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Transition metal chlorides complexes with tetrahydrofuran [MtCl$_4$(THF)$_2$] used as precursors of ethylene polymerization catalysts

Summary — Three complexes of transition metal chlorides with tetrahydrofuran (THF), *viz.*, [TiCl$_4$(THF)$_2$] (**I**), [ZrCl$_4$(THF)$_2$] (**II**), and [HfCl$_4$(THF)$_2$] (**III**), were prepared and studied as the precursors of titanium—magnesium catalysts to be used in low-pressure polymerization (0.5 MPa, 323 K) of ethylene using AlEt$_3$ (most favorable), AlEt$_2$Cl, or Al(i-Bu)$_3$ as cocatalysts. The activity of catalysts increases in the order [HfCl$_4$(THF)$_2$] < [ZrCl$_4$(THF)$_2$] < [TiCl$_4$(THF)$_2$]. Degree of crystallinity (C), density, bulk density, M, MWD, and m.p. were determined for the resulting HDPE. Catalyst activity, found to obey the following ascending type (**III**) < (**II**) < (**I**), increased as the element electronegativity was raised and the partial charge on the transition metal atom in the precursor was diminished. The catalyst surface patterns visualized by a computer supported the experimental data. The uncomplexed, [MgCl$_2$(THF)$_2$]-supported tetrachlorides yielded catalysts less active than (**I**)—(**III**), but following the same general activity correlations.

Key words: polymerization of ethylene, catalysts, transition metal chloride complexes with tetrahydrofuran, molecular modeling.

Transition metal complexes containing Lewis bases play an important role in low-pressure polymerization of olefins. Although the composition of modern catalysts has changed as compared with the early systems developed by Ziegler and Natta, they all derive from the common source, *i.e.*, transition metal complexes. Although the structure of soluble catalysts has been well defined and they offer the possibilities of producing new polymers of outstanding properties, heterogeneous catalysts are still of great industrial importance. The polymers obtained by using such catalysts constitute more than a quarter of the overall polymer production [1]. The activity of a heterogeneous catalyst depends on a number of factors. The nature of the active site is not exactly known and, only few attempts have been made to explain this problem, both theoretically and experimentally [2—12].

We have studied the activity of the catalysts based on [TiCl$_4$(THF)$_2$], [ZrCl$_4$(THF)$_2$] and [HfCl$_4$(THF)$_2$] supported on [MgCl$_2$(THF)$_2$]. The correlation between the activity of the catalysts and the electronegativity of, and

charge on, the transition metal atom in the precursor has been confirmed [8, 9]. We have also considered the interaction between support and precursor by means of molecular modeling.

MATERIALS

The materials used in this study included:
— ethylene (Blachownia, Kędzierzyn-Koźle), purified in the columns of a sodium metal supported on Al$_2$O$_3$ and over 4Å molecular sieves;
— pure-grade argon (99.995%) (Liquid Carbonic, Poland), used after having been passed through a column of sodium supported on Al$_2$O$_3$;
— pure-grade hexane (ORLEN SA, Płock), refined with sulfuric acid, dried over KOH, refluxed from sodium metal and benzophenone in an argon atmosphere, and stored over 4 Å molecular sieves;
— Fluka's pure grade triethylaluminum, diethylaluminum chloride, and triisobutylaluminum, used without further purification;
— Aldrich's titanium tetrachloride, zirconium tetrachloride, and hafnium tetrachloride.

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T a b l e 2. Properties of the polyethylene obtained in ethylene polymerization in the presence of catalytic system: [MgCl$_2$(THF)$_2$]/precursor/AlEt$_3$. [Mt] = 0.01 mmol · dm^{-3}, [Al] = 5 mmols · dm^{-3}, Mg:Ti mole ratio = 10:1, T$_p$ = 323 K, ô$_a$ = 15 min, P$_{ethylene}$ = 0.5 MPa

Precursor	Density[*] g·cm^{-3}	Bulk density[**] g·cm^{-3}	C[***], %	m.p.[****] K	MWD
trans-[TiCl$_4$(THF)$_2$]	0.958	125	61.7	412.4	8.62
cis-[ZrCl$_4$(THF)$_2$]	0.960	107	58.2	411.7	5.76
cis-[HfCl$_4$(THF)$_2$]	0.955	122	57.3	412.1	6.31
TiCl$_4$	0.951	115	54.0	411.1	9.27
ZrCl$_4$	0.948	111	57.1	410.8	4.12
HfCl$_4$	0.950	104	57.0	410.5	8.65

