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Probing the Coordinative Unsaturation and Local Environment of Ti³⁺ Sites in an Activated High-Yield Ziegler Natta Catalyst

Elena Morra,[a,b,c] Elio Giamello,[a] Sabine Van Doorslaer,[c] Giuseppe Antinucci,[d] Maddalena D'Amore,[d] Vincenzo Busico,[d] and Mario Chiesa*[a]

[a] E. Morra, Prof. E. Giamello, Prof. M. Chiesa

Dipartimento di Chimica
Università degli Studi di Torino
Via Giuria 7, 10125 Torino, Italy
E-mail: mario.chiesa@unito.it

[b] E. Morra

Dutch Polymer Institute(DPI)
P.O. Box 902, 5600 AX Eindhoven, The Netherlands

[c] E. Morra, Prof. S. Van Doorslaer

Department of Physics
University of Antwerp
Universiteitsplein 1, B-2610 Antwerp-Wilrijk, Belgium

[d] G. Antinucci, Dr. M. D'Amore, Prof. V. Busico

Dipartimento di Scienze Chimiche
Università degli Studi di Napoli Federico II
Via Cintia 21, 80126 Napoli, Italy

Abstract: The typical activation of a 4th-generation Ziegler Natta catalyst TiCl₄/MgCl₂/phthalate with triethyl-aluminum generates Ti³⁺ centers that are investigated by multi-frequency continuous wave and pulse EPR methods. Two families of isolated, molecular like Ti³⁺ species have been identified. Comparison of the experimentally derived g tensors and ^{35,37}Cl hyperfine and nuclear quadrupole tensors with DFT-computed values suggests that the dominant EPR-active Ti³⁺ species is located on MgCl₂(110) surfaces (or equivalent MgCl₂ terminations with tetra-coordinated Mg). O₂ reactivity tests show that a fraction of these Ti sites is chemically accessible, an important observation in view of the search for the true active sites of olefin polymerization.

Despite major research efforts, MgCl₂-supported Ziegler Natta (ZN) catalyst systems for the industrial production of isotactic polypropylene[1] remain elusive. Efforts have been produced to characterize model systems,[2,3] but no direct insight in the complex, polycrystalline working catalysts at the molecular level has been obtained so far. Progresses have been made in the elucidation of MgCl₂ surface structure and stability,[4] and periodic DFT studies suggested that MgCl₂(110) terminations are the only surfaces where TiCl₄ (the most common precursor of the active species) can lead to moderately stable adsorbates.[5] How the system is impacted by the modifying action of certain Lewis bases and, at a later stage, by the AlR₃ co-catalyst,[1] is still largely unknown and seminal experimental[3,6-9] and theoretical[5,10-14] investigations failed to accommodate all known facts. Activation is usually performed by reacting the pre-catalyst with aluminum alkyl compounds (typically triethyl-aluminum, TEA). In this process tetravalent Ti ions assume a lower oxidation state[15] and both Ti³⁺ and Ti²⁺ have been proposed. Ti³⁺ centers are believed to play an important role in ZN catalysis however, their exact role and nature is still obscure.

Due to the paramagnetic nature of Ti³⁺ (3d¹, S=1/2), Electron Paramagnetic Resonance (EPR) is the ideal technique to unravel the nature and local coordinative environment of these sites. Conventional X band continuous wave (CW) EPR techniques have been used primarily to monitor the amount of reduced Ti species.[16-21] However, modern EPR techniques offer a whole arsenal of specific experiments capable of investigating the local environment of paramagnetic species. Here we employ a combination of multi-frequency CW and pulse EPR experiments, complemented with DFT calculations, to elucidate the nature and reactivity of Ti³⁺ centers generated by reacting a 4th-generation MgCl₂/TiCl₄/dibutylphthalate pre-catalyst (Ti 2.0 % by weight and dibutylphthalate 8.9 % by weight) with TEA vapors.[1] The sample was kindly supplied by SABIC.

