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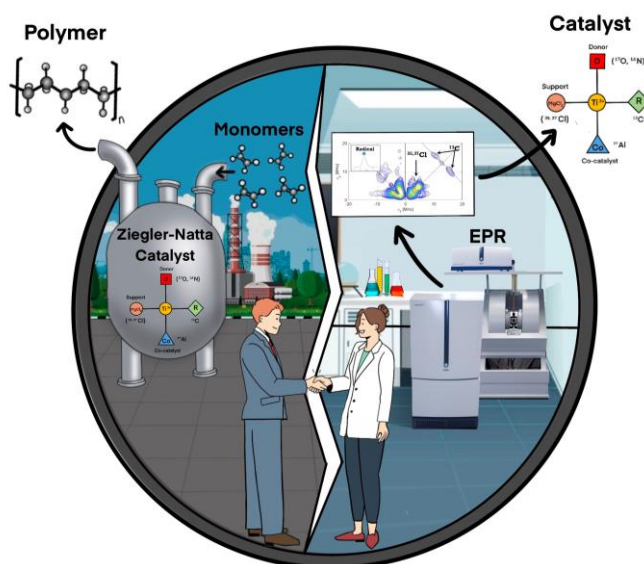
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Paramagnetic species in Ziegler-Natta catalysts



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Summary

This doctoral thesis investigates the nature and behavior of paramagnetic Ti(III) species in industrial Ziegler-Natta catalysts (ZNCs) used for the polymerization of polyethylene and polypropylene and is the result of a collaborative effort between the EPR laboratories of the University of Torino, the University of Antwerp and the Giulio Natta R&D Centre of Basell Poliolefine Italia, carried out as part of the H2020 MSCA-EJD PARACAT project (grant agreement No 813209).

The study focuses on the use of advanced Electron Paramagnetic Resonance (EPR) spectroscopy to examine the role of Lewis bases on the active sites in the (pre-)catalysts. EPR allows to monitor paramagnetic species, such as Ti(III) sites and organic radicals formed during catalysis. The research involves a systematic bottom-up analysis of the paramagnetic species in the ZN-materials starting from the MgCl_2 support to pre-catalysts, activated catalysts, and pre-polymerized samples. The presence of radical species distributed in the MgCl_2 support was found to be related to the presence of the Lewis base. The addition of different Lewis bases to a $\text{MgCl}_2/\text{TiCl}_4$ system was found to have also a direct effect on the distribution and coordination geometry of Ti(III) species on the surface of MgCl_2 , which in turn affects the activity and selectivity of the final catalyst. The nature of the Ti(III) species was found to be depend on whether the activation process was performed in liquid or gas phase with a suitable co-catalyst. In the pre-polymerized samples, a dilution of the paramagnetic species was observed with the increase in polymer weight, but no change in the species was found. The current research provides insights into the behavior and activity of the ZNCs and contributes to the understanding of the catalytic mechanism.

Samenvatting

Deze doctoraatsverhandeling onderzoekt de aard en het gedrag van paramagnetische Ti(III)-species in industriële Ziegler-Natta-katalysatoren (ZNC's) die worden gebruikt voor de polymerisatie van polyethyleen en polypropyleen. Het is het resultaat van een samenwerking tussen de EPR-laboratoria van de Universiteit van Turijn en de Universiteit Antwerpen, en het Giulio Natta R&D-centrum van Basell Poliolefine Italia, uitgevoerd als onderdeel van het H2020 MSCA-EJD PARACAT project (projectovereenkomst No 813209).

Het onderzoek richt zich op het gebruik van geavanceerde Elektron Paramagnetische Resonantie (EPR)-spectroscopie om de rol van Lewisbasen op de actieve sites in de (pre-)katalysatoren te onderzoeken. EPR laat toe om de paramagnetische species, zoals Ti(III) sites en organische radicalen, te bestuderen die tijdens de katalyse worden gevormd. Het onderzoek omvat een systematische bottom-up analyse van paramagnetische species in de ZN-materialen, te beginnen bij de MgCl_2 -drager tot pre-katalysatoren, geactiveerde katalysatoren en geprepolymeriseerde monsters. De aanwezigheid van radicalen in de MgCl_2 -drager kon gerelateerd worden aan de aanwezigheid van de Lewisbase. De toevoeging van verschillende Lewisbasen aan een $\text{MgCl}_2/\text{TiCl}_4$ systeem bleek een direct effect te hebben op de distributie en coördinatiegeometrie van Ti(III)-soorten op het oppervlak van MgCl_2 , wat op zijn beurt de activiteit en selectiviteit van de finale katalysator beïnvloedt. De aard van de Ti(III)-centra hing af van de fase waarin het activeringsproces werd uitgevoerd (vloeibare of gasfase met een geschikte co-katalysator). In de geprepolymeriseerde monsters, werd een verdunning van deze paramagnetische species waargenomen bij toenemend polymeergewicht, maar werd geen verandering in deze centra gevonden. Het huidige onderzoek biedt inzicht in het gedrag en de activiteit van de ZNCs en draagt bij aan het begrip van het katalytische mechanisme.

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List of Abbreviations

AMB	Alkylmagnesium Butoxide
BPI	Basell Poliolefine Italia S.r.l., LyondellBasell Group
CW	Continuous Wave
DEAC	Diethylaluminum chloride
DFT	Density Functional Theory
DQ	Double Quantum
EADC	Ethylaluminum dichloride
ED	External Donor
ELDOR	Electron-electron Double Resonance
ENDOR	Electron-Nuclear Double Resonance
EPR	Electron Paramagnetic Resonance
ESEEM	Electron Spin Echo Envelope Modulation
EXAFS	Extended X-ray Absorption Fine Structure
FID	Free Induction Decay
HDPE	High-density Polyethylene
HFI	Hyperfine Interaction
HTA	High Turning Angle
HYSCORE	Hyperfine Sublevel Correlation
ID	Internal Donor
LB	Lewis Base
LDPE	Low-Density Polyethylene
LEED	Low Energy Electron Diffraction
LLDPE	Linear Low-Density Polyethylene
MCDMS	Methyl-Cyclohexyl-Dimethoxy Silane
mw	Microwave frequency
MW	Molecular Weight
MWD	Molecular Weight Distribution
NMR	Nuclear Magnetic Resonance
NQI	Nuclear Quadrupole Interaction
PE	Polyethylene
PP	Polypropylene
PSD	Particle Size Distribution
SMART	Single Matched Resonance Transfer
SQ	Single Quantum
TEA	Triethylaluminum
TEMPO	2,2,6,6-tetramethyl-1-piridinylloxy
TDS	Temperature Programmed Desorption
TIBA	Triisobutylaluminum
XANES	X-Ray Near Edge Spectroscopy
XRD	X-Ray Diffraction
XPS	X-Ray Photoelectron Spectroscopy
ZNC	Ziegler-Natta Catalyst

Symbols

A	Secular hyperfine coupling
$\mathbf{A}$	Hyperfine interaction tensor
a_{iso}	Isotropic hyperfine interaction
$\mathbf{B}_0$	External magnetic field
g_e	Free-electron g value (2.002331)
g_n	Nuclear g value
h	Planck constant ($6.6260755 \times 10^{-34} \text{ J}\cdot\text{s}$)
$\hbar$	Reduced Planck constant ($1.05457266 \times 10^{-34} \text{ J}\cdot\text{s}$)
$\mathcal{H}$	Hamiltonian
$\mathbf{I}$	Nuclear spin operator
I	Nuclear spin quantum number
$\mathbf{Q}$	Nuclear quadrupole tensor
$\mathbf{S}$	Electron spin operator
S	Electron spin quantum number
$\mathbf{T}$	Dipolar hyperfine interaction tensor
T	Secular dipolar hyperfine interaction coupling
T_m	Phase memory relaxation time
β_e	Bohr magneton ($9.27400899 \times 10^{-24} \text{ J}\cdot\text{T}^{-1}$)
β_n	Nuclear magneton ($5.05078317 \times 10^{-27} \text{ J}\cdot\text{T}^{-1}$)
μ_0	Magnetic constant (vacuum permeability) ($4\pi \times 10^{-7} \text{ N}\cdot\text{A}^{-2}$)
ν	Frequency

General introduction

Polymers and plastics have become among the most common and important materials used in everyday life and comprise nowadays nearly 80% of the worldwide chemical industry output, which corresponded to \$ 961,300,000,000 in 2014 [1]. Among existing polymers, polyethylene (PE) and polypropylene (PP) are the most used ones, as they together sum up to more than 50% of the overall plastics production. Such mass production of PE and PP became possible only after the discovery of transition metal-based catalysts in the 1950s, thanks to joined academic and industrial efforts in both USA and Europe. In 1953, the Italian chemist Giulio Natta (1903–1979) [2], building on work by the German chemist Karl Ziegler (1898–1973) on organometallic catalysts was able to produce isotactic polypropylene. The latter two, later shared the 1963 Nobel Prize in Chemistry for their work on polymers. Later, Professor Natta also produced syndiotactic polypropylene.

So called Ziegler–Natta catalysts (ZNC) are currently used to produce PP. In 1957, the Italian company Montecatini, then Montedison (and now Basell Polyolefin Italia), who sponsored Natta's work, were the first to produce isotactic polypropylene commercially in a plant in Ferrara, Italy. It is in this very place that part of this thesis was carried out, with the ambitious goal of applying advanced Electron Paramagnetic Resonance (EPR) spectroscopy to catalysts of industrial relevance and elucidating the role of open-shell species in ZNCs.

1.1. Overview of the Thesis

The aim of this thesis is the investigation of heterogeneous ZNCs produced in the Basell Polyolefin Italia (BPI) research centre of Ferrara (Italy), focusing on the nature and structure of open-shell (radical) species. Despite that open-shell Ti(III) species are meant to be the catalytic active sites, the paramagnetic species in the Ziegler Natta catalysis have been relatively poorly explored. Clearly, electron paramagnetic

resonance (EPR) represents a powerful technique to characterize the active sites on ZNC and their surrounding environment. Whilst most of these studies have utilized the more readily available continuous wave (CW)-EPR method, the advantages of modern pulsed EPR techniques offer a far greater step forward in terms of the information that can be extracted on the structure of the paramagnetic sites. In this work, thanks to the support of the BPI research center, I followed a bottom-up approach (Figure 1.1), using EPR to characterize heterogeneous Ziegler – Natta catalyst systems of increasing complexity.

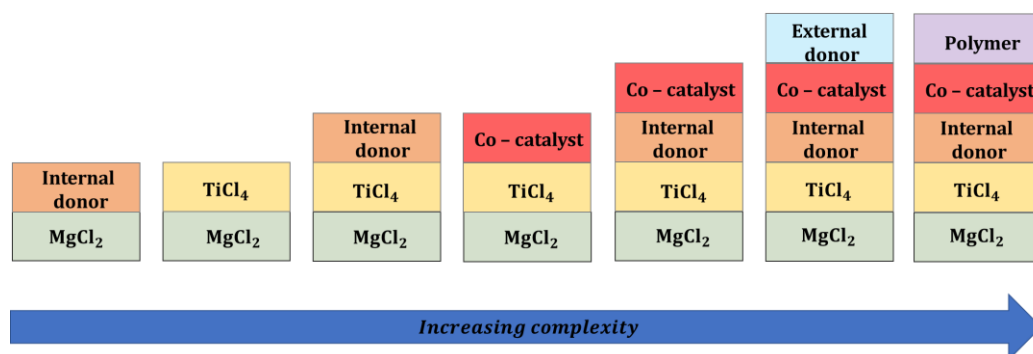


Figure 1.1 Scheme of the bottom-up approach of investigation employed in this thesis.

The thesis is organized as follows. In Chapter 1 a general introduction on the nature and structure of Ziegler-Natta catalysts, including a historical perspective is given. Chapter 2 provides the fundamental background on EPR spectroscopy, while the methodological aspects are described in Chapter 3. In Chapter 4, results obtained on highly active MgCl_2 support samples containing Lewis bases (internal electron donors) are reported and the radical species as observed by CW-EPR spectra are discussed. Following the characterization of the paramagnetic properties of the MgCl_2 support, pre-catalysts of the type $\text{MgCl}_2/\text{TiCl}_4$ with and without the presence of Lewis bases (internal donors) have been studied showing, in addition to organic radicals, also the presence of Ti(III) species before any activation. Such “native” Ti(III) species, introduced, during the impregnation of the MgCl_2 support with TiCl_4 were used as paramagnetic probes to explore the relation between the EPR spectral features and the nature of the sample and of the Lewis bases (*i.e.* internal and external donors). Finally, in Chapter 5, results obtained on activated and pre-polymerized catalysts, containing different amounts of polyethylene, are presented, and discussed. Chapter 6 summarizes the main results of this work and presents future outlooks.

1.2. Ziegler-Natta catalysts. Composition and preparation

The first catalyst discovered by Ziegler in 1953 using a combination of TiCl_4 and aluminum alkyls led to the polymerization of PE under mild reaction conditions [3]. Natta employed the same catalyst system and successfully synthesized PP [4]. However, this catalyst showed low productivity and stereospecificity, leading to the need to improve the catalyst composition [5]. As a result of further studies, the original ZNC systems have gradually changed in composition over the decades, leading to the development of several generations of catalysts (Table 1.1). This development has been correlated with notable advancements in activity and stereochemical control in each generation. The first generation of ZNC was developed using prolonged ball-milling of TiCl_3 with either AlCl_3 or AlEt_2Cl [5,6]. These catalysts were characterized by low productivity and stereospecificity, attributed to the fact that only a small fraction of Ti atoms were available as potential active sites [7,8]. The second generation was the result of additional advancements in the synthesis made by Solvay in the 1970s, leading to a catalyst with a much higher surface area, productivity, and an isotactic index of approximately 95% [9,10]. The third generation was developed by using highly active surface supports, mainly activated MgCl_2 , which can chemically anchor TiCl_4 [11]. The use of MgCl_2 as support enables the dilution of Ti atoms on a high-surface-area carrier, leading to an improvement in catalyst efficiency because a large number of surface Ti atoms become available for polymerization [12]. The first catalysts of this generation were mainly used in PE polymerization, given their low stereoselectivity for PP polymerization [5]. Improvements for the use in PP polymerization were achieved by comilling MgCl_2 , TiCl_4 , and a Lewis base, referred to as an “internal donor” (ID), and activating this pre-catalyst with triethylaluminum (TEA) in the presence of a second Lewis base, named as an “external donor” (ED). The Lewis bases used in the third generation were ethyl benzoate as the ID and methyl p-toluate or ethyl p-ethoxybenzoate as the ED [13,14]. The other generations were developed mainly using different new combinations of Lewis bases. Fourth-generation alkylphthalates were employed as ID and alkoxy silanes as ED [15]. Significant improvements in activity and isotacticity have been achieved in the fifth generation by introducing diethers or succinates as ID, either alone or in combination with alkoxy silanes [16]. Diethers remain on the surface of the MgCl_2 support even after activation with TEA and are not involved in secondary reactions with Ti-C, Al-C, and Ti-H bonds during polymerization [17].

The sixth generation of supported ZNC was developed by Basell, using succinate as an ID [18]. The development of more efficient and practical catalysts is still ongoing [19].

Table 1.1 Generations of ZNCs for propylene polymerization [5].

Generation	Year	Catalyst Composition	Productivity (kg _{pp} /g _{cat})	Isotactic Index (%)
1 st	1954	δ -TiCl ₃ · 0.33 AlCl ₃ + AlEt ₂ Cl	2 – 4	90 – 94
2 nd	1970	δ -TiCl ₃ + AlEt ₂ Cl	10 – 15	94 – 97
3 rd	1971	MgCl ₂ /TiCl ₄ /phthalate + AlR ₃ /benzoate	15 – 30	95 – 97
4 th	1980	MgCl ₂ /TiCl ₄ /phthalate + AlR ₃ /silane	40 – 70	95 – 99
5 th	1988	MgCl ₂ /TiCl ₄ /diether + AlR ₃	100 – 130	95 – 98
		MgCl ₂ /TiCl ₄ /diether + AlR ₃ /silane	70 – 100	98 – 99
6 th	1999	MgCl ₂ /TiCl ₄ /succinate + AlR ₃ /silane	40 – 70	95 – 99

The preparation procedure of heterogeneous ZNC consists of two major steps: the synthesis of the pre-catalyst, consisting of MgCl₂, TiCl₄, and ID, and the activation process with a co-catalyst, usually an alkylaluminum compound mixed with an ED [5,12]. In contrast to catalysts for polyethylene, which can be used also without electron donors, electron donors must be employed in the catalyst composition in order to obtain isotactic PP [20–26].

A variety of routes to prepare the Ziegler-Natta pre-catalysts for PE and PP polymerization have been proposed, divided into three main general procedures: the mechanical route, the mechanical plus chemical route, and the chemical route.

- In the mechanical route, MgCl₂, TiCl₄, and, optionally, an ID are milled together in a ball mill under an inert atmosphere for a certain period of time [27–33]. The activity of the catalysts prepared via this route depends on the milling time and the ratio of MgCl₂, TiCl₄, and ID [5,12].
- In the mechanical plus chemical route, there are two approaches for preparing the pre-catalyst. The first consists of either milling MgCl₂ alone or co-milling it with an ID and then reacting it with an excess of TiCl₄ at approximately 80 °C. This pre-catalyst is then washed with hydrocarbons to remove the excess TiCl₄ [34–43]. In the second approach, all catalyst components are co-milled together and washed afterward with a halogenated or aromatic solvent [44–48].

- The chemical route involves reactions that result in the formation of an active MgCl_2 support and its interaction with TiCl_4 and ID. These reactions can be divided into four main groups:
 - The reaction of a precursor, such as Mg(OR)_2 and Mg(OR)Cl , with an ID and excess TiCl_4 , during which the active form of MgCl_2 is obtained from the reaction of the precursor with TiCl_4 accompanied by the release of Ti-alkoxides as byproducts, which are removed by washing [49–56].
 - The formation of an MgCl_2 and Lewis base (e.g., an alcohol) complex, which is then treated with excess TiCl_4 in the presence of an ID at 80 °C. The solid is then extensively washed with hydrocarbon solvents [57–64].
 - Formation of the active form of MgCl_2 from the reaction of a solution of MgCl_2 or a precursor [e.g., Mg(OR)_2 , Mg(OCOR)_2 , MgR_2] in a suitable solvent (ROH, trialkyl-phosphate, titanium alkoxides, etc.) with a chlorinating agent. The precipitate is then treated with TiCl_4 and ID [65–74].
 - The reaction of MgR_2 or MgRCl with a chlorinating agent (eg. SiCl_4) to obtain the active form of MgCl_2 , which may or may not be treated with a Lewis base (e.g., alcohol) before its final treatment with an ID and excess TiCl_4 [75–83].

From the above preparation routes for heterogeneous ZNC, the chemical route is the most preferable in the industrial sector. By using the chemical route instead of the mechanical route, particles with controlled shapes (either spherical or granular), sizes, and size distributions can be obtained. In contrast, powders with no morphology control in terms of shape, size, and size distribution were obtained using the mechanical route. The generation of spherical catalyst particles is particularly important because of the replication phenomenon (see Section 1.5), where the polymer mimics the shape of the catalyst [5,12].

The activation process of MgCl_2 -supported ZNC is performed using alkyl aluminum compounds such as triethylaluminum (TEA) and triisobutylaluminum (TIBA), which are used as alkylation and reduction agents to reduce the Ti(IV) center to the Ti(III) center bearing a Ti–C bond and a vacancy. Additionally, it has been shown that the co-catalyst affects the polymer's stereoregularity, comonomer sequence distribution, and molecular weight [84,85].

The main goals of the polyolefin industry regarding catalyst optimization, of which most have been achieved, are as follows:

- High yield (with chlorine level less than 50 ppm)
- High Isotactic Index, higher than 97% Index, expressed as the polymer fraction insoluble in xylene at room temperature
- Control of polymer parameters like molecular mass (MW) and molecular mass distribution (MWD)
- Control of polymer morphology through the control of catalyst particle morphology [5]

The potential of ZNCs is still under investigation. Many questions regarding the structure of the active sites and the mechanism of these catalysts remain still not fully answered.

1.3. The fundamental components of heterogeneous Ziegler-Natta Catalysts

Following the basic Ziegler-Natta catalyst composition described above and the chemical composition evolution over several decades, a description of each of the key components of heterogeneous Ziegler-Natta catalysts will be given in this section to better understand the catalyst function.

The main components of the heterogeneous ZNCs include the highly active compounds MgCl_2 , TiCl_4 , aluminum alkyl compounds, and electron donors employed as ID in the preparation step of the pre-catalyst and ED added during the activation process. The structure of each component influences the structure of the active sites and overall catalyst productivity.

1.3.1. TiCl_3 : The Essential Component in Ziegler-Natta Catalysts

The most stereospecific catalysts are obtained from transition metal compounds of the MX_3 type (M – transition metal, X – halogen). The presence of a center of chirality is necessary for the isospecific polymerization of α -olefins. In the ZNCs, this center is likely to be the active site. In these catalytic systems, TiCl_3 is the key component, and it exists in four crystalline modifications: α , β , γ , and δ . Modifications α , γ , and δ are characterized by a violet color and layered structure (Figure 1.2a), and modification β by a brown color

and a fiber-like structure (Figure 1.2b) [5]. In all modifications, each titanium atom is positioned such that it can octahedrally coordinate six chlorine atoms [86].

