

A New Method for Measuring the Number of Active Centers in Heterogeneous Ziegler–Natta Catalysts

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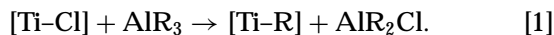
A new chemical method is developed for the measurement of the number of active centers in heterogeneous titanium-based Ziegler–Natta catalysts. The method can be applied to polymerization reactions of various alkenes using AlMe₃ as a cocatalyst. After a polymerization reaction is completed, the solid phase (a mixture of a catalyst and a polymer) is separated from the liquid phase and thoroughly washed with fresh solvent to remove monomers and the cocatalyst. In the absence of an alkene and cocatalyst, active centers with growing polymer chains undergo the β-hydrogen elimination reaction and generate Ti–H bonds. The washed solid is reslurried in a small quantity of a hydrocarbon and treated with benzoyl chloride which is converted by the Ti–H species into benzaldehyde. After removal of excess benzoyl chloride from the slurry (in a reaction with additional AlMe₃), the liquid layer is analyzed by the GC method. The amount of benzaldehyde and its reaction products with AlMe₃ is the measure of the concentration of Ti–H bonds derived from active centers. Several examples of the active site measurement are presented for polymerization and copolymerization reactions of ethylene, propylene, and 1-hexene with different catalyst systems.

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Key Words: Ziegler–Natta catalysts; active centers, measurement method; active centers, alkene polymerization with.

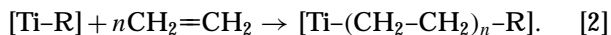
INTRODUCTION

Titanium-based heterogeneous Ziegler–Natta catalyst systems for alkene polymerization are usually prepared from two components, a solid component (called a catalyst) containing Ti–Cl bonds on the surface of catalyst particles, and an organoaluminum compound, AlR₃ or AlR₂Cl (called a cocatalyst). Active centers in these systems, C*, are formed in reactions of the Ti–Cl bonds and the cocatalyst. The reaction produces Ti–R groups:

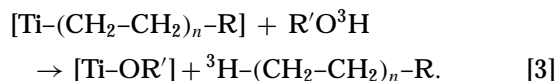


Some of these Ti–R groups become active centers in polymerization reactions; they insert alkene molecules into their Ti–C bonds with the formation of growing polymer chains

attached to the Ti atoms. For example, in the case of ethylene polymerization, the chain growth reaction is

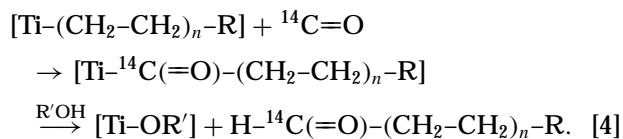


Several methods have been developed in the past for the C* measurement in Ziegler–Natta catalysts based on reacting the polymerization centers with different chemical compounds [see reviews in Refs. (1–5)]. Two of the methods are the most popular. The first one is based on quenching a polymerization reaction with tritium-labeled alcohols R'O³H (6, 7) or water (8). The alcohols react with growing polymer chains and convert them into Ti alkoxides and polymer molecules containing tritium atoms on their ends:



The quantity of tritium in the polymer should correspond to the number of growing polymer chains at the moment of alcohol introduction. Unfortunately, most Ziegler–Natta systems contain another type of species, polymer chains carrying AlR₂ groups on their ends, which also react with R'O³H with the formation of labeled polymer molecules. [Polymer chains with AlR₂ end groups are generated in chain transfer reactions with cocatalysts (1)]. The chains containing AlR₂ groups gradually accumulate over the course of polymerization reactions, which makes the C* measurement with labeled alcohols uncertain.

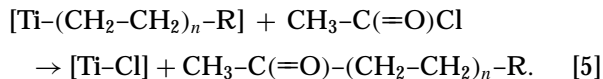
The second method of C* measurement involves addition of ¹⁴C-labeled CO to a polymerization reaction (9, 10). It is generally assumed that CO inserts into a growing polymer chain with the formation of a ¹⁴C-labeled carbonyl end group in the chain. Such an end group cannot insert alkene molecules anymore and, when the reaction is eventually terminated with an alcohol, it is separated from the Ti atom:



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CO is a powerful poison for Ziegler-Natta catalysts because it coordinates with Ti atoms in active centers (1). It is not certain, however, how fast and how irreversible the C=O insertion reaction into the Ti-C bond is and whether it involves all active centers. Model studies (11, 12) demonstrated high complexity of CO interaction with polymerization centers.

Several years ago, Fan and co-workers published a series of articles detailing a new method for the C* measurement in Ziegler-Natta catalysts (13-16). The method is based on the reaction between the growing polymer chain and acetyl chloride:



This idea has a significant appeal: directionality of the reaction (formation of the Ti-Cl bond and a polymer chain with the carbonyl end group) appears reasonable, and the presence of the ketone group in the polymer yields itself to dependable identification. There are, however, two obstacles to the immediate transfer of this technique to the most interesting types of Ziegler-Natta catalysis, polymerization of light alkenes, such as ethylene and propylene, with solid and supported catalysts:

1. The technique, as originally designed, was used for the study of a homogeneous reaction, polymerization of 1-octene with the $\text{TiCl}_4/\text{MgCl}_2-\text{AlEt}_3$ catalyst system at 30°C. Poly(1-octene) is completely soluble in the reaction medium, *n*-heptane. The measurement of carbonyl groups in the polymer was carried out with the UV-vis method after reacting the ketone produced in reaction [5] with 2,4-dinitrophenylhydrazine [it generates a hydrozone (13)]. Polymerization of light alkenes with Ziegler-Natta catalysts results in insoluble polymers, and the UV-vis method cannot be used.

