Novel Binary Chlorides Containing TiCl₃ as Components of Coordination Catalysts for Ethylene Polymerization. II. Behavior of the Resulting Catalyst Systems

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Synopsis

Binary chlorides described in part I yielded very active catalyst systems for HDPE synthesis when they were associated with $(i\text{-}C_4H_9)_3Al$. Very high initial polymerization rates were observed for systems bases on $MnCl_2 \cdot TiCl_3$, $MnCl_2 \cdot 2TiCl_3$, or $FeCl_2 \cdot 2TiCl_3$ (III), but high yields, i.e., above 30 kg polymer/g Ti, could be reached only using moderate pressure of ethylene. Hydrogen consumption during ethylene polymerization was observed in the case of catalysts based on $AlCl_3 \cdot 3TiCl_3$, $CrCl_3 \cdot 3TiCl_3$, and other binary chlorides containing elements of the VIII group. Relevant amounts of ethane were found in the case of systems III, V, and VIII. All the mixed chlorides studied were able to reduce cyclohexene in the presence of H_2 and $(i\text{-}C_4H_9)_3Al$, even though with different kinetic courses. Compounds II, III, V, and VIII and $(MgCl_2)_{1.5} \cdot TiCl_3$ and $AlCl_3 \cdot 3TiCl_3$ were very active. The results have been explained on the basis of solubilization processes involving the heterogeneous catalysts which actually were experimentally verified during cyclohexene reduction. Analogous processes may occur also during HDPE synthesis.

INTRODUCTION

In part I,[1] new binary chlorides $CrCl_3 \cdot 3(TiCl_3)$ (I), $MoCl_3 \cdot 3TiCl_3$ (II), $FeCl_2 \cdot 2TiCl_3$ (III), $MnCl_2 \cdot 2TiCl_3$ (IV), $NiCl_2 \cdot 2TiCl_3$ (V), and $MnCl_2 \cdot TiCl_3$ (VI) containing usually the γ-modification of $TiCl_3$ were described. Their ability to give catalyst systems for the low-pressure polymerization of ethylene when associated to AlR_3 was also mentioned.

In this paper, the dependence of the polymerization rate on time and the influence of hydrogen used as regulator of the polymer molecular weight on some side processes, i.e., monomer hydrogenation and catalyst solubilization, are presented. Relevant differences have been encountered among the systems based on different binary halides and depending on the element associated with $TiCl_3$ in the solid solution.

RESULTS AND DISCUSSION

Ethylene Polymerization

Products I through VI, and also $VTi_{1.1}Cl_{6.7}$ (VII) and $CoTi_{1.6}Cl_{6.6}$ (VIII), have been associated with $Al(i\text{-}C_4H_9)_3$ to investigate their catalytic activity toward low-pressure ethylene polymerization. By working in the presence of H_2 as

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molecular weight regulator and under experimental conditions typical for HDPE synthesis, the results reported in Table I were obtained. They are referred to the catalytic activity shown by $AlCl_3 \cdot 3TiCl_3$, while the possible contribution to the catalyst efficiency of the binary chloride due to the second transition metal has been neglected only in a first approximation. In fact, this assumption is not rigorous.[2] However, Table I shows that catalyst systems based on III, IV, and VI are about three times more efficient than the system based on $AlCl_3 \cdot 3TiCl_3$. The hydrogen sensitivity, i.e., the dependence of the polymer molecular weight on the H_2 concentration, can be considered satisfactory in the case of VI, whereas it is rather poor in the case of III and I.

In part I, mention has been made of the difficulty to relate the overall catalyst efficiency to the surface area (SA) value of the binary chlorides used. Analogous difficulties in correlating the catalytic activity and SA values were encountered in the case of $TiCl_2$- and $TiCl_3$-based systems.[9] They have been attributed to fragmentation of the catalyst during polymerization so that fresh catalyst surface could be formed.

In our work a relation was found betweeen the SA value of the adducts and the initial polymerization rate as shown by the kinetic curves reported in Figure 1 (cf. the curves obtained with III, IV, and VI, which have high SA values). However, the decay of the initial efficiency is markedly dependent on the type of adduct. In fact, the system based on III reaches after the first hour of polymerization a constant reaction rate which, however, is lower than that of the catalyst based on $AlCl_3 \cdot 3TiCl_3$. On the contrary, IV- and VI-based systems do not attain a constant activity in the range of time explored. After 5 hr of polymerization the reaction rate displayed by VI is double that observed with the system based on $AlCl_3 \cdot 3TiCl_3$.