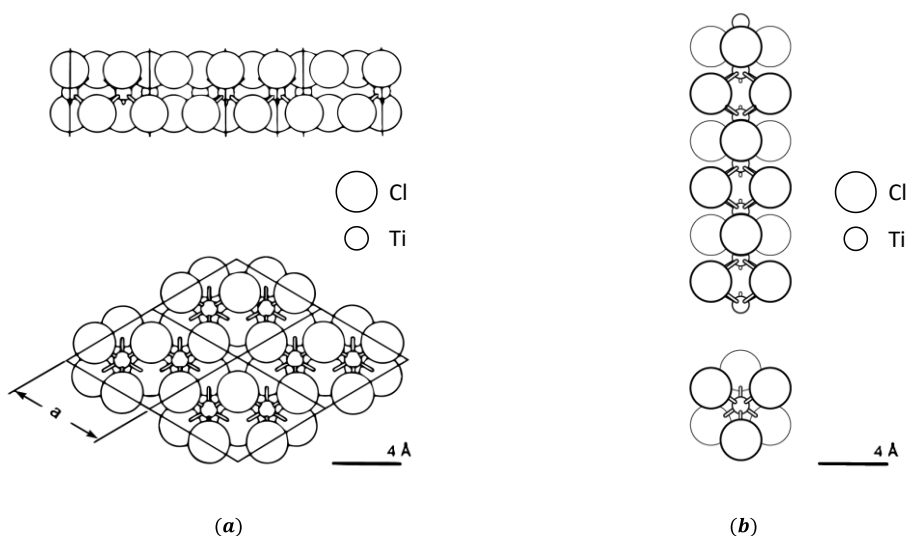


Figure 1.2 Stereochemical model of a) layered structure for α , γ , and δ modifications of TiCl_3 , and b) linear structure for β modification of TiCl_3 . Adapted from ref. [86]

The layered structures in modification α , γ , and δ constitute of bi-dimensional macromolecules of TiCl_3 with a regular assembly of structural Cl – Ti – Cl triple layers, where two bridge bonds created by chlorine atoms connect each titanium atom to each of the three adjacent ones (Figure 1.2) [86]. The difference between the three modifications lies in the Cl packing mode. The α form displays hexagonal packing, the γ form cubic packing, and the δ form features a sporadic trend of hexagonal and cubic packing. The structural layer can be easily represented by stating the order of the two chlorine atom planes, that is, AB, AC... (for further understanding, the reader is advised to read Ref. [87]), which is ABABAB for the α phase, ABCABC for the γ phase, and statistical for the δ phase (Figure 1.3). The Ti – Cl distance in the layered modifications is 2.46 Å and the distance between adjacent titanium atoms is 3.54 Å, whereas in the linear modification, β , the Ti – Cl distance is 2.45 Å, and the distance between titanium atoms is 2.91 Å, which is lower than that in the layered modifications [86].

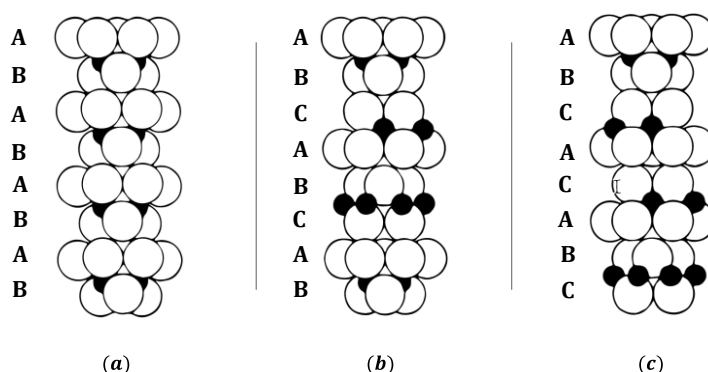


Figure 1.3 Different TiCl_3 modifications: (a) α - TiCl_3 , (b) γ - TiCl_3 , and (c) δ - TiCl_3 . Reproduced from ref. [5].

Several methods have been reported for the synthesis of different TiCl_3 modifications, and the reduction method used determines both the composition and crystalline modification [5,19]. α - TiCl_3 can be synthesized by reducing TiCl_4 with H_2 at $500^\circ\text{--}800^\circ\text{C}$, or with aluminum powder at lower temperatures (approximately 250°C). The β -modification (free of Al) is formed by the decomposition of CH_3TiCl_3 or (with Al) by the reduction of TiCl_4 with Al-alkyls or chloro-alkyls. The γ modification is formed by heating the β modification (at $100^\circ\text{--}200^\circ\text{C}$); the higher the temperature, the quicker the change. The β modification can be with or without aluminum content. The presence of aluminum in the β - modification is reported to affect the speed of the transformation of β to γ . For a β modification containing one Al per three Ti, the transformation takes only several hours at about 140°C [19]. The δ crystalline modification was synthesized by prolonged dry milling of the α and γ forms. Milling reduces the crystallite size and increases the surface area, resulting in higher activity.

The presence of AlCl_3 did not affect the stereoregularity abilities of the α , γ , and δ types of TiCl_3 . In contrast, β - TiCl_3 was less active and isospecific when combined with AlEt_2Cl [19]. A summary of the various synthetic methods used over the years is presented in Table 1.2.

The composition, structure, and morphology of the TiCl_3 modifications play an important role in their catalytic properties [19]. In particular, layered TiCl_3 polymorphs are significantly more stereoselective than β - TiCl_3 [88,89].

Table 1.2 Synthesis methods for different TiCl_3 modifications

No.	Modification	Composition	Preparation	Reference
1	α	TiCl_3	$\text{TiCl}_4 + \text{H}_2$ (500-800 °C)	[90,91]
2	α	TiCl_3	$\text{TiCl}_4 + \text{H}_2$ on W wire (1000-1100 °C)	[92]
3	α	$\text{TiCl}_3 \cdot 0.5\text{AlCl}_3$	$\text{TiCl}_4 + \text{Al}(+\text{AlCl}_3)$ at 200 °C	[93]
4	α	$\text{TiCl}_3 \cdot 0.02\text{AlCl}_3$	$\text{TiCl}_4 + \text{Ti} + \text{Al}$ at > 200 °C	[7,8,94]
5	β	$\text{TiCl}_3 \cdot 0.33\text{AlCl}_3$	$\text{TiCl}_4 + \text{Al}$ at < 100 °C	[8,95]
6	β	$\text{TiCl}_3 \cdot x\text{AlCl}_3$	$\text{TiCl}_4 + \text{TEA, DEAC, or EAD}$ at < 25 °C	[96,97]
7	γ	$\text{TiCl}_3 \cdot 0.33\text{AlCl}_3$	$\text{TiCl}_4 + \text{Al}(+\text{AlCl}_3)$ at ~ at 160 °C in inert solvents	[8,95]
8	δ	TiCl_3	Milling α or γ - TiCl_3	[8,98]
9	δ	$\text{TiCl}_3 \cdot 0.33\text{AlCl}_3$	Milling α or γ - $\text{TiCl}_3 \cdot 0.33\text{AlCl}_3$	[99]
10	δ	$\text{TiCl}_3 \cdot x\text{AlCl}_3$	Milling of TiCl_3 with AlCl_3	[8,86,99]

1.3.2. MgCl_2 support

With the introduction of the active form of MgCl_2 as a support for ZNCs, a progression from self-supported Ziegler-Natta systems to supported systems has been achieved [100–103]. As briefly discussed above, catalytically active sites are formed on a high-surface-area carrier, in which the support acts as a polar solvent. During this process, a dilution of the potential active sites occurs on the surface of the support. In addition to MgCl_2 , supports such as SiO_2 , TiO_2 , MgO , and Al_2O_3 have also been reported [104,105]; however, the samples analyzed in this thesis are MgCl_2 -supported ZNCs. The inclusion of MgCl_2 as a support in this thesis is attributed to its widespread utilization within the industrial sector. This choice is motivated by its superior activity and stereospecificity compared to other supports in polypropylene (PP) polymerization. Chien [106] summarized several reasons why MgCl_2 is preferred as a support in ZNCs, it is chemically inert so it does not need deashing to remove it from the polymer, it has a lower electronegativity than TiCl_3 which promotes the coordination of the monomer molecule to Ti atom via π – back donation, it is highly porous and resistant in mechanical manipulation but weak enough to break during polymerization. Therefore, the further discussion is based on the structure and properties of the MgCl_2 support.

Moreover, MgCl_2 is isomorphous with TiCl_3 , possessing a similar crystal structure to TiCl_3 with ionic radii of Mg^{2+} (0.65 Å) and Ti^{4+} (0.68 Å) close to each other. MgCl_2 is a layered crystalline having octahedral six-coordinated Mg atoms bonded to chlorine atoms [103]. MgCl_2 exists in two ordered polymorphic modifications, rhombohedral α - MgCl_2 , and hexagonally closed-packed β - MgCl_2 , and in one rotationally disordered polymorph δ - MgCl_2 [100,103,107–109]. The α -form has a layered structure with cubic-closed-packing ABCABC, similar to γ - TiCl_3 . The β -form also has a layered structure with a packing sequence ABABAB, similar to α - TiCl_3 , and the δ -form has a disordered structure in which the crystal order in the stacking direction is lost by the translation and rotation of the structural Cl-Mg-Cl layers [5].

Active sites are formed through reactions occurring on the surface of MgCl_2 . In theory, the grafting of TiCl_4 can occur at many MgCl_2 surface terminations as revealed by computational calculations and XRD measurements [110–114], and the precise facets housing the catalytically active Ti species remain a matter of debate. To become useful for catalytic reactions, MgCl_2 is transformed into its active δ -form either before or during the grafting of TiCl_4 . The activation of MgCl_2 into its active δ -form, which is characterized by a higher disorder and surface area, is performed either mechanically or chemically. During the activation process, the formation of non-basal planes (104) and (110) from the cleavage of the MgCl_2 crystal has been reported. These facets are of significant interest for catalysis, whereas the (001) basal planes are not as relevant for catalysis. [107]. As has been shown by experimental and quantum-chemical investigations, the (104) surface, which exposes pentacoordinated magnesium sites, is thermodynamically more stable than the (110) surface, which exposes tetra-coordinated magnesium sites. However, the addition of Lewis bases (electron donors) to the system changes this energy in favor of the (110) surface [114–117], which is discussed in more detail in the next section.

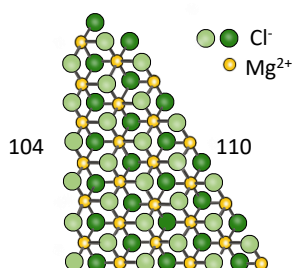


Figure 1.4 Representation of (110) and (104) lateral cuts of MgCl_2 support. Adapted from ref. [12].

It is still not completely understood how TiCl_4 is adsorbed on the surface of MgCl_2 . It has been reported that several different active sites are formed on the surface of the MgCl_2 support, possessing different symmetries, activities, and stereoregularities. This has been related to the formation of different Ti species (monomeric, dimeric, clusters, etc.) [118,119]. According to Corradini, TiCl_4 is epitactically adsorbed either as a binuclear (Ti_2Cl_8) or mononuclear (TiCl_4) species on the surface (104) or as a mononuclear species (TiCl_4) on the surface (110). The binding of mononuclear TiCl_4 gives a five-coordinate Ti on the (104) surface and either a six- or four-coordinate Ti on the (110) surface. On the other hand, the binding of binuclear Ti_2Cl_8 gives six-coordinate Ti on the (104) surface. The chirality of the active center controls the stereochemistry of the monomer insertion [12,120,121]. The dimer species Ti_2Cl_8 has the right chirality for the formation of isospecific active sites, whereas monomeric TiCl_4 does not have intrinsic chirality, leading to the formation of non-stereoselective active sites [12] (Figure 1.5).

Similar models have been proposed by Chien [122], who also reported three types of epitaxial placement of TiCl_4 in the (100) facet, two in complex pairs, and one as a monomer TiCl_4 . The main difference from the previous model of Corradini *et al.* is the assumption of the presence of tetracoordinated, instead of hexacoordinated, monomeric species on the (110) facet.

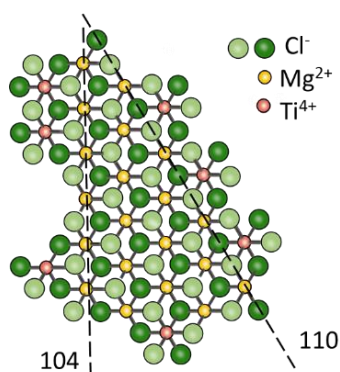


Figure 1.5 Modes of epitactic adsorption of TiCl_4 species on MgCl_2 . Adapted from ref. [12]

Many other experimental and theoretical approaches have been used to deeper understand the structure of active sites formed on the two most relevant MgCl_2 facets. Cavallo *et al.* [117] proposed another hypothetical MgCl_2 model that considered recent experimental and computational findings. They considered that, in real heterogeneous ZNC systems, models of active species different from those derived from standard TiCl_4 adsorption on perfect (104) and (110) lateral cuts should also be considered. This also depends on the

used support size and its defects. They reported that during the harsh conditions used for the preparation of the catalyst, MgCl_2 units can be removed from the corner of (104)-edged MgCl_2 crystallites. This creates a short (110) stretch joining the (104) lateral cuts, as shown in Figure 1.6, in which the adsorption of TiCl_4 can occur. This species has been reported to promote propene polymerization, leading to the formation of atactic polypropylene.

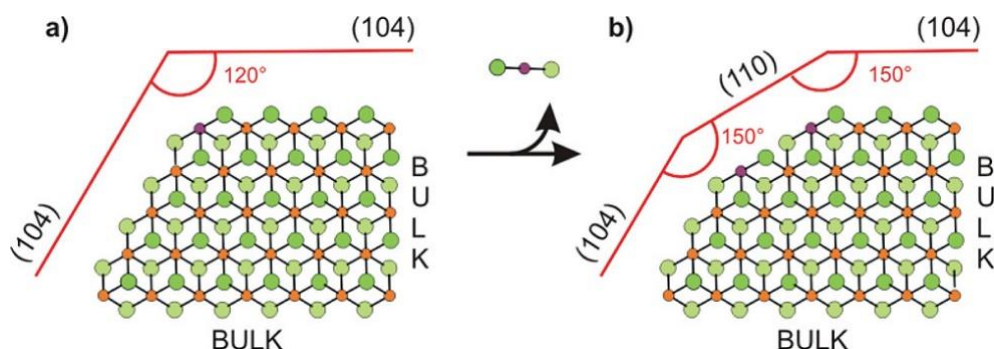


Figure 1.6 Schematic representation of the model proposed by Cavallo *et al.* [117]. The orange balls represent Mg, the dark green balls represent the Cl atoms above the Mg plane, and the light green balls represent the Cl atoms below the Mg plane.

All the above-mentioned models of isospecific and nonspecific active species have been proposed for PP polymerization. In principle, these centers are also active in PE polymerization. Some studies have proposed that besides Ti(III) species, Ti(II) species are also active in ethylene polymerization [12,100,123]. However, few studies have been dedicated to the modeling of active centers for ethylene polymerization.

1.3.3. Electron donors – the fine-tuning components of ZNCs

The breakthrough achieved in the third generation of ZNCs was obtained not only by dispersing the active sites on high-surface-area support, such as MgCl_2 support, but also by discovering that the implementation of Lewis bases in the catalyst synthesis leads to more active and stereoselective catalysts [5,12]. The role and mechanism of action of Lewis bases in Ziegler-Natta catalytic systems are still far from being fully understood. In the beginning, their role was believed to be only in the selective poisoning of nonspecific centers; today, it is well understood that they also play a major role in catalyst

productivity, kinetic profile, polymer molecular weight (MW), and molecular weight distribution (MWD) [124].

In industrial terms, Lewis bases are named electron donors. These can be added either alone or as a pair of ID and ED [17,125–128]. The ID is added in the pre-catalyst and its primary function is to control the distribution of TiCl_4 on potential MgCl_2 cuts and stabilize the MgCl_2 crystallites [12]. During the activation process, the ID interact with AlR_3 a Lewis acid-base reaction forming complexes that can be removed from the surface. The main role of the ED is to replace the ID that has been washed from the MgCl_2 surface [12,17,129]. Except for the fifth-generation ZNCs, which can contain only one electron donor, ID, in all other catalyst systems, the electron donors are added in pairs [5]. The ID in the fifth generation is strongly bonded to the support and is hardly removed from the surface in the activation process, therefore there is no need for an external donor.

For electron donors to be added in pairs, it is necessary to match their chemical nature. In this regard, the nature of the ID is the determining factor of whether an ED is needed and what type of ED needs to be used. A general selection rule for choosing the right pair of electron donors is presented in Table 1.3 [5].

Table 1.3 Some useful rules for choosing the appropriate electron donor [5].

Internal donor type	Best external donor type
Monofunctional (aromatic monoester)	Monofunctional (aromatic monoester)
Bifunctional (aromatic diester)	Polyfunctional (silylether) or monofunctional (TMP)
Bifunctional (1,3-diether)	None or bifunctional (silane, diether)

The search for the most appropriate couple of donors is still ongoing, and when choosing the right pair of donors, the following interaction of the electron donors with other catalyst components should be taken into consideration besides the selection rules in Table 1.3 [12,17,130,131]:

- the donors should effectively bind to the MgCl_2 surface
- The donor should not form complexes with AlR_3 , TiCl_4 , or the Ti–C, and Ti–H bonds of the polymerization centers.

Meeting these properties is important to achieve a high stereospecific catalyst which depends on the amount of a Lewis base in the catalyst. Aromatic monoesters, phthalates,

monoethers, diethers, and succinates are mostly used as IDs, whereas the most frequently used EDs include mono- or polyfunctional carboxylic acids, carboxylic anhydrides, carboxylic esters, ketones, ethers, alcohols, lactones, organophosphorus compounds, and organosilicon compounds [5,132,133]. Bidentate internal donors have been reported to be more firmly bound to the MgCl_2 surface in comparison to monodentate donors. Therefore, the bidentate donors tend to be more stable towards the reaction with AlR_3 and remain on the surface even upon activation [12].

Another critical parameter that determines the catalyst performance and polymerization kinetics is the concentration of the donors used and the ED/Al (or ED/Ti) ratio. However, this parameter depends largely on the particular ID/ED combination. The increase in the ED/Al ratio increases the isotactic index and average MW of the polymer [5].

In addition to the long-lasting question of which site of the MgCl_2 surface the active sites of ZNC coordinate, with many models proposed (see section 1.3.2), another related question is how electron donors interact with the MgCl_2 surface and how they interact with the other components. Several experimental and theoretical studies have attempted to answer these questions [114,124,128,129,134–138]. Moreover, it is still not fully understood how they control or influence the stereospecificity of the active sites [12]. As discussed above (section 1.3.2), for the two most relevant MgCl_2 surfaces, (104) and (110), the more acidic facet (110), as confirmed by simple electrostatic calculations, is thermodynamically less stable [115,139–141]. It has been reported that TiCl_4 is preferably coordinated on the (110) lateral cut, which represents a nonstereoselective site [114]. This scenario is changed by the introduction of electron donors, which have a higher affinity towards the (110) facet, preventing the possible formation of non-stereoselective sites (Figure 1.7) [139,140,142,143]. However, some donors also show a preference towards the (104) facet, such as phthalates that coordinate on both (104) and (110) surfaces, whereas diethers are reported to have a preference for the (110) facet [139,143–145]. This depends on the differences on the binding energies of the different Ti species (TiCl_4 , TiCl_3 , Ti_2Cl_8 , Ti_2Cl_6 ,) and of the different donors to the MgCl_2 substrate, for which the reader is referred to the papers [112,113,119,144,146].

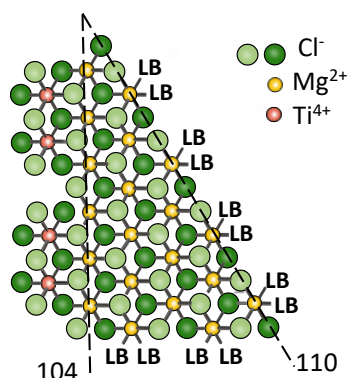


Figure 1.7 An adsorption model of Ti_2Cl_6 species and Lewis bases (LB) on lateral cuts of MgCl_2 . Adapted from ref. [12]

Electron donors have mostly been used in PP polymerization; however, the patent literature [21–23,147] also shows that electron donors affect PE polymerization, mostly in improving the quality of linear low-density polyethylene (LLDPE).

1.3.4. Co-catalyst – the activating agent

In ZNC systems, the co-catalyst bears one of the key functions – the formation of active sites and influences the overall catalyst performance. Active sites are formed by the reduction and alkylation of surface TiCl_4 using an alkyl-aluminum compound, such as R_3Al , R_2AlCl , $\text{R}_3\text{Al}_2\text{Cl}_3$, RAlCl_2 , $\text{R}_2\text{AlOR}'$, or R_2AlH [5,100]. Alkyl-aluminum compounds are useful because of their reducing and alkylating abilities, capacity to act as scavengers for different molecules that act as poisons for Ziegler-Natta catalysts, and ability to complex external donors to moderate the polymer properties [6,148].