2. The usefulness of the Fan technique hinges on the absence of a significant reaction between acetyl chloride and the cocatalyst. Investigation of the reaction between acetyl chloride and $\text{Al-}i\text{-Bu}_3$ at 30°C (13) showed that it produces 4-methyl-2-pentanone, but the reaction is slow and can be neglected if the hydrozone is analyzed quickly. However, this reaction may greatly accelerate at higher temperatures typical for Ziegler-Natta catalysis, usually in the 70-90°C range.

PRELIMINARY RESULTS

Our initial attempts of modifying the Fan method for polymerization of light alkenes at high temperatures were focused on two subjects:

1. The search for an alternative method for measuring the concentration of carbonyl groups in polymers, which could be applied to insoluble polymers.

2. Investigation of reactions between AlR_3 and acid chlorides and between AlR_3 and ketones produced in reaction [5]. Such reactions are well known (17) and their outcome can affect the analysis results.

The C=O stretching mode has one of the highest absorption coefficients in IR spectra of organic compounds; it was reasonable, therefore, to use the IR method for the ketone measurement (after removal of excess acetyl chloride and a cocatalyst). In a preliminary experiment, an ethylene polymerization reaction was performed at 85°C with a supported Ti-based catalyst activated with AlEt_3 , and acetyl chloride was added to it after 15 min. Indeed, the IR spectrum of the purified polymer, after subtraction of the spectrum of a similarly produced blank polymer, contained a small $\nu(\text{C}=\text{O})$ band. However, it was positioned at 1741 cm^{-1} , which is typical for the ester group rather than for a ketone expected in reaction [5] (1719-1716 cm^{-1}). These data suggest that the ketone underwent secondary reactions, an observation which makes the C* measurement method described in Refs. (13-16) less straightforward.

It is well known that acid chlorides readily react with organoaluminum compounds (17):

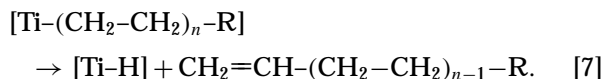


However, GC tests showed that a reaction between $\text{Al}(\text{C}_6\text{H}_{13})_3$ and acetyl chloride does not end with the expected 2-octanone but produces a variety of other organic compounds as well. The reasons for this became obvious when the mixture containing five ketones $\text{CH}_3\text{C}(=\text{O})\text{R}$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_4\text{H}_9, n\text{-C}_5\text{H}_{11},$ and $n\text{-C}_6\text{H}_{13}$) was reacted, in two separate experiments at 20°C, with AlMe_3 and $\text{Al}(\text{C}_6\text{H}_{13})_3$ followed by decomposition of excess AlR_3 with methanol. In both cases, all ketones rapidly reacted with the AlR_3 compounds with the formation of a variety of products. This is an expected result in view of the well-known chemistry of organoaluminum compounds (see details below). These reactions limit the applicability of the C* measurement method described by Fan *et al.* Depending on reaction conditions, one can expect that both the quenching agent, an acid chloride, and ketones formed in reactions [5] and [6] may react with a cocatalyst and that the nature of these products depends on the ratio between the acid chloride and the cocatalyst and on reaction conditions in general. To overcome this problems, we developed a different C* measurement method based on the use of acid chlorides.

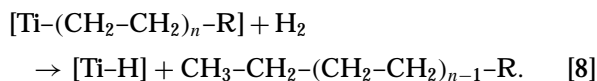
THE BASIS OF THE NEW C* MEASUREMENT METHOD

All C* measurement methods using either tritiated alcohols (reaction [3]) or ^{14}CO (reaction [4]) suffer from one principal uncertainty: they both determine total amounts of labels in polymers without detailed information about the positions of the labels in polymer chains. We propose a

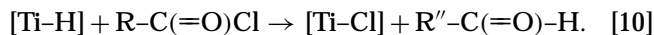
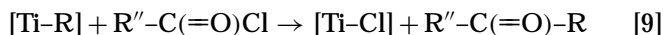
different method in which the exact chemical nature of the measured species is unambiguously known. The method is based on well-established kinetic details of alkene polymerization reactions (1, 19). If, in the course of a polymerization reaction, a monomer is depleted or removed and a cocatalyst is also removed, the growing polymer chains eventually separate from active centers in the β -hydrogen elimination reaction and leave Ti-H bonds in the catalyst:



Under usual polymerization conditions, this reaction is relatively slow in comparison with other reactions of chain termination (20). Approximate estimations, based on literature kinetic data on propylene polymerization with supported Ti-based catalysts (1), showed that the half-conversion time for reaction [7] at 70°C is in the range of 0.5–2.5 min; one can expect that it is lower at higher temperatures. The formation of Ti-H bonds in a catalyst is, of course, greatly accelerated if hydrogen (the most often used chain termination agent) is present:



If the monomer and the free cocatalyst are removed from a reaction system and then an acid chloride is added to it, two different reactions of organotitanium species will take place, those with Ti-H bonds formed in reaction [7] and with Ti-R groups formed in reaction 1 and not affected by polymerization:



Reaction [9] produces a ketone and reaction [10] an aldehyde.

