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Electron Spin Resonance, Titanium Oxidation State, and Ethylene Polymerization Studies of a Model-Supported Ziegler–Natta Catalyst. Spectroscopic Detection of Titanium Tetrachloride

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ABSTRACT: Electron spin resonance spectra have been recorded for model Ziegler–Natta catalysts prepared by depositing alkylmagnesium butoxide (AMB) and titanium tetrachloride onto a silica support. Depending on the reagent stoichiometry and loading, one or more of four different singlet resonances are observed which account for no more than 17% of all the titanium present. By examining trends in the spectra as a function of Mg to Ti ratio and of temperature, one ESR site ($g = 1.895$) is proposed to arise from an interaction between $[\mathrm{Ti(3+)}]_n$ clusters and $\mathrm{TiCl_4}$. In situ dosing experiments and wet chemistry titanium oxidation state determinations support this proposal, while ethylene polymerization experiments on selected preparations show that catalyst activity increases by increasing the Ti(4+) content. In the case of the in situ dosing experiments, the $g = 1.895$ signal can be created or eliminated by exposing the catalyst to $\mathrm{TiCl_4}$ or diethylaluminum chloride vapors, respectively. The titanium oxidation state determinations show that even under the most extreme reducing conditions used ($\mathrm{AMB/TiCl_4}$ molar ratio 10/1), only a negligible fraction (0.8%) of all titanium is reduced to Ti(2+). All Ti(3+) determinations by cyclic voltammetry on filtrates of extracted catalysts show that there is two to nine times more Ti(3+) present than is detected by ESR. All of the above findings are consistent with the equilibrium process shown below:

$$\underset{\text{ESR silent}}{[\mathrm{Ti(3+)}]_n} + m\mathrm{TiCl_4} \rightleftharpoons \underset{\text{ESR active}}{[\mathrm{Ti(3+)}]_n(\mathrm{TiCl_4})_m}$$

Through comparisons with ESR spectra reported for other similar catalysts, it is proposed that these or related cluster sites exist in many titanium Ziegler–Natta catalysts on magnesium-based supports. Ironically, then, ESR can be used to detect the presence of the diamagnetic molecule $\mathrm{TiCl_4}$ in these catalysts.

Introduction

While magnesium-based supported Ziegler–Natta catalyst preparations number in the thousands, our search of the literature indicates only four published electron spin resonance (ESR) studies of these catalysts.[1-4] In reviews of supported Ziegler–Natta catalyst chemistry,[5-8] including those dealing with speculation on the number and kinds of different active sites, references to ESR results are absent. On the basis of these facts, we infer that workers in the field have found ESR to be of little value. This is because, by and large, ESR spectra for supported Ziegler–Natta catalysts are composed of broad singlet resonances the total intensity of which accounts for no more than 10–20% of all the titanium present. Consequently, spectral assignments have been highly speculative and incomplete. The result is that correlations between ESR spectra and catalyst behavior have not been forthcoming, except in the sense that the spectra have provided a fingerprint identification of the catalyst preparations.

In a break from the previous work, we will present the first use of ESR spectroscopy in which the spectra provide an experimentally verifiable clue about the structure of an ESR-active site in the catalyst. Supporting evidence for the spectral assignment made is provided by wet chemistry titanium oxidation state determinations. A correlation between the catalyst Ti oxidation state distribution, the identified ESR active site, and catalyst ethylene polymerization activity will be presented. From comparisons with reported ESR spectra, we believe that structural features associated with this ESR-active site are commonly found in other Ziegler–Natta catalysts based on titanium and magnesium components.

Experimental Section

Sample Preparation. All manipulations were carried out in a nitrogen or argon atmosphere by using typical drybox and Schlenk techniques. Solvents were spectral grade and dried over molecular sieves and sparged with nitrogen. Davison grade MS952 silica (surface area and pore volume 275 ± 10 $\mathrm{m^2/g}$ and 1.75 $\mathrm{cm^3/g}$, respectively) was dehydrated in flowing dry nitrogen at 800 °C prior to use. The alkylmagnesium butoxide (AMB) was prepared by slowly adding 0.5 mol equiv of butanol under vigorous stirring to 1.0 mol equiv of "butyl ethyl magala" (Texas Alkyls) in heptane. As alcohol was added, a gelatinous mass formed which slowly dissolved to yield a water white, clear solution of AMB.