Choosing the right co-catalyst type is crucial, as it not only affects the catalyst productivity but also the polymer structure. The main roles of the co-catalyst are as follows:

- activating the potential active sites dispersed in the pre-catalyst,
- altering the kinetic stability of the catalyst,
- participating in chain transfer reactions,
- influencing the isotacticity and molecular weight of the polymer.

Some of the most prominent co-catalysts used in the industrial manufacturing of polyolefins include triethylaluminum (TEA), triisobutylaluminum (TIBA),

diethylaluminum chloride (DEAC), and ethyl aluminum dichloride (EADC) [6,85,149–151]. The stability of the active centers depends widely on the choice of the co-catalyst and whether these are employed alone or combined [150–152]. While in the first generations of ZNCs, DEAC was widely used, with the development of supported ZNCs TEA became one of the most used co-catalysts in the industrial sector. Its advantage over DEAC lies in its higher reducing power and the lower amount of neutralization additives needed in the reactor, as TEA does not contain chloride which would lead to the release of HCl upon contact with moisture [6].

The co-catalyst is usually added to the system together with an external donor. Considerable work has been devoted to elucidating the nature of the interaction of the co-catalyst with different external donors [125,153–156]. Given the acidic nature of the co-catalyst and the basic nature of the external donor, a complex interaction is likely to happen. These complexes interact with the pre-catalyst surface generating isospecific active sites [5].

The concentration of the cocatalyst used plays an important role as well. Low co-catalyst concentrations affect the number of the formed active sites, as many potential active sites can remain inactive. Furthermore, the full removal of impurities is also affected by low co-catalyst concentrations. On the opposite, high concentrations can also lead to a smaller number of active sites, caused by over-reduction of the catalytic active sites. In both cases, the catalyst activity decreases [157–160].

1.4. The catalytic mechanism of ZNCs

A thorough description of the ZNC mechanism in the polymerization process of ethylene and propylene is still not understood well. Over the years several mechanisms have been proposed [161–163] but the most accepted one nowadays is the monometallic mechanism proposed by Cossee and Arlman (Figure 1.8). According to this mechanism, the active sites of a ZNC are surface titanium ions possessing an incomplete octahedrally coordination with a chloride vacancy and an alkyl group in the coordination sphere. These active sites are formed by alkylation (formation of a Ti-C bond) accompanied by the reduction of Ti atoms to lower oxidation states due to the reaction with the co-catalyst. The formed active sites possess the required asymmetry for α -olefin insertion to the Ti-C bond and to keep this asymmetry for the next monomer insertion a relocation of the growing polymer chain happens as presented in Figure 1.8 [164–166].

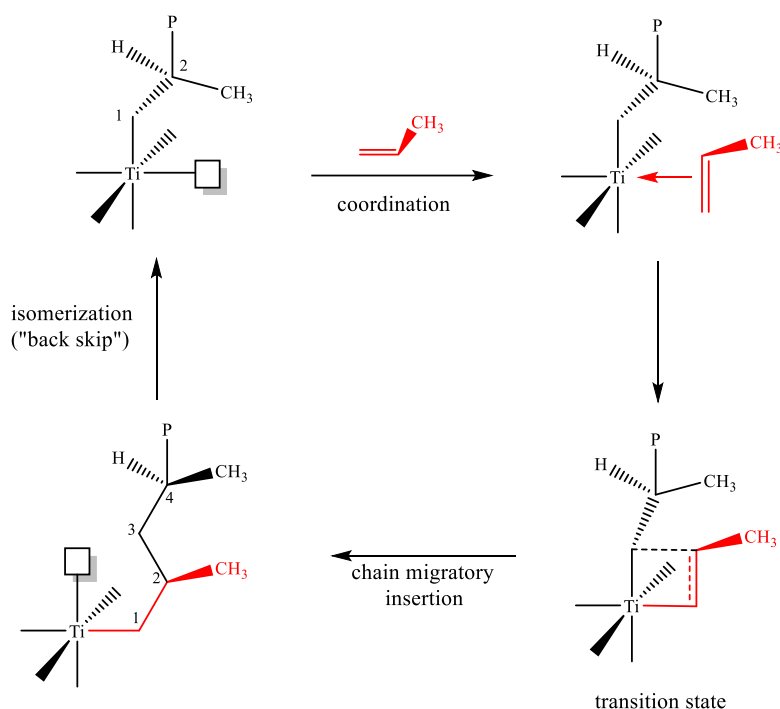
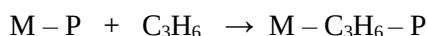


Figure 1.8 Cossee-Arlman mechanism for ethylene polymerization on a ZNC. The growing polymer chain is shown by P. Adapted from ref. [12].

The multiple insertions of α -olefin in the Ti-C bond have been proven by ^{13}C NMR studies [167] using ^{13}C -enriched aluminum and zinc alkyls to activate different ZNCs. In this study enriched ^{13}C end groups have been detected in each of the end products, supporting the mechanism proposed by Cossee and Arlman:



Where M represents the transition metal of the active site and P the growing polymer chain. According to Allegra the relocation of the growing chain in its original position is an irrelevant step and can be avoided. This study still supports the monometallic polymerization mechanism proposed by Cossee and Arlman but it takes into consideration also the influence of steric effects in the complexation and the addition step. It assumes that the chirality of the coordination around the Ti atom determines the chirality of the olefin-metal complex [168].

1.5. Pre-polymerized Ziegler-Natta Catalysts

A technique called "pre-polymerization" is often used in the polymer industry for polyolefin production by using highly active ZNCs [6]. This technique is usually employed in gas-phase reactors, where some difficulties and problems, like polymer powder breakage and polymer agglomeration, might be experienced by using highly active ZNCs [6,169,170]. By using a pre-polymerization step the catalyst-activation stage is separated from the actual polymerization stage, leading to efficient heat removal [171]. The pre-polymerization step takes place in a smaller reactor under mild conditions, where the catalyst is suspended in a suitable solvent and exposed to a co-catalyst, low monomer concentrations, and hydrogen at low temperatures. The initial catalyst is normally left to pre-polymerize until it reaches around 30% of the total weight of the final polymer. The pre-polymerized catalyst is then moved to the main polymerization reactor and it will have about the same amount of activity per particle as the bare catalyst [6,170]. The main advantages of using a pre-polymerization step before the actual polymerization process can be summarized as follows:

- prevents thermal overheating of the catalyst particle in the early stages of polymerization,
- preserves catalyst morphology by controlling the fragmentation of the catalyst support.
- controls the polymer growth and shape.

The phenomenon of particle replication is a key feature of heterogeneous polypropylene catalysts. In the first steps of polymerization, the polymer grows gradually around each active center forming a small sphere or "glomerule" of polymer which continues to grow. To facilitate the continuation of polymerization, the glomerule undergoes fragmentation into smaller spheres, each harboring a minute portion of the active catalyst. These fragments act like a nucleus around which the polymer continues to grow. They become trapped and scattered within the growing polymer mass, progressing outward in proportion to the localized volumetric expansion attributed to the process of polymerization (Figure 1.9).

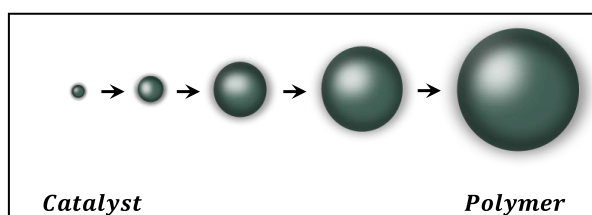


Figure 1.9 Schematic representation of the replication phenomenon. The polymer particle grows mimicking the morphology of the catalyst particle. Adapted from ref. [6].

However, this depends on the speed of the catalyst support fragmentation, which leads to higher polymer yields. Fast fragmentation may result in unwanted particle shapes [170,172,173]. By using the pre-polymerization step, the support breaks slowly allowing fragmentation control. Three different models of polymer growth have been proposed including the core-shell model, the multigrain model, and the polymeric flow model [173].

In industry, either a semi-batch or continuous pre-polymerization process is used. In the semi-batch process, the pre-polymer is first dried by a nitrogen gas flow and then fed to the main polymerization reactor, whereas, in the continuous process, the pre-polymer is directly fed to the main polymerization reactor [174]. Although the importance of the pre-polymerization step is well understood in the production of polyolefins on large scales at industrial sites, more research in understanding the kinetics and powder morphology is still needed.

1.6. Characterization of Ziegler-Natta Catalysts

Being a multi-component system composed of extremely sensitive components, the thorough characterization of Ziegler-Natta Catalysts is quite difficult and requires a combination of theoretical studies and several experimental methods. Although many analytical techniques are used in this direction there is still a lack of information on the catalyst's true structure, mechanism, and performance in the polymerization process.

Several experimental methods are used to get a detailed microscopic description of the Ziegler-Natta system including UV/Vis, IR, and Raman spectroscopies [175,176], optical and electronic microscopies [177,178], TDS (Temperature Programmed Desorption)[179], LEED (Low Energy Electron Diffraction) [180], EXAFS (Extended X-ray Absorption Fine Structure), XRD (X-ray diffraction) [181], XPS (X-ray Photoelectron Spectroscopy) [179], XANES (X-ray Near Edge Spectroscopy) [181], NMR (Nuclear Magnetic Resonance) [182], EPR (Electron Paramagnetic Resonance)

[183–185]. On the other hand, theoretical studies are more focused on the elucidation of the structure and performance of the catalyst, with a special focus on the interaction of the different components of the catalysts [18,117,131,186,187]. It can be challenging to assess the validity of computational analyses in many situations because there are rarely any relevant experimental data available.

To elucidate the nature of the believed active sites, bearing a Ti(III)-C bond, and observed organic radical sites, EPR spectroscopy has been used in this thesis. Therefore, further discussion will be focused on this technique and its application in ZNC systems.

Chapter 2

Brief introduction into EPR Spectroscopy

Since its discovery by Zavoisky in 1944 [188], electron paramagnetic resonance (EPR) spectroscopy is the technique of choice in the study of a variety of samples containing paramagnetic centres. The technique detects unpaired electrons and gives detailed information on the electronic and geometric structure and on the dynamics of paramagnetic species. It is extensively used to study systems containing organic radicals, transition-metal ions, inorganic radicals, biological samples, photoexcited molecules, point defects in crystals, *etc.* Therefore, EPR spectroscopy finds a wide application in different fields [189–194]. In this chapter some basic EPR concepts are introduced including the main techniques that have been used in this work to study industrial ZNC samples prepared and already analysed by other techniques in BPI laboratories in Ferrara, Italy. For a deeper understanding of EPR spectroscopy the reader is advised to read the papers and books [191,195–202], on which the writing of this section was based.

2.1. The resonance phenomenon and electron Zeeman interaction

The fundamental principles of EPR spectroscopy rely on the intrinsic property of the free electron called spin. The electron spin is characterized by the angular momentum vector $\mathbf{S}$ with spin quantum number $S = \frac{1}{2}$ that has associated with it a magnetic moment $\boldsymbol{\mu}$. The two vectors are parallel to each other but with opposite direction. Their relation is given by:

$$\boldsymbol{\mu} = -g_e \mu_B \mathbf{S} \quad (2.1)$$

where, g_e is the free electron g -factor ($g_e = 2.0023$) and μ_B is the Bohr magneton ($\mu_B = e\hbar/2m_e = 9.274 \times 10^{-24} \text{ JT}^{-1}$).

An electron with spin $S = \frac{1}{2}$ has two possible spin states, called the α -spin with $m_s = +\frac{1}{2}$ and the β -spin with $m_s = -\frac{1}{2}$. In the absence of a magnetic field the two electron spin

states are degenerate. When in a magnetic field, the energy level of the electron spin will split. This splitting is essential in EPR and is called the Zeeman effect, named after the Dutch Nobel prize winner Pieter Zeeman. The interaction energy (E) between the magnetic moment μ and the external magnetic field $\mathbf{B}_0$ is in classical terms given by:

$$E = -\mu \cdot \mathbf{B}_0 \quad (2.2)$$

Moving to quantum mechanics, in the presence of the magnetic field the electron spin energy will assume two values along the z-direction (*i.e.* direction of magnetic field) (Figure 2.1):

$$E = g_e \mu_B m_s B_0 = \pm \frac{1}{2} g_e \mu_B B_0 \quad (2.3)$$

In an EPR experiment, the sample containing paramagnetic centers is irradiated with microwaves in the presence of an external field. The β -spin electron in the lowest energy will get excited in the upper level by absorbing a quantum of microwave radiation energy. The resonance condition is achieved when the energy difference (ΔE) created by the applied field is equal to the energy of the absorbed microwave radiation ($h\nu$):

$$\Delta E = h\nu = E_2' - E_1' = g_e \mu_B B_0 \quad (2.4)$$

where ν is the radiation frequency. In a continuous wave (CW) experiment, the resonance absorption signal is more often plotted as a first derivative (Figure 2.1b), rather than in absorption mode (Figure 2.1a).

At thermal equilibrium, under the influence of the external applied magnetic field, the spin population is split between the two levels according to the Maxwell–Boltzmann law:

$$\frac{N_\alpha}{N_\beta} = \exp\left(-\frac{g\mu_B B_0}{k_B T}\right) \quad (2.5)$$

where k_B is Boltzmann's constant which is equal to $1.3806 \times 10^{-23} \text{ JK}^{-1}$, T is the absolute temperature and N_α and N_β are the spin populations characterized by the m_s values $+1/2$ and $-1/2$, respectively.

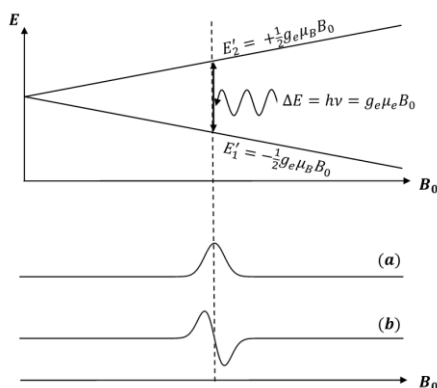


Figure 2.1 Schematic representation of the electron Zeeman effect and the resonance condition. By increasing the magnetic field, the energy gap increases linearly. At resonance condition the absorption of continuously irradiated microwave energy leads to an electron spin flip resulting in an EPR signal that can be presented either in (a) absorption or (b) derivative mode. Adapted from ref. [203].

This fundamental interaction between the unpaired electron and the external magnetic field, gives the resonant field position that is determined by the g -value. The g -value is to some extent analogous to the chemical shift in NMR and similarly independent of the operating frequency of the instrument. For the free electron $g_e = 2.0023$. This value changes for bounded unpaired electrons in a macroscopic system due to the interaction with the environment. The shift in the g -value is due to the coupling of the electron spin with the orbital angular momentum and to the local magnetic field B_{local} experienced by the unpaired electron in a molecular environment. For organic radicals the g -value shift is small ($g \sim 2$), while for transition-metal complexes this shift is larger. Therefore, the g -value can be used as an identifier for a given paramagnetic center.

As discussed above, the electron Zeeman interaction, described by the g -factor, represents the fundamental interaction in EPR spectroscopy. In a macroscopic system this interaction will have a more complex character. The unpaired electron occupies orbitals of different configuration and symmetry in different atoms. Therefore, the spin-orbit coupling $\lambda \cdot \mathbf{L} \cdot \mathbf{S}$ needs also to be taken into consideration. The complete Hamiltonian that represents the interaction of the electron spin $\mathbf{S}$ with the external magnetic field, also considering the spin – orbit coupling interaction, is given by:

$$\mathcal{H} = \mu_B \mathbf{B}_0 \cdot (\mathbf{L} + g_e \mathbf{S}) + \lambda \cdot \mathbf{L} \cdot \mathbf{S} \quad (2.6)$$

where λ is the spin – orbit coupling constant. As already mentioned, the experimental g -values deviate from g_e due to the spin orbit – orbit coupling interaction. This effect can

be introduced in equation (2.6) by a $\mathbf{g}$ -tensor that is defined using second-order perturbation theory, with elements given by:

$$\mathbf{g} = g_e \mathbf{U} + 2\lambda \mathbf{A} \quad (2.7)$$

where $\mathbf{U}$ is the 3x3 unit matrix and $\mathbf{A}$ is the symmetric tensor:

$$A_{ij} = \sum_{n \neq 0} \frac{\langle \psi_0 | L_i | \psi_n \rangle \langle \psi_n | L_j | \psi_0 \rangle}{E_0 - E_n} \quad (2.8)$$

where A_{ij} are the elements of the symmetric 3x3 $\mathbf{A}$ matrix, E_0 and E_n are the energies of the ground and excited orbital states.

With this definition the spin Hamiltonian takes the form:

$$\mathcal{H}_{EZ} = \frac{\mu_B}{\hbar} \mathbf{B}_0 \cdot \mathbf{g} \cdot \mathbf{S} \quad (2.9)$$

In an anisotropic environment the g -value is replaced with a $\mathbf{g}$ -tensor, a 3x3 matrix reflecting the anisotropic environment:

$$\mathbf{g} = \begin{bmatrix} g_{xx} & g_{xy} & g_{xz} \\ g_{yx} & g_{yy} & g_{yz} \\ g_{zx} & g_{zy} & g_{zz} \end{bmatrix} \quad (2.10)$$

The six off diagonal elements (g_{yx} , g_{zx} , g_{zy} , g_{xy} , g_{xz} , g_{yz}) are zero in the principal axes (x, y, z) of the $\mathbf{g}$ -tensor. This is named as a diagonal tensor ($\mathbf{g}_{\text{diag}}$):

$$\mathbf{g}_{\text{diag}} = \begin{bmatrix} g_{xx} & 0 & 0 \\ 0 & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{bmatrix} \quad (2.11)$$

The anisotropy of the $\mathbf{g}$ -tensor provides additional information about the symmetry, bonding, structure and electronic configuration of the paramagnetic center. Depending on the electronic distribution it is classified as either isotropic ($g_x = g_y = g_z = g_{\text{iso}}$), axial ($g_x = g_y \neq g_z$), or rhombic ($g_x \neq g_y \neq g_z$). The EPR spectra of the different anisotropies are illustrated in Figure 2.2.

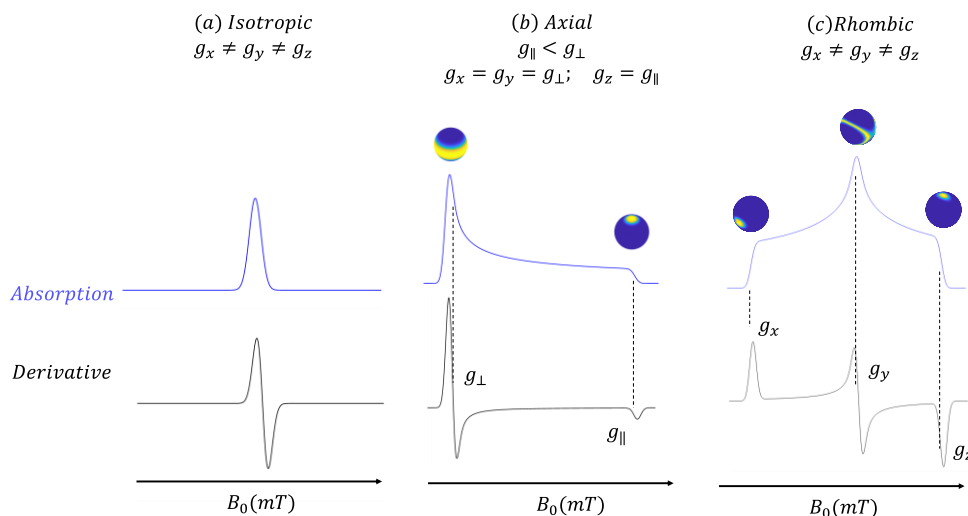


Figure 2.2 Absorption (blue line) and first derivative (black line) EPR spectra for a randomly oriented $S=1/2$ spin system with (a) isotropic, (b) axial, and (c) orthorhombic symmetry. For the axial and orthorhombic symmetries, the orientation selection spheres are also shown. Note that an axial system may also have $g_{\perp} > g_{\parallel}$, a case that is not presented here.