Evidently, one important obstacle to C^* measurement by this method (using Reaction [9]) is the possibility that the Ti-R species unaffected by polymerization may be converted to Ti-H species. This conversion may occur because of two reactions, (a) hydrogenation of the Ti-R species with H_2 and (b) when such Ti-R species have hydrogen atoms in the β -position and undergo β -hydrogen elimination:



The Ti-*i*-Bu₃ group is especially prone to this reaction. Ti-H species formed in reaction [11] are indistinguishable from those formed in reaction [7]. Both of these complications can be avoided, however, if hydrogen is not used in the polymerization reaction and if the R group in the cocatalyst does not have hydrogen atoms in the β -position, for example, when $\text{R}=\text{CH}_3$.

The number of active centers in heterogeneous Ziegler-Natta catalysts is small, usually 1–3% of all Ti atoms in the catalysts (1). Therefore, a sufficiently sensitive analytical method is required to determine small quantities of aldehydes and ketones generated in reactions [9] and [10]. Because both the aldehydes and the ketones are low-molecular-weight compounds, the GC method was chosen as the primary analytical tool. The choice of the acid chloride is also dictated by the convenience of GC analysis. If acetylchloride is used in reactions [9] and [10], the respective aldehyde (acetaldehyde) and ketones generated from common cocatalysts (2-propanone from AlMe_3 , 2-butanone from AlEt_3) have low boiling points and can easily escape from the reaction mixture. In addition, polymerization systems always contain extraneous light organic products, such as light hydrocarbons in the solvent, light oligomers, etc. These impurities may interfere with the analysis of light aldehydes and ketones. After several trials, we chose benzoyl chloride as the acid chloride for the C^* measurement.

EXPERIMENTAL

Three solid catalysts were used: δ -TiCl₃, a supported TiCl₄/Mg(OEt)₂/SiO₂ catalyst for ethylene polymerization containing 3 wt% of Ti (18), and a supported TiCl₄/dioctyl phthalate/MgCl₂ catalyst for propylene polymerization containing 2.3 wt% of Ti. The cocatalysts were AlMe_3 , AlEt_3 , and $\text{Al-}i\text{-Bu}_3$.

Most polymerization reactions were carried out in 10-cm³ glass vials sealed with rubber septa. In a typical experiment, 0.1 g of a solid catalyst was slurried in 3–5 cm³ of *n*-heptane and activated with 0.4–0.5 mmol of a cocatalyst. In 1-hexene polymerization experiments and ethylene/1-hexene copolymerization experiments, 1-hexene was added to the vial in an amount of 3–10 vol% with respect to the solvent. The vial was pressurized with a gaseous monomer, ethylene or propylene, at a monomer partial pressure of 1.0–1.5 kPa and a polymerization reaction was carried out at 80–85°C under vigorous stirring with a magnet stirrer. The experiments continued for different periods of time, depending on the activity of the catalyst and its kinetic behavior evaluated in separate experiments (19, 20). Polymer yields were kept low, 5–10 g/g of catalyst. The vial was then cooled, depressurized, and centrifuged, and all liquid from it was removed with a syringe under a nitrogen blanket. The remaining solid phase, a mixture of the catalyst and the polymer, was washed three times at 85°C with 3-cm³ aliquots of *n*-heptane. After the last wash was removed from the vial, a nearly dry solid was reslurried in 1 cm³ of *n*-heptane, 0.035 mmol (3 μ l) of benzoyl chloride was added to the slurry, and it was heated at 85°C for 10 min. Unreacted benzoyl chloride was neutralized (at 80–85°C for 10 min) either with a large excess (0.5-cm³, 12 mmol) of methanol, or, preferably, with a fresh aliquot

of the cocatalyst (0.5–0.6 mmol), after which the fresh cocatalyst was decomposed with 12 mmol of methanol. The rationale for the latter procedure is described below. Finally, 1 μ l of an internal GC standard with a high boiling point, *n*-dodecane or 7-methyltridecane, was added to the vial. Polymerization reactions at higher pressures were carried out using a 500-ml stainless-steel autoclave, as described earlier (19).

GC analysis was carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a FID detector and a 60-m column containing a cross-linked silicon resin (MTX-1, Restek). Both the injector and the detector were kept at 350°C; the column was heated from 40 to 300°C at a 5°C/min rate. GC-MS analysis was carried out with a Hewlett-Packard 5890 gas chromatograph equipped with a HP 5971 MS detector. Analysis of Ti and Mg by the inductively coupled plasma emission spectrometry was carried out with a Jarrel TJA 61E instrument.