The trend of the kinetic curves decaying in Figure 1 seems attributable to the instability of the active centers which, in turn, depend on the type of metal

TABLE I
Polymerization of Ethylene at Low Pressure with Catalysts Based on Binary Chlorides Containing $TiCl_3$[a]

Compound No.	Binary chloride		Polymer yield, g/l	Overall catalyst efficiency, kg plo/g Ti	$MFI_{2.16}$, g pol/10 min	$MFI_{21.6}/ MFI_{2.16}$
	Type	Quantity, mg				
Ref.[b]	$AlTi_3Cl_{12}$	22.2	59	11.0	0.64	40.1
I	$CrTi_3Cl_{12}$	34.1	75	9.0	0.12	58.3
II	$MoTi_3Cl_{12}$	42.0	10	1.0	n.d.	—
III	$FeTi_2Cl_8$	33.1	173	24.0	0.05	50.9
IV	$MnTi_2Cl_8$	35.7	175	22.6	0.72	43.8
V	$NiTi_2Cl_8$	46.2	43	4.2	n.d.	—
VI	$MnTiCl_5$	30.5	165	28.1	1.36	36.7
VII	$VTi_{1.1}Cl_{6.7}$	30.0	130	24.2	0.58	52.0
VIII	$CoTi_{1.6}Cl_{6.6}$	30.0	120	19.1	n.d.	—
Ref.[b,c]	$(MgCl_2)_{1.5} \cdot TiCl_3$	8.7	185	132.0	1.1	40.0

[a] Experimental conditions: n-hexane = 1000 cm^3; $[Al(i\text{-}C_4H_9)_3]$ = 4.0 mmole/l; T = 85°C; C_2H_4 = 5 atm; H_2 = 5 atm; time = 2 hr.

[b] Reference run.

[c] Prepared according to ref. 3 (see experimental section).
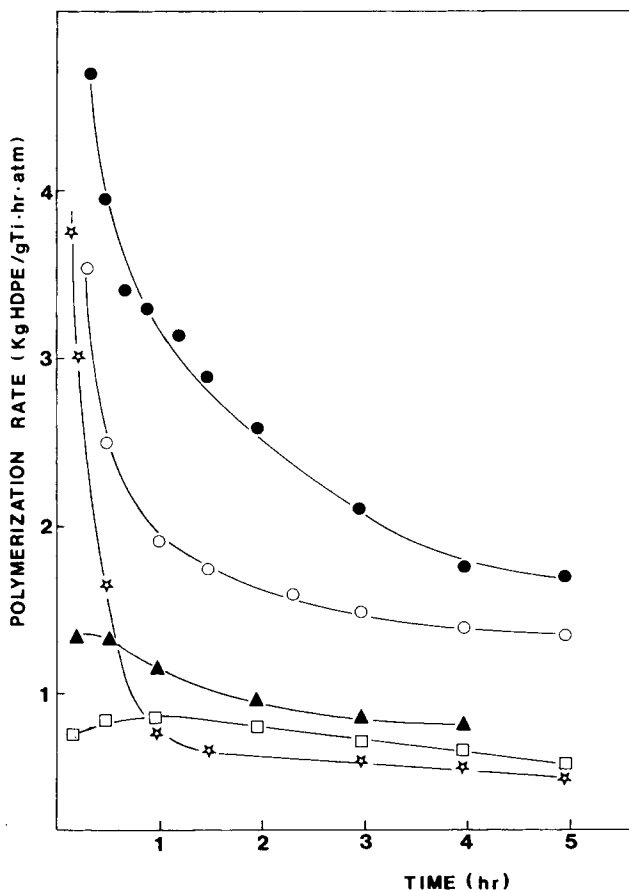
Fig. 1. Polymerization rate as function of time. Conditions: n-heptane = 2.5 l.; $p_{C_2H_4} = p_{H_2} = 5$ atm; $T = 85°C$; binary halide = 15 mg/l; (i-C_4H_9)$_3$Al = 4.0 mmole/l. Type of binary halide: (●) VI; (○) IV; (▲) AlCl$_3$·3TiCl$_3$; (□) I; (☆) = III.

chloride associated with TiCl$_3$ to give the same crystalline structure.[1] On the other hand, the initial polymerization rate, extrapolated to zero time, is exceptionally high in the case of MnCl$_2$-based mixed chlorides, and this result seems related to the high proportion of active Ti atoms. Very likely, a relatively high number of Ti atoms, descending from the high SA values of the binary chlorides containing MnCl$_2$, is converted into active sites.

