Ethylene Polymerization Reactions with Multicenter Ziegler-Natta Catalysts—Manipulation of Active Center Distribution

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ABSTRACT: This article describes ethylene/1-hexene copolymerization reactions with a supported titanium-based, multicenter Ziegler-Natta catalyst. The catalyst was modified by pretreating its solid precursor with $AlEt_2Cl$ and with similar organoaluminum chlorides, $Al_2Et_3Cl_3$, $AlEtCl_2$, and $AlMe_2Cl$. Testing of the untreated and the pretreated catalysts in copolymerization reactions under standard reaction conditions demonstrated that the modifying agents produce two changes in the catalyst. First, the pretreatment significantly reduces the reactivity of active centers that produce high molecular weight, highly crystalline copolymer components with a low 1-hexene content. Second, the pretreat- ment noticeably increases the reactivity of active centers that produce low molecular weight copolymer components with a high 1-hexene content. The first effect is caused by Lewis acid-base interactions of the modifiers with the active centers, whereas the second (activating) effect is due to the removal of catalyst poisons (organosilicon compounds generated in the process of the catalyst synthesis) by $AlEt_2Cl$. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 4219–4229, 2010

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INTRODUCTION Supported Ti-based Ziegler-Natta catalysts used for ethylene polymerization reactions consist of two components, solid components called catalyst precursors and cocatalysts, trialkylaluminum compounds. The active catalyst species are formed when the two catalyst components are combined, usually immediately before the polymerization reactions. A large number of competing synthetic procedures for the preparation of the Ti-containing catalyst precursors are described in numerous patents. Several of the techniques are reviewed in ref. 1.

Our earlier work on the kinetics of ethylene homopolymerization and copolymerization reactions with different Ti-based catalysts has demonstrated that they all exhibit several common features. The catalyst performance can be described in terms of a multicenter reaction scheme as follows[1–4]:

1. All the catalysts contain several (usually four or five) types of active centers. One of the principal differences between the centers is the average molecular weight of the polymer molecules they produce under given reaction conditions. Each type of center produces polymer molecules with a narrow molecular weight distribution described by the Flory theory,[5] with the M_w/M_n ratio of 2.0. Similar to the earlier publications,[1–4] different centers in this article are arbitrarily numbered from I to V in the order of increasing molecular weights of the polymer components they produce: $M_w(\text{Center I}) < M_w(\text{Center II}) < M_w(\text{Center III}) < M_w(\text{Center IV}) < M_w(\text{Center V})$. The differences between molec- ular weights of the polymer components produced by different centers are quite large, as several examples below demonstrate; for example, the ratio between the $M_w(\text{Center V})$ and the $M_w(\text{Center I})$ values can be as high as 80 to 90.

2. Centers of different types vary greatly in their ability to copolymerize α-olefins with ethylene. This ability steadily decreases from Center I to Centers IV and V. Centers IV and V have poor copolymerization ability. Even when α-olefins are present in the copolymerization reactions in significant concentrations, the copolymer molecules produced by Centers IV and V have low α-olefin contents, and these materials are highly crystalline.

3. Centers of different types significantly vary in their kinetic behavior; they are formed and decay at different rates. Centers I and II are formed rapidly but they decay rapidly and become practically inactive after 20 to 30 min. On the other hand, Centers IV and V are formed much slower, during a period of 15 to 30 min, but they are much more stable and can polymerize ethylene for several hours without any significant loss of activity.

4. Ziegler-Natta catalysts are sensitive to the presence of the majority of inorganic and organic chemicals. Most chemical compounds poison the active centers. Some chemical compounds do it indiscriminately, whereas others selectively poison only certain types of the centers. Although the poisoning selectivity is never complete, it is still significant enough to be useful as a means of modifying the catalysts.[1]

This article describes the modification of one type of a precursor of a supported Ti-based Ziegler-Natta catalyst by pretreating it with organoaluminum chlorides. The principal experimental tool for the study of the modification effects is the comparison of the untreated and the pretreated catalysts in ethylene/1-hexene copolymerization reactions under standard reaction conditions. Analysis of the produced copolymers by three techniques, the gel permeation chromatographic method (GPC), the crystallization fractionation method (Crystaf), and the differential scanning calorimetry (DSC), provided detailed information about different types of active centers in the catalyst and about the extent and the nature of the catalyst modification.

EXPERIMENTAL

Catalyst Precursor

The majority of the copolymerization experiments were carried out with a single supported catalyst precursor. Its preparation procedure was reported previously.[1,2,6,7] The support was amorphous microspherical porous silica, which was precalcined at 700 °C to remove most of the silanol groups from its surface. Heptane slurry of the calcined silica was contacted at 50 °C for 40 min with a solution of $MgBu_2$ in hexane (purchased from FMC) at a $[MgBu_2]$:[silica] ratio of 1.0 mmol/g. Commercial $MgBu_2$ is a mixture of MgR_2 compounds with R = n-Bu (45 mol %), sec-Bu (45 mol %), and n-C_8H_{17} (10 mol %). Next, $Si(OEt)_4$ was added to the slurry at a $[Si(OEt)_4]$:[silica] ratio of 0.44 mmol/g, and the mixture was stirred at 50 °C for 40 min. Then the mixture was reacted with $TiCl_4$ at a $[TiCl_4]$:[silica] ratio of 1.0 mmol/g for 40 min at 50 to 60 °C. Finally, the liquid phase of the slurry was removed by evaporation, and the remaining solid material, the catalyst precursor, was dried under a nitrogen flow. It contains ~3.0 to 3.5 wt % of Ti and can be used in ethylene polymerization reactions at 80 to 90 °C in combination with any standard organoaluminum cocatalyst,[6,7] such as $AlEt_3$ in this study.

This precursor was pretreated with ethylaluminum chlorides, $AlEt_xCl_{3-x}$ (x = 2, 1.5, and 1), with $AlMe_2Cl$, and with two other organoaluminum compounds $AlEt_2F$ and $Al(n$-$C_{10}H_{21})_3$. The pretreatment was carried out in hexane slurry at 55 °C for 30 min at different molar ratios between the organoaluminum compounds and $TiCl_4$. After removing the liquid phase from the slurries, the precursors were dried at 55 °C for 2 h under a nitrogen flow.

Catalyst Analysis

Chemistry of the preparative steps of the catalyst precursor was studied by gas chromatography (GC). Two Hewlett–Packard gas chromatographs were used. HP 5880A was equipped with a wide-bore, 60-m, 0.75-mm i.d. SUPELCO SPB-1 column and was used in splitless mode with He as a carrier gas (5 cc/min). The column was held at 30 °C for 15 min and then heated at a rate of 2 °C/min. HP 5890A was equipped with two columns, 60-m and 30-m, 0.28-mm i.d. capillary RESTEK MTX-1 columns; both were used in split-flow mode (1:70) with N_2 as a carrier gas (1 cc/min). The columns were heated from 40 to 300 °C at a rate of 5 °C/min. GC analysis of model reactions between $Si(OEt)_4$ and $MgBu_2$ was carried out at different [Si]:[Mg] ratios, with and without silica. It required the estimation of response factors for various organosilicon compounds. Some of them were determined experimentally [for $Si(OEt)_4$, $Si(n$-$Bu)_4$, $Si(OEt)_3Et$, $Si(OEt)_2Et_2$], others were calculated based on the additivity principle.