EXPERIMENTAL RESULTS AND DISCUSSION

Chemical Reactions in Model Mixtures

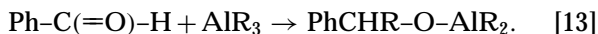
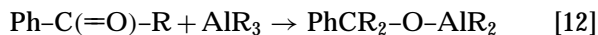
Solid Ziegler-Natta catalyst systems always contain significant quantities of chemisorbed organoaluminum compounds (1), both the original cocatalysts and the products of their reactions with Ti-Cl bonds (reaction [1]). Supported catalysts may contain the organoaluminum compounds associated both with their Ti components and with the supports (such as silica). To remove these compounds completely by washing catalyst systems (either before or after polymerization) with clean solvents is difficult. Therefore, to develop a reliable technique for the C^* measurement based on the use of acid chlorides, one has to take into account secondary reactions between organoaluminum compounds remaining in solid polymer-catalyst mixtures and aldehydes and ketones produced in reactions [9] and [10]. For this purpose, a series of reactions was carried out in which all components of polymerization systems (in the absence of monomers) and various model compounds were reacted with benzoyl chloride and with different organoaluminum compounds. The following chemical reactions were established (by GC-MS and by spiking GC samples):

1. Benzoyl chloride rapidly reacts with all tested organoaluminum compounds with the formation of alkylphenyl ketones PhC(=O)R (reaction [6]). If the cocatalyst is AlMe_3 , acetophenone is produced.

2. If benzoyl chloride is not completely consumed in reaction [6], it reacts with methanol with the formation of methyl benzoate and HCl.

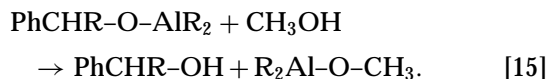
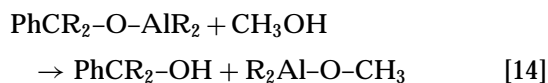
3. Ketones formed in reactions [6] and [9], as well as benzaldehyde formed in reaction [10], rapidly react with organoaluminum compounds with the formation of several products (17). The most important of these reactions is the

addition (alkylation) reaction with the formation of dialkylaluminum alkoxides with substituted α -carbon atoms in alkoxy groups:



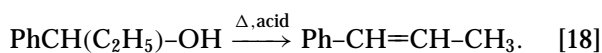
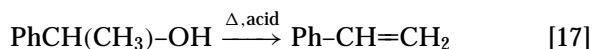
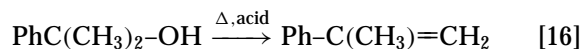
However, other reactions of ketones and aldehydes can also take place. If the alkyl group R in AlR_3 has a β -H atom, reduction of ketones to another type of dialkylaluminum alkoxides, PhCHR-O-AlR_2 , and reduction of aldehydes to alkoxides $\text{PhCH}_2\text{-O-AlR}_2$ also takes place, especially if $\text{Al}^i\text{-Bu}_3$ is used.

4. Alkoxides formed in reactions [12] and [13] are decomposed in excess methanol with the formation of tri- and disubstituted carbinols, respectively:



In the case of AlMe_3 , the respective products are 2-phenyl-2-propanol, $\text{PhC(CH}_3)_2\text{OH}$ (reaction [14]), and 1-phenylethanol, $\text{PhCH(CH}_3)\text{OH}$ (reaction [15]). Reactions [12]–[15] also readily occur when the organoaluminum compounds are chemisorbed, e.g., on silica. Similarly, when a blank catalyst system produced in the reaction between the $\text{TiCl}_4/\text{Mg(OEt)}_2/\text{SiO}_2$ catalyst and AlMe_3 and separated from free AlMe_3 was treated, in sequence, with benzoyl chloride and methanol, it produced not only acetophenone as expected in reaction [6] but also ca. 30% of the secondary product, $\text{PhC(CH}_3)_2\text{OH}$, from the acetophenone and organoaluminum compounds chemisorbed in the catalysts (reactions [12] and [14]).

5. GC experimentation involving either acid chlorides or reaction products of organoaluminum compounds and alcohols (such as $\text{MeAl(OCH}_3)_2$ and $\text{Al(OCH}_3)_3$ from AlMe_3 and methanol) results in gradual accumulation of an acidic residue in the injection port of the GC instrument. This residue decomposes some of the organic compounds produced in reactions [6], [9], [10], [14], and [15]. The carbinols generated in reactions [14] and [15] are the most sensitive. A combination of a high temperature and the acidic contamination in the injection port results in their decomposition to styrenes, e.g.:



In addition, model experiments showed that acetophenone

also slowly decomposed under acidic conditions in the GC injection port with the formation of a small quantity of styrene. This reaction is slow: experiments with acidic alumina placed in the injection port showed that even under these extreme conditions the conversion in this reaction reaches only ca. 25%; it does not exceed 5% in the case when the acidic accumulation occurs in the course of the usual C* analysis. Nevertheless, the presence of styrene from this acetophenone decomposition reaction interferes with the measurement of styrene derived from Ti-H bonds (reactions [10], [13], [15], and [17]). Therefore, the analytical procedure was designed in such a way that acetophenone was eliminated from the mixture (in reactions [12] and [14]) prior to GC analysis.