The catalyst activation was performed in situ by contacting a weighted amount of pre-catalyst (typically 0.06 g) with TEA vapors in a specially designed cell described elsewhere.[22]

Upon reaction with TEA vapors the sample underwent a slight color change from dark yellow to pale brown and an intense EPR signal appeared. The X and W band CW EPR spectra are reported in Figure 1a and 1b respectively. The spectra show the typical g values (Table 1) expected for a system with a singly occupied molecular orbital (SOMO) comprised predominantly of a 3d orbital of Ti. Quantification of the EPR signal in Figure 1 indicates that the amount of EPR active Ti^{3+} is of the order of 15 ± 5 % of the total Ti content. The g tensor elements were determined by computer simulation of the spectra at the two frequencies (Figure 1), indicating the presence of three species (Table 1). Two of them (S1 and S2), with different relative contribution, account for the majority of the spectral intensity. The relative abundance of the three species was found to vary slightly from experiment to experiment. Both set of g values for the principal species (S1 and S2) are in line with values reported in the literature for Ti^{3+} species observed in ZN catalysts.[23]

To probe the local environment of the Ti^{3+} species, hyperfine sublevel correlation spectroscopy (HYSCORE) experiments at Q band frequency were performed (no electron spin echo was detected at X band frequency).

The Q band HYSCORE spectrum (Figure 1c) is dominated by correlation peaks at (6,2.8) and (2.8,6) MHz arising from the hyperfine (hfi) interaction with ^{35}Cl and ^{37}Cl nuclei. Given the superposition of the spectral features of S1 and S2, the HYSCORE spectra reflect hfi and nuclear quadrupole (nqi) interactions associated with both Ti^{3+} species

Table 1. Spin Hamiltonian parameters extracted from computer simulation of the experimental spectra^[a]. All hfi and nqi values are in MHz, while Euler angles are given in degrees.

		g_1	g_2	g_3	% ab		A_1	A_2	A_3	α, β, γ	e^2qQ/h	η	α', β', γ'
Ti^{3+}	S1	1.936±0.01	1.888±0.01	1.84±0.01	76	^{35}Cl	-3.5	-0.5	7.0	90,46,50	-9	0.3	10,55,0
	S2	1.960±0.01	1.945±0.01	1.89±0.01	23		±1.5	±2.5	±3.5	±20	±3	±0.2	±20
	S3	1.976±0.005	1.968±0.005	1.96±0.01	1								
O_2		2.0035±0.0002	2.0106±0.0002	2.0209±0.0002	100	1H	0.5	0.5	8.5	0,90,0			
						±0.3	±0.3	±0.5	±5				
	^{27}Al					8	8	11	---				
						±1	±1	±1					

[a] The g -matrix principal values were determined from the simultaneous simulation of the W band CW EPR spectrum, while the hyperfine parameters were determined from simulations of HYSCORE data (Figures 1 and 3, as well as the Supporting Information). The Euler angles α, β, γ define the passive rotation of the hyperfine and quadrupole principal axes system into the g -matrix principal axes system, $\mathbf{A}=\mathbf{R}(\alpha, \beta, \gamma) \mathbf{A}_{diagonal} \mathbf{R}^+(\alpha, \beta, \gamma)$. Signs of the proton hyperfine elements are based on the point-dipole model.

For the simulation of the HYSCORE spectrum spin-Hamiltonian parameters, recently obtained for $TiCl_3$ molecular complexes[24] and the results of DFT computations (vide infra) were used as starting values. An example of a reasonable simulation is shown in Figure 1c (see also Supporting Information). The main feature of the experimental spectra could be reproduced considering a Cl hfi tensor characterized by a fairly large dipolar component and relatively small Fermi contact contributions and nqi (e^2qQ/h) in the range 6 - 12 MHz. These values are in line with experimental and computed values for directly coordinated Cl to Ti^{3+} molecular complexes.[24] The same spin-Hamiltonian parameters have been used to fit W band ELDOR- detected NMR spectra, which are reported as Supporting Information.

