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NOTES

Magnetic Susceptibility Study of a Model Supported Ziegler–Natta Catalyst: Evidence for Reduced Titanium Clusters

We report magnetic susceptibility data from 4 to 290 K for four supported Ziegler–Natta model catalysts of general formulation $SiO_2 + x\text{AMB} + y\text{TiCl}_4$, where AMB is an alkylmagnesium butoxide reagent. For each variation of the formulation, the spin concentration measured by magnetic susceptibility is nearly equal to the spin concentration measured by electron spin resonance (ESR) spectroscopy. By both methods we obtain [spins/Ti] values between 4.0 and 20.5%. For the three most reduced catalyst preparations studied—1.2, 1.3, and 1.4 ($1 < x/y < 10$)—these values are three to nine times lower than the [Ti(3+)/Ti(total)] ratios found for the catalysts by electrochemical methods [measurements of Ti(2+) concentration by hydrogen evolution show that Ti(2+) is negligible in these formulations]. The near equivalence of [spins/Ti] values measured by ESR and magnetic susceptibility and the deficiency of these values compared with Ti(3+) measured electrochemically establish that the reduced formulations contain clusters of Ti(3+) ions, $[\text{Ti}(3+)]_n$ where $n > 1$. Apparently, in those cases where n is even, the titanium (3+) ions in the clusters are spin paired, whereas where n is odd, there is one unpaired electron per cluster. It has been shown previously by ESR that $TiCl_4$ can bind to these reduced clusters and render them ESR active. Now, the magnetic susceptibility data also suggest that, on binding to the $[\text{Ti}(3+)]_n$ clusters, $TiCl_4$ breaks Ti(3+)–Ti(3+) bonds. Thus, in the case of the most oxidized formulation 1.1 ($x/y = 0.55$), which contains only 9% Ti(3+) by electrochemical determination, a much higher fraction of the Ti(3+) (65–95%) is detected by ESR and magnetic susceptibility.

INTRODUCTION

We have reported recently (*1*) the results of a titanium oxidation state, ethylene polymerization activity, and ESR spectral study of the model supported Ziegler–Natta catalyst formulation

$$\underset{\mathbf{1}}{SiO_2 + x\text{AMB} + y\text{TiCl}_4}$$

where AMB is an alkylmagnesium butoxide reagent. AMB and similar magnesium reagents, and $TiCl_4$, are frequently cited as important synthetic reagents in the Ziegler–Natta catalyst patent literature (*2*) and are often employed in the same catalyst synthesis. In our previous study (*1*), the x and y values (in mmol/g SiO_2) for the products examined were varied over a wide range. Initial work showed that one of the singlet resonances found in the more oxidized formulations ($x/y < 1$), nominally assigned $g = 1.89$, results from coordination of $TiCl_4$ to a $[\text{Ti}(3+)]_n$ site, where n is some integral number. If the $TiCl_4$ concentration is too low or it is thermally or chemically removed, then the $g = 1.89$ signal is absent. This reversible interaction is

$$\underset{\text{ESR silent}}{[\text{Ti}(3+)]_n} + m\text{TiCl}_4 \leftrightharpoons \underset{\text{ESR active}}{[\text{Ti}(3+)]_n(\text{TiCl}_4)_m} \tag{1}$$

We also found that for all samples, including those containing ~100% Ti(3+) (d^1 ions), [spins/Ti] concentrations measured by ESR were never greater than 19% and the ratio of spins detected by ESR to [Ti(3+)] measured by electrochemistry was never greater than 65%. These experimental facts suggest that a majority of the reduced titanium is bound in ESR silent titanium clusters ($n \geq 2$) (*1*). However, it is not

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possible by ESR alone to determine whether the spectroscopically silent reduced titanium is indeed clustered or, if clustered, what type of Ti–Ti interactions result. Consequently, in a case such as this where only a modest fraction of all potentially paramagnetic ions are accounted for by ESR, it is useful to independently measure spin densities by magnetic susceptibility methods (*3*). Such measurements on four products of general formulation **1** form the basis of this work. These magnetic susceptibility measurements extend the lower limit of the temperature range over which these samples have been studied from 100 down to 4 K. To our knowledge, this is the first published application of magnetic susceptibility to the characterization of supported Ziegler–Natta catalysts.