Choice of Cocatalyst

Three organoaluminum compounds were investigated in regard to their suitability for the C* measurement: AlMe₃, AlEt₃, and Al*i*-Bu₃. There are three big potential problems with the cocatalysts which can disqualify them from the proposed technique:

1. A possibility of reaction [11] which leads to generation of additional Ti-H bonds, apart from those formed in reaction [7].
2. A similar reaction of the cocatalyst itself, decomposition to a dialkylaluminum hydride:



R'₂AlH can react with benzoyl chloride with the formation of benzaldehyde and thus can interfere with the C* measurement. Only AlMe₃ is free from these two complications.

3. A possibility of several parallel reactions between aldehydes and ketones with trialkylaluminum compounds. For example, reduction of acetophenone with AlEt₃ and alkylation of benzaldehyde with the same compound both give PhCH(C₂H₅)-O-AlEt₂ as an intermediate product.

Therefore, a model investigation was required in each particular case: both acetophenone and benzaldehyde were tested under conditions adopted for the C* measurement for possible interference. These tests produced the following results:

1. AlMe₃ reacts both with benzoyl chloride and with acetophenone with the formation (after treatment with methanol) of the same product, PhC(CH₃)₂OH (reactions [6], [12], and [14]). The latter partially decomposes in the GC injection port to α-methylstyrene (reaction [16]). All these reactions are unaffected by the presence of inert solids (silica) or Ti-based catalysts.
2. Benzaldehyde is equally cleanly converted to PhCH(CH₃)OH (reactions [13] and [15]) and, eventually, to styrene (reaction [17]).

In some experiments in the presence of catalyst components and monomers, two sets of products can be detected simultaneously: (a) acetophenone, 2-phenyl-2-propanol, and α-methylstyrene from reactions of Ti-CH₃ groups, and (b) benzaldehyde, 1-phenylethanol, and styrene from reactions of Ti-H groups. This situation is not optimal when the concentration of Ti-H groups in the catalyst is measured, and a special procedure was developed (see below) to reduce the number of reaction products.

3. AlEt₃ converts benzaldehyde to PhCH(C₂H₅)OH (reactions [13] and [15]) and the latter partially decomposes in the GC injection port to β-methylstyrene (reaction [8]). Unfortunately, benzoyl chloride also reacts with AlEt₃ with the formation of PhCH(=O)C₂H₅ and PhCH(C₂H₅)OH (the reduction reaction), in addition to the expected PhC(C₂H₅)₂OH. This circumstance, as well as a possibility of reaction [11], makes AlEt₃ unsuitable as a cocatalyst for the proposed C* measurement method.

4. Al*i*-Bu₃ is strongly susceptible to reduction reactions with aldehydes and ketones. For example, the main product of its reaction with benzoyl chloride is benzyl alcohol rather than tri- or disubstituted carbinols expected in alkylation reactions of ketones. This reaction also produces a small quantity of benzaldehyde. When free Al*i*-Bu₃ was removed after its contact with a solid catalyst at 85°C in a blank reaction, and when AlMe₃ rather than Al*i*-Bu₃ was used to eliminate excess of benzoyl chloride, only very small quantities of benzaldehyde and styrene were detected in the reaction products with the catalyst residue, most probably due to conversion of Ti-CH₂-CH(CH₃)₂ species to Ti-H bonds and isobutene (reaction [11]). Therefore, this modification of the analytical procedure can be, in principle, used for the C* measurement with Al*i*-Bu₃.

Analytical Procedure

When benzoyl chloride is added to an active polymerization system (after removal of monomers and the free cocatalyst), its reactions with Ti species (reactions [9] and [10] and its reactions with chemisorbed AlMe₃ (reactions [6], [12], and [14]) occur in rapid succession, and the yields of respective products are mostly determined by the ratios between the reactants and by diffusion rates of different chemicals to active centers on the catalyst surface. To make these reactions controllable, the following analytical procedure was adopted (see also *Experimental*).

At the end of a polymerization reaction, the reactor (a 10-cm³ glass vial) is centrifuged and the liquid layer in it (it contains most of cocatalyst) and the gaseous monomer are removed under a nitrogen blanket. After that, the solid phase, which contains the catalyst residue and the polymer, is repeatedly washed with a fresh clean solvent at a high temperature (usually the same as the polymerization temperature) to eliminate the remaining cocatalyst and the monomer. This step usually lasts 10–15 min. The τ_{0.5} value

for reaction [7] at 80–85°C is estimated as ca. 1 min. Therefore, one can expect that most growing polymer chains have sufficient time to complete the β -hydrogen elimination reaction and that only two types of Ti species capable of reacting with benzoyl chloride remain on the catalyst surface, the Ti–H bonds formed in reaction [7] and those Ti–Me bonds which are not involved in the polymerization reaction.