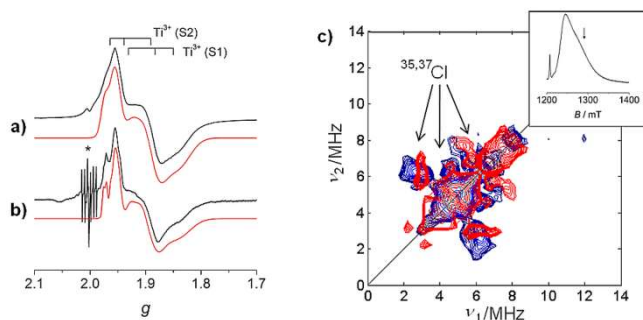


Figure 1. a) Experimental (black) and simulated (red) X band CW EPR spectra of the activated catalyst; b) W band CW EPR spectra of the same sample. Spectra were recorded at $T = 77$ K. The asterisk indicates a Mn^{2+} impurity. The spectral deconvolution is shown as Supporting Information; c) Q band experimental (blue) and simulated (red) HYSCORE spectra measured at the position indicated in the inset ($B_0 = 1290.0$ mT), showing ^{35}Cl and ^{37}Cl signals. The HYSCORE spectrum recorded at the maximum ESE intensity is reported as Supporting Information together with the full experimental details.

In order to interpret the spectroscopic data in terms of microscopic models, DFT calculations have been carried out (details in Supporting Information). Two models representative of Ti^{3+} on the (110) and (104) $MgCl_2$ surfaces have been considered (Figure 2a and 2b respectively). The DFT-computed spin Hamiltonian parameters are reported in Table 2. The hfi tensors show a large dipolar character with consistent departure

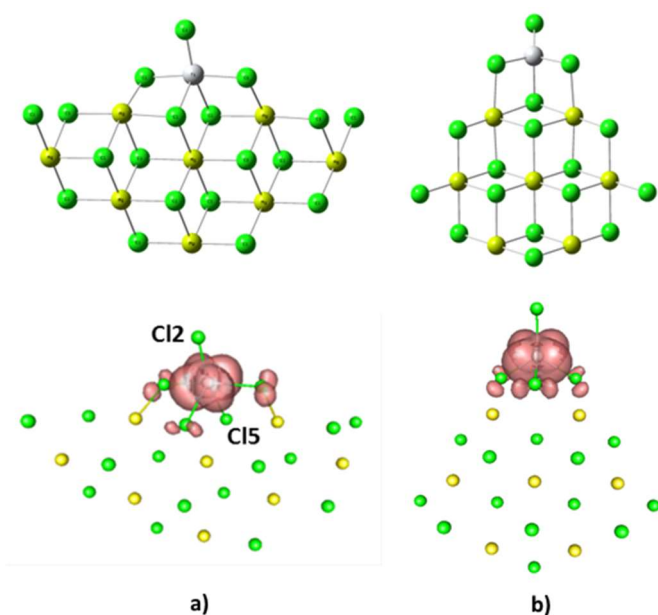


Figure 2. DFT model structures and corresponding spin density plots of $TiCl_3$ localized at a) $MgCl_2(110)$ surfaces and b) $MgCl_2(104)$ surfaces. Spin densities are displayed for an isosurface value of 0.002

from axial symmetry in line with a large spin density in the Cl p orbitals.

Overall the computed hfi and nqi Cl tensors are compatible with the experimental HYSCORE spectrum and concur with the results obtained on $TiCl_3$ molecular complexes.[24] The computed g tensors for the two models are consistent with the single electron occupying a d_{xy} or $d_{x^2-y^2}$ orbital (Figure 2). Distinctly different g tensor elements are computed for the two models, with the case of the tetra-coordinated Ti^{3+} located at the $MgCl_2(110)$ surface (Figure 2a) being in better agreement with the experimental values relative to the most abundant Ti^{3+} species (S1). The experiments illustrated in Figure 1 thus show that the

reaction of the pre-catalyst with TEA yielded isolated molecular-like Ti³⁺ species with directly bound Cl ions.

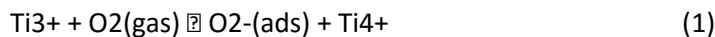
Table 2. Computed DFT spin Hamiltonian parameters for the models reported in Figure 2. All *hfi* and *nqi* values are in MHz.