Model catalysts were prepared by anaerobically adding sufficient AMB solution to about 4 g of the silica slurried in 30 mL of hexane to give between 0.1 and 2.0 mmol of Mg/g of silica. After a reaction time of 1 h under stirring, sufficient $\mathrm{TiCl_4}$ stock solution (12.8% by weight in hexane) was added to give the desired Mg to Ti molar ratio. The diluent was removed in vacuo to yield a dry, free-flowing solid. Elemental analyses (either from Galbraith, Knoxville, TN, or from our own analytical labs) on selected catalyst samples are organized in Table II.

Polymerization Tests. Selected catalysts were tested for ethylene polymerization activity by using a stainless-steel autoclave of nominal 2-L capacity. To the nitrogen-purged reactor was added 1000 mL of isobutane spiked with 6.2 mmol of Al as $\mathrm{Al(C_2H_5)_3}$ followed by 80 mmol of hydrogen from a calibrated charge pot. The reactor was heated to 75 °C and the reactor pressure (ca. 1340 kPa) was increased to 1825 kPa with the admission of ethylene. Solid catalyst was injected to the reactor and ethylene added on demand to maintain reactor pressure. At the end of the polymerization time (40 min) the reactor was vented and cooled. Polyethylene was obtained as a white, granular solid and dried for 4 h at 50 °C prior to analysis. Resin melt index (MI) and melt index ratio (MIR) were measured in accordance with ASTM Test D1238 (condition E). Polyethylene product molecular weights were determined using a Waters Gel permeation chromatograph (GPC) equipped with three ultrastryrogel columns having nominal pore sizes of 10^6, 10^4, and 500 $\mathrm{\AA^3}$. The GPC was calibrated with four polyethylene NBS standards and 16 narrow MWD polystyrene standards. Samples were eluted at 145 °C in trichlorobenzene at a rate of 1 mL/min. Infrared spectra of pressed polymer films were recorded using a Digilab FTIR.

ESR Spectroscopy. Freshly prepared samples were sealed under vacuum in oven-dried 4-mm o.d. quartz tubes. Spectra were recorded on an IBM/Bruker 100D electron spin resonance spectrometer equipped with an IBM CS9001 computer and variable-temperature probe.

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Table I
Model-Supported Catalyst Preparations and Their Spin Densities As Measured by ESR

	mmol of reagent/g of silica		
	RMg (O-*n*-Bu)	$TiCl_4$	spins/Ti (by ESR)[a]
1	0.1	0.4	0.01
2	0.1	0.2	0.005
3	0.3	0.9	0.023
4	0.5	0.4	0.050
5a	0.5	0.9	0.040
5b			0.058
6a	1.0	0.2	0.11
6b			0.16
7	1.0	0.4	0.17
8	1.4	0.3	0.13
9a	2.0	0.1	0.15
9b			0.16
10	2.0	0.2	0.11
11a	2.0	0.4	0.10
11b			0.13

[a] Measured by numerical double integration and comparison with doubly integrated ESR spectrum of freshly prepared *fac*-$TiCl_3(PMe_2Ph)_3$ standard. Titanium concentration in model catalysts estimated by assuming 100% of both reagents bind to and remain on silica.

The following instrument settings were employed for recording all spectra: modulation amplitude 7–10 G, microwave attenuation 7 dB, modulation frequency 100 kHz, time constant 80–160 ms, sweep time 200 s. Spin concentrations were derived from comparisons of numerical double integrations of spectra for the samples with those for established Ti(3+) spin standards. For *g* value measurements, the magnetic field was calibrated with polyacetylene or diphenylpicrylhydrazyl (dpph) standards.[9]

For in situ reactions followed by ESR, typically 100 μL or so of neat $TiCl_4$ or diethylaluminum chloride was placed in the bottom of an ESR tube followed by a loose, dry, quartz wool plug about 0.5 cm thick and spaced a centimeter or so above the $TiCl_4$. After the plug was in place, a charge of the catalyst to be dosed was deposited on the plug. The contents were cooled with liquid nitrogen and sealed under vacuum. Spectra were then recorded periodically at room temperature for up to 2 days.