A similar interpretation was proposed by Haward et al.[3] for the system based on MgCl$_2$·TiCl$_3$, obtained by reducing TiCl$_4$ with alkylmagnesium halides and containing usually significant amounts of Ti^{2+}. There are, however, some analogies between our adduct VI and the binary chloride studied by Haward et al. Both, in fact, have similar composition, high SA values, and a very low crystallinity due to a very small size of the crystallites. Actually, (MgCl$_2$)$_{1.5}$ TiCl$_3$-based catalyst, tested under comparable conditions, is five times more efficient than MnCl$_2$·TiCl$_3$ (cf. the last run of Table I). The role played by MgCl$_2$ in association with TiCl$_3$ seems responsible of this result, but it is rather difficult to describe adequately the influence of MgCl$_2$ on the basis of the results so far published.[3,9,16–19]

Certainly, $MgCl_2$ is inert toward trialkylaluminum compounds, i.e., the co-catalytic components of these systems, as demonstrated by contacting $MgCl_2$ or $(MgCl_2)_{1.5}TiCl_3$ with an excess of $Al(i\text{-}C_4H_9)$ in hydrocarbon solution at 85°C. Only traces (less than 0.01%) of the initial amount of Mg and Ti put in contact with $Al(i\text{-}C_4H_9)_3$ was found in the hydrocarbon solution.

In the case of $MnCl_2$ and $MnCl_2 \cdot TiCl_3$, 0.1% Mn and 2.9% Ti were solubilized. On the other hand, $AlCl_3$, present in another reference binary chloride, i.e., $AlCl_3 \cdot 3TiCl_3$, participates actively in ligand exchange with AlR_3, since it produces alkylaluminum halides.[4] The layer lattice structure of γ-$TiCl_3$ is capable of incorporating $MgCl_2$ and also $MnCl_2$ even though the latter yields a larger deformation of the $TiCl_3$ structure, due to the higher ionic radius of Mn^{2+} (0.82 Å) with respect to that of Mg^{2+} (0.65 Å) and of Ti^{3+} (0.67 Å).[1] As a consequence, the solid solutions of the binary chlorides described in this work lead to very disordered structures when the difference between the ionic radius of Ti^{3+} and that of the second metal ion is significant.[1] From these disordered structures a high number of exposed Ti atoms, i e., potential active centers,[5] can result, and this means, in principle, high catalyst efficiency.[6]

This potentiality can become an actual result when the environment of the Ti atom can stabilize the active centers resulting from the interaction with AlR_3. This seems the case of $MgCl_2 \cdot 3TiCl_3$ solid solution, whereas $AlCl_3 \cdot 3TiCl_3$, which shows a more ordered crystalline structure,[1] may loose many potential active centers because of the strong interaction with AlR_3 and the preferred coordination of R_2AlCl formed inside the solid solution. It is known that α-$TiCl_3$-based systems activated by $AlEt_3$ are more efficient than those activated by Et_2AlCl.[7] The same results were observed with catalysts based on $TiCl_4$ supported on annealed SiO_2 and $Al(i\text{-}C_4H_9)_3$ or $(i\text{-}C_4H_9)_2AlCl$.[8]

The higher efficiency of systems based on AlR_3 instead of R_2AlCl agrees with the conclusion derived from kinetic investigations[9] according to which ethylene alkylates only Ti ions having high coordination insufficiency. Further insight into the peculiar behavior and the performance of the catalysts based on the binary chlorides described in this work has been reached by studying the effect of hydrogen both on the course of the ethylene polymerization and the hydrogenating ability of the same systems toward a nonpolymerizable olefin (see next section).

Binary chlorides, reported in Table I, do not reach high yields of polyethylene since overall catalyst efficiencies are not higher than 30 kg polymer/g Ti. The rapid decrease in the average polymerization rate during the first hour of polymerization does not allow to improve significantly the overall efficiency by increasing the polymerization time. As is well known,[12] an increase of the H_2 concentration reduces both the molecular weight of the polymer and the catalyst efficiency, as found also for the system based on VI (Table II).