In the next step, the solid is reslurried in a small volume of a fresh solvent and benzoyl chloride is added to the slurry in significant excess with respect to the expected amounts of Ti–H and Ti–Me bonds (see their estimations below). At this point, two alternative procedures for the C^* measurement can be utilized:

Method 1: Neutralization of unreacted benzoyl chloride with excess methanol. This reaction produces methyl benzoate. The reaction is not very fast; its progress can be also monitored with GC. GC analysis of the products in a blank experiment ($\text{AlMe}_3 + \text{PhC(=O)Cl} + \text{excess methanol}$) showed the formation of all four expected reaction products, PhC(=O)OCH_3 (from benzoyl chloride), PhC(=O)CH_3 , $\text{PhC(CH}_3)_2\text{OH}$, and α -methylstyrene. The ratio between the last two compounds depends on the condition of the GC injection port. The reaction of excess benzoyl chloride with methanol also produces HCl. The latter rapidly destroys GC columns and should be scrubbed before analysis. Due to this complication, as well as the fact that PhC(=O)CH_3 , under acidic conditions in the GC injection port, can produce a small quantity of styrene (see above), a more preferred alternative procedure was developed.

Method 2: Neutralization of unreacted benzoyl chloride with additional AlMe_3 . This reaction converts unreacted benzoyl chloride into PhC(=O)CH_3 (reaction [6]) and the latter is further converted into an aluminum alkoxide (reaction [12]). After that, a large excess of methanol is added to the vial (isopropanol can also be used). It decomposes the second aliquot of AlMe_3 into the mixture of $\text{MeAl(OCH}_3)_2$ and $\text{Al(OCH}_3)_3$, and converts the aluminum alkoxide formed in reaction [12] into PhCMe_2OH (reaction [14]).

As mentioned before, carbinols formed in reactions [14] and [15] partially decompose in the GC injection port with the formation of styrenes. (If acid chlorides of alkanolic acids are used instead of benzoyl chloride, these reactions produce alkenes.) If free AlMe_3 is removed from the catalyst/polymer blend, α -methylstyrene mostly derives from two reactions of benzoyl chloride, those with Ti–Me bonds and with chemisorbed AlMe_3 , and unsubstituted styrene derives from benzyl aldehyde produced in reaction [10]. Conversions in reactions [16] and [17] depend on the quality of the dispersing agent in the GC injection port (usually glass wool). $\text{MeAl(OCH}_3)_2$ and $\text{Al(OCH}_3)_3$ are partially soluble in *n*-heptane; they precipitate in the hot injection port and produce acidic deposits. Consequently, the ratio

between the styrenes (from reactions [16] and [17] and the carbinols (from reactions [14] and [15]) gradually increases. The most reasonable procedure is to replace glass wool in the injection port often and to use the combined yield of $\text{PhCH(CH}_3)\text{OH}$ and styrene as the measure of the Ti–H bond amount.

C^* Measurement in Different Catalysts

A series of C^* measurements in alkene polymerization reactions was carried out using three Ti-based catalysts, δ - TiCl_3 and two supported catalysts, $\text{TiCl}_4/\text{Mg(OEt)}_2/\text{SiO}_2$ (catalyst for ethylene polymerization) and $\text{TiCl}_4/\text{dioctyl phthalate}/\text{MgCl}_2$ (catalyst for propylene polymerization). AlMe_3 was used as the cocatalyst and as the second reactant in method 2. Four types of polymerization reactions were investigated: homopolymerization reactions of ethylene, propylene, and 1-hexene, and the ethylene/1-hexene copolymerization reaction. All reactions were carried out at 80–85°C at relatively low monomer concentrations and to low yields (5–10 g/g of catalyst) to prevent formation of large quantities of polymers and thus to avoid diffusion problems in reactions of Ti species on the surface of catalyst particles (surrounded by a polymer layer) and the required reactants, benzoyl chloride, AlMe_3 , and methanol.

Table 1 gives several examples of the measurements. The results are reported in two formats, as the C^* concentration in the catalysts, millimoles per gram of catalyst, and as the C^* fraction with respect to the number of Ti atoms in the catalysts.

In the beginning, several blank experiments without monomers were carried out with the $\text{TiCl}_4/\text{Mg(OEt)}_2/\text{SiO}_2$ catalyst to determine the level of error inherent to the method. Two such measurements, after reacting the slurry containing the catalyst and AlMe_3 at 85°C for 2 h in the absence of a monomer, showed that a small quantity of styrene was still formed, amounting to $\sim 2.5 \times 10^{-3}$ mmol/g of catalyst. The sources of this systematic error are not known but, obviously, necessary corrections should be introduced to all measurements.

1-Hexene polymerization reactions with the supported catalyst were the easiest to study due to a low monomer pressure in the reactor. The data are generally reproducible: from 1.0 to 1.5% of all Ti atoms in the catalyst are active centers. When ethylene is polymerized, either alone or in combination with 1-hexene, the concentration of active centers noticeably increases. Differences between results produced with methods 1 and 2 are not large, indicating that the amount of styrene formed in method 1 due to acidic/thermal decomposition of acetophenone is quite low.