In EPR spectroscopy mostly we work in the solid state, *i.e.* with powders or frozen solutions, for which the isotropic case is rarely encountered. In solid state the isotropic case is mostly encountered for systems in cubic or higher symmetry. The axial and rhombic g -tensors are more informative with respect to isotropic g -tensors, but also more difficult to examine. In a non-viscous solution, the anisotropy is averaged out and results in an isotropic g -value:

$$g_{\text{iso}} = \frac{g_x + g_y + g_z}{3} \quad (2.12)$$

2.2. The spin Hamiltonian

The interpretation of EPR spectra is based on the full spin Hamiltonian that enables to calculate the energy levels of the spin system. So far only a brief description of the interaction of an unpaired electron with the external magnetic field due to the electron Zeeman interaction was given. In the EPR spectra of many paramagnetic molecules more interactions can be seen, contributing to the field position and the shape of the EPR line and need to be taken into consideration. For a system with electron spin $\mathbf{S}$ and m nuclei with spin $\mathbf{I}_k$ in an external magnetic field $\mathbf{B}_0$, the interaction energy can be described by the spin Hamiltonian:

$$\mathcal{H} = \mathcal{H}_{\text{EZ}} + \mathcal{H}_{\text{ZFS}} + \mathcal{H}_{\text{HF}} + \mathcal{H}_{\text{NZ}} + \mathcal{H}_{\text{NQ}} =$$

$$\frac{\mu_B \mathbf{B}_0 g \mathbf{S}}{\hbar} + SDS + \sum_{k=1}^m SA_k I_k - \mu_n \sum_{k=1}^m \frac{g_{n,k} \mathbf{B}_0 I_k}{\hbar} + \sum_{I_k > \frac{1}{2}} I_k P_k I_k \quad (2.13)$$

where $\mathcal{H}_{\text{EZ}}$ is the electron Zeeman interaction discussed earlier, $\mathcal{H}_{\text{ZFS}}$ is the zero-field splitting in case of $S > 1/2$, $\mathcal{H}_{\text{HF}}$ the hyperfine coupling between the electron spin and the m nuclear spins, $\mathcal{H}_{\text{NZ}}$ the nuclear Zeeman interaction and $\mathcal{H}_{\text{NQ}}$ the nuclear quadrupolar coupling for nuclear spins with magnetic quantum number $I > 1/2$. The individual terms will be discussed below.

2.2.1. The Nuclear Zeeman Interaction

Analogously to the electron spin, many nuclei possess a spin I that gives rise to a magnetic moment given by:

$$\mu_z = g_n \mu_n I \quad (2.14)$$

The spin Hamiltonian that describes the interaction of the nuclear spin with magnetic field $\mathbf{B}_0$ is given by:

$$\mathcal{H}_{\text{NZ}} = -\frac{g_n \mu_n}{\hbar} \mathbf{B}_0 I \quad (2.15)$$

where g_n is the nuclear g -factor and μ_n is the nuclear magneton ($\mu_n = e\hbar/2m_p = 5.051 \times 10^{-27} \text{ JT}^{-1}$) which depends on the proton mass. Due to the much higher mass of the proton, the nuclear Zeeman interaction is much weaker than the electron Zeeman interaction.

2.2.2. The Hyperfine Interaction

One of the most important sources of information in EPR comes from the interaction between the magnetic dipoles of unpaired electrons and surrounding nuclei, called the hyperfine interaction (HFI). In the case of nuclear spins with a non-zero nuclear spin the

electron spin will experience an additional magnetic field in its vicinity. This will give rise to a further splitting of the energy levels that is independent from the applied external magnetic field. The Hamiltonian describing the hyperfine interaction is given by:

$$\mathcal{H}_{\text{HF}} = \sum_{k=1}^m \mathbf{S} \mathbf{A}_k \mathbf{I}_k \quad (2.16)$$

where $\mathbf{A}_k$ are the hyperfine matrices and $\mathbf{I}_k$ are the nuclear spin operators. The hyperfine interaction ($\mathbf{A}$) consists of two contributions: the isotropic or Fermi contact interaction and the anisotropic term resulting from the electron-nuclear dipolar coupling:

$$\mathbf{A} = a_{\text{iso}} \mathbf{U} + \mathbf{T} \quad (2.17)$$

where a_{iso} is the isotropic hyperfine coupling constant (the Fermi contact term), $\mathbf{U}$ is the unit matrix and $\mathbf{T}$ is the dipolar part of the hyperfine matrix. The isotropic hyperfine coupling arises from the presence of finite electron spin density at the nucleus, and is proportional to the probability of finding the electron spin at the nucleus ($|\psi_0(0)|^2$):

$$a_{\text{iso}} = \frac{8\pi}{3} g_e \mu_B g_n \mu_n |\psi_0(0)|^2 \quad (2.18)$$

in which a_{iso} is expressed in energy units. However, the isotropic hyperfine coupling constant is typically expressed in frequency units (MHz), thus a_{iso}/h . The spin Hamiltonian describing the isotropic part of the hyperfine interaction is given by:

$$\mathcal{H}_{\text{iso}} = a_{\text{iso}} \mathbf{S} \mathbf{I} \quad (2.19)$$

The hyperfine interaction becomes purely isotropic if the unpaired electron occupies an s-orbital, but in most cases the isotropic part represents the fraction of the s-orbital included in the molecular wave function of the unpaired electron. An isotropic contribution may also occur when the unpaired electron resides in a p-, d-, or f-orbital, and in this case the electron density on the nucleus is ascribable to spin-polarization effects. Knowledge of a_{iso} provides information on the nature and spatial extent of the orbital in which the unpaired electron resides.

The dipolar or anisotropic part of the hyperfine interaction arises from a dipole – dipole interaction between the unpaired electron and the nearby paramagnetic nuclei. It depends on the relative orientation and distance between the magnetic dipole moments of the electron and nucleus. Therefore, the dipolar part can be used to determine the distance between the unpaired electron and the closeby nuclei (the dipolar component T of the

hyperfine tensor is proportional to $1/r^3$). It also provides information about the relative orientation of the electron-nucleus axis in the principal $\mathbf{g}$ -tensor frame, with the electron-nucleus axis connecting the atom on which the unpaired electron mainly resides and the nucleus interacting with the electron. This can be related to geometric information in the lab frame, if the orientation of the principal $\mathbf{g}$ -tensor axes in this frame is known. The spin Hamiltonian describing the anisotropic part of the hyperfine interaction is given by:

$$\mathcal{H}_{\text{DD}} = \frac{\mu_0}{4\pi\hbar} g_e g_n \mu_n \beta_n \left[\frac{(3\mathbf{S}\mathbf{r})(\mathbf{r}\mathbf{I})}{r^5} - \frac{\mathbf{S}\mathbf{I}}{r^3} \right] = \mathbf{S}\mathbf{T}\mathbf{I} \quad (2.20)$$

where $\mathbf{r}$ is the distance vector between the electron and the nuclear spin and $\mathbf{T}$ is the traceless dipolar coupling matrix. Thus the hyperfine matrix $\mathbf{A}$ takes the form:

$$\mathbf{A} = Ua_{\text{iso}} + \mathbf{R}(\alpha, \beta, \gamma) \begin{bmatrix} T_x & & \\ & T_y & \\ & & T_z \end{bmatrix} \mathbf{R}^{-1}(\alpha, \beta, \gamma) \quad (2.21)$$

where $\mathbf{R}$ transforms the matrix $\mathbf{T}$ from the laboratory frame to the molecular frame through the Euler angles α, β, γ . In many instances, at X-band the hyperfine couplings are too small (in the order of magnitude of a few MHz) to be fully resolved in the CW-EPR spectra, hence one might think of using specific pulse methods.

2.2.3. The Nuclear Quadrupole Interaction

Paramagnetic nuclei with $I > 1/2$ have a non-spherical charge distribution, that gives rise to a quadrupole moment Q and is determined by the internal nuclear structure. A positive quadrupole moment Q implies an elongated charge distribution, whereas a negative Q implies a flattened charge distribution (Figure 2.3).

This quadrupole moment will interact with the electric-field gradient (EFG), generated by the neighboring electrons and nuclei. The interaction is independent from the magnetic field and the spin Hamiltonian that describes this interaction is given by:

$$\mathcal{H}_{\text{NQ}} = \sum_{I_k > \frac{1}{2}} \mathbf{I}_k \mathbf{P}_k \mathbf{I}_k \quad (2.22)$$

where $\mathbf{P}$ is the traceless tensor of the nuclear quadrupole interaction (NQI). In its principal axes system (eigenbasis), the spin Hamiltonian is given by:

$$\mathcal{H}_{\text{NQ}} = P_x I_x^2 + P_y I_y^2 + P_z I_z^2 = \frac{e^2 q Q}{4I(2I-1)\hbar} [3I_z^2 - I(I+1) + \eta(I_x^2 - I_y^2)] \quad (2.23)$$

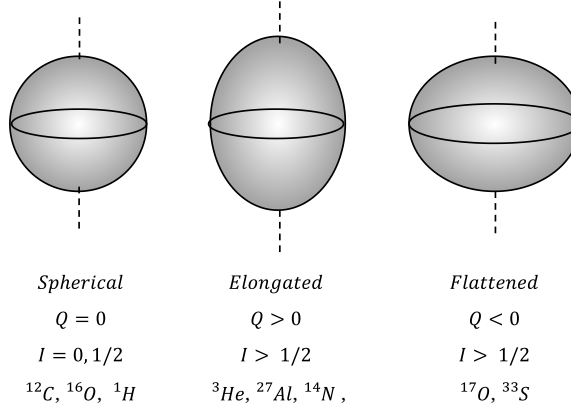


Figure 2.3 Illustration of the relation between nuclear charge distribution shape and the nuclear quadrupole moment Q for some $I > 1/2$ isotopes often investigated in EPR. Adapted from ref. [198].

The nuclear quadrupole tensor can then be written as:

$$\mathbf{P} = \frac{e^2 q Q}{4I(2I-1)\hbar} \begin{bmatrix} -(1-\eta) & & \\ & -(1+\eta) & \\ & & 2 \end{bmatrix} \quad (2.24)$$

where $e^2 q$ is the magnitude of the electric field gradient experienced by the nucleus and Q is the quadrupole moment of the nucleus. The asymmetry parameter $\eta = (P_x - P_y)/P_z$, with $|P_z| > |P_y| > |P_x|$, represents the deviation of the field gradient from axial symmetry and can adopt values in the range $0 \leq \eta \leq 1$.

2.2.4. The zero-field splitting

The zero-field splitting (ZFS) is a phenomenon that occurs in paramagnetic systems where the energy levels corresponding to different magnetic spin quantum numbers are split in the absence of an external magnetic field ($\mathbf{B}_0$). It occurs in paramagnetic systems that contain multiple unpaired electrons ($S > 1/2$), and it arises due to the interaction

between the unpaired electrons, including spin-spin coupling, spin-orbit coupling, and exchange interactions. The spin Hamiltonian describing this interaction is expressed as:

$$\mathcal{H}_{\text{ZFS}} = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} \quad (2.25)$$

where $\mathbf{D}$ is the symmetrical and traceless zero-field interaction tensor.

2.3. Quantification of paramagnetic species by CW-EPR spectroscopy

Performing quantitative CW-EPR spectroscopy requires to carefully follow good practices, by giving special attention to specific issues [204,205]. Importance should be given to choosing a suitable reference standard, temperature, resonator considerations, sample positioning, microwave power saturation, modulation amplitude and frequency, receiver gain, magnetic field scan width, type of cavity, sample amount, sample position in the cavity, dimensions and uniformity of the sample tube, dielectric properties of the solvent at the microwave frequency, *etc.* The accuracy provided by EPR quantification can lay within a few percent accuracy, depending how good one follows the instructions explained in the book of Eaton *et al.* [205]. As for any other analytical method, the key issue is sample preparation. This issue is specifically highlighted for ZNC due to their high sensitivity to O₂ and H₂O. Therefore, the sample tubes need to be filled under inert atmosphere (Ar or N₂) and the tubes need to be air-tight sealed. In this work quantitative EPR was carried out by double integration of the CW-EPR spectra and comparison with a standard as well as by an automatic “spin-count” routine incorporated in the Bruker EPR spectrometer.

2.4. Pulsed EPR Techniques

Very limited amount of information is obtainable by using only CW EPR at X-band or higher frequencies, being limited only to the electron Zeeman interaction, the zero-field splitting (in a few cases) and very large hyperfine interactions. The CW-EPR spectrum provides information on the splitting between energy levels of the electron spin system, of its surrounding environment in case of well resolved hyperfine splitting and of its relaxation mechanism. In most case, the hyperfine effects are so small that they are masked by the inhomogeneous line broadening in CW-EPR experiments. The nuclear Zeeman interaction is not observable in a CW-EPR spectrum since the resonance condition implies $\Delta m_I = 0$ and the quadrupole interaction cause also only secondary effects. Advanced pulsed EPR techniques enable to observe nuclear transitions, *i.e.* small

energy transitions within electron spin manifold, giving thus also information about the surrounding environment of the electron spin. Pulse EPR enables to design experiments that address a specific problem, making it possible to resolve interactions convoluted in the line width of a CW-EPR spectrum. In this section the basics of pulse EPR and the main pulsed techniques applied in this work will be introduced.

2.4.1. The Vector Model for Pulsed EPR and the Quantum Mechanical Picture

To understand how a paramagnetic sample is analysed by pulse EPR techniques, an ensemble of multiple electron spins oriented either parallel or antiparallel to the externally applied magnetic field needs to be considered. The net magnetization of the ensemble behaves as a classical vector with a length and direction in space:

$$\mathbf{M} = \frac{1}{V} \sum_i \boldsymbol{\mu}_i \quad (2.26)$$

where V is the sample volume with all individual magnetic moments. A useful method to simplify the understanding of the motion of magnetization, during a microwave pulse, is to use the rotating and laboratory (or shortly lab) frames, represented in Figure 2.4.

The lab frame in EPR is usually defined as in Figure 2.4a where the magnetic field, $\mathbf{B}_0$ is parallel to the Z' axis, the microwave magnetic field $\mathbf{B}_1$, is parallel to the X' axis, and the Y' axis is orthogonal to the X' and Z' axes. When an electron spin is placed in a magnetic field, the external field exerts a torque on the magnetic moment $\mathbf{M}$ of the electron spin, causing it to precess on a cone about $\mathbf{B}_0$ as illustrated in Figure 2.4b. This causes a time-averaged magnetization vector $\mathbf{M}_0$ along the Z' axis. The precessing frequency is equal to the Larmor frequency:

$$\omega_L = -\gamma \mathbf{B}_0 \quad (2.27)$$

where γ is the gyromagnetic ratio and $\mathbf{B}_0$ is the external magnetic field. When applying a microwave pulse along the X' axis, which is in essence a time-dependent magnetic field $\mathbf{B}_1$ oscillating with the microwave frequency, it becomes very complicated to consider its effects on the magnetization vector in the lab-frame. The magnetization undergoes complex rotations when viewed in this frame. Using the rotating frame perspective, *i.e.* a frame that is rotating about the Z' axis with the microwave frequency, a straightforward understanding of the motion of the magnetization vector $\mathbf{M}_0$ during the microwave pulse

can be obtained. The frame rotation matches the Larmor frequency, rotating exactly at the same rate as the magnetization $\mathbf{M}$. The alternating magnetic field $\mathbf{B}_1$ applied along the X' axis in the lab frame can be described as the sum of two counter-rotating $\mathbf{B}_1$ Figure 2.4c. One of these components is static in the rotating frame, the other is counter-rotating and far from resonance. For a deeper understanding of these frames the reader is advised to check the following references: [197,200,206,207].

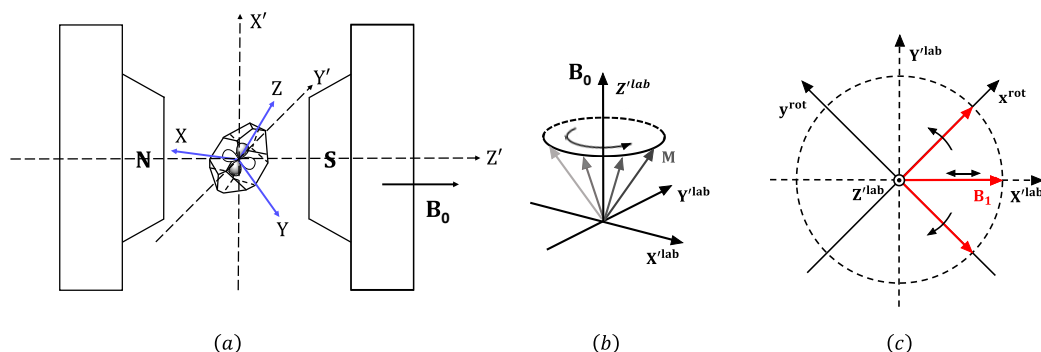


Figure 2.4 (a) A schematic representation of the lab frame (X', Y', Z') used in EPR. (X, Y, Z) is the molecular frame (b) Precession of the total magnetization, indicated here as $\mathbf{M}$, about the external field B_0 . (c) Illustration how the rotating frame $(x^{rot}, y^{rot}, z^{rot})$ is related to the laboratory frame. Also the two counter-rotating components of the linearly polarized B_1 field are shown. Figures taken and combined from ref. [208] and [209].

In the rotating frame, the precession frequency of $\mathbf{M}$ about the z^{rot} -axis is given by:

$$\Omega = \omega_L - \omega_{mw} \quad (2.28)$$

When applying a microwave pulse, the microwave magnetic field B_1 , that is perpendicular to the external magnetic field, causes an additional precession of $\mathbf{M}_0$ about the x^{rot} -axis with angular velocity:

$$\omega_1 = -\gamma B_1 \quad (2.29)$$

where ω_1 is called the Rabi frequency and γ the gyromagnetic ratio. By controlling the time between the turning on and off of the microwave field, it is possible to control how far the magnetization will turn. For a microwave pulse of duration t_p , the angle by which the magnetization vector will rotate, called the flip angle (Figure 2.5), is given by:

$$\alpha = \gamma B_1 t_p \quad (2.30)$$

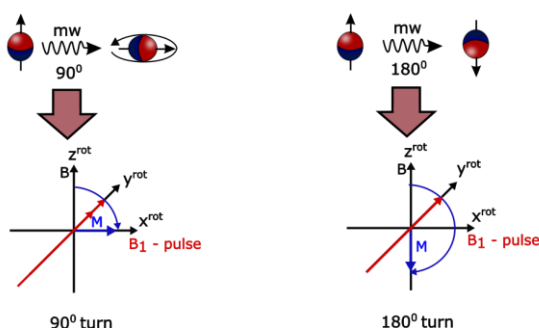


Figure 2.5 Illustration of the flip angles that can be obtained by adjusting the pulse length t_p or the microwave magnetic field strength B_1 . Figure taken from reference [210].

2.4.2. The Hahn Echo

Pulsed EPR techniques are typically based on the so-called spin-echo sequences. To understand the basic pulse sequences used in pulsed EPR and the information that they provide, all that is needed is to understand the motion of $\mathbf{M}_0$ during the microwave pulse and the motion of $\mathbf{M}_0$ and the spin relaxation processes after the application of microwaves. Variation of the magnetization in function of time can be described by the Bloch equations [211]. There are different experimentally observable EPR signals that can be generated by applying one or more microwave pulses [200]. The first signal is called a free induction decay (FID) and represents the simplest pulsed EPR sequence, consisting of a single $\pi/2$ microwave pulse that flips the magnetization $\mathbf{M}_0$ in the xy -plane, described hereafter in the rotating frame without the use of the superscript rot for simplicity (Figure 2.6a). After Fourier transformation, a signal occurs at the resonant frequency of the spin packet. All the pulse-EPR techniques used in this thesis are based on spin echoes and the Hahn echo sequence is the simplest one. It was described for the first time for NMR by E. Hahn [212]. In this experiment the first $\pi/2$ pulse converts the magnetization $\mathbf{M}_0$ from z -axis to the x -axis. It is followed by a period of free evolution τ during which the spin packets fan out. By applying a second π -pulse the magnetization is flipped in the xy -plane and the spin packets refocus along $-x$ after a time τ . This refocussing generates a Hahn echo called spin echo.

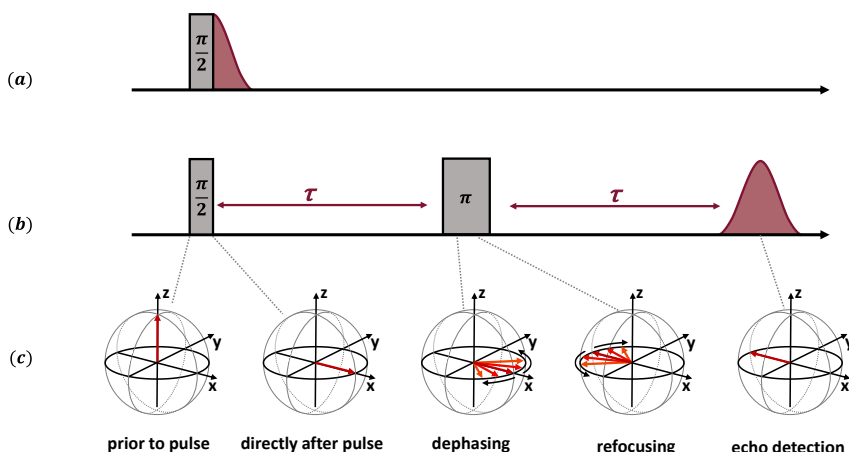


Figure 2.6 (a) The generation of the FID signal by a $\pi/2$ pulse. (b) The two-pulse sequence giving rise to the Hahn spin echo, which is an inverted FID followed by an FID. (c) The evolution of the magnetic moments of individual spin packets (red arrows) as seen in the rotating frame, for the Hahn Echo sequence. Adapted from ref. [208].