Wet Chemistry Titanium Oxidation State Determinations. Titanium(2+) concentrations were determined for three samples of formulaton 1 by measuring the amount of hydrogen gas evolved from decomposition of the catalyst. The catalysts were decomposed by exposure to the vapor of a 1 M aqueous HCl solution (prepared from distilled water which had been degassed by two freeze–pump–thaw cycles) in a H-tube reactor for 2–14 h. After each decomposition, hydrogen gas in the reactor was determined by comparison of the gas chromatographic trace for the sample with the traces for a Matheson 1000 ppm (by volume) H_2-in-ethylene gas standard or for the reaction product of a weighed amount of $TiCl_2$ also decomposed by exposure to the 1 M HCl solution. The accuracy of the measurement is estimated to be ±15%. Titanium(3+) concentration was determined by the following procedure: Inside a dry, nitrogen-purged glovebox, between 0.5 and 4 g of sample was placed in a glass container followed by 8–13 mL of a degassed 7–8 M H_2SO_4 aqueous solution. Each glass container was sealed and transferred to a sonicator where the contents were treated for 3 min. The sonicated mixture was returned to the drybox, filtered, and then washed with two or three 5–7-mL aliquots of the sulfuric acid solution. Between 0.2 and 0.4 g of tartaric acid was added to the filtrate. The extracted silica was evacuated to dryness. Both the filtrate and extracted silica were analyzed by ICPES. Within 1–5 days after an extraction, the Ti(3+) concentration in the filtrate was measured at Radian Corp. (Austin, TX) via cyclic voltammetry. Concentrations of titanium trichloride standard solutions used for calibration ranged from 0.005 to 0.156 M. In one case, prior to the cyclic voltammetry measurement the $TiCl_3$ standard solution was combined with dehydroxylated silica, sonicated for 3 min and isolated by filtration in the same manner as the titanium was isolated from the model catalyst samples. This procedure was followed so we could determine whether sonication caused any change in the Ti(3+) concentration. No change was found.

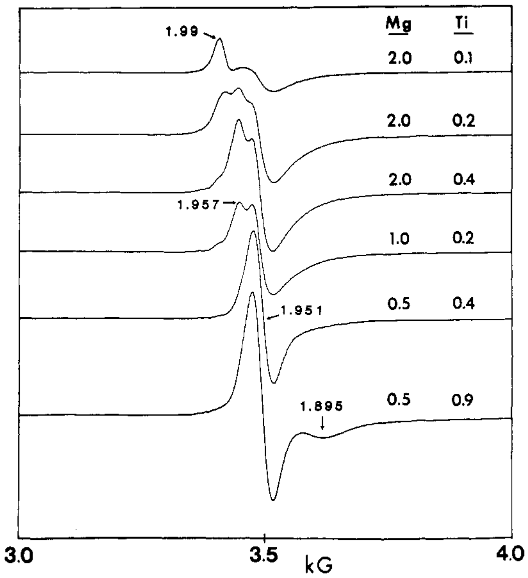

Figure 1. Room-temperature ESR spectra of SiO_2 + AMB + $TiCl_4$ preparations made by using different reagent stoichiometries. The millimolar quantities listed for AMB and $TiCl_4$ are on a per-gram basis of SiO_2. Arrows indicate nominal *g* value assignments for four different resonances discerned.

Table II
Elemental Analyses for Selected Samples

	sample,[a] mmol of reagent/g of SiO_2		% element found[b]		
	AMB	$TiCl_4$	Ti	Mg	Cl
4	0.5	0.4	1.67 (1.67)	1.01 (1.10)	4.88 (4.96)
5b	0.5	0.9	3.40 (3.46)		
7	1.0	0.4	1.68 (1.58)		
10	2.0	0.2	0.72 (0.72)	3.58 (3.69)	2.41 (2.15)
11b	2.0	0.4	1.30 (1.42)		

[a] Sample numbering scheme follows Table I. [b] Calculated values in parentheses.