	g_x	g_y	g_z	3Q	A_x	A_y	A_z	e^2qQ/h	η
TiO ₂ MgCl ₂ (110)	1.888	1.788	1.939	Cl1	-3.6	-2.8	-1.9	-8.4	0.83
				Cl2	-2.7	0.07	10.6	-14.1	0.56
				Cl3	-5.2	-1.9	10.1	-12.4	0.87
				Cl4	-3.6	-0.6	5.6	-9.8	0.57
				Cl5	-1.0	0.5	0.8	-9.6	0.2
TiO ₂ MgCl ₂ (104)	1.850	1.968	1.909	Cl1	-3.7	-1.6	8.9	-10.4	0.34
				Cl2	-6.1	-3.0	5.1	-8.6	0.13
				Cl3	-3.8	-1.7	9.6	-10.4	0.41
				Cl4	-3.9	-3.7	1.1	5.7	0.77

The observation of well-defined molecular-like sites in an industrial heterogeneous catalyst is per se remarkable, considering the complexity of the system. Comparison between experimental and DFT-computed EPR parameters suggests that the dominant EPR active Ti³⁺ species is characterized by a well-defined and homogeneous environment, compatible with MgCl₂(110) or equivalent surfaces.

The important question arises as to whether the isolated Ti³⁺ centers observed by EPR are chemically accessible or not. To answer this question the sample was reacted with molecular oxygen (50 mbar at room temperature).

Oxygen is a well-known electron scavenger and readily reacts with Ti³⁺ according to the following equation:



Upon reaction with O₂ (Figure 3a), we observe a consistent decrease of the Ti³⁺ signal (down to ~60 % of the initial intensity) and the appearance of the spectrum of surface-adsorbed O₂⁻ species. The g matrix (Table 1) is typical for an ionic superoxide species stabilized at a Ti⁴⁺ site.[25-29] Remarkably, the Q-band EPR spectrum (Figure 3b) indicates that one single O₂⁻ species was formed, implying a single stabilizing Ti⁴⁺ surface site. The presence of unreacted Ti³⁺ sites (~40 % of the EPR-active Ti³⁺ species), in turn, indicates that the activation process also gave rise to Ti³⁺ species which are chemically inactive under the mild experimental conditions, due to coordinative saturation and/or because they are buried underneath the catalyst surface.

The O₂⁻ ions can also be exploited as paramagnetic probes to further monitor the local environment of the adsorption site. In particular X and Q band HYSCORE spectra (Figure 3c,d) allow resolving hfi couplings with nearby ¹H, ²⁷Al and ^{35,37}Cl nuclei.

A ¹H X band HYSCORE spectrum of the formed O₂⁻ radicals is shown in Figure 3c. Simulation of the spectra recorded at different magnetic field settings (Supporting Information) provided the full hyperfine matrix (Table 1), from which a O₂⁻-H distance of 0.33 nm can be estimated using the point-dipole approximation. This proton may have different sources and we cannot make a definitive assignment at this stage.

The Q band HYSCORE spectrum (Figure 3d) shows the presence of signals due to ^{35,37}Cl and ²⁷Al nuclei. The most interesting features are the ²⁷Al cross peaks, separated by ~10 MHz, indicating a large isotropic (Fermi contact) contribution and direct interaction of the radical with a nearby Al ion (see Supporting Information for a detailed analysis). A similar case was found for O₂⁻ radicals generated at the surface of MgO doped with Na atoms[30] and a related scheme (Scheme 1) may explain the present experimental results.

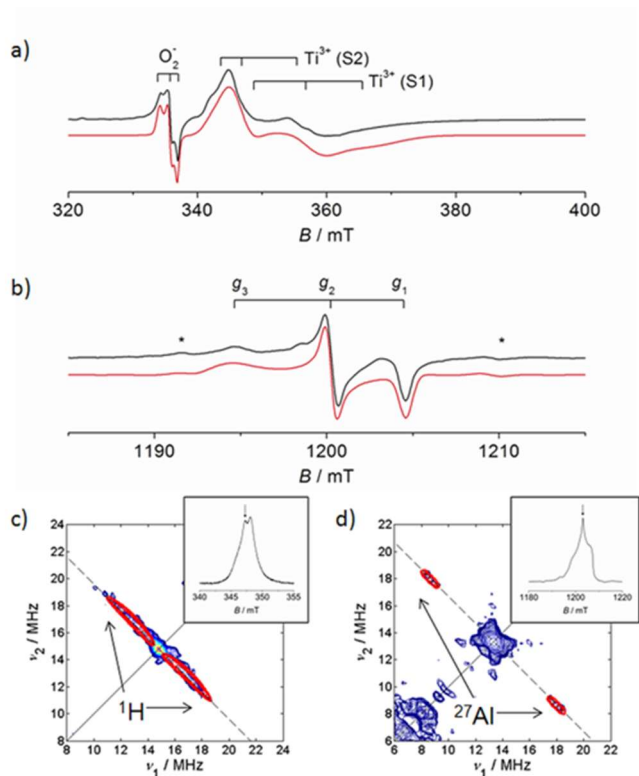
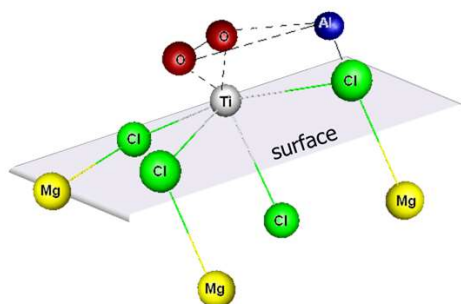