2.4.3. Hyperfine spectroscopy

Determining the couplings between the paramagnetic center of interest and the nearby nuclei is important to characterize the electronic and geometric structure of a paramagnetic center. As already mentioned in section 2.3.2 for many systems the hyperfine couplings are too small (in the order of magnitude of a few MHz) to be fully resolved in the CW-EPR spectra. Hence, high-resolution techniques based on specific pulse sequences need to be used to obtain information on the hyperfine interactions that are not resolved in the CW-EPR spectra. In this work two types of hyperfine spectroscopy techniques that allow the detection of nuclear-transition frequencies have been used: (1) electron-spin-echo envelope modulation (ESEEM) and (2) electron-nuclear double resonance (ENDOR). In the sections below, the basic pulse sequences of these techniques will be briefly introduced.

2.4.3.1. ESEEM pulse sequences

Electron Spin Echo Envelope Modulation or ESEEM is a time-domain experiment used to determine the nuclear frequencies of weakly coupled nuclei to the unpaired electron. ESEEM experiments make it possible to observe the mixing of allowed and forbidden EPR transitions by indirectly monitoring the NMR frequencies [213,214]. These

experiments are based on pulse sequences that create a spin echo, whose intensity decays as a function of time. Fourier transformation of the decaying echo time trace transforms the time-domain spectra to frequency-domain spectra that allow the identification of the nuclear frequencies. The pulse sequences of an ESEEM experiment can be subdivided in three different building blocks as shown in Figure 2.7 including the preparation period followed by the first evolution time, the mixing period followed by a second evolution time and the detection period [215]. The function of each building block will be further explained for each ESEEM sequence used in this work.

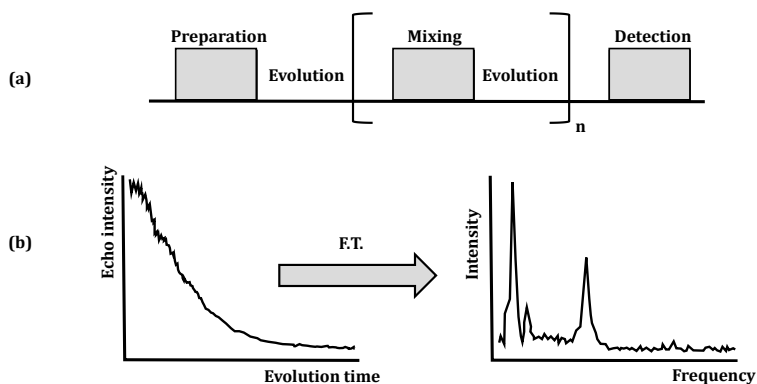


Figure 2.7 General outline of an ESEEM experiment. (a) A schematic representation of the preparation, mixing, and detection building blocks. (b) A standard two-pulse ESEEM time-domain spectra and its corresponding frequency – domain spectra obtained after Fourier transformation. Adapted from ref. [215].

2.4.3.2. Two-pulse ESEEM

The simplest ESEEM experiment is based on the earlier-mentioned Hahn echo sequence [213,214] $\pi/2 - \tau - \pi - \tau - \text{echo}$ (Figure 2.8). In the two pulse ESEEM sequence the preparation period consists of a $\pi/2$ pulse which creates electron coherence, that evolves during the time τ . The mixing period consists of a π pulse that mixes the electron coherences. After a second evolution time τ an electron spin echo is generated.



Figure 2.8 Two-pulse ESEEM sequence

The intensity of the generated spin echo decays as a function of τ , depending also on the phase-memory time T_m of the electron spin. This decay is modulated with nuclear frequencies of magnetic nuclei coupled to the unpaired electron. Assuming ideal pulses the resulting echo modulation for a $S=1/2$, $I=1/2$ system is given by:

$$V_{2P}(\tau) = 1 - \frac{k}{4} \left[2 - 2 \cos(\omega_\alpha \tau) - 2 \cos(\omega_\beta \tau) + \cos(\omega_- \tau) + \cos(\omega_+ \tau) \right] \quad (2.31)$$

where the modulation depth, k , is defined as:

$$k = \left(\frac{B\omega_I}{\omega_\alpha \omega_\beta} \right)^2 \quad (2.32)$$

with ω_I the Larmor frequency and the nuclear frequencies ω_α and ω_β defined as:

$$\omega_\alpha = |\omega_{12}| = \left[\left(\omega_I + \frac{A}{2} \right)^2 + \frac{B^2}{4} \right]^{1/2} \quad (2.33)$$

$$\omega_\beta = |\omega_{34}| = \left[\left(\omega_I - \frac{A}{2} \right)^2 + \frac{B^2}{4} \right]^{1/2} \quad (2.34)$$

and $\omega_\pm = \omega_{12} \pm \omega_{34}$ are the combination frequencies. A and B are the secular and non-secular terms of the hyperfine interaction [215].

The main advantage of the two-pulse ESEEM is the short time needed to record a two-pulse ESEEM spectrum that allows to quickly identify nearby magnetic nuclei. However, there are several disadvantages emerging from this experiment. One of them is that besides the nuclear frequencies also the sum and differences of these frequencies will be detected. This becomes a major drawback when the electron spin interacts with several nuclei. The spectra obtained in this case are composed of broad lines with overlapping features. Other limitations come from the short T_m (hence broad lines) and the spectrometer deadtime that can lead to distortions or artifacts in the frequency domain spectra.

2.4.3.3. Three-pulse ESEEM

Some of the drawbacks in the two-pulse ESEEM experiment are bypassed by a three-pulse ESEEM [214,216] experiment with sequence $\pi/2 - \tau - \pi/2 - T - \pi/2 - \tau - \text{echo}$. The first two $\pi/2$ pulses ($\pi/2 - \tau - \pi/2$) in the preparation period will create nuclear coherences that will evolve during time T (evolution period) and transformed afterwards to a detectable electron coherence from the last $\pi/2$ pulse.



Figure 2.9 Three-pulse ESEEM sequence. mw = microwave.

For a $S=1/2$, $I=1/2$ system the echo modulation from the three-pulse ESEEM experiment is given by:

$$V_{3P}(\tau, T) = 1 - \frac{k}{4} \left\{ [1 - \cos(\omega_\beta \tau)] [1 - \cos(\omega_\alpha (T + \tau))] + [1 - \cos(\omega_\alpha \tau)] [1 - \cos(\omega_\beta (T + \tau))] \right\} \quad (2.35)$$

In the three-pulse ESEEM experiment, the echo intensity decays as a function of T that is varied, and the decay depends now on the phase memory time of the nuclear spins T_m^n which is much longer than the phase memory time T_m of the electron spins. This leads to much narrower lines in the three-pulse ESEEM spectra. In addition, the combination frequencies $\omega_\pm$ are no longer observed, leading to fewer frequency lines compared to the two-pulse ESEEM experiment. Nevertheless, the three-pulse ESEEM experiment has also some disadvantages, one of them being the influence of τ leading to τ -dependent blindspots. To avoid the effect of blindspots, the three-pulse ESEEM experiment should be recorded for a series of different τ values making the experiment more time-consuming. Besides that, phase cycling is also needed in order to remove spurious signals. This requires application of pulses in different vector space [215,217].

2.4.3.4. HYSCORE

Hyperfine Sublevel Correlation Spectroscopy or HYSCORE is a two-dimensional four-pulse ESEEM technique, with sequence $\pi/2 - \tau - \pi/2 - t_1 - \pi - t_2 - \pi/2 - \tau - \text{echo}$, where an additional π -pulse is introduced between the second and third $\pi/2$ pulse of the three-pulse ESEEM sequence, improving the interpretation of ESEEM spectra [218].

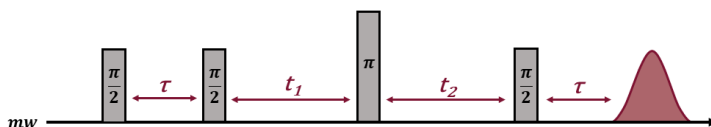


Figure 2.10 Four-Pulse HYSCORE sequence. mw = microwave.

The introduction of a second dimension in the HYSCORE experiment makes the overlapping features in the two- and three-pulse ESEEM now observable. The preparation period in the HYSCORE experiment consists of $\pi/2 - \tau - \pi/2$, which leads to the generation of nuclear coherences and polarizations, same as in the three-pulse technique. After a first free evolution time t_1 , the nuclear coherences will be transferred from one m_s manifold to the other by a strong mixing pulse and allowed to evolve during a second time t_2 . 2D Fourier transformation of the time-domain data along the two dimensions generates a 2D frequency-domain spectra where cross peaks relate to corresponding nuclear frequencies. These cross peaks appear either in the $(+, +)$ or $(-, +)$ quadrant of the 2D spectra (Figure 2.11). The $(+, +)$ quadrant displays signals from weakly coupled nuclei ($|A| < 2\omega_I$), whereas $(-, +)$ displays signals from strongly coupled nuclei ($|A| > 2\omega_I$). Figure 2.13a and Figure 2.13b show the energy level schemes for an $S=1/2$, $I=1/2$ system in the weak and strong coupling, respectively. In the exact cancellation condition, both quadrants will display intense cross peaks due to a large k value.

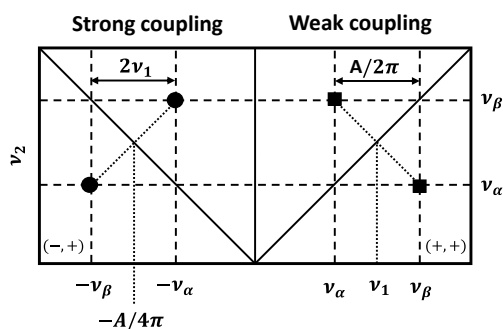


Figure 2.11 Schematic representation of the appearance of the cross peaks in different quadrants in the HYSCORE spectra in case of weak hyperfine coupling (■) and strong hyperfine coupling (•) for a $S=1/2$, $I=1/2$ spin system. Adapted from ref. [215].

For the more usual cases of randomly oriented systems, such as powders or frozen solutions, the cross peaks are no longer sharp features. They appear as broad ridges representing the sum of individual orientations. The HYSCORE spectra for a powder

sample of an $S=1/2$, $I=1/2$ spin system is represented in Figure 2.12. For randomly oriented systems the HYSCORE spectra need to be recorded at different field positions.

The information obtained from HYSCORE spectra is mostly based only on the analysis of peak positions. While for single crystals, the cross-peak intensity is distributed between the two quadrants, for disordered systems the analysis of the peak intensities in a HYSCORE spectrum is not a straightforward process. Therefore, one might observe that not all cross peaks will appear equally intense in the different quadrants. This is because of orientation selection and additional amplitude effects due to destructive interferences [219].

From the simulation of the peak positions in the HYSCORE spectra it is possible to extract the hyperfine couplings. The anisotropy of the hyperfine coupling interaction T , can be determined from the shift of the curvature ridges from the anti-diagonal given by:

$$\Delta\omega_{\max} = \frac{9T^2}{32|\omega_I|} \quad (2.36)$$

in which T is the dipolar component of the hyperfine tensor.

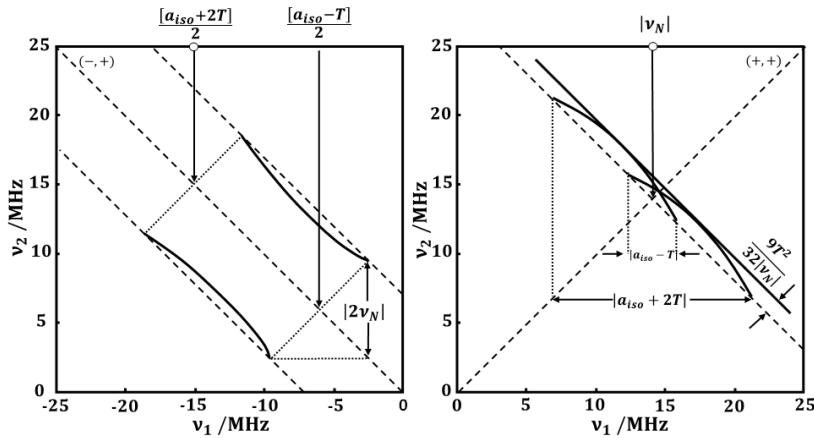


Figure 2.12 Schematic representation of HYSCORE spectra of a powder sample for an $S = 1/2$, $I = 1/2$ spin system with an axial hyperfine tensor. (left) Strong-coupling case with $v_1 = 3.5$ MHz, $a_{\text{iso}} = 18$ MHz, and $T = 6$ MHz. (right) Weak-coupling case with $v_1 = 14$ MHz, $a_{\text{iso}} = 2.5$ MHz, and $T = 6$ MHz. Adapted from ref. [196].

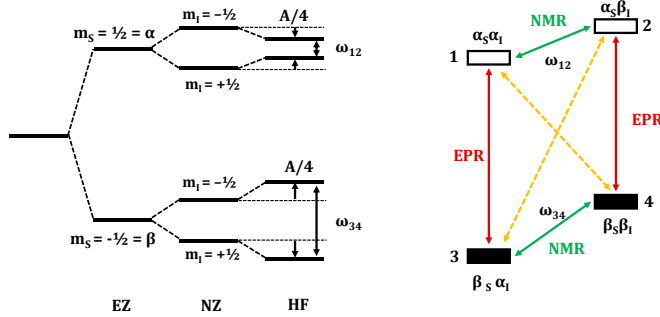
For spin systems with nuclei $I \geq 1$ and non-zero quadrupole interaction the HYSCORE spectra become more complicated due to single-quantum (SQ: $|\Delta m_I|=1$) and double

quantum (DQ: $|\Delta m_I|=2$) transitions. The double-quantum nuclear frequencies are given by:

$$\omega_{\alpha,\beta}^{\text{DQ}} = 2 \sqrt{\left(\omega_I \pm \frac{A}{2}\right)^2 + \left(\frac{e^2 q Q}{4h}\right)^2 (3 + \eta^2)} \quad (2.37)$$

where A is the hyperfine coupling at the observer position. The DQ cross peaks are less broad and more intense compared to the SQ ridges in the HSCORE spectra. This is because the nuclear quadrupole interaction is contributing in first order in the SQ frequencies, while for DQ frequencies this interaction is contributing in second order.

(a) $A > 0, g_n > 0, 2|\omega_I| > |A|$



(b) $A > 0, g_n > 0, 2|\omega_I| < |A|$

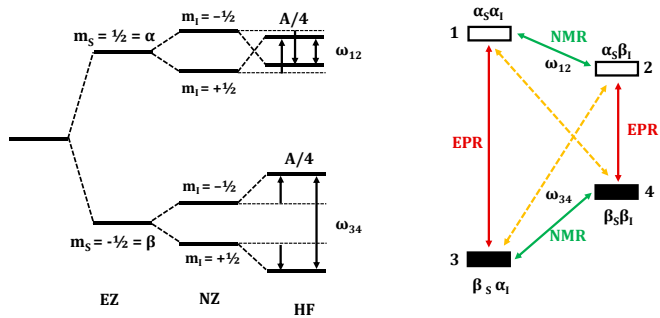


Figure 2.13 Energy-level diagrams for an $S = 1/2, I = 1/2$ spin system; (a) Weak coupling case, $2|\omega_I| > |A|$, with $A > 0, g_n > 0$; (b) Strong coupling case $2|\omega_I| < |A|$. The red lines correspond to allowed EPR transitions, the dotted yellow lines to forbidden EPR transitions and the green lines to NMR transitions. Adapted from ref. [198].

HYSCORE spectroscopy has some drawbacks. For the same reason as for the three-pulse ESEEM experiment, also in a HYSCORE experiment phase cycling is necessary and this leads to an increase in the recording time. An increase in recording time comes also from the need to record spectra at different τ values to prevent blindspots in the spectra. Furthermore, for systems containing several paramagnetic nuclei the analysis of HYSCORE spectra still represents a challenge.

2.4.3.5. Matched HYSCORE

High turning-angle (HTA) pulses of proper length called matched pulses are used in ESEEM experiments to enhance the sensitivity of these experiments [220–222]. To perform an ESEEM experiment with matched pulses for the case of weakly coupled nuclei, one or more of the pulses have to be matched to the nuclear Zeeman frequency, while in the strong coupling case, one needs to apply the maximum available mw field strength. In standard HYSCORE, non-selective mw pulses are used, and the sensitivity depends solely on the spin system. In matched HYSCORE the second and fourth pulse are replaced by HTA pulses used to optimize the creation of nuclear coherence and then transfer back to electron coherence. An optimal HTA pulse length needs to be determined and its choice depends on the system that will be analysed.

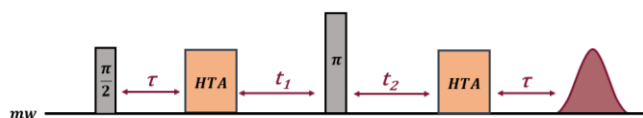


Figure 2.14 Matched HYSCORE sequence. mw = microwave.

2.4.3.6. Six-pulse HYSCORE

The six-pulse HYSCORE [223] is used to obtain HYSCORE spectra that are less affected by cross suppression and to recover signals from weakly modulating nuclei. In the six-pulse experiment an additional π – pulse is introduced. The first three pulses in the six-pulse HYSCORE sequence produce nuclear spin coherence. After a variable evolution time t_1 a mixing π – pulse is added followed by a two-pulse echo sequence after t_2 , after which an echo is observed.

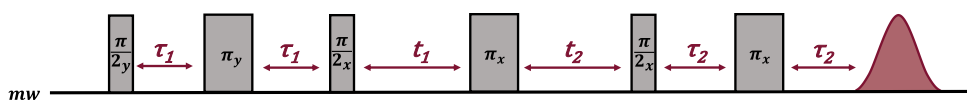


Figure 2.15 Six-pulse HYSCORE sequence. mw = microwave.

In six-pulse HYSCORE the intensity ratio of cross peaks to diagonal peaks is significantly enhanced, making it possible to reveal nuclei which remain undetected in the four-pulse HYSCORE. Another advantage of the six-pulse HYSCORE experiment is the absence of the combination frequencies. However, the addition of an extra mw pulse leads to a loss in the signal intensity.

2.4.4. Pulsed ENDOR

Electron nuclear double resonance or ENDOR represents another pulsed EPR technique for measuring hyperfine and nuclear quadrupole interactions by combining the tools of EPR and NMR. In a pulsed ENDOR experiment short pulses of microwaves (mw) in the order of ns and radiofrequencies (rf) in the order of μs are used [224]. The rf pulse induces polarization changes. This is then transferred to electron coherence and detected via a spin echo, whose amplitude is measured as a function of the variable radiofrequency, with all the time intervals fixed in the detection period. For a system to be analysed by a pulsed ENDOR experiment two main criteria need to be fulfilled: the phase memory time T_m needs to be longer than the spectrometer deadtime and the systems should have a long spin-lattice relaxation time T_1 . Two common pulsed ENDOR experiments are used in this work: Davies-ENDOR [225] and Mims-ENDOR [226].

2.4.4.1. Davies ENDOR

The Davies ENDOR sequence $\pi_{\text{mw}} - T - \pi/2_{\text{mw}} - \tau - \pi_{\text{mw}} - \tau - \text{echo}$ (Figure 2.16) is based on the application of a selective microwave pulse π that inverts the polarizations of a particular EPR transition. Then during time T , an rf pulse is applied to invert one of the NMR transitions. The radiofrequency is swept and upon resonance with the nuclear transition, the effect on the electron polarization will be detected by a conventional Hahn echo sequence, but FID detection can also be used.

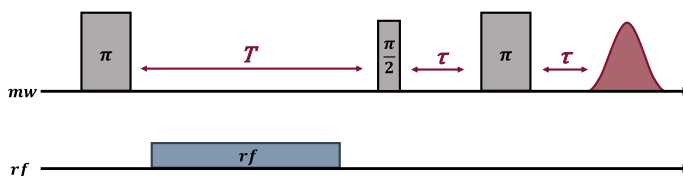


Figure 2.16 Pulse sequence of Davies ENDOR experiment. mw = microwave, rf = radio frequency.

2.4.4.2. Mims ENDOR

The Mims ENDOR sequence $\pi/2_{\text{mw}} - \tau - \pi/2_{\text{mw}} - T - \pi/2_{\text{mw}} - \tau - \text{echo}$ (Figure 2.17), is based on the stimulated echo sequence, with three non-selective $\pi/2$ microwave pulses, where the first two pulses create nuclear coherences and polarization. The nuclear polarizations are changed during time T by a selective rf pulse, whose frequency is swept during the experiment. The final $\pi/2$ microwave pulse generates the simulated echo.

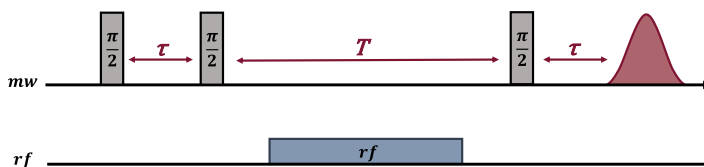


Figure 2.17 Pulse sequence of Mims ENDOR experiment. mw = microwave, rf = radio frequency.