EXPERIMENTAL

The silica (Davison 952, surface area 280 m^2/g) supported formulations **1** were prepared following procedures described previously (*1*). Briefly, the silica was dehydrated at 800°C under flowing dry nitrogen. The alkylmagnesium butoxide reagent was prepared by slowly adding 0.5 mol of butanol under vigorous stirring to 1.0 mol of "butyl ethyl magala" (Texas Alkyls) in heptane. Each model catalyst was prepared by adding sufficient AMB solution to about 4 g of the silica slurried in hexane to give between 0.1 and 2.0 mmol Mg/g of silica. About an hour later, sufficient $TiCl_4$ stock solution was added to give the desired Mg/Ti molar ratio. The diluent was removed *in vacuo* to yield a dry, free-flowing solid. Elemental analyses for the four samples examined herein are given in Table 1. All samples studied by magnetic susceptibility had been previously examined (*1*) by ESR and by wet chemical determinations for Ti(2+) and Ti(3+) concentrations.

Magnetization data were obtained between 4 and 290 K using an automated George Associates Faraday magnetometer. The samples were sealed in a precalibrated quartz and Tygon sample holder in a helium-filled dry box (Vacuum Atmospheres; equipped with recirculator). Various tests have demonstrated that such sample holders are vacuum-tight after being sealed. Magnetization-versus-magnetic field (*H*) isotherms were obtained below 8 kG at several temperatures for each sample between 77 and 295 K to determine the contribution of ferromagnetic impurities to the measured magnetizations. These data were linear above 5 kG but nonlinear below this field.

TABLE 1

Compositions of SiO_2 + xAMB + $y$$TiCl_4$ Model Catalysts

Sample	mmol reagent/g SiO_2		Elemental analysis (%)				
	AMB	$TiCl_4$	Ti	Mg	Cl	C	H
1.1	0.5	0.9	3.40 (3.46)[a]				
1.2	0.5	0.4	1.67 (1.67)	1.01 (1.10)	4.88 (4.96)	2.95 (2.1)	0.65 (0.4)
1.3	2.0	0.4	1.30 (1.42)				
1.4	2.0	0.2	0.72 (0.72)	3.58 (3.69)	2.41 (2.15)	9.66 (8)	2.04 (1.2)

[a] Found value (calculated value). Calculated values are based on the assumption that 100% of each reagent binds to the silica support.

TABLE 2

Magnetic Susceptibility Data for $SiO_2 + x$AMB $+ y$TiCl$_4$ Model Supported Ziegler–Natta Catalysts

Sample	mmol reagent/g silica		χ_0 (10^{-7} cm^3/g)	C_g (10^{-5} cm^3-K/g)	% (Spins = ½)/Ti	M_{sat} (77 K) (G-cm^3/g)	Ferromagnetic impurity atoms per Ti (ppm)	θ (K)
	AMB	TiCl$_4$						
1.1	0.5	0.9	−4.52	1.99	8.1	8.1×10^{-4}	107	−5.0
1.2	0.5	0.4	−4.02	0.48	4.0	8.0×10^{-4}	200	0
1.3	2.0	0.4	−4.37	1.83	19.2	1.50×10^{-3}	480	−1.9
1.4	2.0	0.2	−4.46	1.08	20.3	7.3×10^{-4}	420	−0.8

RESULTS AND DISCUSSION

The zero-field intercepts, denoted M_{sat}, of the high-field linear $M(H)$ data were found to be nearly independent of temperature for each of the samples; the values at 77 K are listed in Table 2. These ferromagnetic impurity saturation magnetizations correspond to 100 to 400 atomic ppm with respect to Ti of ferromagnetic iron impurities, similar to the iron impurity concentrations obtained by inductively coupled plasma emission spectroscopic analysis of the silica support used for our preparations.

The magnetic susceptibility (χ) is the high-field slope of the $M(H)$ isotherms. The susceptibility data were obtained by measuring the magnetization in a fixed field of 6.3 kG upon sweeping the temperature at less than 1 K/min. $\chi(T)$ is then obtained using the relation $\chi(T) = [M(T) - M_{sat}(T)]/H$ to correct for the contribution of ferromagnetic impurities.

The inverse gram magnetic susceptibility χ_g versus temperature for the four samples is plotted in Fig. 1. Above about 10 K the data are nearly linear, closely following the relation

$$\chi = \chi_0 + C/(T - \theta) \qquad (2)$$

which is the sum of the temperature-independent diamagnetic contribution χ_0 and a Curie–Weiss term arising from unpaired spins on Ti(3+) sites. The values of χ_0, the Curie constants C, and the Weiss temperatures θ were determined from least-squares fits of Eq. (2) to the data. The results are listed in Table 2. As shown in Fig. 1, these least-squares fits describe the data well.