Improved catalyst efficiencies can be achieved with our systems working at moderate ethylene pressure, i.e., up to 20 atm, as shown in Table III for catalysts based on VI and IV. By choosing the appropriate amount of H_2, the entire range of molecular weights having commercial interest [melt flow index (MFI) between 0.1 and 40 g/10 min] can be obtained. The shear sensitivity, i.e., the ratio $(MFI)_{21.6}/(MFI)_{2.16}$, which gives an indication of the molecular weight distribution,[11] is higher in the case of IV (45–50) than of VI (35–40). Microstructure analysis confirms that the polymer is highly linear (low content of methyls) and

TABLE II
Dependence of Polymer MW and Catalyst Efficiency on C_2H_4 and H_2 Concentration[a]

Run no.	$P_{C_2H_4}$, atm	p_{H_2}, atm	Average polymerization rate, g pol/g Ti-hr-atm	$MFI_{2.16}$, g pol/10 min	$MFI_{21.6}/MFI_{2.16}$
1	7.0	3.0	3050	n.d.	—
2	5.0	5.0	2800	1.36	36.7
3	4.0	6.0	2100	2.76	38.6
4	3.3	6.7	2450	3.90	41.8
5	3.0	7.0	2450	3.96	41.8
6	6.6	13.4	2300	18.6	n.d.
7	13.2	26.8	2040	24.6	n.d.

[a] Catalyst $MnTiCl_5$ (Ti = 3–6 mg/l.); conditions as in Table I.

contains vinyl and viylidene unsaturations typical of HDPE. The amount of waxes is usually a few percent of the entire polymer when $MFI \leqslant 10$ g/10 min. As expected, the wax content increases when the polymer molecular weight decreases. The polymers are colorless, and residual catalyst are too low to induce undesired effects during processing steps.

Hydrogen Consumption During Ethylene Polymerization

It can be observed in Table I that catalyst systems displaying similar overall efficiency (systems based on III, IV and VI) show different hydrogen sensitivity as evidenced by MFI data. The molecular weight of polyethylene is regulated by all the chain transfer reactions occurring in the polymerization system, and H_2 contributes relevantly to this regulation.[12] Of course, when the H_2 concentration in the polymerization medium decreases, the MW of the resulting polymer increases. This result was actually observed, under our experimental conditions, with some of the catalyst systems based on binary chlorides when samples of polymer produced at different times were examined.

The direct analysis of the H_2 concentration in the gas phase of the polymerization system confirmed that in the case of catalysts based on I, III, V, VIII, $AlCl_3 \cdot 3TiCl_3$ and $(MgCl_2)_{1.5} \cdot TiCl_3$, an effective H_2 consumption occurred (Fig. 2). Meanwhile, the continuous formation of ethane was detected, corresponding approximately to the decrease in the H_2 concentration, at least in the case of III, V, and VIII (Fig. 3). It is noteworthy that no evidence was found of isobutane formation, i.e., the volatile product resulting from the hydrogenolysis[12] of $Al(i$-$C_4H_9)_3$ present as cocatalyst.

Furthermore, the amount of H_2 consumed to form all the polymer chains during a typical polymerization experiment accounts for no more than 2 vol. % of H_2 concentration decrease. Even if one takes into account the formation of waxes (3%–5% and $\overline{M}_n = 2000$ when the polymer's $\overline{M}_n$ is 5×10^4), the overall consumption of H_2 does not exceed 5% of the initial concentration. Actually, the system based on III, V, and VIII showed respectively 56, 62, and 92 vol-% decrease of H_2 concentration, within 5 hr of polymerization 23, 50, and 70 vol-%

TABLE III

HDPE Synthesis with Catalyst Systems Based on $MnTiCl_5$ (VI) and $MnTi_2Cl_8$ (IV)[a]