Figure 3. Experimental (black/blue) and simulated (red) spectra recorded upon reaction at room temperature of the activated catalyst with molecular O_2 . a) X band CW EPR spectrum recorded at 77 K; b) Q band FID-integral detected EPR spectrum of the superoxide radical anion recorded at 40 K. To facilitate the comparison with the CW X band spectrum the first derivative of the absorption is presented. The asterisks indicate a Mn^{2+} impurity; c) 1H X band HYSCORE spectrum of the surface O_2^- , recorded at the position indicated in the inset ($B_0 = 347.3$ mT); d) ^{27}Al Q band HYSCORE spectrum recorded at the position indicated in the inset ($B_0 = 1200.5$ mT). All HYSCORE spectra were recorded at 40 K. The spin-Hamiltonian parameters used in the simulations are listed in Table 1. The full set of spectra is shown in the Supporting Information.

Summarizing, monomeric and well defined EPR-active Ti^{3+} species are formed by activating an industrial $MgCl_2$ -supported ZN pre-catalyst with TEA. Such species account for ≈ 15 % of the total Ti content and are characterized by a well-defined environment compatible with $MgCl_2(110)$ or equivalent surfaces exposing tetra-coordinated Mg ions. Only a fraction (≈ 60 %) of these Ti^{3+} species is chemically accessible and reacts via an electron transfer mechanism with O_2 . A fraction of the reacted oxygen is stabilized on Ti^{4+} sites in the form of surface O_2^- radical ions in the proximity of Al^{3+} ions.



Scheme 1. Schematic representation of the proposed O_2^- coordination. The proton is not shown in the scheme.

In conclusion, we demonstrated the presence of a non negligible amount of Ti^{3+} in the form of monomeric isolated and chemically accessible centers. Even though we have, at present, no evidence that these are the actual catalytic sites operating in heterogeneous ZN catalysts, this is the first time Ti^{3+} centers formed upon activation of a heterogeneous industrial ZN catalyst are characterized at a molecular level, accomplishing a crucial step towards the identification of the potential active sites and the resolution of one of the most exciting open problems of modern catalysis.

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Keywords: Ziegler-Natta • Heterogeneous catalysis • EPR • Polymerization