Copolymerization Reactions

The ethylene/1-hexene copolymerization reactions were carried out in a 3.8-L autoclave under standard conditions. The detailed description of the copolymerization experiments was presented earlier.[2–4,7] $AlEt_3$ (Akzo Nobel, 25-wt % solution in hexane) was used as a cocatalyst in an amount of 3 to 4 mmol. The amount of the catalyst precursors varied from 0.02 to 0.05 g. Hydrogen was used in the copolymerization reactions as a chain transfer agent to reduce the molecular weight of the copolymers. Typical reactions conditions were temperature 85 °C, 1-hexene concentration in solution 16 and 45 vol %, the total reaction pressure 0.90 to 0.93 MPa, the hydrogen partial pressure P_H from 0.12 to 0.18 MPa, the ethylene partial pressure $P_E \sim$ 0.7 to 0.8 MPa, and reaction time 60 min.

Polymer Analysis

Infrared spectra of the copolymers (thin films hot-pressed at ~140 °C) were recorded with a Perkin–Elmer Paragon 1000 FTIR spectrophotometer. Composition of the copolymers was calculated from IR data as described previously[8]; it is reported as the average molar content of 1-hexene, $(C_{Hex}^{cop})^{av}$, mol %.

Molecular weights and molecular weight distributions of the polymers were determined by two techniques. The first one was GPC. It was performed at 145 °C with a Waters 150C Liquid Chromatograph (two columns 10^6, 10^4, and 10^3 Å) using 1,2,4-trichlorobenzene as a solvent. Resolution of GPC curves into elemental components (Flory components, see the definition in refs. 1 and 9) was carried out with the Scientist program (MicroMath Scientific Software), as described earlier.[9] The second technique used rheological properties of polymer melts for measuring weight average molecular weights of polyethylenes, M_w and the widths of their molecular weight distributions, M_w/M_n ratios. It was based on a correlation between M_w values of polyethylenes and their melt indices I_2 and a correlation between M_w/M_n values and melt index ratios, I_{21}/I_2. Both melt indices were measured at 190 °C with a Kayeness extrusion plastometer according to ASTM method D-1238, Conditions E and F. In the case of polymers with a medium-broad molecular weight distribution prepared with typical Ti-based Ziegler-Natta catalysts ($M_w/M_n \sim$ 4–5, $I_{21}/I_2 \sim$ 25–35), the following empirical correlations were found[2,8]: $\log(I_2) \approx 1.440$ to $1.286 \times 10^{-5} \cdot M_w$; $M_w/M_n \approx 0.238 \cdot (I_{21}/I_2)$ to 2.4.

Crystaf analysis of ethylene/1-hexene copolymers was carried out with a Model 110 Crystaf instrument by Polymer Char.[10] A small amount of a copolymer material, ~0.05 g,

was dissolved in 15 mL of 1,2,4-trichlorobenzene at 150 °C; the solution was rapidly cooled to 100 °C and then slowly cooled at a rate of 0.2 °C/min to 30 °C, while the concentration of the copolymer remaining in solution was continuously recorded. Resolution of Crystaf curves into peaks of individual components was carried out similarly to the previously described procedure.[10]
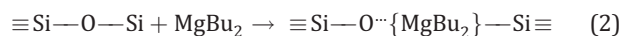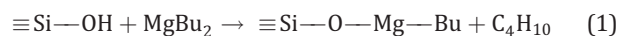
DSC melting curves of the copolymers were recorded using a DuPont 9900 DSC System. First, the samples were melted at 140 °C, slowly crystallized, and annealed by cooling to ~30 °C at a rate of 0.5 °C/min. Then, the melting curves were recorded at a heating rate of 2 °C/min.

Chemistry of Catalyst Synthesis Steps
Every chemical step of the precursor synthesis was studied by GC. In most cases, model mixtures without silica were also analyzed by GC.
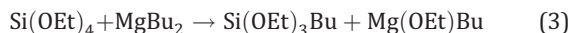
Reactions of Calcined Silica with MgR₂
Calcination of silica at 700 °C leaves a small quantity of silanol groups on its surface, 0.5 to 0.6 mmol/g.[11,12] According to refs. 1 and 13, $MgBu_2$ reacts with such silica at two different sites, one containing a silanol group and another a siloxane group:

$$\equiv Si\text{---}OH + MgBu_2 \rightarrow\ \equiv Si\text{---}O\text{---}Mg\text{---}Bu + C_4H_{10} \quad (1)$$

$$\equiv Si\text{---}O\text{---}Si + MgBu_2 \rightarrow\ \equiv Si\text{---}O\cdots\{MgBu_2\}\text{---}Si \equiv \quad (2)$$

These reactions can be quantitatively examined by GC, if $MgBu_2$ is replaced with $Mg(C_6H_{13})_2$ to avoid the loss of n-butane produced in Reaction 1. Several model experiments were carried out at 55 °C in which the calcined silica was reacted with different amounts of $Mg(C_6H_{13})_2$, then all liquid reaction products were removed, and the solid, after thorough washing with heptane, was reacted with an excess of ethanol to solvolize the remaining Mg—C bonds. Analysis of the evolved n-hexane showed that the conversion of the $\equiv Si$—OH groups in Reaction 1 is high and can approach ~90%.

Reactions with Si(OEt)₄
It is well known in the literature that the interaction of a Mg—R moiety with an alkoxysilane leads to an exchange reaction between the Mg—R and the Si—OR′ bonds.[14] Our experiments with mixtures of solutions of $MgBu_2$ and $Si(OEt)_4$ in the absence of silica showed that these compounds rapidly and irreversibly interact even at 25 °C with the formation of $Si(OEt)_3Bu$, $Si(OEt)_2Bu_2$, $Si(OEt)Bu_3$, and a small quantity of $SiBu_4$:

$$Si(OEt)_4 + MgBu_2 \rightarrow Si(OEt)_3Bu + Mg(OEt)Bu \quad (3)$$

$$Si(OEt)_3Bu + MgBu_2 \rightarrow Si(OEt)_2Bu_2 + Mg(OEt)Bu \quad (4)$$

$$Si(OEt)_2Bu_2 + MgBu_2 \rightarrow Si(OEt)Bu_3 + Mg(OEt)Bu \quad (5)$$

Several isomers of each product with n-Bu and sec-Bu groups are formed. Conversion of $Si(OEt)_4$ in Reactions 3 to 5 depends on the [Si]:[Mg] ratio, is only 25 to 30% at [Si]:[Mg] ~ 4, when the dominant product is $Si(OEt)_3Bu$ (~90%). The number of the formed Si(Bu) bonds in this

reaction significantly exceeds what would be expected if only $MgBu_2$ participated in Reactions 3 to 5, which signifies that $Mg(OEt)Bu$ also reacts with $Si(OEt)_4$:

$$Si(OEt)_4 + Mg(OEt)Bu \rightarrow Si(OEt)_3Bu + Mg(OEt)_2 \quad (6)$$
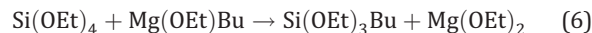
At a [Si]:[Mg] ratio of 0.5, similar to that in the real precursor, the conversion of $Si(OEt)_4$ at 55 °C is ~90%, and the main products are $Si(OEt)_2Bu_2$ (80%) and $Si(OEt)Bu_3$ (15%). Apparently, the driving force in Reactions 3 to 6 is the high thermodynamic stability of the Si(C) bond.
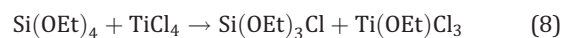
When the real catalyst precursor is synthesized in the presence of silica, a significant fraction of all the $MgBu_2$ is already spent in Reaction 1 and, therefore, the number of the remaining Mg(Bu) bonds is decreased from ~2.0 to ~1.4 mmol/g silica. In this case, the conversion of $Si(OEt)_4$ at $[Si(OEt)_4]$:$[MgBu_2]$ of ~0.5 at 60 °C after 30 min is only 45 to 55%, which is much lower than in the experiments without silica. The main Si-containing products are $Si(OEt)_3Bu$ (~45%) and $Si(OEt)_2Bu_2$ (~5%). They are generated in Reactions 3, 4, and 6, as well as the reaction:

$$\equiv Si\text{---}O\text{---}Mg\text{---}Bu + Si(OEt)_4 \rightarrow\ +\equiv Si\text{---}O\text{---}Mg\text{---}OEt \\ + Si(OEt)_3Bu \quad (7)$$
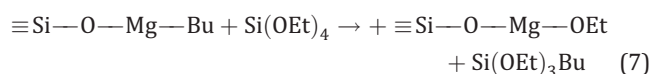
Only ~55% of all the silicon species remain in solution, the rest are absorbed on the silica surface; the fact supported in separate model experiments.

Reactions with TiCl₄
$TiCl_4$ vigorously reacts with all the silicon compounds involved in the precursor synthesis, both the starting $Si(OEt)_4$ and the products of Reactions 3 to 7. Reactions between solutions of $Si(OEt)_4$ and $TiCl_4$ produced viscous heptane-immiscible liquids. GC-MS analysis identified two silicon compounds in them, $Si(OEt)_3Cl$ and $Si(OEt)_2Cl_2$:

$$Si(OEt)_4 + TiCl_4 \rightarrow Si(OEt)_3Cl + Ti(OEt)Cl_3 \quad (8)$$

$$Si(OEt)_3Cl + TiCl_4 \rightarrow Si(OEt)_2Cl_2 + Ti(OEt)Cl_3 \quad (9)$$

Similar model reactions between $TiCl_4$ and two silicon compounds imitating the products of Reactions 3 and 4, $Si(OEt)_3Et$ and $Si(OEt)_2Et_2$, produced single exchange products, apparently, $Si(OEt)_2(Et)Cl$ and $Si(OEt)Et_2Cl$, respectively. The products of all these reactions can be converted back to the products of Reactions 3 to 5 if the reaction with $TiCl_4$ is followed by extensive solvolysis with ethanol-water mixtures.

$TiCl_4$ also readily reacts with all the products of Reactions 3 to 5 formed in the $Si(OEt)_4$–$MgBu_2$ system. These reactions are rapid and produce voluminous dark-brown solids indicative of the reduction of Ti(IV). Reactions 3 to 5 produce two families of products, the silicon compounds and the magnesium compounds. The reactions of $TiCl_4$ with the silicon compounds give $Si(OEt)_xCl_{4-x}$ compounds (Reactions 8 and 9) and $SiBu_x(OEt)_yCl_{4-x-y}$ compounds. The reaction of a Mg—OEt moiety (formed in Reactions 3–7) with $TiCl_4$ should produce Mg—Cl bonds and $Ti(OEt)Cl_3$. In addition, any

TABLE 1 AlR_xCl_{3-x}-Pretreated Catalysts; Composition and Performance in Ethylene/1-Hexene Copolymerization Reactions[a]

| $AlEt_xCl_{3-x}$	[Al]:[Ti] (mol/mol)	Productivity (g/g cat·h)	$(C_{Hex}^{cop})^{av}$ (mol %)	M_w^{av}	M_w/M_n
Part 1. Reaction conditions: $(C_{Hex}/C_E)^{mon} = 5.7-5.9$, $P_H = 0.186$ MPa[b]					
$AlEt_2Cl$	0	5,580	3.5	108,500[b]	4.02[b] (4.0[c])
	3	4,750	5.1	106,900[b]	4.47[b] (4.8[c])
	10	4,150	∼8	102,900[b]	5.20[b]
Part 2. Reaction conditions: $(C_{Hex}/C_E)^{mon} = 2.1$, $P_H = 0.134$ MPa[c]					
$AlEt_2Cl$	0	5,680	1.4	108,800	3.7
	10	3,400	3.7	115,500	
	12.5	3,550	3.4	112,000	5.1
	15	3,100	3.6	115,500	
	25	2,680	3.5	119,500	5.5
Part 3. Reaction conditions: $(C_{Hex}/C_E)^{mon} = 2.8$, $P_H = 0.186$ MPa[c]					
$Al_2Et_3Cl_3$	3	5,450	4.8	100,600	5.8
$AlEtCl_2$	3	4,360	∼5	96,100	7.3

[a] Reaction conditions: cocatalyst $AlEt_3$, 85°C, run time 60 minutes, P_E from 0.69 to 0.74 MPa.

[b] M_w^{av} and M_w/M_n values from GPC data.

[c] Estimations of M_w^{av} and M_w/M_n based on rheological measurements.

Mg—Bu moiety remaining in the system at the end of Reactions 3 to 7 will reduce $TiCl_4$, resulting in the formation of Mg—Cl bonds and the reduced Ti-chloride species. $Ti(OEt)Cl_3$, the product of Reaction 8, may also undergo similar reactions. All these solid products absorb most of the silicon compounds formed in Reactions 3 to 9.