Run No.	Catal. (type)	C_{H_2},[b] %	Overall catalyst efficiency, kg pol/ g Ti	$[\eta]$, dl/g	$MFI_{2.16}$, g pol/ 10 min	Wax content, %	Density, g/cm^3	Microstructure (%) unsaturation		
								CH$_3$ groups	Vinyl	Vinylidene
1	VI	33	175.8	n.d.	0.32	n.d.	0.965	0.10	0.15	0.04
2	VI	37	152.4	2.51	0.39	0.71	n.d.	n.d.	n.d.	n.d.
3	VI	50	104.0	1.79	1.21	n.d.	0.967	0.16	0.14	0.08
4	VI	66	48.9	1.03	24.6	5.0	0.970	0.32	0.16	0.13
5	VI	75	35.9	0.88	38.9	7.0	n.d.	n.d.	n.d.	n.d.
6	IV	37	112.2	2.38	0.28	0.76	0.964	0.10	0.13	0.04
7	IV	50	88.1	1.96	0.92	n.d.	n.d.	n.d.	n.d.	n.d.
8	IV	55	82.6	1.90	1.07	n.d.	0.967	0.15	0.14	0.08
9	IV	70	46.8	1.07	28.7	3.8	0.974	0.20	0.14	0.11
10	IV	75	29.5	0.90	39.2	6.5	n.d.	n.d.	n.d.	n.d.

[a] Experimental conditions as in Table I, except overall pressure = 40 atm.
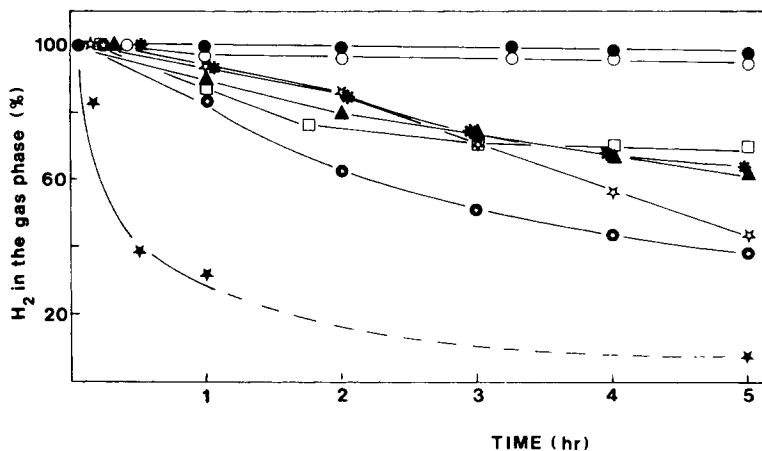[b] $C_{H_2} = p_{H_2}/(p_{H_2} + p_{C_2H_4})$.

Fig. 2. Dependence of hydrogen concentration (referred to initial concentration) on polymerization time.   Conditions and symbols as in Fig. 1, except n-heptane = 1.0 l; binary halide = 30 mg; (⊛) V; (★) VIII; (✳) $(MgCl_2)_{1.5} \cdot TiCl_3$.
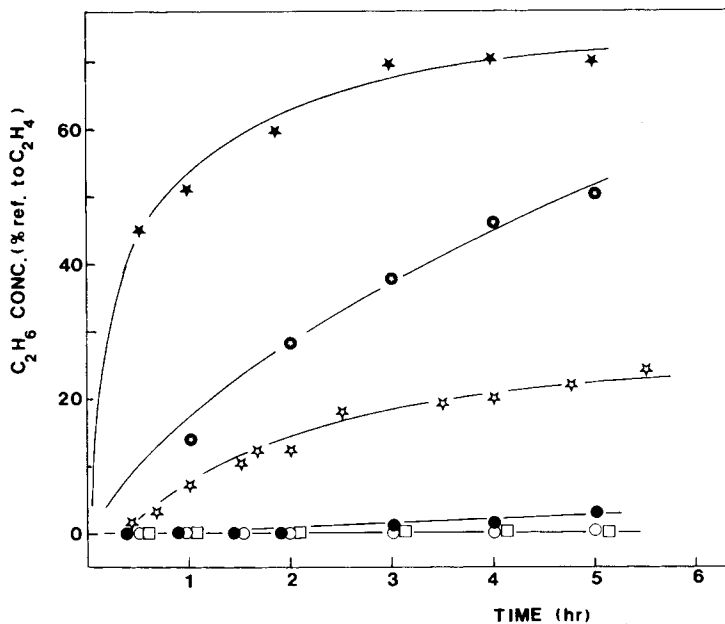

Fig. 3. Formation of ethane during polymerization.   Conditions and symbols as in Fig. 1; ethylene determined by VPC (column Poropack Q, 80–100 mesh; 1.5 m; T = 130°C; carrier = N_2; C. Erba Fractovap Model C instrument).

ethane appeared respectively, in the gaseous phase of the auto clave. Therefore, the olefin hydrogenation is the main side process responsible for the H_2 consumption.