Results and Discussion

The effect of stoichiometry on the recorded spectra was examined for various silica loadings of AMB and $TiCl_4$. Molar ratios and loadings for the different preparations are summarized in Table I. Representative room-temperature spectra for the freshly prepared samples are shown in Figure 1. Depending on the stoichiometry, one or more of four different singlet resonances are observed. These are nominally assigned the following *g* values: 1.99, 1.957, 1.951, and 1.895.

Two trends are apparent in the spectra. First the relative intensities of the signals increase from higher to lower *g* value with increasing Ti to Mg stoichiometry. For example, the *g* = 1.99 and 1.957 signals are strongest at the lowest Ti/Mg ratios (samples **9a** and **9b** and sample **10**) whereas the *g* = 1.951 signal is strongest when the Ti/Mg stoichiometry is approximately 1 (sample **4**), and the *g* = 1.895 signal is only clearly observed for Ti/Mg stoichiometries in excess of one (samples **3** and **5**). A second observed trend relates to total spin density in each sample.

Spins/Ti values for most samples are based on the theoretical titanium concentration in each sample assuming each reagent is bound to the silica without significant weight loss. Selected elemental analyses (Table II) illustrate that this is a reasonable assumption. The spins/Ti detected for these samples range from 0 to 0.17. Most

Table III
Wet Chemical Determinations of Ti(2+) and Ti(3+) Concentrations in Selected Catalysts

	mmol of reagent/ g of silica				Ti(3+) determination	
sample[a]	AMB	$TiCl_4$	% Ti(2+)[b]	[spins/Ti(3+)] (ESR)	% Ti extracted[c]	fraction Ti(3+)[d]
4	0.5	0.4	0	0.05	90.1	0.11
56	0.5	0.9	–	0.058	93.4	0.091
7	1.0	0.4	0.2	0.17	86.3	0.95[e]
10	2.0	0.2	0.8	0.11	89.1	0.97[e]
11b	2.0	0.4	–	0.13	98.2	0.96

[a] Numbering scheme same as in Table I. [b] By measuring hydrogen evolved after decomposing catalyst with water vapor. See Experimental Section. [c] From the silica support using 7–8 M H_2SO_4. [d] Determined by cyclic voltammetry. See Experimental Section for details. [e] Corrected for Ti(2+) contribution.

samples have spins/Ti values of 0.11–0.17. Deviations toward lower spin concentrations are associated with two reaction conditions, i.e., low Mg concentration (less than 1.0 mmol/g of SiO_2) and high Ti to Mg molar ratio (greater than one, regardless of the Mg reagent concentration). These relationships are evident in Table I. Low spins/Ti values result from low Mg concentrations because the AMB is the reducing agent for $TiCl_4$, as illustrated below:

$$\mathrm{RMgOBu} + \mathrm{TiCl_4} \rightarrow \mathrm{ClMgOBu} + \mathrm{RTiCl_3}$$

$$2\mathrm{RTiCl_3} \rightarrow 2\mathrm{TiCl_3} + \mathrm{R_2}$$

As the magnesium loading is reduced, an increasing percentage of the magnesium alkyl groups is consumed by reaction with the residual silanol groups on the silica surface (about 0.9 mmol of OH/g of SiO_2 for 800 °C treated silica).[10] Of course, all other factors remaining constant, spins/Ti values would also be expected to fall once the Ti/Mg stoichiometry exceeds one, as the alkylmagnesium butoxide clearly becomes the limiting reagent.

Even when titanium reduction should be nearly complete, as in those cases where the Mg/Ti ratio is in the 2–5 range (samples 6–11), the total number of spins detected still accounts for only 10–20% of all the titanium present.