The reaction between $TiCl_4$ and the reaction products in the ternary $MgBu_2$/silica/$Si(OEt)_4$ systems was also studied with GC. Even before the addition of $TiCl_4$, these systems contain only a fraction of the silicon derivatives remaining in the supernatant solution, mostly $Si(OEt)_4$ itself and $Si(OEt)_3Bu$. Addition of $TiCl_4$ results in a nearly complete disappearance from solution of all silicon compounds. Apparently, these reactions produce principally the same species as those formed in the absence of silica, but they all either precipitate in the silica pores or are strongly adsorbed on the silica surface. The ≡Si—O—Mg—OEt species, the product of Reaction 7, can also undergo exchange reactions with $TiCl_4$ or with $Ti(OEt)Cl_3$:

$$TiCl_4 + \equiv Si—O—Mg—OEt \rightarrow Ti(OEt)Cl_3 +$$
$$\equiv Si—O—Mg—Cl \quad (10)$$
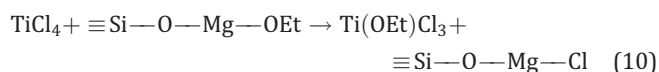
To summarize, the solid catalyst precursor used in this study contains several families of compounds, which affects the formation and functioning of active centers. They include such species (all either bonded to the silica surface or strongly adsorbed on it) as Mg—Cl moieties, $Si(OEt)_xCl_{4-x}$, $SiBu_x(OEt)_yCl_{4-x-y}$, as well as titanium chlorides and titanium ethoxychlorides in which the Ti atoms are in various oxidation states. All the Mg species and all the Si species are absorbed within the silica pores in the precursor. Virtually, no organometallic compounds were found in the supernatant after the $TiCl_4$ addition and practically no butane was found

in the solvolysis/hydrolysis products of the final precursor indicating the absence of any remaining Mg—C or Ti—C bonds.

Polymerization Reactions: Pretreatment of Catalyst Precursor with $AlEt_2Cl$

Two aspects of the ethylene/1-hexene copolymerization reactions give the most significant information about the performance of the multicenter catalysts. The first one is the structure of the produced copolymers, the presence in the components with different molecular weight and different composition. The second source is the copolymerization kinetics, which reflects differences in stabilities of different types of the centers.

General Effects

Parts 1 and 2 in Table 1 give the pretreatment conditions with $AlEt_2Cl$ and the basic testing results in the copolymerization reactions at 85 °C at two different monomer concentration ratios $(C_{Hex}/C_E)^{mon}$, one high, ∼5.8, and another low, 2.1. In general, the pretreatment with $AlEt_2Cl$ has a significant effect on the performance of the catalyst system. Its activity deteriorates slightly, especially at higher $[AlEt_2Cl]$:[Ti] ratios, whereas the catalyst becomes much more responsive to the presence of 1-hexene in the copolymerization reaction: the $(C_{Hex}^{cop})^{av}$ value increases from ∼3.5 to > 8 mol % in Part 1 of the table and from 1.4 to 3.5 mol % in Part 2. Concurrently, the molecular weight distributions of the copolymers become broader.

To evaluate the effects of the copolymerization conditions, the precursor pretreated at $[AlEt_2Cl]$:[Ti] = 10 was tested in a series of reactions at three different $(C_{Hex}/C_E)^{mon}$ ratios, 5.85, 2.60, and 2.17. As expected, as the $(C_{Hex}/C_E)^{mon}$ ratio decreases, so does the $(C_{Hex}^{cop})^{av}$ value also decreases from ∼8 to 3.4 mol %. This dependence was analyzed with the

copolymer composition equation in the case of low α-olefin contents,[1] $[C_{Hex}/(1 - C_{Hex})]^{cop} \approx (1/r_1)\cdot(C_{Hex}/C_E)^{mon}$. The reactivity ratio r_1 for the untreated catalyst is ∼80 to 100, that is, ethylene is much more reactive in the copolymerization reaction compared with 1-hexene.[1,3] However, the r_1 value for the pretreated catalyst decreased to ∼50 reflecting the increased sensitivity to 1-hexene.

Part 3 in Table 1 gives the copolymerization data for the same catalyst precursor pretreated with two other ethyl-aluminum chlorides, $Al_2Et_3Cl_3$ and $AlEtCl_2$. The results are similar: the pretreated catalysts become more responsive to the presence of 1-hexene in the copolymerization reactions and their molecular weight distribution becomes broader.

Nature of Catalyst Modification

Up to this point, the general results on the pretreatment with $AlEt_2Cl$ do not differ much from several similar studies of other ethylene polymerization catalysts. The most perti-nent results of this type were published in 1992 to 2000 in a series of articles, which examined the $AlEt_2Cl$ pretreatment of a well-defined crystalline Ti-Mg complex $[Mg_2(\mu\text{-}Cl)_3\cdot(THF)_6]^+ [TiCl_5\cdot THF]^-$ and silica-supported catalysts using this complex.[15–19] The pretreatment of the complex at $[AlEt_2Cl]:[Ti]$ ratios from 1.4 to 8.6 was also accompanied by significant changes in the catalyst behavior. In particular, this pretreatment also significantly increased the sensitivity of the catalysts to α-olefins and broadened the molecular weight distribution of the copolymers. These are the same effects that were found in this study, although the catalyst precursor we used was synthesized from different reagents and in a completely different procedure.

Catalyst modification is usually viewed in the literature as chemical reactions between precursors of active centers and the modifying chemical compounds, that is, as reactions which change the nature of the active centers. For example, the changes in the behavior of the $AlEt_2Cl$-pretreated Ti—Mg com-plex described in refs. 15–19 were ascribed to a change in the ratio between isolated and clustered Ti^{3+} species after the reaction of the pretreated complex with the cocatalyst $AlEt_3$.

However, the use of modern polymer characterization techni-ques provides more nuanced information about the nature of the catalyst modification. The modifiers interact with the pre-cursors of active centers and their action can be partially selective; that is, they may reduce the number or reactivity of some types of active centers, while leaving other centers mostly intact or even increasing their number or reactivity. The data discussed in the following sections demonstrate that, indeed, viewing catalyst modifiers as the agents of redistribu-tion in the relative populations of different active centers can explain the experimental findings presented in Table 1.

Changes in Molecular Weight Distribution

As described in Introduction, all heterogeneous Ziegler-Natta polymerization catalysts contain several populations of active centers which differ in the molecular weights of polymer components they produce. If only one type of center exists in a catalyst, polymers prepared with it have a narrow
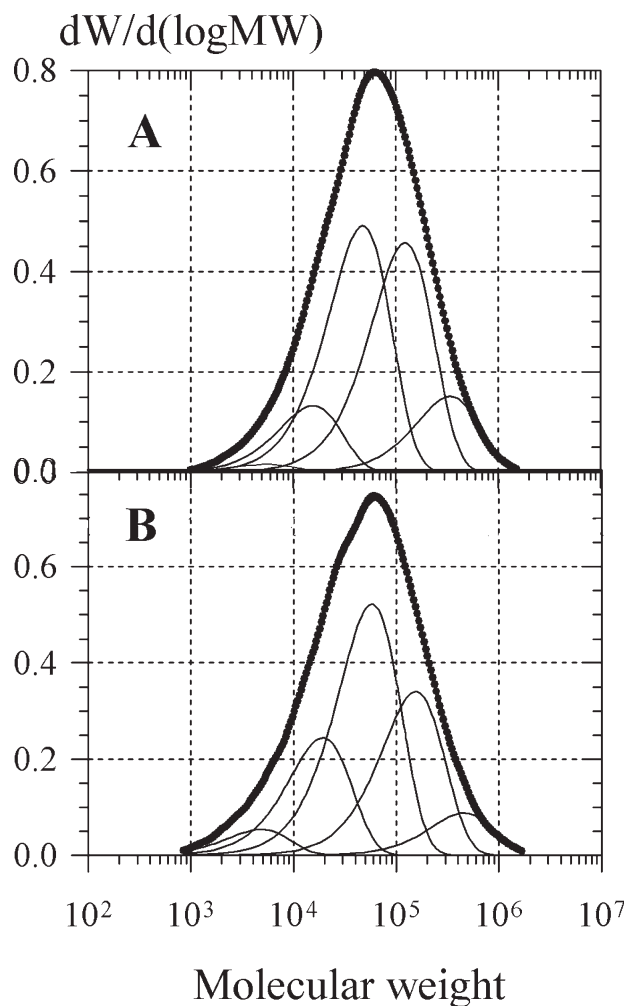