Even though the system $TiCl_3$ + AlR_3 has been described as a hydrogenation catalyst,[13] it is difficult to account for the different behavior of all the systems investigated.   In fact, they are structurally very similar, but the H_2 consumption

induced by them is very different, being pronounced when the metal associated with TiCl₃ belongs to group VIII of the Periodic Table.

A work hypothesis put forward to explain the results of Figure 2 may be the transformation (at least in part) of heterogeneous catalyst systems into homogeneous ones, under the simultaneous influence of the alkylaluminum derivative and the monomer. Homogeneous systems based on transition metals and mainly on group VIII elements are known to be hydrogenation catalysts more efficient than analogous heterogeneous catalysts.[14]

We have tried to verify this hypothesis by using a nonpolymerizable olefin (cyclohexene) which allows an easier study of the reaction products and of the solubilized amount of catalyst.

Hydrogenation of Cyclohexene

The polymerization systems based on the binary chlorides described above have been used in hydrogenation experiments with cyclohexene, which is unable to polymerize under the adopted conditions. The hydrogenation reaction has been followed by measuring the H_2 pressure decrease with time, and the results are plotted in Figure 4 for the systems based on $AlCl_3 \cdot 3TiCl_3$, I, III to VI, and
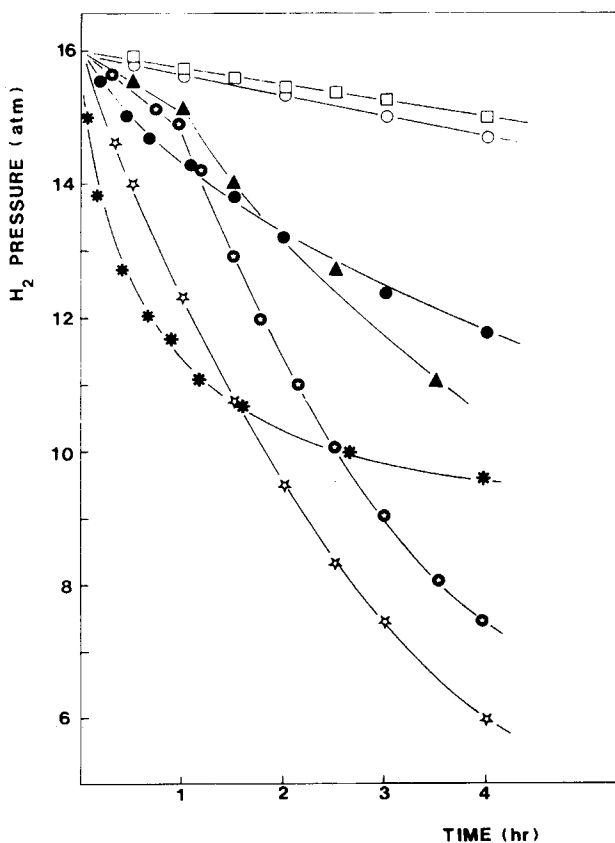

Fig. 4. Hydrogen consumption as function of time during cyclohexene hydrogenation. Conditions reported in Table IV. Symbols as in Figs. 1 and 2.

$(MgCl_2)_{1.5} \cdot TiCl_3$.   In Table IV are reported the amount of cyclohexane, Ti, and transition metal found in the liquid phase (n-heptane) after 8 hr of reaction; also the data concerning the systems based on II and VII are given.

According to Table IV, all the systems studied are able to hydrogenate cyclohexene, while Figure 4 shows that I and VI originate systems that are scarcely efficient. $AlCl_3 \cdot 3TiCl_3$, $(MgCl_2)_{1.5} \cdot TiCl_3$, and IV are more active, while II, III, V, and VIII are very active.   In the last group are included binary halides containing elements of group VIII of the Periodic Table.