*) Polish Standard PN-80/C-89035
**) Polish Standard PN-80/C-04532
***) DSC-TA Instruments
****) GPC-Waters 150-C

cocatalyst applied (Table 1). The organoaluminum compound used as cocatalyst plays an important role in the catalytic system. It is the alkylating and reducing agent for a transition metal atom. It also transfers growing polymer chains and interacts with the other components of the catalytic system. With AlEt$_3$ as a cocatalyst, catalyst activities are several times greater than those involving other cocatalysts. The high-density polyethylene obtained is characterized by specific density of 0.955–0.958 g·cm^{-3}, bulk density of 107—125 g·dm^{-3}, crystallinity of 57.3—61.7%, melting point of 411.7—412.4 K, and molecular weight distribution of 5.76—8.62.

The activities of the catalysts obtained from the tetrachlorides (titanium, zirconium and hafnium) complexed with tetrahydrofuran and supported on [MgCl$_2$(THF)$_2$] are a few times greater than those for catalytic systems based on corresponding chlorides (without THF) and supported on [MgCl$_2$(THF)$_2$]. Density, crystallinity and melting point of PE are similar and MWD is narrower.

The changes in the activities of the catalysts correspond to changes in the electronegativity of transition metal atoms. For instance, titanium, which is the most electronegative of the three elements, forms the most active catalyst. This can be attributed to the lower stabilization of the π-complex by the positive charge on the transition metal atom [8, 9]. Electronegativities, charges on transition metal atoms as well as activities of catalysts are given in Table 3.

In the heterogeneous catalysis interactions between catalyst components are of great importance. Therefore, we studied the compatibility of the precursor and support surfaces during the catalyst preparation step. In our calculations we used the model of accessible surface developed by Connolly [15]. In this model, the probe of a given radius is rolled on the van der Waals surface of the molecule. The crystallographic data necessary for calculations of the precursor and support interactions were taken from [16—19]. Catalyst surfaces are shown in Figs. 2—6. Numerous Miller planes for cleaving the
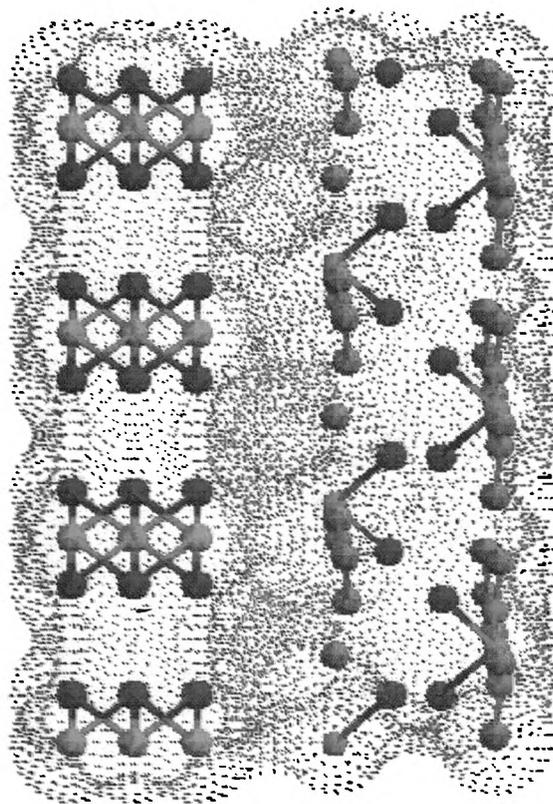
Fig. 2. Catalyst surface: (left) interface between MgCl$_2$ cleft with the (110) Miller plane and (right) trans-[TiCl$_4$(THF)$_2$]
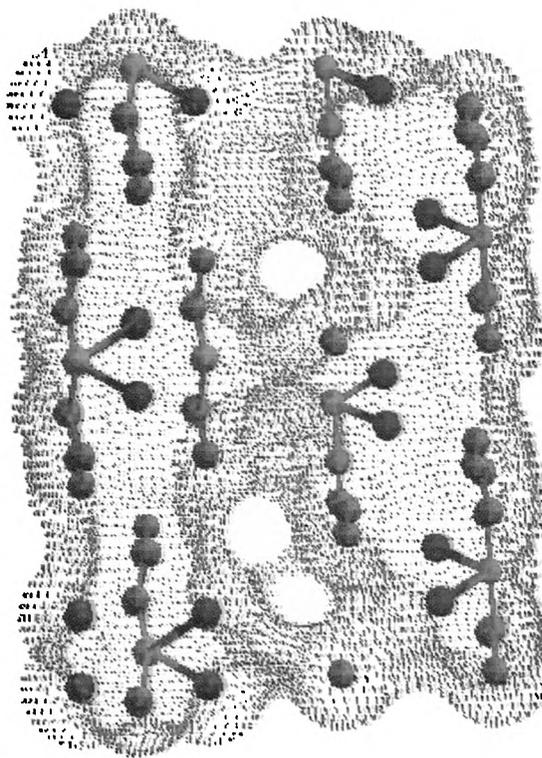
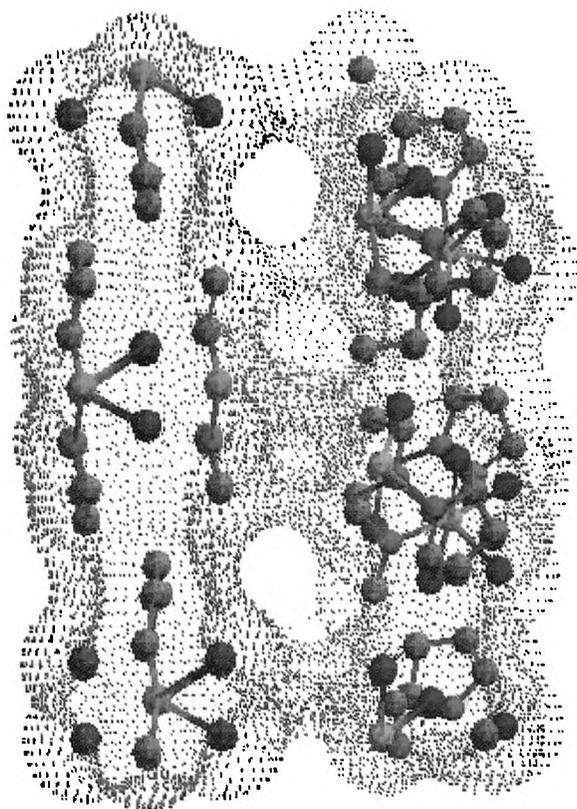Fig. 3. Catalyst surface: (left) interface between [MgCl$_2$(THF)$_2$] cleft with the (100) Miller plane and (right) trans-[TiCl$_4$(THF)$_2$] cleft with (011)