FIGURE 1 GPC curves of ethylene/1-hexene copolymer pro-duced with the untreated catalyst (top) and with the precursor pretreated at $[AlEt_2Cl]:[Ti] = 10$ (bottom) (see Table 1).

molecular weight distribution $(M_w/M_n \sim 2.0)$[1,9]; their GPC curves are narrow and have a characteristic asymmetric appearance.[9] The M_w/M_n ratios of the polymers prepared with supported Ti-based Ziegler-Natta catalysts usually vary between 3.5 and 5.5 (Table 1). GPC curves of such polymers are quite broad and can be resolved[1,9] into GPC curves of their elemental components, each component representing a polymer material produced by a single type of active center or by several types of centers producing polymer compo-nents with similar average molecular weights.

Figure 1 shows two examples of such resolution, one for an ethylene/1-hexene copolymer prepared with the untreated catalyst and another a copolymer prepared with the catalyst pretreated at $[AlEt_2Cl]:[Ti] = 10$. Table 2 gives the results of the GPC resolution. Each catalyst contains five types of active centers, which differ greatly in the M_w values of the polymer components they produce, from ∼5000 for the component produced by Center I to ∼420,000 for the component pro-duced by Center V. Taking into account, the unavoidable uncertainty in resolution of curves of a complex shape into

TABLE 2 GPC Curve Resolution Results for Ethylene/1-Hexene Copolymers Produced with Untreated and AlEt$_2$Cl-Pretreated Catalysts at a High 1-Hexene Concentration (Part 1 in Table 1)

$(C_{Hex}^{cop})^{av}$ Center	[AlEt$_2$Cl]:[Ti] = 03.5 mol %		[AlEt$_2$Cl]:[Ti] = 35.1 mol %		[AlEt$_2$Cl]:[Ti] = 10 ∼ 8 mol %	
	M_w	Fraction (%)	M_w	Fraction (%)	M_w	Fraction (%)
I	∼5,600	∼1	4,700	2.2	4,800	4.3
II	15,700	10.6	17,000	13.4	19,200	19.6
III	47,900	39.4	53,300	42.7	57,700	41.8
IV	124,400	36.6	144,700	34.0	154,300	27.2
V	342,000	12.2	430,800	7.7	452,700	7.1

several closely spaced elemental peaks[9] (Fig. 1), it can be stated that modification with AlEt$_2$Cl does not affect the performance of individual centers: the average molecular weight of each polymer component remains approximately the same. What changes with the pretreatment are the contents of the polymer components: as the [AlEt$_2$Cl]:[Ti] ratio increases, the fractions of the components produced by Centers IV and V gradually decrease and the fractions of the components produced by Centers I and II increase.

This redistribution of the copolymer components is universal. For example, the same effect was observed in the copolymerization reactions at a significantly lower $(C_{Hex}/C_E)^{mon}$ ratio of 2.1: the catalyst pretreated at [AlEt$_2$Cl]:[Ti] = 15 produced a copolymer with 6% less of components IV and V. This change was sufficient to increase the 1-hexene content in the copolymer from 1.4 to 3.6 mol %.

Changes in Compositional Distribution

The Crystaf method is an effective technique for the analysis of the compositional distribution in ethylene/α-olefin copolymers.[10,20,21] Crystaf curves of compositionally uniform copolymers prepared with catalysts containing only one type of active center have single narrow crystallization peaks.[1,10] In contrast, Crystaf curves of ethylene/α-olefin copolymers produced with multicenter Ziegler-Natta catalysts are broad and consist of several overlapping peaks at crystallization temperatures from 83 to ∼35 °C (Fig. 2).

These Crystaf data were quantified using the earlier developed computerized method,[10] which is based on resolution of the Crystaf curves into their elemental components. Each such component consists of copolymer molecules of approximately the same composition; the lower is the α-olefin content in a copolymer, the higher is its crystallization temperature. The components in the Crystaf curves are arbitrarily marked as A, B, C, etc., in the order of decreasing crystallization temperature. Complex cocrystallization phenomena between copolymer components of different compositions[10] result in a strong dependence of half-widths of the elemental peaks on their mutual proximity obvious from Figure 2. The range of compositions for different components is quite broad, from 0.3 to 0.5 mol % of 1-hexene for the highly crystalline material of peaks A and B (the material produced by Centers IV and V) to ∼5.5 to 6 mol % for the peak F, which

is mostly produced by Center II. In addition, a significant fraction of the copolymers does not crystallize even at the lowest temperature in the Crystaf procedure, 30 °C.[10] This dissolved material is nearly completely amorphous, it is mostly produced by Center I.

Table 3 lists parameters of elemental peaks in the Crystaf curves of ethylene/1-hexene copolymers prepared under conditions given in Part 1 in Table 1 with both the untreated catalyst and the one pretreated at [AlEt$_2$Cl]:[Ti] = 10. Both curves contain peaks with maximums at approximately the same crystallization temperatures; therefore, the compositions of the elemental components (estimated as described in ref. 10) are also close for the two copolymers. As shown in Table 3, the most obvious difference between the copolymers is the relative areas of different Crystaf peaks. The pretreated catalyst produced a copolymer with a lower fraction of components A–C and with a much higher fraction of the soluble amorphous material. Of course, these changes are
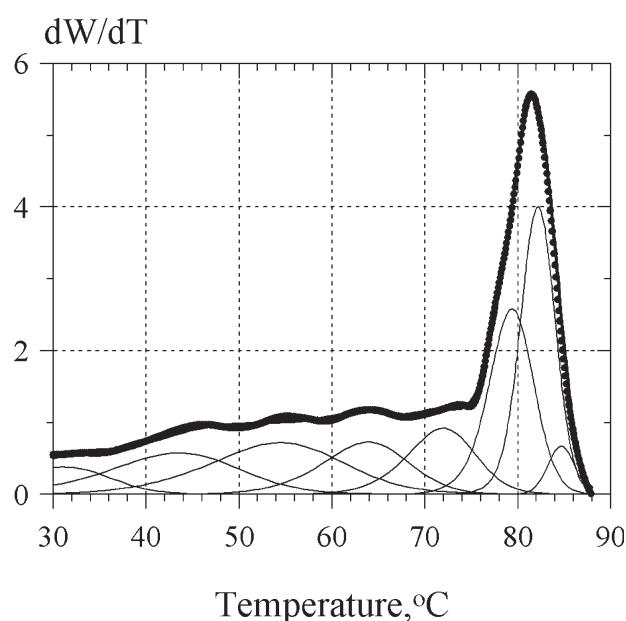

FIGURE 2 The Crystaf curve of an ethylene/1-hexene copolymer produced with the untreated catalyst and its resolution into elemental components.