2.5. CW EPR and pulse EPR spectra of Ti(III) species in Ziegler-Natta systems

Due to the low natural abundance of the isotopes ^{47}Ti ($I = 5/2$, natural abundance 7.75%) and ^{49}Ti ($I = 7/2$, natural abundance 5.51%), the dominating interactions in a CW-EPR spectrum observed for Ti(III) species in Ziegler-Natta catalysts systems arise mainly from the electron Zeeman interaction characterized by the $\mathbf{g}$ -tensor. Ti(III) has a $3d^1$ configuration with $S=1/2$. The principal components of the $\mathbf{g}$ -tensor are influenced by the local symmetry of the Ti(III) and this influence can be explained by using the perturbation formulas based on the one- spin-orbit (SO)-parameter mode [193,199]. Depending on the crystal field experienced by the Ti(III) ion, the five-fold degeneracy of the d orbitals of the Ti(III) ion are split into a doublet e_g ($d_{x^2-y^2}$ and d_{z^2}) and a t_{2g} (d_{xy} , d_{xz} , and d_{yz}) state. In a tetrahedral field the doublet has lower energy, while the contrary is observed in an octahedral field. Further distortions lead to further splitting of these states as shown in

Figure 2.18 and Figure 2.19. If the metal ion is tetrahedrally coordinated, and depending on the degree of the tetragonal distortion whether there is a compression or an elongation, different g -values are observed that can be evaluated based on these equations here:

$$g_{\parallel} = g_e \quad \text{and} \quad g_{\perp} \cong g_e - \frac{6\lambda}{\Delta_{Td}} \quad (2.38)$$

$$g_{\parallel} \cong g_e - \frac{8\lambda}{\Delta_{Td}} \quad \text{and} \quad g_{\perp} \cong g_e - \frac{2\lambda}{\Delta_{Td}} \quad (2.39)$$

where λ is the spin-orbit coupling constant (154 cm^{-1} for Ti(III)) and Δ_{Td} is the energy separation between the degenerate triplet and doublet levels in the cubic tetrahedral field (Figure 2.18). For a tetragonal compression $g_{\perp} < g_{\parallel}$ (Eq. 2.38) and for a tetragonal elongation $g_{\parallel} < g_{\perp} \cong g_e$ (Eq. 2.39).

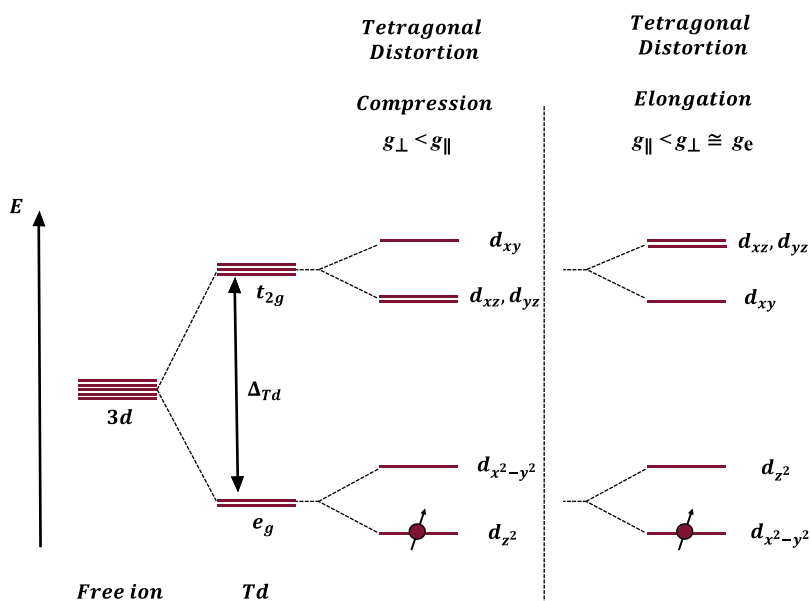


Figure 2.18. Splitting of the d orbitals of Ti(III) with tetrahedral (T_d) symmetry into a doublet e_g and triplet t_{2g} state in a tetragonally distorted tetrahedral crystal field, with further splitting due to compression or elongation. Adapted from ref. [193].

When the metal ion is octahedrally coordinated, anisotropic g -values are observed that depend on the type and degree of the tetragonal or trigonal distortion. The tetragonal

distortion can be compressed or elongated, and the corresponding principal g -values can be evaluated based on the following equations:

$$g_{\parallel} \cong g_e - \frac{8\lambda}{\delta_2} \quad \text{and} \quad g_{\perp} \cong g_e - \frac{2\lambda}{\delta_1} \quad (2.40)$$

where δ_1 and δ_2 are the energy separations between the d orbitals (Figure 2.19).

In the case of a trigonally distorted octahedral symmetry, the g -values are given by these equations:

$$g_{\parallel} \cong g_e \quad \text{and} \quad g_{\perp} \cong g_e - \frac{2\lambda}{\delta} \quad (2.41)$$

Where δ is the energy separation between d orbitals in a trigonally distorted octahedral symmetry.

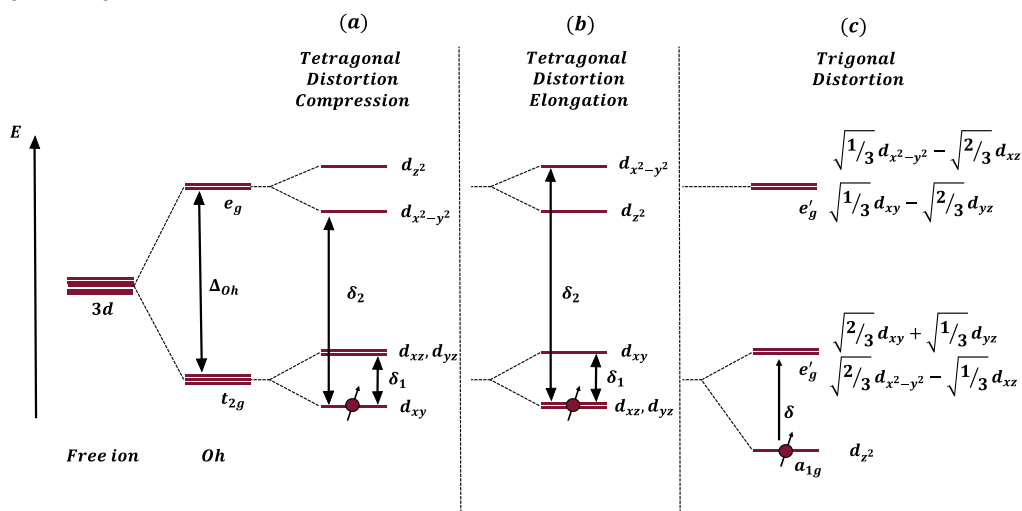


Figure 2.19 Splitting of the d orbitals of Ti(III) with octahedral (O_h) symmetry into a doublet e_g and triplet t_{2g} state undergoing either a tetragonal or a trigonally octahedral distortion. Adapted from ref. [193].

Most of the published EPR spectra include overlapping signals arising from different Ti(III) species with either axial ($g_{\perp} > g_{\parallel}$ and $g_{\perp} < g_{\parallel}$) or rhombic ($g_x \neq g_y \neq g_z$) g -values ranging from 1.89 to 1.99. Depending on the composition of the Ziegler-Natta catalyst, small deviations are observed in different ZNC systems. Several factors contribute to the deviations in the g values, all of which are related to the influence of the chemical environment on the paramagnetic species. Some of the most common reasons, for the slight deviation of the g values in the ZNC, include the localisation of Ti(III) species at different surface terminations of MgCl_2 support (lateral cut 110

and 104), the nature of Lewis bases and even the nature of the co-catalyst used in the activation process.[185,227,228]. However, CW-EPR spectra provide information mostly on the local symmetry of Ti(III) species without giving further information on the metal-ligand interactions. For obtaining such information from the first and second coordination shells, pulsed EPR experiments are performed.

2.5.1. EPR studies of Ti(III) species in ZNC systems reported in the literature

EPR spectroscopy represents an important method for the characterization of transition-metal complexes in heterogeneous systems [194,229]. MgCl_2 -supported ZNC systems remain the most used systems for the industrial production of PE and PP. Specific active sites, located on the surface of a highly active MgCl_2 support, are responsible for the catalytic reactions. These potential active sites are assumed to be paramagnetic Ti(III) species bearing a Ti–C bond, formed after the reductive activation of TiCl_4 with different alkyl-aluminum compounds (usually with TEA), which play the role of co-catalysts [5,19]. The paramagnetic nature of Ti(III) species ($3d^1$, $S = \frac{1}{2}$) makes EPR spectroscopy the ideal spectroscopic technique to obtain specific information on the chemistry of the active sites of ZNC [193]. The exact role of Ti(III) centers in Ziegler-Natta catalysis is still only vaguely defined. Several questions are still open, summarized as follows: (i) which faces of MgCl_2 host the catalytically active Ti species; (ii) how these surfaces are modified by certain Lewis bases [often referred to as internal donors (ID)]; and (iii) by the AlR_3 co-catalyst. Due to the paramagnetic nature of Ti(III), EPR spectroscopy is in principle the ideal technique to answer such questions. However, the EPR characterization of these catalysts in terms of electronic, chemical, and structural properties represents a non-trivial task. Upon activation with AlEt_3 , different species are formed, most of which is EPR silent due to strong dipolar and exchange interactions between the paramagnetic centers. Moreover, a further complication arises from the heterogeneity of the support, the low concentration of the active sites, and the ease of contamination. During the reductive activation of Ti(IV), several studies report also the formation of Ti(II) species besides the formation of Ti(III) species [230]. Characterized with a $3d^2$ electronic configuration ($S = 1$), Ti(II) represents a non-Kramer system, whose zero-field splitting (ZFS) affects strongly the EPR response. Due to the large ZFS, the non-Kramer ion can become observable only in very high microwave frequency and magnetic field, except in some rare systems. These required conditions exceed the available highest frequencies in EPR spectroscopy, therefore Ti(II) is mostly EPR silent [231]. To our knowledge, there are only a few EPR studies reported on Ti(II) spectra in other systems[228,230,232–234], while there are no direct EPR studies on Ti(II) species

present in ZNCs. Taking this into account and the fact that Ti(IV) is diamagnetic, with no unpaired electrons, EPR is perfectly suited to study the electronic structure and the surrounding environment of the proposed active sites in ZNCs.

Due to the complicated composition of the real industrial working catalysts systems, EPR investigation in working models is more widely reported. Brant *et al.* [185], described an EPR investigation on a model ZNC prepared by the deposition of alkylmagnesium butoxide (AMB) and titanium tetrachloride onto silica support. Their work provided an important correlation between Ti spin concentrations and different Ti/Mg ratios, without going into much detail regarding the structures of the active sites themselves. Higher Ti(III) intensity and catalyst activity has been observed when increasing the Ti-Mg ratio. Using a wet chemical route, they demonstrated that the amount of Ti(III) and Ti(II) formed after the reduction of Ti(IV) was 95% and 0.8%, respectively. However, the total amount of EPR-active Ti(III) detected only represented 10-20% of all the titanium ions, suggesting the presence of considerable quantities of EPR-silent Ti(III) centers.

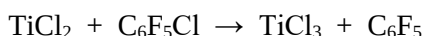
Morra *et al.* [227], investigated an industrial catalyst consisting of $\text{TiCl}_4/\text{MgCl}_2$ /dibutylphthalate, activated by TEA by using a combination of multifrequency (X-, Q-, and W-band) CW and pulsed EPR techniques (including HYSCORE and electron-electron double resonance (ELDOR)-detected NMR). Three distinct EPR-active Ti(III) species were reported, with principal g -values: $g_x = 1.936 \pm 0.01$, $g_y = 1.888 \pm 0.01$ and $g_z = 1.84 \pm 0.01$ for the first species 1 (with 76% abundance), $g_x = 1.960 \pm 0.01$, $g_y = 1.945 \pm 0.01$ and $g_z = 1.890 \pm 0.01$ for the second species 2 (with 23% abundance) and finally $g_x = 1.976 \pm 0.005$, $g_y = 1.968 \pm 0.005$, and $g_z = 1.960 \pm 0.01$ (with only 1% abundance) for the third species 3 as extracted from the X- and W-band. From the Q-band HYSCORE spectra, a hyperfine coupling between Ti(III) and $^{35,37}\text{Cl}$ was observed, suggesting a direct coordination of Cl nuclei to the two more abundant Ti(III) species. The catalyst was subsequently exposed to molecular oxygen, to demonstrate the reactivity and the accessibility of the EPR-active sites. A decrease of the Ti(III) signal intensity was observed immediately, due to oxidation to the EPR-silent Ti(IV) center along with the concomitant appearance of surface superoxide (O_2^-) signal. The latter superoxide signal was used as a spin probe to reveal the presence of Al nuclei, originating from the co-catalyst, in close proximity to the Ti(III) species. Moreover, a hyperfine interaction with ^1H nuclei was resolved in X-band HYSCORE measurements, translating into an $\text{O}_2^- \cdots \text{H}$ distance of 0.33 nm. Finally, analysis of the Q-band HYSCORE revealed that the large isotropic (Fermi contact) hyperfine interaction with ^{27}Al , indicated that the O_2^- radical is stabilized on the Ti(IV) center and experiences a direct interaction with the ^{27}Al nucleus of the co-catalyst.

Advanced EPR studies were also used to provide meaningful information on the nature of paramagnetic metal-olefin complexes. These experiments, performed on ZNCs, revealed important information on the π -coordination mode of the olefins at the paramagnetic center, and thus in turn informed on how the stereoselectivity of the catalyst is directed. In particular, standard hyperfine sublevel correlation (HYSCORE) and single-matched resonance transfer (SMART)-HYSCORE experiments (the latter providing higher sensitivity and an absence of any blind spots), in combination with DFT calculations, were performed by Morra *et al.* [235]. The study was performed on mono-ethylene complexes with trivalent titanium centers, produced by the adsorption of C_2H_4 and ^{13}C -enriched C_2H_4 on reduced TiAlPO-5 zeotype materials. This study provided experimental proof for the π -coordination of ethylene to the paramagnetic Ti(III) center, in addition to the electronic and geometric structure of the ethylene-Ti(III) intermediate complex. The HYSCORE spectrum revealed the presence of two distinct ^{13}C couplings, confirming that the two carbon nuclei of ethylene are inequivalent, with C_2 displaying a larger coupling to the Ti compared to C_1 . This affirmed an asymmetry in the spin density delocalization between the two carbons of ethylene. From this study, it was shown that the reactivity of the ethylene molecule and the stereoselectivity of the catalyst are a consequence of the electronic effects.

Another study was performed by Allouche *et al.* [236], using HYSCORE in combination with X-ray crystallography and DFT calculations, to investigate two model systems of low coordinated bis(alkoxide) Ti(III) alkyl complexes formed upon ethylene polymerization. In this study, they provided structural assignment for $(\equiv Si_2O)(\equiv SiO)_2Ti(III)-R$ surface species as key intermediates in the ethylene polymerization activity of the silica-supported titanium hydrides. From the CW-EPR spectra, they observed rhombic g tensors for both complexes, bearing different degrees of g -anisotropy. After the reaction of the complexes with ^{13}C -labelled ethylene, weak ^1H couplings were observed in the HYSCORE spectra to the first coordination sphere of Ti(III), and the closest proton to the Ti(III) center was found to be from the C_α carbon of the alkyl ligand. The HYSCORE spectra also showed the characteristic ^{13}C hyperfine coupling.

2.5.2. Quantification of Ti(III) species in Ziegler-Natta Catalyst by EPR spectroscopy

To better interpret the working mechanism of the catalyst, besides understanding the nature and surrounding environment of Ti(III) species, it is also important to determine the amount of the potential active sites. A correlation between the fraction of isolated Ti(III) species and the catalyst activity has been reported by several studies [237–239]. Due to the over-reduction of Ti(IV) species during the activation process, quantification of all Ti species in the different oxidation states, present before and after activation, in ZNCs is important. EPR spectroscopy enables the direct quantification of Ti(III) species [199], and indirectly the quantification of Ti(II) [155,240–242]. One of the indirect routes to determine Ti(II) by EPR, uses selective oxidizing reactions of Ti(II) to Ti(III) with water or pentafluorochlorobenzene [155,240–242]:



Nevertheless, there is a problem to determine the total amount of Ti(III) species by EPR spectroscopy in ZNC systems, which is related to the presence of EPR-silent Ti(III) species. Their origin is still poorly understood, but it is likely to be correlated to superexchange and dipolar interactions, present in cluster organizations of Ti(III) species [155,185,230]. Several EPR studies in ZNCs have pointed out the problem of EPR-silent Ti(III) species, proposing different methods to convert EPR – silent Ti(III) species to EPR-active Ti(III) species [243,244]. Their amount depends on the catalyst composition and they are more likely to be formed in high Ti content ZNC [240].

By knowing the total amount of Ti present, usually determined by another quantification method, and the amount of the two ions Ti(III) and Ti(II), the amount of Ti(IV) can also be determined [155]. Zakharov *et al.* reported the absence of Ti(II) species in ZNC with low Ti content, while their presence is most likely observed in ZNC systems with a high Ti content (>1 wt %) [238]. The total Ti content has a direct effect also in the amount of isolated Ti(III) species in the system. In the ZNC with low Ti content (<1 wt %) the Ti-Ti interactions disappear leading to the formation of a higher fraction of isolated Ti(III) species (30 – 70% of the total Ti content), characterized with a higher catalytic activity but lower stereoselectivity [239]. While in ZNC with high Ti content (>1 wt %), the fraction of isolated Ti(III) is smaller (5 – 35%) [158,185,230,242,245]. Our work is focused on the quantification of isolated EPR-active Ti(III) species, excluding the investigation of EPR-silent Ti(III) and Ti(II) species in the analyzed systems.

Materials and methods

In this chapter, a description of the composition of the samples analyzed in this thesis is given, following a bottom-up approach from the simplest system to the most complicated one. Subsequently, a description of the treatment procedures applied in the samples is given, followed afterwards with the EPR measurement details.

3.1. Materials

All the samples represent industrial working models and real samples, prepared in the laboratories of Giulio Natta R&D Centre of Basell Poliolefine Italia S.r.l.(BPI), LyondellBasell Group following standard procedures. The pre-polymerized samples were prepared by myself during my secondment period in BPI while all the other samples were prepared by colleagues from BPI.

3.1.1. MgCl_2 support samples containing internal Lewis bases

Two samples containing a diether as an internal electron donor and two samples containing fluorene as an inert additive instead of a donor, have been provided from BPI. Fluorene was chosen as the inert additive as it has no functional groups that can adsorb on MgCl_2 surfaces. The amount of donors was set to the molar ratio of MgCl_2 :donor = 10:1. The samples have been prepared with different co-milling times (conditions in Table 3.1 and Table 3.2 below).

A planetary ball mill was used for the co-milling of all the samples. All the operations, in particular the transfer of the solids to the jar of the mill, were carried out under N_2 atmosphere. The jar was closed to avoid contact with air. Samples were washed with iso-hexane (technical grade, mixture of C5 – C6 isomers, conditions in Table 3.1 and Table 3.2 below). The synthesis conditions of the four samples are presented in Table 3.1 and Table 3.2. No treatments with TiCl_4 were carried out. After the milling the solid was washed two times with iso-hexane at 70 °C for 10 minutes and one time at 25 °C for 10 minutes. The solvent was siphoned off and the solid was dried under vacuum.

Table 3.1 Synthesis conditions for the MgCl₂ support containing diether as an internal donor

Sample	Synthesis			
	MgCl ₂ (g)	diether (g)	Mg/diether (mol/mol)	Milling Time (h)
MgCl ₂ /diether	20.81	5.48	10	8
MgCl ₂ /diether	20.37	5.33	10	16

Table 3.2 Synthesis conditions for the MgCl₂ support containing fluorene as an internal donor

	Synthesis			
	MgCl ₂ (g)	Fluorene (g)	Mg/fluorene (mol/mol)	Milling Time (h)
MgCl ₂ /fluorene	20.33	3.47	10	8
MgCl ₂ /fluorene	20.06	3.49	10	4

3.1.2. Ziegler-Natta pre-catalyst systems with and without internal Lewis bases

Six pre-catalysts systems, sample 1-6 in Table 3.3, with and without intentionally added TiCl₃ were provided by BPI. The samples include three binary systems MgCl₂/TiCl₄ (sample 1 without TiCl₃, sample 2 with Mg/Ti(III) = 40 mol/mol, and sample 3 with Mg/Ti(III) = 20 mol/mol), one ternary system MgCl₂/TiCl₄/monoether (sample 4 without TiCl₃), and two ternary systems MgCl₂/TiCl₄/diester (sample 5 without TiCl₃ and sample 6 with Mg/Ti(III) = 50 mol/mol). The samples contain a high Ti content (2.4 – 4.9 %wt) and represent working models similar to industrial solid catalyst precursors. All samples were washed with iso-hexane after the synthesis. The composition of each sample is represented in Table 3.4.