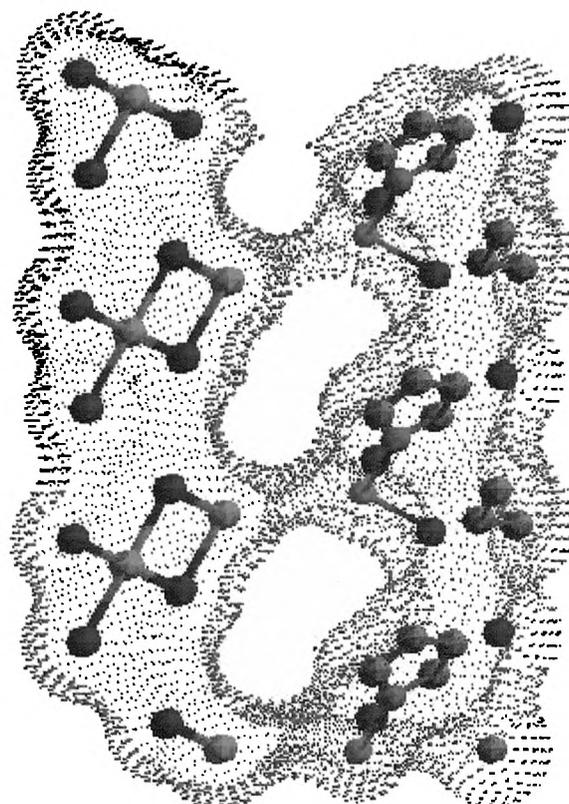*Fig. 4. Catalyst surface: (left) interface between [MgCl$_2$(THF)$_2$] cleft with the (100) Miller plane and (right) cis-[ZrCl$_4$(THF)$_2$] cleft with (011)*

