2.2 g (yield 98.9%).

Dry grinding of metal chlorides mixtures were carried out in a 200-cm^3 stainless steel rotating mill (60 rpm) containing 100 stainless steel balls (diameter 0.9 mm), at least for 24 hr. Polymerization experiments were carried out with a 2-liter stainless steel autoclave fitted with a mechanical stirrer (400 rpm), manometer, and thermometer pocket. A thermostatic system utilizing an electrical heating jacket and external water cooling provided a constant reaction temperature.

After having purged the reactor with N_2 and evacuated it, a solution of 1 cm^3 $\text{Al}(i\text{-C}_4\text{H}_9)_3$ (4.0 mmole) in 100 cm^3 *n*-hexane and containing in suspension also 8–30 mg binary chloride (0.5–2 atom Ti) was siphoned into the autoclave. Within 10–15 min, the autoclave was heated to the chosen temperature and measured pressures of H_2 and C_2H_4 were admitted. The demand of monomer was compensated by feeding C_2H_4 in order to maintain the operating pressure. The polymerization was stopped by venting the gases and introducing 10 cm^3 isopropanol in the autoclave. The polymer, after separation of the solvent, was dried to constant weight.

Kinetic measurements were done with the equipment above described, except that gas inlet rates were measured using calibrated rotameters. Temperature control was within $\pm 1^\circ\text{C}$.

Analyses

Chemical analyses were carried out on solutions obtained by decomposition of weighed samples with dilute aqueous sulfuric acid. The aluminum content was evaluated by the EDTA– ZnSO_4 method. Magnesium was also determined by EDTA at pH 10. Chlorine was determined according to Volhard's method. The Cr, Ni, and Fe content was obtained by atomic absorption spectroscopy (Perkin-Elmer Model 503 instrument), while in the case of Ti and Mn a colorimetric method (Optika Model CF 4 instrument) was used. When Ti and V were associated, the colorimetric method described by Fritz and Abbink was adopted.²⁸

UV and visible spectra were recorded on a Cary-15 spectrophotometer.

Surface area measurements were carried out with BET's method²⁹ by adsorbing liquid N_2 at low temperature and using a volumetric apparatus. X-Ray powder patterns were collected after the samples were sealed in thin-walled glass capillaries under a dry nitrogen atmosphere. A Debye–Scherrer camera (diameter 114.6 mm) was used with CuK_α radiation ($\lambda = 1.54178\text{ \AA}$).

CONCLUSIONS

The reaction of transition metal carbonyls with TiCl_4 yields binary chlorides showing a defined composition and containing, besides TiCl_3 , a di- or trivalent chloride of the metal present in the initial carbonyl derivative. The presence of an excess of TiCl_4 during the synthesis of these binary chlorides can explain the formation of TiCl_3 only and the absence of Ti^{2+} . The state of oxidation of the transition metal is such to obtain a crystalline phase isomorphous with the TiCl_3 phase to which it is associated. Under our experimental conditions the γ -phase of TiCl_3 is the most stable, and indeed it was observed in products III, IV, V, VI, and VIII, while mixed phases were shown by I ($\alpha + \gamma$) and II ($\beta + \gamma$). Only product VII displayed the δ -phase of TiCl_3 .

The stability of the crystalline products obtained is due to isomorphism phenomena between the different crystalline modification of TiCl_3 and that of the associated chloride. On the basis of x-ray and spectroscopic investigations, the binary adducts described in this work can be considered solid solutions of the couple of chlorides involved. When the mixed chlorides mentioned above are associated with trialkylaluminum derivatives, efficient catalyst systems for the low-pressure polymerization of ethylene are obtained. However no high yield is observed, even though the average polymerization rate measured in the best cases is 2 to 3 times higher than that of unsupported TiCl_3 -based systems. Peculiar aspects have been encountered during the polymerization process, and they will be discussed in the second part of this work.

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