Table 3.3 Type of pre-catalyst samples

Samples	"Sample Definition"	Type of catalyst precursor	TiCl ₃ added during synthesis	Scope
1	MgCl ₂ /TiCl ₄	ID free	No	
2	MgCl ₂ /TiCl ₄	ID free	Mg/Ti(III) = 40 mol/mol	addition of TiCl ₃
3	MgCl ₂ /TiCl ₄	ID free	Mg/Ti(III) = 20 mol/mol	Effect of TiCl ₃ amount
4	MgCl ₂ /TiCl ₄ /monoether	aliphatic monoether	No	
5	MgCl ₂ /TiCl ₄ /diester	aliphatic diester	No	
6	MgCl ₂ /TiCl ₄ /diester	aliphatic diester	Mg/Ti(III) = 50 mol/mol	addition of TiCl ₃

Table 3.4 Composition of pre-catalyst samples presented in Table 3.3.

New Samples	Ti(III) %wt	Mg %wt	Ti(Total) %wt	Cl %wt	solvent(*) %wt	diester %wt	monoether %wt	Ti(III)/Ti(Tot) %
1	0.8	19.2	4.6	69.5	3.6	-	-	17.4
2	0.7	19.1	4.8	70.0	4.0	-	-	14.6
3	0.5	18.8	4.9	70.0	3.9	-	-	10.2
4	0.5	14.3	2.4	48.3	0.7	-	32.6	20.8
5	0.4	15.8	3.1	55.3	13.0	12.4	-	12.9
6	0.4	16.0	3.4	56.4	9.6	13.0	-	11.8

(*) Residual solvent after washing and drying the solids

3.1.3. Industrial and experimental pre-catalysts and the corresponding activated catalyst containing an external Lewis base

Two pre-catalyst systems (named **A1** and **B1**) of the type MgCl₂/TiCl₄/ID (ID = diether), and the corresponding activated catalysts (named **A3** and **B3**) have been provided by BPI (Table 3.5). The pre-catalysts differ between each other in the structure of the diether and the preparation recipe of the pre-catalysts (structural information of the diether is confidential). The pre-catalyst samples were washed with iso-hexane at the end of the synthesis. The activation was performed in a liquid phase in the laboratories of BPI in the same way for both systems at 10 °C, with an excess of 8% TEA solution in iso-hexane (80 g/L, with Al/Ti around 1000 mol/mol) and introducing a silane (TEA/Silane = 20

mol/mol) as an external Lewis base. Methyl-cyclohexyl-dimethoxy silane (MCDMS) was used as an external Lewis base. For this reaction 8 g of solid catalyst precursor, was reacted with 1 g of methyl-cyclohexyl-dimethoxy silane, 44 g of TEA in about 1.5 L of iso-hexane. The precontact time between pre-catalyst and co-catalyst was 30 minutes. The catalyst was washed with iso-hexane to remove the excess of TEA and external donor. The composition of each sample is represented in Table 3.5.

Table 3.5 Composition of pre-catalyst and activated catalysts systems

Sample type	Code	Pre-catalyst	ID	Co-catalyst	ED
Industrial	A1	MgCl ₂ /TiCl ₄	Diether/Structure A	-	-
Industrial	A2	MgCl ₂ /TiCl ₄	Diether/Structure A	TEA	MCDMS
Experimental	B1	MgCl ₂ /TiCl ₄	Diether/Structure B	-	-
Experimental	B2	MgCl ₂ /TiCl ₄	Diether/Structure B	TEA	MCDMS

3.1.4. Pre-polymerized samples

Seven samples (Table 3.6) including an activated catalyst of the type MgCl₂/TiCl₄/diether/TEA (**AC**) and six pre-polymerized samples (**AC1-AC6**) with different degree of pre-polymerization have been prepared in BPI laboratories using catalyst AC. The composition of each sample is represented in Table 3.6. The set up for the preparation of these samples is represented in Figure 3.1.

The samples were prepared at seven different conversion rates (0, 0.3, 0.7, 1, 2, 5 and 10) in which the amount of ethylene varied from 0 to 164 gr. The sample with conversion rate zero represents only the activated catalyst, while with the increase of the conversion rate there is an increase in the ethylene concentration fed in the pre-polymerization step. The activation of pre-catalyst MgCl₂/TiCl₄/diether was performed in the liquid phase using TEA with an Al/Ti molar ratio of 1 mol/mol, in the set up shown in Figure 3.2a.

Afterwards, under N₂ flow, the activated catalyst was added in the autoclave for the pre-contact at 30 °C and left for 30 minutes (Figure 3.1). The temperature of the autoclave was raised to 50 °C and ethylene was added with a flow rate of 135 g/h for 60 min with an instrument error of 10%. Subsequently, the pre-polymerized sample was washed twice with propane.

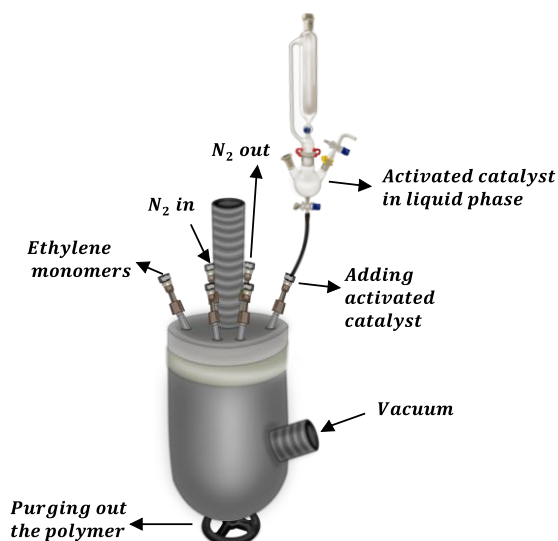


Figure 3.1 Schematic representation of the preparation of the pre-polymerized samples in an autoclave.

Table 3.6 Composition of the activated catalyst $\text{MgCl}_2/\text{TiCl}_4/\text{Diether}/\text{TEA}$ used in the pre-polymerization step at different conversion rates

Sample	Mg wt. %	Ti (total) wt. %	Al wt. %	diether wt. %	Iso- hexane wt. %	Polymer wt. %	Conversion gPE/gcat	P ₅₀ mm
AC	12.3	2.75	1.3	16.3	11.6	0	0	66.7
AC1	9.8	2.2	1.15	13.3	8.4	26.5	0.36	72.2
AC2	7.9	1.8	0.9	10.2	6.3	42.1	0.73	80.7
AC3	6.8	1.55	0.8	4.5	4.5	51.1	1.0	90.1
AC4	4.9	1.1	0.55	5.9	3.0	65.3	1.9	106.3
AC5	2.5	0.7	0.3	3.3	1.9	82.5	4.7	138.5
AC6	1.5	0.4	0.15	2.0	2.4	89.4	8.5	166.9

3.2. Experimental methods

For measurements at X-band all the samples were filled in either 3 or 4 mm outer diameter (o.d.) X-band EPR tubes. For measurements at Q-band the sample has been filled in 1.8 mm o.d. Q-band EPR tubes. And for the experiments at W-band the samples have been filled in 0.8 mm o.d. W-band EPR tubes. All the samples have been handled inside a glove box in argon atmosphere (University of Turin) or nitrogen atmosphere (University of Antwerp). The glovebox conditions were as follows: $\text{H}_2\text{O} < 0.1$ ppm and $\text{O}_2 = 1\text{--}4$ ppm.

All the sample treatments in gas phase have all been performed at the University of Turin on vacuum lines equipped with pump modules that generate a residual pressure of 10^{-5} mbar. The TEA has been purified by the pump-thaw method at 77 K before its use.

3.2.1. Activation of Ziegler-Natta pre-catalysts with triethylaluminum

The activation of the pre-catalysts samples has been performed with TEA in gas and in liquid phase. The gas phase activation has been performed at the University of Turin, while the liquid-phase activation has been performed in BPI laboratories.

The activation in liquid phase has been performed by using the equipment presented in Figure 3.2a. First the equipment is purged with N_2 gas. The solvent is added in the dropping funnel under nitrogen flow. A small amount of the solvent is added from the dropping funnel to the multi-necked flask, followed by the addition of the weighted pre-catalyst and the diluted solution of TEA. Afterwards, the remaining solvent in the dropping funnel was added in the multi-necked flask. All the procedures were performed under nitrogen flow. At the final stage, the activated catalyst has been added to the autoclave from the purging tube. The sample is washed with iso-hexane and dried.

The activation in gas phase was performed *in situ*, by sending vapors of TEA directly in the EPR cell. A specially designed equipment to perform solid-gas phase reactions has been used for this purpose, illustrated in Figure 3.2b. The sample was loaded into a quartz tubular cell equipped with a 3 mm o.d. EPR quartz tube on one side, used for EPR measurements, and a quartz bulb in the opposite site, used for the activation. The cell was filled with sample inside the glovebox and was then attached to the vacuum line and evacuated to a final pressure of 10^{-4} mbar. Before its use, TEA was purified by the freeze–pump–thaw method and delivered on the outgassed sample.

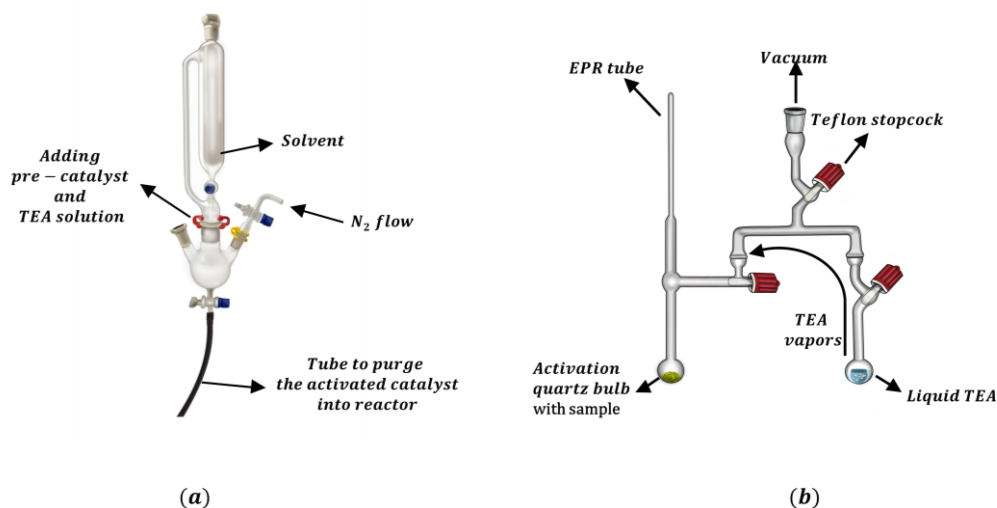


Figure 3.2 Illustration of the experimental set-up used for the activation reaction with TEA at (a) liquid phase and (b) gas phase.

3.2.2. EPR measurements

X-band CW-EPR spectra were recorded in four different EPR instruments: with a Bruker ESP 300E spectrometer operating at a microwave (mw) frequency ~ 9.5 GHz, with a Bruker Elexsys E680 X/W-band spectrometer mounted with an optically accessible ER4104OR resonator working at ~ 9.44 GHz, with a Bruker EMX spectrometer equipped with a ER 4122 SHQ cylindrical cavity operating at ~ 9.7 GHz, and Bruker Elexsys E580 spectrometer operating at a mw frequency of ~ 9.76 GHz. A modulation frequency of 100 kHz was used. The Q-band CW and pulse EPR measurements were performed on a Bruker Elexsys E580 spectrometer operating at a mw frequency of 34 GHz and equipped with helium gas-flow cryostats (Oxford, Inc.). Specific measurement details as the modulation amplitude, microwave power, and temperature are specified in each of the figure captions. For the measurements at 77 K the EPR cell was placed in a finger Dewar filled with liquid nitrogen. CW and pulse EPR experiments at W-band were performed on a Bruker ELEXSYS E680 X/W-band spectrometer (mw frequency 94 GHz) equipped with a continuous liquid-helium flow cryostat.

Electron-spin-echo (ESE)-detected EPR experiments were carried out with the pulse sequence: $t_{\pi/2} - \tau - t_{\pi} - \tau - \text{echo}$ at X- and Q-band frequency. The mw pulse lengths $t_{\pi/2}$

and t_π , and the inter-pulse time intervals (τ values) for each sample are specified in the captions of the figures.

Three-pulse ESEEM measurements were carried out at Q-band by increasing the time delay T of the pulse sequence: $t_{\pi/2} - \tau - t_{\pi/2} - T - t_{\pi/2} - \text{echo}$, with $t_{\pi/2} = 16$ ns. The time interval T was varied in steps of 8 ns starting from 100 ns. A four-step phase cycle was used to eliminate unwanted echoes. To avoid blind-spot effects, two dimensional three-pulse ESEEM spectra were recorded as a function of the interpulse delay τ , which was varied from 100 to 212 ns in steps of 8 ns. Two-dimensional field-dependent 3-pulse ESEEM spectra were obtained by sweeping the magnetic field from 1200 to 1320 mT (70 data points). In this case, a fixed interpulse delay $\tau = 188$ ns was chosen based on the three-pulse ESEEM spectra taken as a function of τ . A 1 kHz repetition rate was used for all experiments. Further experimental details are specified in the figure captions.

HYSCORE experiments [218] were carried out at Q-band with the pulse sequence $t_{\pi/2} - \tau - t_{\pi/2} - t_1 - t_\pi - t_2 - t_{\pi/2} - \tau - \text{echo}$. The inter-pulse delay choice was based on the above-mentioned ESEEM experiments performed as a function of τ . A four-step (for experiments at X-band) or eight-step (for experiments at Q-band) phase cycle was used to eliminate unwanted echoes. The time traces of the HYSCORE spectra were baseline corrected with a third-order polynomial, apodized with a Hamming window and zero filled. After two-dimensional Fourier transformation, the absolute value spectra were calculated.

The six-pulse HYSCORE [223] experiments were performed at Q-band with the pulse sequence $(\pi/2)_y - \tau_1 - (\pi)_y - \tau_1 - (\pi/2)_x - t_1 - (\pi)_x - t_2 - (\pi/2)_x - \tau_2 - (\pi)_x - \tau_2 - \text{echo}$ with microwave pulse lengths $t_{\pi/2} = 16$ ns and $t_\pi = 32$ ns. Two different interpulse delays τ (102 and 112 ns) were used. An eight-step phase cycle was adopted to eliminate unwanted echoes.

The matched HYSCORE [220–222] experiments were performed at X-band with the pulse sequence $\pi/2 - \tau_1 - \text{HTA} - t_1 - \pi - t_2 - \text{HTA} - \tau_2 - \text{echo}$ with microwave pulse lengths $t_{\pi/2} = 16$ ns and $t_\pi = 32$ ns and HTA pulse with length 40 ns. The optimization of the HTA pulse was done from a matched three-pulse ESEEM experiment. Two different interpulse delays τ (112 and 150 ns) were used. An eight-step phase cycle was adopted to eliminate unwanted echoes.

Davies ENDOR spectra [225] were measured at Q-band with the mw pulse sequence $t_\pi - T - t_{\pi/2} - \tau - t_\pi - \tau - \text{echo}$, with hard mw pulses of length $t_{\pi/2} = 16$ ns and $t_\pi = 32$ ns to suppress the signal contributions of the weakly nuclei. A radio frequency pulse from an ENI 3200L RF amplifier was applied during time T ($=17$ μ s) with a length of 14 μ s. ENDOR spectra

were collected in stochastic mode by randomly hopping the RF excitation frequency over a 30 MHz sweep

Mims ENDOR [226] spectra were measured at Q-band with the mw pulse sequence $t_{\pi/2}-\tau-t_{\pi/2}-T-t_{\pi/2}-\tau$ -echo with $t_{\pi/2} = 16$ ns. A radio frequency π -pulse using an ENI 3200L RF amplifier was applied during time $T (=17 \mu\text{s})$ with a length of $14 \mu\text{s}$.

All EPR and ESEEM spectra were simulated using the EasySpin simulation package [246], an Matlab EPR simulation toolbox developed by Stefan Stoll.

3.2.3. Quantification of EPR-active species in heterogeneous Ziegler-Natta Catalysts

The quantification of the EPR-active species has been performed at the University of Turin (Italy) by CW- and pulse EPR measurements performed at X-band and at the University of Antwerp (Belgium) by CW-EPR measurements at X-band.

At the University of Antwerp a standard solution of $\text{Cu}(\text{OTf})_2$ in dimethyl sulfoxide (DMSO) with different molar concentrations in the range of 0.1 – 7 mM was used for the quantification of Ti(III) species. For the quantification of the radical species, a standard solution of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) in toluene with different molar concentrations in the range of 0.8 - 2 mM was prepared. Same experimental conditions have been used for the frozen standard solutions and the frozen powder ZN pre-catalyst samples. The microwave power was selected such as to avoid saturation for both the standard and the sample. The time constant was set equal to the conversion time [204]. Since we are only interested in the double integral of the spectrum, a larger modulation amplitude (1 mT) than normal has been used to improve the S/N, paying attention to not distort the linewidth [205]. This high modulation amplitude was causing a severe distortion of the TEMPO signal, therefore, for the TEMPO standard and the samples containing the radical, a modulation amplitude of 0.1 mT was used. The receiver gain was the only parameter that was changed during the measurements but was corrected at the end for each spectrum.

At the University of Turin, the SpinCount package of Bruker Xenon Software [247] was employed to quantify the spin number (total amount of radical and Ti(III) species) in each sample. No reference standard was used. The length of the tube occupied by the sample and inner diameter of the tube were measured by using a caliber nonius, and the values were inserted in the program for each sample. The spectra were recorded with a microwave power where no saturation of the radical and Ti(III) signals occurs.

All the spectra (at the University of Antwerp and at the University of Torino) were baseline corrected and double integrated, followed at the end by the calculation of the number of spins.

The local average concentration of spins in the samples was obtained by measuring the contribution of the instantaneous diffusion to the phase memory time T_m . A nutation experiment was used to determine the turning angle $\langle \sin^2 \theta_1 \rangle$. Two-pulse echo decays, using a pulse sequence $(\pi/2)_x - \tau - (\pi)_{<x>} - \tau$ -echo, were collected by varying the microwave power of the second pulse. The microwave power was varied by changing the % of the pulse intensity in the $<x>$ channel. The pulse lengths were set to $t_{\pi/2} = 16$ ns and $t_\pi = 32$. The echo was integrated using an integration window of 74 ns.

Investigation of paramagnetic species on pre-active Ziegler-Natta catalyst components by EPR spectroscopy

Supported heterogeneous ZNC systems represent multisite catalysts, where the catalytic active sites involved in the reaction of multiple insertion of olefin units are associated to Ti(III) species, bearing a Ti-C bond. Since their discovery in 1953, these systems have been widely investigated [5,19]. An important challenge on the research of these catalyst systems is to understand the real nature of the active sites and to elucidate their structure, behavior, and their corresponding catalytic performance. In this context, spectroscopic research plays an essential role for a thorough characterization of the active sites in Ziegler – Natta catalysts. The paramagnetic nature of Ti(III) species makes EPR spectroscopy techniques of potential high relevance to gain direct structural information of the believed active sites and their surrounding environment. However, the thorough investigation of heterogeneous ZNCs represents a challenge due to their multi-component composition. For this reason, the approach to use model systems at different levels of simplification, attempting to mimic industrial catalyst systems, has been applied by most research groups in order to characterize the active species in ZNCs [179,185,248–256]. Real industrial samples have been less investigated by means of EPR spectroscopy with only a few reported works [245], due to the complicated nature of the system. Therefore, this thesis is mainly devoted to an EPR investigation of real industrial samples and industrial working models prepared in the laboratories of Giulio Natta R&D Centre of Basell Poliolefine Italia (BPI) following standard procedures.

In this chapter I first focus on the EPR characterization of highly active MgCl_2 support samples containing Lewis bases (Section 4.1), moving then to the exploration of the nature of Ti(III) species on solid ZNC precursors of the type $\text{MgCl}_2/\text{TiCl}_4$ with and without the presence of different Lewis bases (internal donors) before the activation with triethylaluminum (Section 4.2). The investigation of the corresponding activated systems has also been a main goal of this thesis and the results are discussed in Chapter 5. Conclusions are reported in Chapter 6.