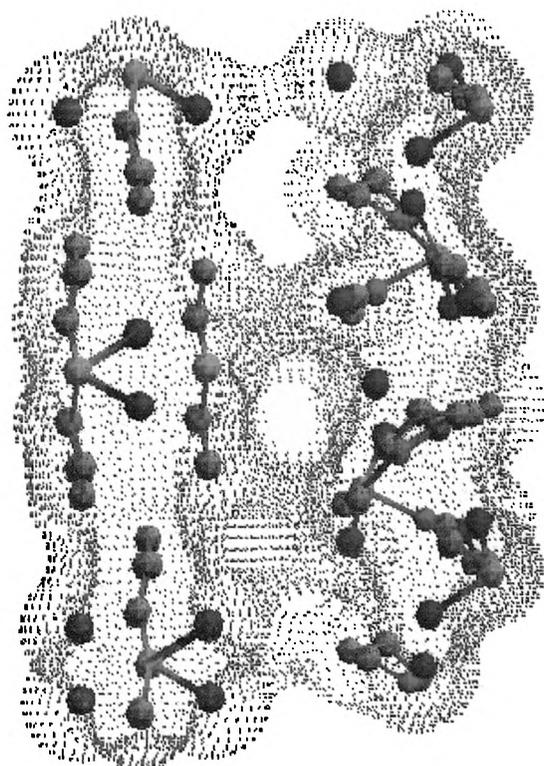*Fig. 6. Catalyst surface: (left) interface between MgCl$_2$ cleft with the (101) Miller plane and (right) trans-[TiCl$_4$(THF)$_2$] cleft with (100)*

Fig. 5. Catalyst surface: (left) interface between [MgCl$_2$(THF)$_2$] cleft with the (100) Miller plane and (right) cis-[HfCl$_4$(THF)$_2$] cleft with (100)

T a b l e 3. Activity of catalysts as a function of electronegativity and charge on transition metal atoms. Catalytic system — [MgCl$_2$(THF)$_2$]/precursor/cocatalyst

Transition metal complex	Charges on transition metal atoms [7]	Electronegativity of transition metal atom		Activity of catalyst kg PE· ·(mol Mt·h)$^{-1}$
		Pauling [21]	Alfred and Ro-chow [21]	
cis-[TiCl$_4$(THF)$_2$]	+0.48	1.54	1.32	10147
trans-[TiCl$_4$(THF)$_2$]	+0.40	1.54	1.32	not examined
cis-[ZrCl$_4$(THF)$_2$]	+0.77	1.33	1.22	1568
cis-[HfCl$_4$(THF)$_2$]	+0.72	1.30	1.23	982

crystals of both support and precursor were examined. Figure 2 illustrates the surface of the catalyst obtained on β-MgCl$_2$ crystal cleft with a (110) plane and a trans-[TiCl$_4$(THF)$_2$] crystal cleft with a (011) plane. The Connolly surface [19] represented by dots surrounding the crystal structures is rather uniform, which indicates strong interactions between the support and the precursor. Moreover, the interface based on [MgCl$_2$(THF)$_2$] cleft by the (100) Miller plane and trans-[TiCl$_4$(THF)$_2$] cleft by the (011) Miller plane (Fig. 3) is also favorable. However, in this case the Connolly surface is not so uniform as in the previous case. The weakest interaction

exists between [MgCl$_2$(THF)$_2$] cleft with (100) and cis-[ZrCl$_4$(THF)$_2$] cleft with (011) (Fig. 4). Therefore chemical anchoring of the precursor on the support surface seems not to be favored. The same applies to the interface between [MgCl$_2$(THF)$_2$] cleft with (101) and cis-[HfCl$_4$(THF)$_2$] cleft with (100) (Fig. 5). Figure 6 shows an example of unfavorable interactions between the support and the precursor. The crystal of MgCl$_2$ is cleft with the (101) Miller plane and the crystal of trans-[TiCl$_4$(THF)$_2$] is cleft with the (100) plane. Both cuts seem to be less suitable for the formation of a catalytic system.

In general, the (011) Miller plane turned out to be the most suitable for cleaving the trans-[TiCl$_4$(THF)$_2$] crystal, whereas (100) is favorable in the case of [MgCl$_2$(THF)$_2$]. These planes are parallel to the THF rings in either of the crystals and the resulting Connolly surfaces are rather flat. For magnesium dichloride, the easy formation of active centers on its surface cleft with the (110) Miller plane has been previously described [20]. Titanium atom bound on MgCl$_2$ cleft by this plane is one of the most stable systems in the formation of heterogeneous catalysts. This fact is confirmed by molecular modeling.

The interaction of β-MgCl$_2$ cleft with a (110) plane and trans-[TiCl$_4$(THF)$_2$] cleft with a [011] plane seems to be the most interesting (Fig. 2). However, it should be noted that the number of active centers which are formed may be smaller because of the fact that the surface is less available to a hexagonal structure than to a linear polymer (such as [MgCl$_2$(THF)$_2$]). Secondly, the donation of THF ligands from the precursor to the support is also possible in this case.

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