The detection of only a minority fraction of the titanium by ESR could be due to very ineffective reduction of the $TiCl_4$, or the reduction could be extensive but a large fraction of the reduced titanium centers may be ESR silent. In order to assess the relative contribution of these two possibilities in each case, we performed Ti(2+) and Ti(3+) determinations on selected samples by wet chemical methods. The procedures used are described in the Experimental Section. Our results are presented in Table III. From these titrations we find that, under the most extreme reducing conditions employed (AMB/$TiCl_4$ molar ratio of 10/1), reduction of Ti(4+) to Ti(3+) is nearly complete (95%) but only a negligible amount (0.8%) of Ti(2+) is formed. For lower AMB/$TiCl_4$ molar ratios the extent of reduction to Ti(3+) and Ti(2+) decreases accordingly. For example, at the AMB/$TiCl_4$ molar ratio of 2.5 the fraction of titanium which exists as Ti(2+) is essentially zero. In all cases the fraction of titanium reduced to Ti(3+) as measured by extraction/cyclic voltammetry is 2–9 times higher than the fraction of titanium detected by ESR. These results show that the majority of the Ti(3+) is not detected by ESR at room temperature. The results are consistent with the presence of ESR-silent $[Ti(3+)]_n$ clusters in these samples.

ESR spectral sensitivity and resolution can be enhanced at lower temperatures, and Ti(3+) not detected at room temperature might then be detected. Most often spectral improvements are realized because relaxation times at lower temperatures are greater.

Consequently, we recorded ESR spectra for several catalysts as a function of temperature. Since Ziegler–Natta catalysts are employed at elevated temperatures (usually (70–90 °C) we chose to record spectra over the range −173 to +93 °C.

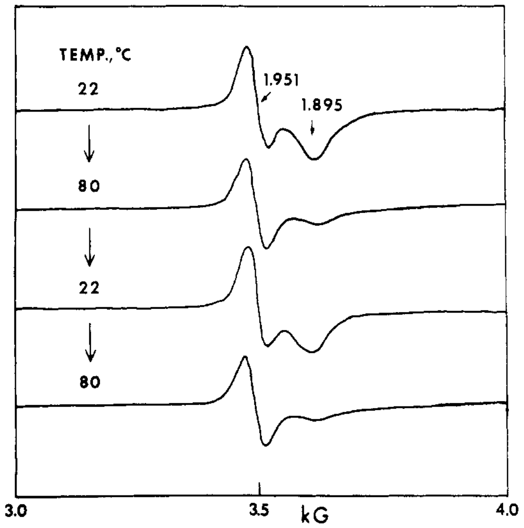

Figure 2. Temperature dependence of signal intensity for sample 3 demonstrating quasi-reversible appearance and disappearance of $g = 1.89$ signal with decreasing and increasing temperatures, respectively.

The variable-temperature spectra of model catalysts prepared with excess AMB reducing agent are fairly standard (roughly Curie behavior; no particular change in spectral envelope). On the other hand, the spectra are very unusual for those models prepared with excess $TiCl_4$. Spectra for such samples give a resonance nominally located at $g = 1.89$. This resonance is markedly enhanced at low temperature but nearly disappears at high temperature. The behavior is quasi-reversible, as shown in Figure 2. Quantification of the signal intensity as a function of temperature for this sample showed that the $g = 1.89$ signal increase was not at the expense of the $g = 1.95$ signal. This same quantification establishes an increasing envelope signal intensity with decreasing temperature (about a factor of 5 increase in signal intensity on cooling samples to −173 °C) for both samples 3 and 4; however the quality of the intensity data is not sufficient to distinguish between (apparent) Curie and non-Curie behavior.

The unusual temperature dependence noted for the $g = 1.89$ signal could be due to changing relaxation time (without any molecular reorganization) of a signal, but it also is consistent with an association–dissociation or other sort of molecular reorganization equilibrium process such as

$$\underset{\text{ESR active}}{A_xB_y} \rightleftharpoons \underset{\text{ESR silent}}{A_xB_y'} \qquad (1)$$

where the species on the left-hand side is structurally different from the species on the right or where the species

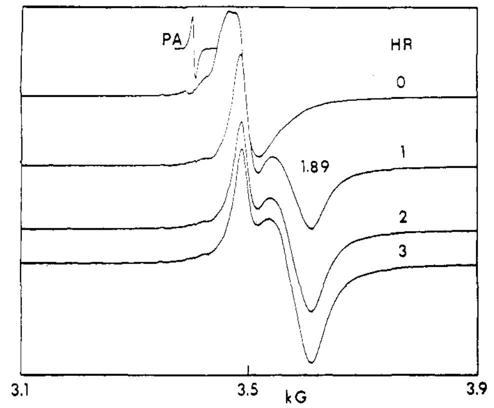

Figure 3. Time dependence of the ESR spectrum of sample 8 contacted with $TiCl_4$ vapor at room temperature.