The values of χ_0 in Table 2 are close to the value (-4.9×10^{-7} cm^3/g) for SiO_2. This is expected, since the bulk of each catalyst consists of the silica support. The θ values are small, indicating negligible coupling between the observed magnetic centers. The spin density N, in units of [spins/Ti], can be obtained from the Curie constant C for each sample using the relation

$$N = (C/C_M)(AW/F) \qquad (4)$$

where C is the measured gram Curie constant, AW = 47.90 g/mol Ti is the atomic weight of Ti, and F is the weight fraction of Ti in the sample (Table 1). C_M is the calculated molar Curie constant for Ti(3+)

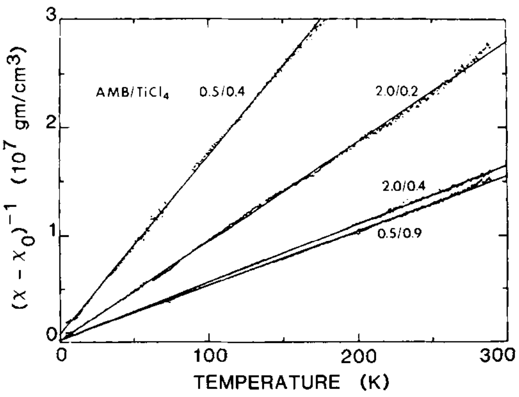

FIG. 1. Inverse susceptibility corrected for temperature-independent terms, $(\chi - \chi_0)^{-1}$, versus temperature for the samples in Table 1. The straight lines are least-squares fits to the data.

$$C_M = N_A(g_{av})^2[S(S + 1)/3k_B]\mu_B^2 \quad (5)$$

where g_{av} is the average gyromagnetic factor, S is the spin on Ti(3+), N_A is Avogadro's number, k_B is Boltzman's constant, and μ_B is the Bohr magneton. Using g_{av} = 1.926–1.945 (taken from half-height position of ESR double integral; Table 3) and $S = \frac{1}{2}$, one obtains C_M values between 0.382 and 0.390 cm^3-K/mol Ti. After converting C_M to an equivalent gram Curie constant and substituting the appropriate C_M value into Eq. (3), values of N are obtained. These are listed in Table 3, along with the values measured by ESR and the values of g_{av}. The spin densities measured independently for these four catalysts by ESR and by magnetic susceptibility agree quite satisfactorily in view of the errors that can be associated with obtaining accurate spin densities by ESR, the more modest errors associated with magnetic susceptibility, and the air sensitivity of the samples.

On the other hand, the spin densities measured by these two methods are usually substantially lower than the Ti(3+) concentration determined by a wet chemical method (*1*). Among the three most reduced samples (1.2, 1.3, and 1.4), we find that only a minority of the Ti(3+) (12–30%) known to be present from wet chemical determinations is detected by either ESR or magnetic susceptibility (cf. Table 3). These chronically low [spins/Ti(3+)] values measured by both methods are consistent with the conclusion that the majority of Ti(3+) spins in these relatively reduced samples are quenched due to ligand-mediated or direct metal–metal bonding. We expect Ti(3+) centers involved in such bonding are within 2.92 Å of each other (*4*).

On the other hand, in the most oxidized sample (1.1), which contains only 9% Ti(3+) by electrochemical analysis, we detect much more of the Ti(3+) (65–89%) by ESR and magnetic susceptibility. This trend is consistent with our systematic ESR findings [Eq. (1)] (*1*) that as samples of formulation **1** become more oxidized and contain more $TiCl_4$, the excess $TiCl_4$ coordinates to diamagnetic $[Ti(3+)]_n$ clusters, and in so doing renders two or more of the Ti(3+) centers in each cluster paramagnetic. Coordination of the $TiCl_4$ can create a mixed valence cluster in which the electrons contributed by the Ti(3+) centers are delocalized as illustrated schematically for the simplest, and not necessarily representative, case of coordination of a $TiCl_4$ molecule to a Ti(3+)–Ti(3+) dimer:

$$\text{Ti(3+)–Ti(3+)–Ti(4+)} \leftrightarrow \text{Ti(3+)–Ti(4+)–Ti(3+)} \leftrightarrow \text{Ti(4+)–Ti(3+)–Ti(3+)}$$

It is perhaps worth commenting on the result that in three of the four samples (1.1, 1.3, and 1.4) studied, higher [spins/Ti] values are detected by magnetic susceptibility