TABLE 3 Parameters of Individual Peaks in Crystaf Curves of Two Ethylene/1-Hexene Copolymers[a]

Crystaf Peak	T (°C)	C_{Hex}^{cop} (mol %)	Fraction (%) at [Al]:[Ti] = 0	Fraction (%) at [Al]:[Ti] = 10
A	83.1–83.2	0.3	9.0	5.2
B	81.5–81.7	0.5	27.3	14.9
C	76.6–77.2	1.0–1.1	8.8	5.6
D	68.2–69.4	1.9–2.0	10.5	6.0
E	58.3–60.3	3.0–3.2	12.8	10.2
F	35.2–40.2	5.3–5.9	15.1	15.6
Soluble fraction			16.6	42.6

[a] Reaction conditions are in Part 1 of Table 1.

reflected in the change in the average copolymer composition: the $(C_{Hex}^{cop})^{av}$ value increases from 3.5 to ~8 mol %.

The conclusions concerning the AlEt$_2$Cl effect on the compositional distribution of the copolymers were corroborated by the data on the melting points and the crystallinity degree of the copolymers, which were measured with the DSC method (Table 4). The position of the main melting peak on the DSC curve of any ethylene/α-olefin copolymer prepared with a Ti-based catalyst reflects the properties of copolymer material with the lowest α-olefin content and the highest crystallinity degree.[1] These copolymer fractions are produced by Centers IV and V; they appear in GPC curves as polymer components IV and V (Fig. 1) and in Crystaf curves as components A and B (Fig. 2). The analysis of the GPC and the Crystaf data from Tables 2 and 3 suggests that the components produced by Centers IV and V under the same copolymerization conditions should have the same characteristics, although the fractions of these materials decrease as the [AlEt$_2$Cl]:[Ti] ratio in the pretreated catalyst increases. The DSC data confirm this prediction: the peak melting points of the copolymers remain practically the same irrespective of the amount of AlEt$_2$Cl used for the catalyst pretreatment. However, the crystallinity degree of these copolymers (also estimated from DSC data) decreases in parallel with the increase of the [AlEt$_2$Cl]:[Ti] ratio; it reflects the decrease of the fraction of the highly crystalline components produced by Centers IV and V.

Polymerization Reactions: Different Types of Catalyst Modification

The term "catalyst modification", when applied to heterogeneous Ziegler-Natta catalysts, is general and can have dif-ferent meanings depending on the nature of interactions between the active centers in the catalysts and the modifiers. The active centers in Ziegler-Natta catalysts are coordinatively unsaturated, and the most common type of such an interaction is poisoning of the active centers in Lewis acid-base reactions.[22] Such reactions can be either completely reversible (with such poisons as CO or allene) or practically irreversible (with amines, conjugated dienes, etc.).[1,3,22,23]

All the data in Tables 2 to 4 demonstrate that increasing the [AlEt$_2$Cl]:[Ti] ratio results in a decrease in the fraction of highly crystalline polymer components with low C_{Hex}^{cop} and high molecular weights and an increase in the fraction of the components of low crystallinity with high C_{Hex}^{cop} and low molecular weights. In principle, all these data can be interpreted either as gradual poisoning of the precursors of Centers IV and V, or as gradual activation of the precursors of Centers I and II, or as both the changes occurring in parallel.

The following approach was used to discriminate between these three possibilities. Table 5 compares absolute yields of different copolymer components produced in reactions under identical conditions (listed in Part 1 of Table 1). Two sets of data are compared; one derived from the Crystaf data and another from the GPC data. To avoid uncertainties related to separation of closely spaced peaks (see Figs. 1 and 2), both the GPC and the Crystaf results were rearranged to produce the data for several distinct large fractions of the copolymers. The results clearly show that the pretreatment of the catalyst precursor with AlEt$_2$Cl produces two different effects. First, it indeed significantly reduces the productivity of active Centers IV and V, those centers which generate high

TABLE 4 Crystaf and DSC Data for Ethylene/1-Hexene Copolymers (Part 1 in Table 1)

[AlEt$_2$Cl]:[Ti]	$(C_{Hex}^{cop})^{av}$ (mol %)	Amorph. Material (%)	Highly Crystalline Fractions A+B (%)	T_m (°C)	Crystallinity Degree (%)
0	3.5	16.6	36.3	126.5	40-42
3	5.1	26.5	23.9	127.1	~39
10	~8	42.6	20.2	126.5	~13

TABLE 5 Yields of Various Components of Ethylene/1-Hexene Copolymers[a] Produced with Untreated and AlEt$_2$Cl-Pretreated Catalysts (Part 1 in Table 1); Data from Crystaf and GPC Analysis

Catalyst:	[AlEt$_2$Cl]:[Ti] = 0	[AlEt$_2$Cl]:[Ti] = 10
Total yield (g/g cat·h)	5,580	4,150
Crystaf data, yields (g/g cat·h)		
Highly cryst. fraction (A + B)	2,025	840
Medium-cryst. Fraction (C–E)	1,790	900
Low-cryst. fraction (F)	840	640
Amorphous material	930	1,770
GPC data, yields (g/g cat·h)		
IV + V	2,720	1,420
III	2,200	1,740
I + II	650	990

molecular weight copolymer components with a low 1-hexene content. The amounts of Crystaf components A and B and the amounts of GPC components IV and V are both reduced by a factor of 2 to 2.5. The data in Table 5 also reveal the second pretreatment effect: the productivity of active centers I and II, the centers producing low molecular weight copolymer components with a high 1-hexene content (the amorphous material in the Crystaf analysis, GPC components I and II), increases by a factor of 1.5 to 2.

Polymerization Reactions: Kinetic Manifestations of Catalyst Modification

Different types of active centers in supported Ziegler-Natta catalysts exhibit different kinetic behavior in ethylene/α-ole-
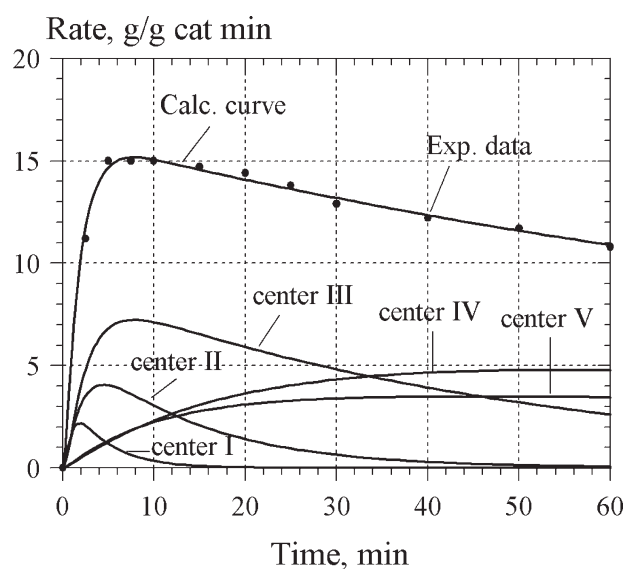