The curves of Figure 4 are very informative in their qualitative trend.   In fact, they show that the hydrogenating efficiency increases with time, independently of any kinetic order or any reaction mechanism, as if the amount of catalyst species were increasing with time.   Furthermore, at least in two cases (systems based on $AlCl_3 \cdot 3TiCl_3$ and V), the kinetic curves show clearly two courses, one slow (within the first hour) and the other faster.   All these facts can be explained by admitting that the systems are initially heterogeneous but become progressively soluble and their hydrogenating ability increases correspondingly.

The particular behavior of $AlCl_3 \cdot 3TiCl_3$ and V may be accounted for by their highly crystalline structure which hinders the solubilization process in the initial stage.   Binary chlorides displaying high SA values do not show kinetic curves with two different courses, as V and $AlCl_3 \cdot 3TiCl_3$ do.   The latter system shows during the polymerization process a kinetic curve (Fig. 2) with two different courses as far as H_2 consumption is concerned.   The diagram pertaining to I is analogous (Fig. 2), whereas the same system is less efficient toward cyclohexene hydrogenation.   However, if one bears in mind that the experimental conditions adopted in the hydrogenation runs were milder than in polymerization experiments (lower Al/Ti molar ratio, lower temperature, and absence of a polymerizable monomer) and remembering that I contains Cr, i.e., a metal able to polymerize ethylene, the behavior of the system based on I may be explained by the same phenomenon of catalyst solubilization which would occur more extensively during the runs of Figure 2 than those of Figure 4.

TABLE IV
Hydrogenation of Cyclohexene with Catalysts Based on Binary Chlorides and $Al(i\text{-}C_4H_9)_3$[a]

| Compound No. | Binary chloride | | Solubilized metal | | Cyclohexane yield, % |
	Type	Quantity, mg	M, %	Ti, %	
Ref.[b]	$AlTi_3Cl_{12}$	208.7	n.d.	4.0	66.1
I	$CrTi_3Cl_{12}$	340.5	0.23	1.8	26.3
II	$MoTi_3Cl_{12}$	211.6	11.0	n.d.	100
III	$FeTi_2Cl_8$	187.0	10.5	2.0	100
IV	$MnTi_2Cl_8$	199.7	0.80	n.d.	58.7
0V	$NiTi_2Cl_8$	200.7	6.9	n.d.	100
VI	$MnTiCl_5$	175.7	0.33	0.2	23.6
VIII	$CoTi_{1.6}Cl_{6.6}$	187.0	17.5	n.d.	100
Ref.[b,c]	$(MgCl_2)_{1.5} \cdot TiCl_3$	231.8	0.35	16.7	55.0

[a] Experimental conditions: cyclohexene = 93.6 mmole; Al $(i\text{-}C_4H_9)_3$ = 1.2 mmole; p_{H_2} = 16 atm; T = 28°C; time = 8 hr.

[b] Reference run.

[c] Prepared according to ref. 3 (see experimental section).

EXPERIMENTAL

Reagents

Binary chlorides were prepared as described in part I.[1] $AlCl_3 \cdot 3TiCl_3$ was a commercial product (Stauffer Co.). A solid solution of $MgCl_2$ and $TiCl_3$ was prepared according to ref. 3 by reducing $TiCl_4$ with an excess of $n\text{-}C_4H_9MgCl$ in ligroin at $-60°C$. A solution of $n\text{-}C_4H_9MgCl$ in ligroin was obtained by reacting powdered Mg (an Eckart-Werke product activated by grinding it in a ball mill with 2% of $Al(C_2H_5)_3$ dissolved in 20 cm^3 toluene and washing it with anhydrous n-pentane) with $n\text{-}C_4H_9Cl$ (a C. Erba product) at $120°C$.[20] The final solid showed the following composition: $(MgCl_2)_{1.5} \cdot TiCl_3$ and a very low crystallinity due to $\beta\text{-}TiCl_3$ as described in ref. 3. Cyclohexene was a commercial product (Fluka); it was washed with a 5% $FeSO_4$ aqueous solution, dried over $MgSO_4$, and distilled from $LiAlH_4$.