- [1] E. Albizzati, U. Giannini, G. Collina, L. Noristi, L. Resconi in *Polypropylene Handbook: Catalysts and Polymerizations* (Ed.: E. P. Moore Jr.), Hanser-Gardner Publications, Cincinnati, 1996, Ch. 2.
- [2] T. Risse, J. Schmidt, H. Hamann, H. J. Freund, *Angew. Chem. Int. Ed.* 2002, 41, 1517-1520; *Angew. Chem.* 2002, 114, 1587-1591.
- [3] a) E. Magni, G. A. Somorjai, *J. Phys. Chem.* 1996, 100, 14786-14793; b) E. Magni, G. A. Somorjai, *Catal. Lett.* 1995, 35, 205-214; c) S. H. Kim, G. A. Somorjai, *Surf. Interface Anal.* 2001, 31, 701-710.
- [4] V. Busico, M. Causà, R. Cipullo, R. Credendino, F. Cutillo, N. Friederichs, R. Lamanna, A. Segre, V. Van Axel Castelli, *J. Phys. Chem. C* 2008, 112, 1081-1089.
- [5] M. Seth, P. M. Margl, T. Ziegler, *Macromolecules* 2002, 35, 7815-7829.
- [6] P. Corradini, V. Barone, R. Fusco, G. Guerra, *Gazz. Chim. Ital.* 1983, 113, 601-607.
- [7] H. Mori, M. Sawada, T. Higuchi, K. Hasebe, N. Otsuka, M. Terano, *Macromol. Rapid Commun.* 1999, 20, 245-250.
- [8] L. Brambilla, G. Zerbi, F. Piemontesi, S. Nascetti, G. Morini, *J. Mol. Catal. A: Chem.* 2007, 263, 103-111.
- [9] T. Taniike, S. Takahashi, T. Wada, K. Tonosaki, S. Dwivedi, M. Terano, *Macromol. Symp.* 2012, 313, 1-7.
- [10] M. Boero, M. Parrinello, H. Weiss, S. Huffer, *J. Phys. Chem. A* 2001, 105, 5096-5105.
- [11] D. V. Stukalov, I. L. Zilberberg, V. A. Zakharov, *Macromolecules* 2009, 42, 8165-8171.
- [12] T. Taniike, M. Terano, *Macromol. Rapid Commun.* 2008, 29, 1472-1476.
- [13] N. Bahri-Laleh, A. Correa, S. Mehdipour-Ataei, H. Arabi, M. N. Haghighi, G. Zohuri, L. Cavallo, *Macromolecules* 2011, 44, 778-783.
- [14] M. D'Amore, R. Credendino, P. H. M. Budzelaar, M. Causà, V. Busico, *J. Catal.* 2012, 286, 103-110.
- [15] C. Beermann, H. Bestian, *Angew. Chem.* 1959, 71, 618-623.
- [16] P. Brant, A. N. Speca, *Macromolecules* 1987, 20, 2740-2744.
- [17] J. C. W. Chien, J. C. Wu, C. I. Kuo, *J. Polym. Sci., Part A: Polym. Chem.* 1982, 20, 2019-2032.
- [18] P. Šindelář, D. Matula, J. Holeček, *J. Polym. Sci., Part A: Polym. Chem.* 1996, 34, 2163-2171.

- [19] V. A. Poluboyarov, V. F. Anufrienko, V. A. Zakharov, S. A. Sergeev, S. I. Makhtarulin, G. D. Bukatov, *React. Kinet. Catal. Lett.* 1984, 26, 347-351.
- [20] A. A. Tregubov, V. A. Zakharov, T. B. Mikenas, *J. Polym. Sci., Part A: Polym. Chem.* 2009, 47, 6362-6372.
- [21] E. I. Koshevoy, T. B. Mikenas, V. A. Zakharov, A. M. Volodin, R. M. Kenzhin, *Catal. Commun.* 2014, 48, 38-40.
- [22] E. Morra, E. Giamello, M. Chiesa, *Chem. Eu. J.* 2014, 20, 7381-7388.
- [23] J. C. W. Chien, Y. Hu, *J. Polym. Sci., Part A: Polym. Chem.* 1989, 27, 897-913.
- [24] S. Maurelli, E. Morra, S. Van Doorslaer, V. Busico, M. Chiesa, *Phys. Chem. Chem. Phys.* 2014, 16, 19625-19633.
- [25] A. M. Prakash, V. Kurshev, L. Kevan, *J. Phys. Chem. B* 1997, 101, 9794-9799.
- [26] K. L. Antcliff, D. M. Murphy, E. Griffiths, E. Giamello, *Phys. Chem. Chem. Phys.* 2003, 5, 4306-4316.
- [27] Z. Sojka, *Catal. Rev.: Sci. Eng.* 1995, 37, 461-512.
- [28] M. Che, A. J. Tench, *Adv. Catal.* 1983, 32, 1-148.
- [29] F. Geobaldo, S. Bordiga, A. Zecchina, E. Giamello, G. Leofanti, G. Petrini, *Catal. Lett.* 1992, 16, 109-115.
- [30] F. Napoli, M. Chiesa, E. Giamello, G. Preda, C. Di Valentin, G. Pacchioni, *Chem. Eu. J.* 2010, 16, 6776-6785.