TABLE 3

Spin Concentrations[a] Determined by ESR and Magnetic Susceptibility, and Distribution of Titanium among Its Three Common Oxidation States

Sample	mmol reagent/g SiO_2		g_{av}	[Spins = ½/Ti]$_{ESR}$ (%)	[Spins = ½/Ti]$_{\chi M}$ (%)	Distribution of titanium among oxidation states (%)			Spins ½/Ti(3+) (%)
	AMB	$TiCl_4$				2+	3+	4+[b]	
1.1	0.5	0.9	1.926	5.8	8.1	0	9.1	90.9	89
1.2	0.5	0.4	1.931	5.0	4.0	0	16.0	84.0	25
1.3	2.0	0.4	1.938	13.0	19.2	0.2	95.8	4.0	20
1.4	2.0	0.2	1.945	11.0	20.3	0.8	97.6	1.6	21

[a] Determined by wet chemical methods. See Ref. (*1*).

[b] By difference.

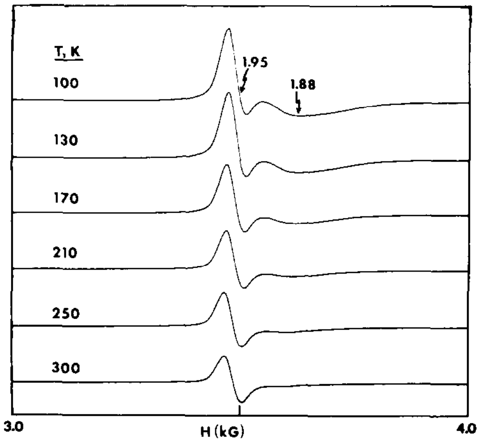

FIG. 2. ESR spectra of sample 1.1 recorded over the temperature range 100–300 K.

than by ESR (Table 3). In the fourth, sample 1.2, the [spins/Ti] are so close (5.0% by ESR, 4.0% by χ_M) that the two are effectively equivalent. The [spins/Ti] comparisons for samples 1.1, 1.3, and 1.4 suggest the presence of a modest population of paramagnetic centers which is not detected by ESR due to relaxation effects. Additionally, in the case of sample 1.1, the most oxidized sample, the higher [spins/Ti] value measured by magnetic susceptibility could also be due, at least in part, to the contribution of more spins with decreasing temperature as a consequence of breaking more Ti(3+)–Ti(3+) bonds through coordination of $TiCl_4$ (*1*) to a greater number of the $[Ti(3+)]_n$ clusters (spins/Ti measured by ESR only at room temperature). This is illustrated in Fig. 2, where the ESR spectrum of 1.1 is shown as a function of temperature. This set of spectra clearly shows the increasing contribution of the $g = 1.88$ signal (with decreasing temperature) to the overall spectrum relative to the $g = 1.95$ signal. Consequently, the [spins/Ti] determined by ESR was also measured at different temperatures down to 100 K. It was expected that increasing [spins/Ti] values would be measured, relative to one of our Ti(3+) standards recorded under the same conditions, with decreasing temperature, but our data so far suggest only simple Curie behavior. Apparently, the increase in spin density in cooling this sample from 300 to 100 K is not sufficient (perhaps on the order of 20% or less) to detectably alter the spin dependence from Curie behavior.

CONCLUSIONS

[Spins/Ti(3+)] values determined from magnetic susceptibility measurements for model supported Ziegler–Natta catalysts **1** are close to those measured previously by ESR. These values are between 12 and 30% for the more reduced model catalyst samples and so account for just a modest fraction of the total quantity of reduced titanium. The low but nearly equivalent values measured by the two different methods arise because the majority of Ti(3+) ions in these catalysts reside in clusters. Presumably, the spins associated with the Ti(3+) ions in $[Ti(3+)]_n$ clusters where n is even are quenched by either ligand-mediated or direct metal–metal bonding. In those clusters where n is odd, we expect (*4*) one unpaired electron per cluster. When a model catalyst sample is relatively oxidized, as is the case for sample 1.1, excess $TiCl_4$ can coordinate to the clusters, breaking Ti(3+)–Ti(3+) bonds [as in Eq. (1)] and resulting in detection of a higher fraction of the total Ti(3+) population. These findings demonstrate a strong propensity for clustering of reduced titanium in this model catalyst formulation and are consistent with the proposal for clustering of titanium in other related Mg/Ti-based Ziegler–Natta catalysts (*5*).

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