Procedure

Polymerization experiments were carried out as described previously.[1] Measurements of the solubilization of $MgCl_2$, $MnCl_2$, $(MgCl_2)_{1.5} \cdot TiCl_3$, and $MnCl_2 \cdot TiCl_3$ by an excess of $Al(i\text{-}C_4H_9)_3$ (8.0 mmole) were carried out in n-heptane (12 cm^3, 0.25 g metal chloride) for 4 hr at $85°C$. Negligible amounts (less than 0.01%) of Mg, Ti, and Cl were found in the hydrocarbon solution (after separation of the solid phase) in the case of $MgCl_2$ and $(MgCl_2)_{1.5} \cdot TiCl_3$.

In the case of $MnCl_2$ 0.1% Mn was solubilized, and 3% chlorine was found in the solution, indicating reduction of Mn^{2+}; 2.9% Ti and 0.1% Mn were solubilized in the case of $MnCl_2 \cdot TiCl_3$. Cyclohexene hydrogenation experiments were carried out in a stainless steel autoclave (volume 200 cm^3) containing a magnetic stirrer. Results and experimental conditions are reported in Table IV. The amount of formed cyclohexane was determined by a VPC [EAS (diethyl ester of succinic acid) column, length 3 m, $T = 62°C$, carrier N_2] after separation of the solid phase of the catalyst. Part of the liquid phase was analyzed to determine the amount of solubilized metals.

Analyses

Elemental analysis of the binary chlorides was carried as reported previously.[1] The molecular weight of HDPE was obtained through viscometric measurements in decalin at $135°C$.[21] Also melt flow index data (ASTM D 1238 method) were used to calculated $\overline{M}_w$ from the empirical relation $\log \overline{M}_w = -0.29 \log (MFI) + 5.01$, which was found to hold for a number of samples. An index of the molecular weight distribution was obtained from the ratio of two MFI measurements carried out respectively with a load of 21.6 and 2.16 kg.[11] The content of waxes in the polymer was determined by extraction of a polymer sample with boiling n-heptane (Kumagawa Equipment) for 48 hr.

Microstructure data were collected from IR measurements (Perkin–Elmer Model 225 instrument) according to the ASTM D 2238-64 T method. Also density measurements were obtained according to the ASTM D 1505 method. Corrosivity tests were carried out by casting the polymer at $250°C$ for 30 min between Cr-based steel plates and determining the content of Cr eventually

present in the water eluted on the plates after removal of the polymer.   The polymer color was determined by means of a Zeiss reflection spectrophotometer (Elrepho Model) and by comparison with a standard white surface (the average value of many samples was 95%).

CONCLUSIONS

Some of the binary chlorides described in this work have shown a very high reaction rate in the initial period of the low-pressure polymerization of ethylene, but its rapid decrease with time prevents the formation of polymer in high yield. However, by using moderate pressure of ethylene, the catalyst systems based on $MnCl_2 \cdot TiCl_3$ (VI) and $MnCl_2 \cdot 2TiCl_3$ (IV) give overall efficiencies in the range of high yields.

All the systems studied display a hydrogenating ability toward olefins which is particularly enhanced when the second element of the solid solution belongs to group VIII of the Periodic Table.   Interestingly, the system based on IV shows a hydrogenating ability rather poor and practically negligible during HDPE synthesis, whereas in the case of $AlCl_3 \cdot 3TiCl_3$ and $(MgCl_2)_{1.5} \cdot TiCl_3$ the consumption of H_2 is conspicuous.

The loss of catalytic activity with time has been ascribed to the partial transformation of the initial heterogeneous system into soluble species which actually have been found in the hydrocarbon phase where the cyclohexene reduction has been performed.   This process of degeneration of heterogeneous catalysts, which occurs under the influence of cocatalyst and olefin, is common to systems containing $TiCl_3$ chemically bonded to a support[8] or dispersed into a solid solution[3] as may be inferred from the decay of the polymerization activity with time. According to our work, the type of metal chloride associated with $TiCl_3$ in solid solutions can reduce the degenerative effect but cannot eliminate it completely as far as binary chlorides I through VII, $(MgCl_2)_{1.5}TiCl_3$, and $AlCl_3 \cdot 3TiCl_3$ are concerned.

It is noteworthy that recent kinetic results obtained during the polymerization of propylene with different kinds of $TiCl_3$ are along the same line of our conclusions.   According to Kokta and Valade,[10] the decay of active centers is a kinetically important termination step that reflects the molecular weight of the polymer.   Furthermore, direct evidence of the solid-phase destruction of catalyst has been obtained by means of electron microscopy measurements.[15]

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