FIGURE 3 Kinetic curves of ethylene consumption by different types of active centers in ethylene/1-hexene copolymerization reactions with the untreated catalyst at 80 °C at $(C_{Hex}/C_E)^{mon}$ = 2.0.

fin copolymerization reactions.[1–4] Figure 3 gives one example of kinetic curves of ethylene consumption by different types of active centers in ethylene/1-hexene copolymerization reactions with the untreated catalyst at 80 °C. The method used for the generation of these kinetic curves was thoroughly described in refs. 3 and 4. When such copolymerization reactions are carried out at 80 to 90 °C, Centers I and II are formed rapidly within ∼10 min, but they decompose rapidly and become inactive after 20 to 30 min. In contrast, Centers IV and V are formed much slower, during a period of ∼25 to 30 min, but they are significantly more stable, whereas Centers III exhibit an intermediate behavior.

These kinetic differences provide additional information about the nature of the catalyst modification with AlEt$_2$Cl. Figure 4(A) shows kinetic curves of ethylene consumption in the copolymerization reactions with the untreated and the AlEt$_2$Cl-pretreated catalysts. When the untreated catalyst precursor is used, the kinetic curve (which is the sum of the
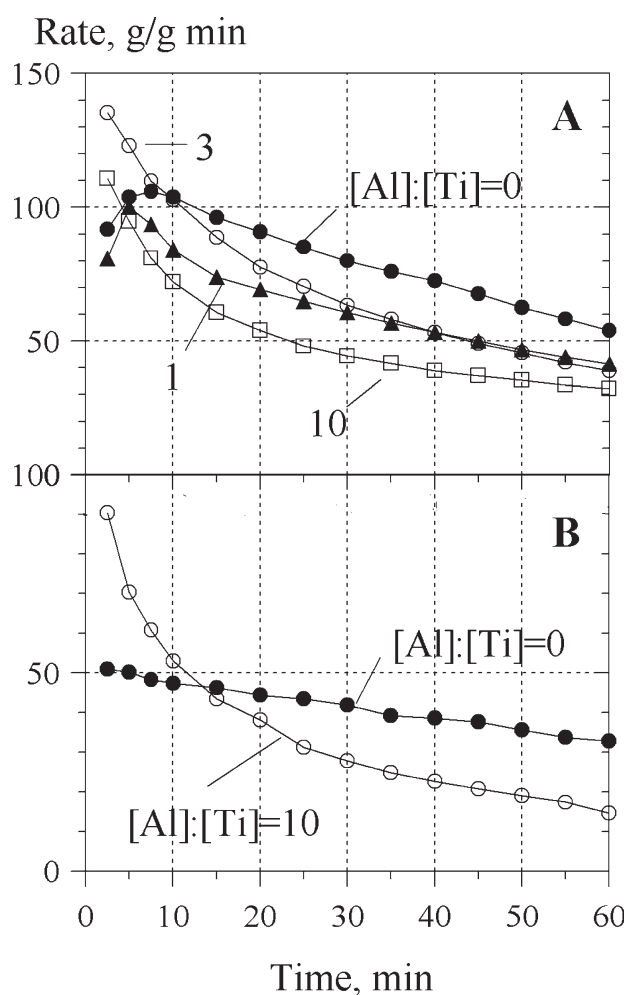

FIGURE 4 Kinetic curves of ethylene consumption in ethylene/1-hexene copolymerization reactions. Reaction conditions are in Part 1 of Table 1. A: Standard catalyst; numbers give [AlEt$_2$Cl]:[Ti] ratios. B: Catalyst precursor prepared at [Si(OEt)$_4$]:[MgBu$_2$] ∼0.68, pretreatment at [AlEt$_2$Cl]:[Ti] = 10.

kinetic curves of all five types of active centers, as shown in Fig. 3) reaches a maximum at ~8 to 10 min and then gradually declines. When this precursor is pretreated with $AlEt_2Cl$, two changes in the catalyst behavior become apparent:

1. At the end of the copolymerization reactions (60 min in these experiments), the reaction rates decrease as the $[AlEt_2Cl]:[Ti]$ ratio increases:

$$[AlEt_2Cl]:[Ti] \text{ in the precursor}: \quad 0 \quad 1 \quad 3 \quad 10$$
$$\text{Relative rate after 60 minutes}: \quad 1 \quad 0.78 \quad 0.72 \quad 0.58$$

As Figure 3 shows, Centers I and II and a large fraction of Centers III have already decomposed after 60 min; therefore, this decline in activity reflects the reduction in the number of Centers IV and V, in agreement with the data in Table 5.

2. In the beginning of the copolymerization reactions, the reaction rates increase as the $[AlEt_2Cl]:[Ti]$ ratio increases. This change supports the second conclusion from the data in Table 5: the pretreated catalysts contain a higher number of Centers I and II, which become active soon after the start of the polymerization reaction.

Both effects were even more apparent when another similar catalyst precursor was tested. It was prepared following the same procedure (see Experimental section) but using a lower $[MgBu_2]:[silica]$ ratio, 0.85 mmol/g, and a higher $[Si(OEt)_4]:[silica]$ ratio, 0.68. This precursor was prepared at the same $[TiCl_4]:[silica]$ ratio of 1.0 mmol/g, and therefore, the principal chemical difference between it and the standard precursor is the higher molar $[Si(OEt)_4]:[MgBu_2]$ ratio, ~0.68 versus 0.44. This second precursor was also modified with $AlEt_2Cl$. The untreated precursor with this formulation contains a low number of Centers I and II and its activity is dominated by Centers IV and V, and the respective kinetic curve in Figure 4(B) is nearly flat (see Fig. 3 for comparison). The pretreatment at $[AlEt_2Cl]:[Ti] = 10$ brought about the same two changes as those in the standard catalyst precursor. First, the reaction rate at the end of the copolymerization reaction decreased by ~55% due to poisoning of Centers IV and V, and second, the initial rate increased by ~80% due to activation of Centers I and II. Both these changes transformed a relatively stable catalyst of moderate activity into a rapidly decaying one.

Other Organoaluminum Modifiers

Three other organoaluminum compounds were tested as modifiers for the standard catalyst precursor. Its treatment with $AlMe_2Cl$ was carried out at $[AlMe_2Cl]:[Ti] = 10$, and the pretreated precursor was tested under the copolymerization conditions in Part 2 of Table 1. As expected, the pretreatment with $AlMe_2Cl$ produced the results similar to those caused by the pretreatment with $AlEt_2Cl$: the 1-h productivity decreased from 5680 to 4950 g/g cat, and the $(C_{Hex}^{cop})^{av}$ value increased from 1.4 to 3.3 mol %. GPC resolution data also showed a similar pattern: the combined content of components IV and V decreased by ~7% and the combined content of components I and II increased by ~30% compared

with the data for the untreated precursor. Crystaf analysis confirmed these results: the fraction of components A and B decreased from >67% to ~62%, the fraction of components of low crystallinity increased from ~16 to ~23%, and the fraction of the soluble amorphous material increased from ~5 to 14.5%.