The propylene polymerization catalyst system $\text{TiCl}_4/\text{dioctyl phthalate}/\text{MgCl}_2\text{-AlMe}_3$ has approximately 1.4% of its Ti atoms as active centers. Crystalline δ - TiCl_3 has a specific surface area of 20 m²/g, and only 2.5% of all Ti atoms in the solid are situated on its surface (1). Taking this into

TABLE 1

C* Measurements in Alkene Polymerization Reactions with Heterogeneous Ti-Based Ziegler–Natta Catalysts (AlMe₃ Cocatalyst)

Catalyst	C _E , M	C _{Alkene} , M	Time, min	Method	C*, mmol/g _{cat}	C*/[Ti] _{cat} , %
Ethylene Polymerization at 85°C						
TiCl ₄ /Mg(OEt) ₂ /SiO ₂	0.14	0	120	2	2.1 × 10 ⁻²	3.3
Ethylene/1-Hexene Copolymerization at 85°C						
TiCl ₄ /Mg(OEt) ₂ /SiO ₂	0.05	0.26	120	1	1.7 × 10 ⁻²	2.7
TiCl ₄ /Mg(OEt) ₂ /SiO ₂	0.14	0.26	20	2	1.3 × 10 ⁻²	2.0
TiCl ₄ /Mg(OEt) ₂ /SiO ₂	0.05	0.26	20	2	9.4 × 10 ⁻³	1.5 ^a
δ-TiCl ₃	0.14	0.26	20	2	6.6 × 10 ⁻³	0.15
1-Hexene Polymerization at 85°C						
TiCl ₄ /Mg(OEt) ₂ /SiO ₂	0	0.52	120	1	7.5 × 10 ⁻³	1.2
TiCl ₄ /Mg(OEt) ₂ /SiO ₂	0	0.52	120	1	7.5 × 10 ⁻³	1.1
TiCl ₄ /Mg(OEt) ₂ /SiO ₂	0	0.52	240	2	6.5 × 10 ⁻³	1.0
TiCl ₄ /Mg(OEt) ₂ /SiO ₂	0	0.52	120	2	8.6 × 10 ⁻³	1.3
TiCl ₄ /Mg(OEt) ₂ /SiO ₂	0	0.52	120	2	1.0 × 10 ⁻²	1.5 ^a
δ-TiCl ₃	0	0.26	20	2	4.1 × 10 ⁻³	0.08
Propylene Polymerization at 80°C						
TiCl ₄ /dioctyl phthalate/MgCl ₂	0	0.63	10	2	6.4 × 10 ⁻³	1.4

^a Isopropanol was used instead of methanol.

consideration, the results for δ-TiCl₃ can be interpreted in the following way: polymerization centers account for ~6% of all surface Ti atoms in ethylene/1-hexene copolymerization reactions and ~3% in the case of 1-hexene polymerization.

Tagging methods for the C* measurements (see Introduction) in ethylene and propylene polymerization reactions usually give very diverse results, depending on the technique and the catalyst (1). For example, the C* values for supported Ti-based catalysts reported in the literature vary from 0.2–0.4% of Ti atoms (21) to 3–5% (22) and up to ~30% (3). Our technique based on benzoyl chloride gives C* estimations (usually 2–3% of Ti atoms) which are in the middle of the range.

When method 1 is employed for the C* measurement, it also affords an approximate estimation of the combined quantity M–CH₃ bonds in the catalysts (after free AlMe₃ is removed prior to the analysis). These M–CH₃ bonds include Ti–CH₃ bonds which are formed in reaction [1] and do not participate in polymerization reactions and Al–CH₃ bonds in organoaluminum compounds chemisorbed on the catalyst surface. The total amount of the M–CH₃ species present in the TiCl₄/Mg(OEt)₂/SiO₂–AlMe₃ catalyst system at 85°C after 2 h is ~ (3–5) × 10⁻² mmol/g_{cat} in 1-hexene polymerization and (6–7) × 10⁻² mmol/g_{cat} in ethylene/1-hexene copolymerization. This amount is 10 to 20 times higher than that of the Ti–H species. One should take into account that polymerization reactions with the formation of crystalline polymers (polyethylene, polypropylene) can indirectly affect both the amount of chemisorbed organoaluminum compounds and conversion in reaction [1]. Such polymers break and disperse original catalyst particles (due

to purely mechanical action) and expose new Ti–Cl bonds for reaction [1] and a new catalyst surface for adsorption of organoaluminum compounds. On the other hand, poly(1-hexene) is soluble in *n*-heptane and its formation does not result in the catalyst particles' breakup.

The use of the C* measurement method can also provide insight into the nature of species which are present in solution over solid Ziegler–Natta catalysts. Analysis of liquids over catalyst–cocatalyst mixtures showed that, in the absence of polymerization reactions, the liquids merely contain the cocatalyst (Table 2). This is an expected result: even when supported catalysts contain small quantities of potentially soluble Ti species [free TiCl₄, TiCl_x(OR)_y, etc.], they are rapidly reduced by the cocatalyst and form insoluble Ti³⁺ species. Blank experiments showed that liquids separated from catalyst–cocatalyst slurries are not active in alkene polymerization.

The results are different when the same liquids are removed after polymerization reactions. These liquids contain three types of products:

1. Products derived from reactions between the free cocatalyst and benzoyl chloride (PhC(=O)CH₃, PhC(CH₃)₂OH, *α*-methylstyrene), the same as in the absence of monomers.

2. Alkene oligomers (low-molecular-weight components of polymers or copolymers) which are soluble in the reaction medium. The structure of these products was described earlier (23).