on the left-hand side dissociates into two different molecules on the right. If such an equilibrium exists, then one would expect signal intensity could also be changed by changing the concentration of reagent A or B at constant temperature. We chose $TiCl_4$ for in situ dosing experiments to test this hypothesis. This choice was based on the spectral trends noted earlier for changes in AMB/$TiCl_4$ stoichiometry, the analytical results which showed substantial amounts of Ti(4+) in these samples, and the volatility of $TiCl_4$.

Reactions between catalyst samples **7** and **8** and $TiCl_4$ vapor at room temperature were monitored in the ESR cavity. The ESR spectra recorded during one dosing experiment are shown in Figure 3. Both dosing experiments yielded an intense $g = 1.89$ signal where there was none before, and total signal intensity increased about threefold. From these in situ reactions, we infer that bonding of diamagnetic $TiCl_4$ to an originally ESR-silent Ti(3+) species is required for appearance of the $g = 1.895$ signal.

Conversely, the $g = 1.895$ signal should disappear if the proposed excess $TiCl_4$ is removed from a catalyst that originally exhibits the $g = 1.895$ signal. Consequently, we first attempted to remove the $TiCl_4$ from samples by extended pumping in vacuo at room temperature, but the signal shrinks only marginally. After these initial results, a second approach involving selective reduction of the $TiCl_4$ was tried. The intent was to deplete $TiCl_4$ from sample **3** by selective reduction with diethylaluminum chloride (DEAC) which is known to reduce Ti(4+) to Ti(3+) but does not reduce Ti(3+) to Ti(2+).[6] The spectra recorded during one in situ reaction between DEAC vapor and sample **3** at room temperature are shown in Figure 4. We found that the $g = 1.895$ signal was selectively eliminated. In addition, the loss of the 1.895 signal was accompanied by a substantial gain in intensity of the 1.951 signal through reduction of the $TiCl_4$. Total integrated signal intensity remained approximately constant throughout the dosing experiment.

The combined results from examining the effects of stoichiometry, temperature, and in situ reactions on the catalyst spectra clearly demonstrate that the $g = 1.895$ signal is "turned on" by combination of $TiCl_4$ with otherwise ESR-silent $[Ti(3+)]_n$ sites. The unusual temperature dependence of the signal could be from an association–dissociation (signal on–signal off) mechanism where the binding of one or more $TiCl_4$ molecules to a cluster disrupts Ti(3+)–Ti(3+) bond(s) or from an antiferromagnetic interaction(s). Alternatively, the association of $TiCl_4$ with the $[Ti(3+)]_n$ clusters might slow spin–lattice relaxation (T_1) sufficiently to render the signal discernible.

Ethylene polymerization tests were carried out on four catalysts. The polymer yields obtained for the catalysts tested are given, along with selected polymer product properties, in Table IV. The two most extensively reduced catalysts tested (virtually 100% Ti(3+)), 7 and 10, were not active, whereas the two catalysts having a large fraction of Ti in the 4+ oxidation state, 4 and 5b, were active. Thus, there is a clear trend between the concentration of Ti(4+), as deduced from wet chemical measurements or from ESR ($g = 1.895$), and the activity of the catalyst. The higher the Ti(4+) concentration and the stronger the $g = 1.895$ signal, the higher the activity. In this particular model formulation, the Ti(3+) clusters (without bound $TiCl_4$) and isolated sites are not active for ethylene polymerization. With use of more elaborate catalyst synthesis conditions, we believe that both the Ti(3+) clusters and isolated sites are active polymerization centers.