In contrast, the pretreatment of the catalyst precursor with $Al(n\text{-}C_{10}H_{21})_3$ and $AlEt_2F$ resulted in severe deterioration of the catalyst activity. Both compounds indiscriminately destroyed precursors of the active centers of all types and produced no changes in the contents of the polymer components.

DISCUSSION

The catalyst described in this article was designed to produce linear low-density polyethylene (LLDPE) resins, that is, semicrystalline ethylene/α-olefin copolymers with the α-olefin content of 3.0 to 3.5 mol %. The main practical requirements for such catalysts are high productivity, the ability to copolymerize well α-olefins with ethylene, and the ability to produce copolymers with a moderately broad molecular weight distribution characterized by a M_w/M_n ratio of 4.0 to 5.0.

The application of various distributive analytical techniques, such as GPC and Crystaf, allows reformulation of these general requirements into specific, active center-oriented goals: a deliberate manipulation of the active center distribution. From the practical point of view, it is desirable to reduce the productivity of Centers IV and V (the centers producing high molecular weight and highly crystalline copolymer components) and to enhance the productivity of Centers II and III.

The aforementioned results show that the pretreatment with $AlEt_2Cl$ or with $AlMe_2Cl$ does not substantially change the chemical structure of individual active centers in the catalyst, but it changes the proportion among the different types of centers. Two major changes occur in parallel: a significant reduction in the activity of Centers IV and V and a noticeable increase in the activity of Centers I and II. The existence of these two unrelated effects calls for two different explanations.

According to ref. 22 active Centers IV and V contain reduced Ti atoms. These centers readily polymerize ethylene, but they copolymerize α-olefins with ethylene poorly, and they do not homopolymerize α-olefins. Our approximate estimations of the productivity of these two centers in several untreated catalysts prepared according to the same recipe (described in Experimental section) with different amounts of $MgBu_2$ and $Si(OEt)_4$ showed that the productivity of Centers IV and V in the copolymerization reactions does not depend on the $[Si(OEt)_4]:[MgBu_2]$ ratio and remains nearly constant, 2500 to 2700 g/g cat h. Thus, the reactivities of Centers IV and V are independent of the presence of $Si(OEt)_4$ and the products of its reactions during the synthesis of the precursor (Reactions 3–9). Judging by the data in Table 5, selective poisoning of these centers with $AlEt_2Cl$, which is

also obvious from the kinetic data in Figure 4, is most probably caused by Lewis-acidic properties of the modifier.

Active Centers I and II behave differently compared with Centers IV and V. These centers easily copolymerize α-olefins with ethylene, and they can homopolymerize α-olefins, mostly to atactic polymers and polymers of a low isotacticity level. When the untreated catalyst precursors are prepared with different amounts of $Si(OEt)_4$, the higher the amount of the used $Si(OEt)_4$ the lower the productivity of Centers I and II. Centers I and II are especially active in the beginning of the copolymerization reactions, the time periods when Centers IV and V are only starting to form (Fig. 3). The initial polymerization rate for the untreated precursor prepared at $[Si(OEt)_4]:[MgBu_2] = 0.44$ is ~110 g/g cat min [Fig. 4(A)], but it decreases to 45 to 50 g/g cat min at $[Si(OEt)_4]:[MgBu_2]$ ~0.68 [Fig. 4(B)].

As discussed in Section 3.1, reactions between silica, $MgBu_2$, and $Si(OEt)_4$ in the course of the precursor synthesis generate several organosilicon compounds of the general formula $Si(OEt)_xBu_{4-x}$ in Reactions 3 to 7. Then these compounds are converted by $TiCl_4$ into organosilicon chlorides $Si(OEt)_x$-Bu_yCl_{4-x-y} in Reactions 8 and 9 Apparently, some of these organosilicon products coordinate with the predecessors of Centers I and II and either prevent the formation of the active centers from them or partially poison the centers after they are formed. The higher is the amount of $Si(OEt)_4$ with respect to the number of the Mg—C bonds present during the precursor synthesis the higher the poisoning degree.

This type of selective poisoning by alkylalkoxysilanes is well researched. When Ti-based Ziegler-Natta catalysts are used for homopolymerization of propylene and other α-olefins, alkylalkoxysilanes of the general formula $Si(OR)_xR'_{4-x}$ (where $x = 2$ and 3; R = Me, Et; R′ = isoBu, isoPr, cyclohexyl, and cyclopentyl) are widely used for selective poisoning of active Centers I and II, the centers which form atactic polymers. This poisoning improves the fractional isotacticity of α-olefin polymers.[1,24–26] The effects of $Si(OR)_xR'_{4-x}$ compounds in ethylene/α-olefin copolymerization reactions are also known.[22] When these compounds are admitted into the copolymerization reactions, the average catalyst activity decreases (all these silicon compounds are poisons), the initial polymerization rates decrease, α-olefin contents in the copolymers decrease, and the average molecular weights of the copolymers increase. All these data are in agreement with the conclusion that the compounds $Si(OEt)_xBu_{4-x}$ formed in Reactions 3 to 7 and their chlorinated derivatives $Si(OEt)_xBu_yCl_{4-x-y}$ may indeed be selective poisons of active Centers I and II.

Apparently, $AlEt_2Cl$ and other organoaluminum chlorides react with these compounds, convert them into nonpoisonous products, and thus restore the predecessors of Centers I and II. $AlEt_2Cl$ is usually used in a significant excess with respect to the Si—OEt bonds remaining in the catalyst precursor after Reactions 3 to 7 (Table 1), and one can assume that the primary reaction between the Si—OEt bond and $AlEt_2Cl$ is similar to its reaction with the Grignard reagent.[27]

$$\equiv Si\!-\!OEt + AlEt_2Cl \rightarrow Si\!-\!Et + Al(Et)(OEt)Cl \qquad (11)$$
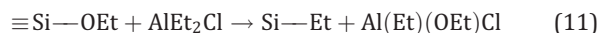
However, the final products could be species containing both Al and Si atoms, which are linked via bridging OEt groups.

The modifying effect of $AlEt_2Cl$ on supported Ziegler-Natta catalysts in ethylene/α-olefin copolymerization reactions has important practical implications. These catalysts are often used to copolymerize ethylene and 1-hexene in gas-phase, fluidized-bed reactors. An improvement in the overall ability of such catalysts to effectively copolymerize 1-hexene with ethylene allows the operation of the reactors at lower [1-hexene]/[ethylene] ratios and, therefore, at higher ethylene partial pressures and with higher productivity. Another advantage of the catalysts that incorporate 1-hexene well is their ability to produce low density LLDPE resins in gas-phase fluidized-bed reactors, a target that is difficult to reach when using unmodified catalysts.

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