3. Products which can be assigned to reactions of Ti–H bonds. Relative yields of these products are quite significant (Table 2).

TABLE 2

Ti-H Bonds in Solution: Alkene Polymerization Reactions with Heterogeneous Ti-Based Ziegler-Natta Catalysts at 85°C (AlMe₃ Cocatalyst)

Catalyst	C _E , M	C _{Alkene} , M	Time, min	Method	[Ti-H] _{sol} , mmol/g _{cat}	[Ti-H] _{sol} /[Ti] _{cat} , %	[Ti] _{sol} , %	[Mg:Ti] _{sol}
Blank Experiments								
TiCl ₄ /Mg(OEt) ₂ /SiO ₂	0	0	120	1	~0			
TiCl ₄ /Mg(OEt) ₂ /SiO ₂	0	0	120	2	6.9 × 10 ⁻⁴	0.1		
Ethylene Polymerization								
TiCl ₄ /Mg(OEt) ₂ /SiO ₂	0.14	0	120	2	8.0 × 10 ⁻³	1.2		
Ethylene/1-Hexene Copolymerization								
δ-TiCl ₃	0.05	0.14	20	1	3.3 × 10 ⁻²	0.75	3.2	~0
TiCl ₄ /Mg(OEt) ₂ /SiO ₂	0.05	0.26	120	1	2.7 × 10 ^{-2 a}	4.3	2.3	<0.1
1-Hexene Polymerization								
δ-TiCl ₃	0	0.26	20	1	8.7 × 10 ⁻³	0.17	1.2	~0
TiCl ₄ /Mg(OEt) ₂ /SiO ₂	0	0.52	120	1	1.6 × 10 ⁻²	2.4	8.4	0.12

^a Isopropanol was used instead of methanol.

The presence of species with Ti-H bonds in the liquid phase can be accounted for by two sources. The first source is trivial: very small catalyst particles which remain suspended in the liquid even after centrifuging the slurries. The second possible source is soluble compounds with Ti-H bonds which are apparently formed in the polymerization reactions. To separate these two possibilities, several liquid layers after polymerization experiments were analyzed for Ti and Mg (last two columns in Table 2). The supported catalyst used in the two experiments in Table 2 has a [Mg] : [Ti] weight ratio of 0.5; therefore, purely mechanical contamination of the liquid layers with catalyst/polymer particles cannot be solely responsible for the results. It appears that polymerization reactions of alkenes, both in the case of the supported catalyst and δ-TiCl₃, cause separation of a fraction of polymerization centers (carrying insoluble polymer chains) from the catalyst surface. After the monomer is removed and reaction [7] comes to completion, these centers produce heptane-soluble Ti-H species which are not associated with the Mg component in the supported catalyst. The amount of the dissolved Ti-H species can be quite significant and comparable to that of the active centers on the catalyst surface. To my knowledge, this is the first instance when solubilization of some Ti-based active species in heterogeneous Ziegler-Natta catalysts was observed. Relative reactivity of these species cannot be easily estimated and the mechanism responsible for their formation is still the subject of speculation; it may be purely mechanical in nature.

CONCLUSIONS

The proposed technique for the measurement of the number of active centers in heterogeneous Ti-based

Ziegler-Natta catalysts activated with AlMe₃ is based on the standard kinetic model (1). The model states that growing polymer chains attached to Ti atoms, if left without a monomer and a free cocatalyst, gradually disengage from the active centers in β-hydrogen elimination reactions and leave Ti-H species on the catalyst surface. The latter react with benzoyl chloride (although other acid chlorides can be used for this purpose as well) with the formation of three products (depending on reaction conditions): benzaldehyde, PhCH(CH₃)OH, and styrene. Yields of all these compounds are measured with the GC method.

The proposed method has several advantages over the existing C* tagging techniques (mostly those with tritiated alcohols and ¹⁴CO). One of them is chemical distinctiveness: the compounds derived from Ti-H species are easily distinguished from other products formed in a catalyst system exposed to an acid chloride. The most important of the latter are the products derived from Ti-CH₃ species that are not involved in polymerization reactions. Other organometallic compounds present in the reaction products also generate products which are different from those derived from Ti-H species: the chemisorbed cocatalyst produces the same compounds as the Ti-CH₃ species, dead polymer molecules attached to Al atoms, Me₂Al-polymer, produce high-molecular-weight ketones, etc. Another advantage of the proposed method is its experimental simplicity: only easily available chemicals in small quantities are used, and there is no need for radioactive isotope storage, handling, and counting equipment, etc.

The method has several disadvantages:

1. Only AlMe₃ can be dependably used as a cocatalyst.
2. Polymer yields should be relatively small to facilitate reactions of benzoyl chloride with catalyst particles coated with polymer.

3. Special care should be given to separating solid products from free cocatalyst and to assuring that the β -hydrogen elimination reaction (reaction [7]) goes to completion.

4. Hydrogen cannot be used in the polymerization reactions: it can hydrogenate inactive Ti-CH₃ species to Ti-H species.

5. The method is unsuitable (without significant modifications) for the study of soluble catalysts.

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