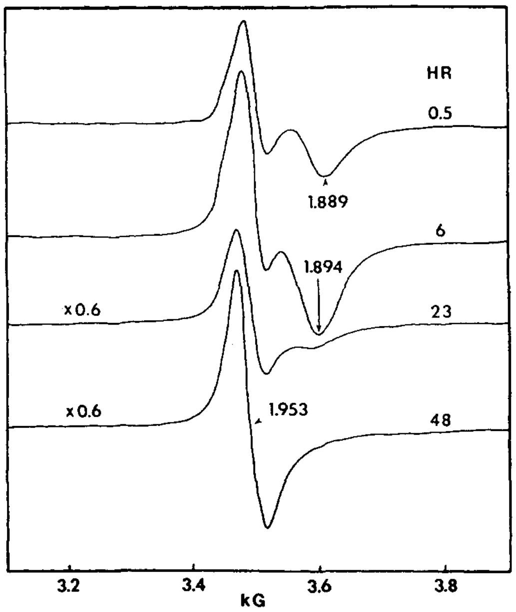

Figure 4. Time dependence of the ESR spectrum of sample 3 contacted with $AlEt_2Cl$ at room temperature.

Table IV
Model Catalyst Activity and Selected Polyethylene Product Properties

	mmol of reagent/ g of silica[a]		C_2 polymerizatn activity, kg of PE/(g of Ti·h·mol/L)	HLMI	$10^5 M_w$[b]
	AMB	$TiCl_4$			
10	2.0	0.2	0	–	–
7	1.0	0.4	0	–	–
4	0.5	0.4	19.6	1.8	2.780
5b	0.5	0.9	48.1	2.6	2.261

[a] Sample numbering scheme follows Table I. [b] Weight average molecular weight.

A review of the literature shows that clusters similar to (but clearly not identical with) those we have identified in this work have been observed in ESR spectra of other magnesium–titanium based Ziegler–Natta catalysts. In particular the results of this study can be used to reexamine ESR assignments made in two recent publications.

In 1982, Chien and Wu[3] published the results of an ESR study of a "high mileage" magnesium chloride supported titanium catalyst. The catalyst was prepared by ball-milling anhydrous $MgCl_2$ together with ethyl benzoate, reacting this product with 4-methylphenol in heptane, and then reacting this product with neat triethylaluminum (up to this point the ESR spectrum was blank). This promoted support was treated with $TiCl_4$ followed by hexane wash and finally dried. At this point, the catalyst gave two ESR signals at room temperature: one at $g = 1.945$ and one at

$g = 1.913$. Although not shown, a spectrum of this sample was also recorded at 77 K. At this temperature the spectrum envelope was unchanged except for a fivefold increase in intensity. The total signal intensity measured accounted for 20% of all Ti(3+) (total Ti(3+) determined by wet chemistry methods) and 6% of all titanium in the sample, while approximately 48% of the titanium was stated to be present as Ti(4+).[11] The two-peak ESR pattern was assigned to a *single* Ti(3+) species proposed to have D_{3h} symmetry. These workers further proposed that the remaining Ti(3+) is present in ESR-silent $[\mathrm{Ti}(3+)]_n$ clusters. In 1984, Zakharov and co-workers published[4] the results of a study designed to identify the state(s) of titanium ions in magnesium chloride supported catalyst formulations for olefin polymerization. In this work, ESR spectra were recorded for three basic catalyst preparations: $TiCl_3$ (AA version) ball milled 1 h with an activated form of $MgCl_2$ (surface area 60 M^2/g) at three different Ti loadings of 0.7, 1.4, and 2.8 wt %; $TiCl_4$ adsorbed onto the high surface area $MgCl_2$ in hexane, then washed, dried, and reduced with either triethylaluminum or diethylaluminum chloride; and finally a brown precipitate with composition $(TiCl_{2.95})(MgCl_2)_{0.55}$ prepared by reacting $TiCl_4$ with dibutylmagnesium.

Each catalyst gave the same pattern of three ESR signals with g values of 1.97, 1.940, and 1.915–1.925. Naturally, the relative intensities of the signals changed with the details of each synthesis. All signals were ascribed to Ti(3+) sites. The 1.97 signal was assigned to Ti(3+) tetrahedrally coordinated on the surface of $MgCl_2$ while the 1.940 signal was assigned to six-coordinate Ti(3+) sites dissolved in $MgCl_2$. The 1.915–1.925 signal was claimed to be from $[\mathrm{Ti}(3+)]_n$ *clusters*. These authors further noted that, in one variable-temperature study, the 1.940 signal was dominant at room temperature while the 1.915–1.925 signal was dominant at low temperature. From the figure shown in this work, it appears that the change in relative intensity is due to growth of the 1.915–1.925 signal rather than shrinkage of the 1.940 signal. They also found that the 1.915–1.925 signal intensity decreased with increasing addition of triethylaluminum. Finally, these authors believe that the $g = 1.940$ and 1.915–1.925 signals they observe are the same as those previously reported by Chein and Wu. Consequently, they dispute the assignment of these two signals by Chein and Wu to a single axially distorted Ti(3+).

On the basis of our own findings, we agree with Zakharov and co-workers that the 1.940 and 1.915–1.925 signals from the high mileage catalyst arise from two separate titanium centers, not one as claimed previously. The intensity of the 1.915–1.925 signal can vary largely independent of the 1.951 signal, both by changing temperature and by changing $TiCl_4$ content. It is also partially true that the 1.915–1.925 signal originates from $[\mathrm{Ti}(3+)]_n$ clusters.

What we add to these conclusions is the essential new fact that the signal from $[\mathrm{Ti}(3+)]_n$ clusters is actually silent in the absence of $TiCl_4$; that it is the coordination of this diamagnetic molecule to the cluster which produces the paramagnetic signal. In this sense, the signal is actually a probe of both $TiCl_4$ and $[\mathrm{Ti}(3+)]_n$ clusters. The changes in relative intensity of the 1.915–1.925 signal with catalyst preparation changes in the previous studies are consistent with this result. Under less reducing synthesis conditions where substantial $TiCl_4$ remains in the product, the 1.915–1.925 signal is strong, and under more reducing conditions the 1.915–1.925 signal is weakened or nearly eliminated.

An element common to all these syntheses, then, is that a large percentage of the Ti(3+) exists in $[\mathrm{Ti}(3+)]_n$ clusters. Work aimed at determining the size and structure of such clusters, how many $TiCl_4$ molecules bind to a cluster, and whether or not the $TiCl_4$ actually dissociates from the cluster would be rewarding.

Conclusions

The model catalyst system [SiO_2 + alkylmagnesium alkoxide + $TiCl_4$] can give rise to one or more ESR signals at 1.99, 1.97, 1.953, and 1.895. The relative signal intensities follow two trends; higher Mg to Ti molar ratios favor the higher g value signals while low Mg loadings, regardless of $TiCl_4$ concentration, favor weak or absent signals. This second observation is consistent with consumption of Mg–R groups by residual silica surface hydroxyl groups, leaving no Mg–R groups (limiting reagent) for reduction of the Ti(4+).

As with past ESR studies of Ziegler–Natta catalysts, we cannot provide much insight as yet regarding the structures which give rise to the signals with g values of 1.99, 1.97, and 1.951.

On the basis of the results of this study, substantially more can be concluded about the local structure of the site or sites which give rise to the fourth signal at $g = 1.895$. A required component of the site giving rise to this signal is $TiCl_4$. If $TiCl_4$ is absent or is chemically or thermally removed, this ESR signal can be eliminated. The thermal loss is demonstrated to be quasi-reversible. Thus the $TiCl_4$ "turns on" previously ESR-silent Ti(3+) sites. Ethylene polymerization activity of the catalysts increases with increasing $TiCl_4$ content and with increasing intensity of the $g = 1.895$ signal (which is indicative of the presence of $TiCl_4$). It is proposed that the ESR silent Ti(3+) exists in clusters of as yet undetermined size, although we speculate that the clusters are linear and small (two Ti per cluster appears to be reasonable).

This proposal is consistent with a topotactic model[12] for the deposition and subsequent reduction of $TiCl_4$ onto magnesium substrates. It is predicted that these findings will have general relevance to the interpretation of ESR spectra of other magnesium-based supported Ziegler–Natta catalysts.

Registry No. $TiCl_4$, 7550-45-0; polyethylene, 9002-88-4.

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