4.1. Radical species on MgCl_2 support

In heterogeneous ZNCs, the formation of catalytic active sites occurs on the surface of a highly active MgCl_2 support, and this process is generally regarded as a dilution process in which the highly active MgCl_2 support acts as a solid polar solvent. As already explained in more detail in Section 1.1.2. the grafting of TiCl_4 , in principle, can occur at different surface terminations of MgCl_2 and the actual facets hosting the catalytically active Ti species remain to a large extent matter of controversy. The (104) and (110) facets have been identified as the relevant surfaces, with some authors proposing that specific point defects localized on such surfaces are the relevant adsorption sites [117,145]. The (015) surface has also been proposed as an alternative relevant surface [116]. In general, consensus has been reached about (104) surfaces, exposing penta-coordinated magnesium sites, as being thermodynamically more stable than (110) surfaces, exposing tetra-coordinated magnesium sites [115,116]. However, this energetic scenario, is known to be profoundly altered by the adsorption of Lewis bases, favoring the (110) sites. The use of Lewis bases as modifiers (known as internal and external electron donors in industrial terms) in the catalyst preparation is of particular importance to modify the surface of supported ZNCs by improving the stereospecificity, stereoselectivity and activity of the catalyst. However, their role and their interaction with other catalyst components is still not fully understood. Depending on their nature and structure, Lewis bases can interact with the MgCl_2 support by adsorption on one of the MgCl_2 facets [143,257], with TiCl_4 by forming $\text{TiCl}_4 \cdot \text{Lewis Base}$ complexes [258,259], and with the co-catalyst [129,137,260]. Therefore, during this PhD work, one of the main goals was understanding the influence of different Lewis bases on the nature of Ti(III) species. In principle, coordination of an electron donor to Ti(III) is expected to modify the ligand field felt by the metal ion and this is reflected by a change in the EPR spectrum. Hence, $\text{MgCl}_2/\text{Lewis-base}$ samples were first investigated, before moving to a more complicated catalyst system. Four MgCl_2 support samples have been explored by means of CW-EPR spectroscopy without the treatment with TiCl_4 , two samples containing diether as an internal electron donor and two samples containing fluorene as an inert additive, used for comparison. Fluorene was chosen as the inert additive as it has no functional groups that can adsorb on MgCl_2 surfaces. The amount of donors was set to the molar ratio $\text{MgCl}_2:\text{donor} = 10:1$. The samples have been prepared with different co-milling times of 4, 8 and 16h, washed afterwards with iso-hexane and dried. Even though nowadays the physical activation by ball-milling is less used in industrial practice, for our purpose it is more appealing due to its chemical simplicity as well as to the ease of controlling the activation process through the grinding time. Our interest was focused on the interaction of the organic compounds with the MgCl_2 surfaces. The preparation of

MgCl₂/TiCl₄ pre-catalysts, with and without Lewis bases, by ball milling has been reported to generate higher surface areas and to form crystal defects leading to an increased number of TiCl₄ adsorption sites. While ball milling can influence the particle size, shape, and surface characteristics of materials, it might not offer precise control over the specific "type" of surface facet generated [261–263]. The X-band CW-EPR spectra have been recorded at liquid nitrogen temperature. The results, presented in Figure 4.1 show the presence of an intense peak at about $g = 2.003$ amenable to radical species arising from the C-C bond breakages (an approximate bond energy of 80 kcal/mol) of the organic compounds present during the milling process. It is known that ball milling reduces the C-C bonding force that may even lead to C-C bond breakage for systems containing organic compounds [264]. According to Zhang *et al.* [264], besides the effect on C-C bonds, ball milling has also an effect on oxygen-containing functional groups. They reported a reduction of C=O to C-O after ball milling. The spectra in Figure 4.1 reveal that the EPR signal for the sample containing a diether as an internal donor has a broader linewidth ($\Delta B_{pp} = 0.85$ mT) compared to the system containing fluorene ($\Delta B_{pp} = 0.55$ mT). Also, the two spectra recorded after the same milling time show different intensities (Figure 4.2), suggesting that the presence of the diether favors the localization of carbon-based radicals.

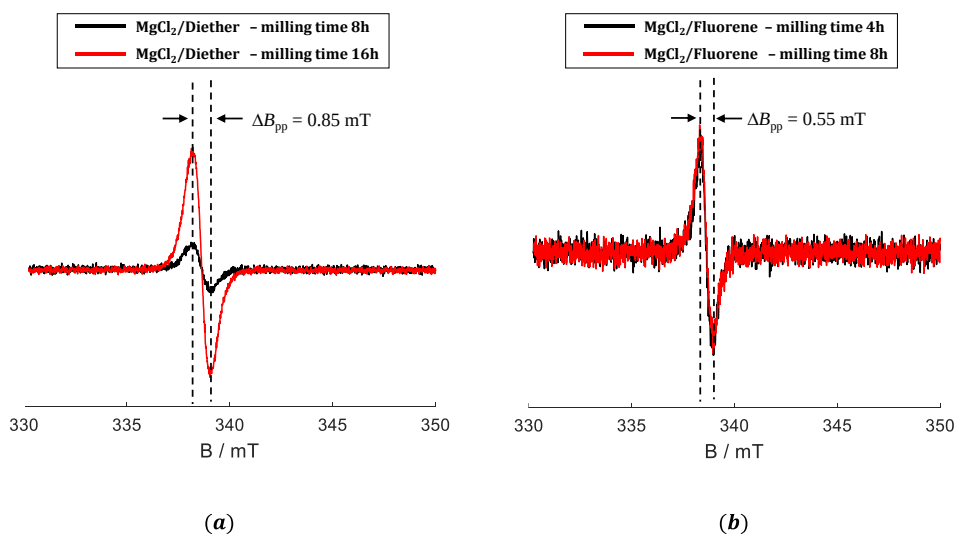


Figure 4.1 X-band ($\nu_{mw} = 9.5$ GHz) CW-EPR spectra for: (a) MgCl₂/Diether co-milled for 8h (black spectra) and 16h (red spectra) and (b) MgCl₂/Fluorene co-milled for 4h (black spectra) and 8h (red spectra). All spectra were recorded at liquid nitrogen temperature (77 K) and normalized by the mass of sample.

Moreover, for MgCl₂/Diether, the signal intensity correlates with the milling time (*i.e.* largest intensity for longer milling time Figure 4.2). Interestingly, the sample analysis results from the BPI laboratories (Table 4.1), obtained from wet chemistry, also indicate

a higher percentage of the bounded organic phase for the system containing the diether and milled for 16 h. Also, in the case of fluorene, the sample analysis from BPI reveals a higher intensity of the radical signal for a longer milling time (Table 4.2). This would also explain why in this system we observe a higher intensity of the radical species, which remain in the surface after washing with the solvent.

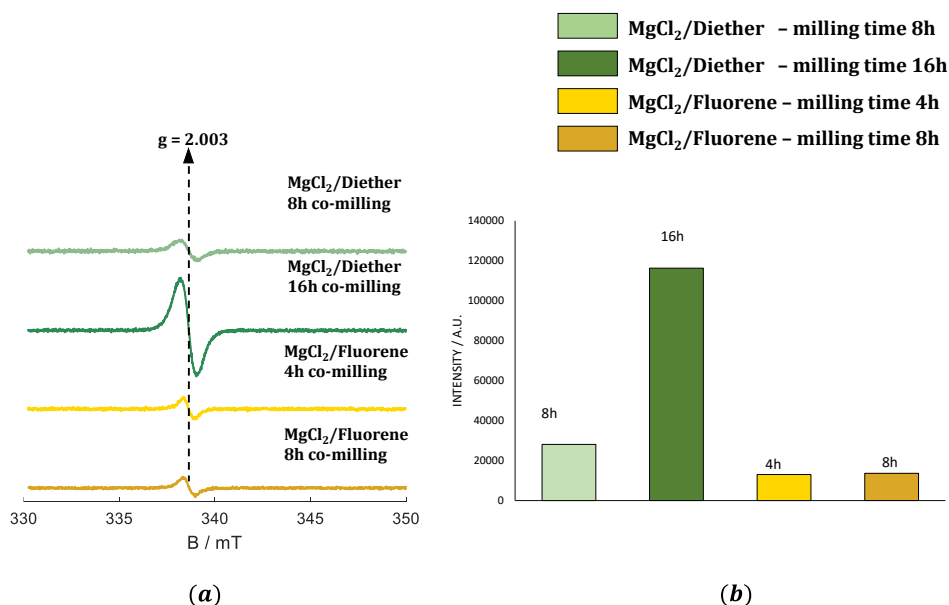


Figure 4.2 X-band ($\nu_{mw} = 9.5$ GHz) CW-EPR spectra for sample MgCl₂/Diether co-milled for 8h (light green spectra) and 16h (dark green spectra) and sample MgCl₂/Fluorene co-milled for 4h (light yellow spectra) and 8h (gold spectra). The intensity of the active species is presented in arbitrary units. All spectra were recorded at liquid nitrogen temperature (77 K) and normalized by the mass of sample.

Table 4.1 MgCl₂/Diether sample analysis performed in the BPI laboratories.

Sample	Analysis					
	Mg wt% <i>mol/mol(Mg)</i>	Cl wt% <i>mol/mol(Mg)</i>	diether wt% <i>mol/mol(Mg)</i>	Tot w%	Mg/diether found	diether bonded (*)
Mg/diether milled for 8h	19.6 1.00	57.5 2.01	13.7 0.07	90.8	15.0	67%
Mg/diether milled for 16h	19.6	57.5	16.3	93.4	12.6	80%

(*) diether bonded with respect to initial amount charged to mill

(*) composition is indicated as both %wt, and as a molar ratio with respect to Mg

Table 4.2 MgCl₂/Fluorene sample analysis performed in the BPI laboratories

Sample	Analysis					
	Mg wt% <i>mol/mol(Mg)</i>	Cl wt% <i>mol/mol(Mg)</i>	fluorene wt% <i>mol/mol(Mg)</i>	Tot wt%	Mg/fluorene found	fluorene bonded (*)
Mg/fluorene milled for 4h	24.7 1.00	73.9 2.05	0.5 0.0019	99.1	516.4	2%
Mg/fluorene milled for 8h	24.4 1.00	72.7 2.04	0.6 0.0036	97.7	278.2	4%

(*) fluorene bonded with respect to initial amount charged to mill

(*) composition is indicated as both %wt, and as a molar ratio with respect to Mg

Recent evidences suggest that the molecular structure of the donors and their basicity, play an important role in driving stereochemical selectivity by interacting with certain MgCl₂ facets [265,266]. While fluorene is a weak acid (pK_a = 22.6 in DMSO), diethyl ether acts as a base (pK_b = 17.5 in DMSO). The higher the basicity the stronger the coordination to the more acidic sites of the MgCl₂ support, which correspond to the facet (110) [260,265]. There are no XRD data available for the samples analyzed in this thesis. In this context, experimental and computational studies have shown that diethers favorably coordinate on the (110) facet [124,135,143]. They remain on the surface even after the washing with solvents and activation with alkyl aluminum compounds and give narrow molecular weight [268]. However, the EPR signal does not give any information on the radical structure or with which of the MgCl₂ facets the radical interacts.

4.2. Investigation of Ti(III) species on pre-active ZNCs

Studying Ti(III) species of titanium sites supported on MgCl₂ provides insight into the typical EPR parameters that can be used for interpreting the results of the more complex activated catalysts. Recent computational and experimental results show a preferential binding of TiCl₄ monomers to the (110) surface, as explained in chapter 1.3.3 [114]. In this model, titanium forms two additional bonds with surface chloride, resulting in a pseudo-octahedral titanium site or in a distorted pyramidal coordination (the latter in the case of a complexed TiCl₃ monomer). On the other hand, coordination to the (104) MgCl₂ termination would give a tetrahedral coordination of the Ti(III) ions [245]. The titanium coordination modes on the two surfaces are shown in Figure 4.3.

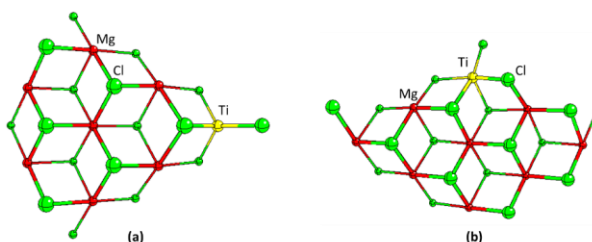


Figure 4.3 Coordination modes of TiCl_3 at (a) (104) MgCl_2 surface giving a tetrahedral coordination of the Ti(III) ions and (b) on a (110) surface resulting in a distorted pyramidal coordination.

In Section 4.2.1 I exploit the presence of Ti(III) species in pre-active ZNCs as spin-probes to understand the influence of different Lewis bases on the local coordination structure of the reduced metal sites. In particular three systems have been explored before activation with triethylaluminum: a binary system $\text{MgCl}_2/\text{TiCl}_4$ and two ternary systems where two different Lewis bases, a diester and a monoether, were incorporated. In Section 4.2.2 I will turn the attention to the influence of Lewis bases of the same family in the distribution of the Ti(III) species.

4.2.1. Isolated Ti(III) Species on the Surface of a Pre-active ZNCs Containing Different Lewis Bases

The EPR characterization of the three systems before activation was carried out at three different microwave frequencies (X-, Q-, W-band) shown in Figure 4.4. CW-EPR spectra at X- and W-band, and ESE-detected spectra at Q-band were collected. All spectra show the presence of a weak isotropic signal resonating at $g = 2.003$, which is assigned to radical impurities, and signals due to different Ti(III) species. The intensity of the radical species was found to vary in the different samples being particularly intense in the ternary system containing the diester Lewis bases (Figure 4.4c). The CW-EPR spectra at W-band also shows the presence of Mn(II) impurities for all the samples and the presence of two other peaks resonating at $g = 2.012$ and $g = 1.99$ for the system containing a monoether (highlighted with a red asterisk sign (*)). The first approach on analyzing the species with a g -value of 2.012 was based on considering the presence of a superoxide species. However, the signal of superoxide species is characterized with a rhombic g -tensor [245,269–271], while in our system the signal is isotropic. Moreover, we have also the presence of the signal resonating at $g = 1.99$ which we do not observe in the X- and Q-band spectra. Taking into account the absence of this signal in the X- and Q-band EPR spectra, the signal is more likely to arrive from some impurities from the sealing method used for the tubes rather than superoxide or Ti(III) species. The W-band EPR tubes were

first closed inside the glovebox by vacuum grease and then sealed with flame outside the glovebox.

The spectrum of Ti(III) in the binary $\text{MgCl}_2/\text{TiCl}_4$ mixture is reported in Figure 4.4a and features a complex EPR powder pattern indicating the presence of at least two EPR active species. These are characterized by g values and line widths typical of isolated Ti(III) species but experiencing different local environments [183,184,237,238,272–274]. A dramatic change in the spectrum is observed for Ti(III) at the ternary system $\text{MgCl}_2/\text{TiCl}_4/\text{monoether}$ (Figure 4.4b). In this case the spectrum is dominated by the contribution of a Ti(III) species with an axial g tensor and $g_{\perp} > g_{\parallel}$ (Ti(III)-A', Figure 4.4b). Furthermore, a signal around $g = 1.87$ is also related to Ti(III) species and this signal will be treated in more detail in section 4.2.1.2. A reversed g -tensor situation is observed for the ternary system $\text{MgCl}_2/\text{TiCl}_4/\text{diester}$ (Ti(III)-B, Figure 4.4c). In this case the spectrum is dominated by the spectral pattern of a different species, with a pseudo-axial g tensor with $g_{\perp} < g_{\parallel}$. This comparison reveals that in the binary system, two Ti(III) species with different g tensor symmetry are present, while the introduction of the Lewis bases selectively suppresses one of the two species, depending on the nature of the molecule. Reproducibility was checked using a second batch of the same samples.

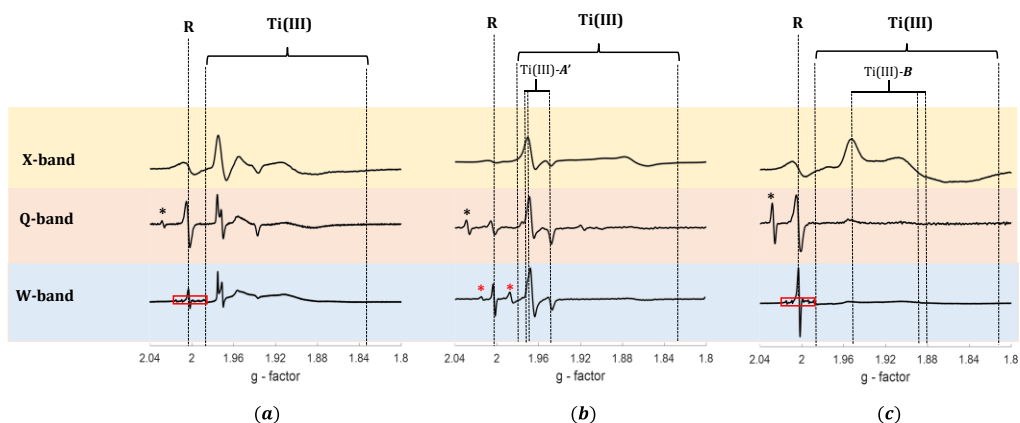


Figure 4.4 Experimental CW-EPR at X- and W-band frequency and the first derivative of the ESE-detected spectra at Q-band of (a) $\text{MgCl}_2/\text{TiCl}_4$ binary system, (b) $\text{MgCl}_2/\text{TiCl}_4/\text{monoether}$ ternary system, and (c) $\text{MgCl}_2/\text{TiCl}_4/\text{diester}$ ternary system recorded at 77 K at X-band ($\nu_{\text{mw}} = 9.5$ GHz), 30 K at Q-band ($\nu_{\text{mw}} = 33.8$ GHz), and 10 K at W-band ($\nu_{\text{mw}} = 94$ GHz). The black asterisk (*) accounts for a spurious signal of the Q-band EPR cavity; the red asterisk (*) implies the presence of some impurities of unknown nature; and the highlighted red square implies the presence of Mn impurities for the W-band spectra.

4.2.1.1. The $\text{MgCl}_2/\text{TiCl}_4$ binary system

To obtain the spin-Hamiltonian parameters of the different species briefly described above, computer simulation of the X-band CW-EPR and corresponding Q-band ESE-detected EPR spectra were carried out.

The experimental and simulated spectra are shown in Figure 4.5, while the spin Hamiltonian parameters extracted from the simulation are listed in Table 4.3. The two Ti(III) species contributing to the EPR spectrum are labelled Ti(III)-**A** and Ti(III)-**B** and are indicated by stick diagrams in Figure 4.5, while the radical species is indicated with **R**. The simulations of the spectra recorded at the two different frequencies were carried out using the same set of spin Hamiltonian parameters, only changing the line width and the relative abundance of the species. This is justified because both depend on the frequency-dependent relaxation properties and different experimental conditions. The relative abundance reported in Table 4.3 refers to the simulation of the X-band CW-EPR spectra.

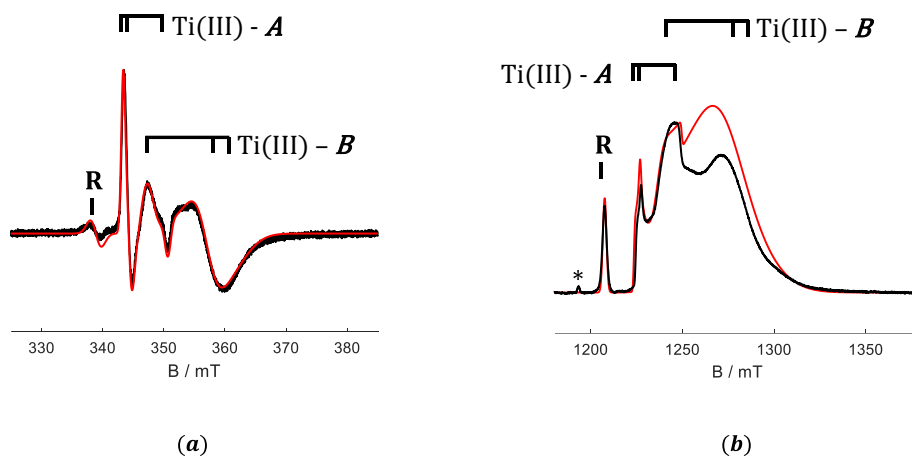


Figure 4.5 Experimental (black) and computer-simulated (red) EPR spectra of Ti(III) species in the $\text{MgCl}_2/\text{TiCl}_4$ binary system. (a) X-band ($\nu_{\text{mw}} = 9.5$) CW-EPR recorded at 77 K; (b) Q-band ($\nu_{\text{mw}} = 33.8$ GHz) ESE detected EPR recorded at 50 K. The stick diagrams indicate the two Ti species, R the organic radical and * a spurious signal of the Q-band EPR cavity. The g-values for species Ti(III)-**A** and Ti(III)-**B** are reported in Table 4.3

By using the perturbation formulas (equation 2.38 – 2.41 in Chapter 2) from the crystal-field theory, in our case we observe a significant departure from g_e suggesting that a d_{z^2} ground state is unlikely. Although the actual situation may be more complicated than what described in those equations due to lower local symmetry, these may provide some useful guidelines to determine the ground state of the Ti(III) species. In particular, based

on this analysis, Ti(III)-**A** ($g_{\perp} > g_{\parallel}$) is amenable to a $d_{x^2-y^2}$ or d_{xy} ground state associated to tetrahedral elongation or octahedral coordination respectively, while Ti(III)-**B** ($g_{\perp} < g_{\parallel}$) can be associated to a d_{xy} ground state associated to an octahedral coordination, provided that $\delta_2 > 4\delta_1$, where δ_1 and δ_2 are the separation energies between the e_g (tetragonal distortion) and the t_{2g} (octahedral field) d orbitals. In other words, Ti(III)-**B** can only be associated to a pseudo octahedral coordination, while Ti(III)-**A** may be related to both octahedral or tetrahedral coordination.

Table 4.3 Spin Hamiltonian parameters obtained from the simulation of the EPR spectra of Ti(III) in the three samples before activation. The relative abundance of the different species refers to the X-band CW-EPR experiments.

Sample	Species	g_x	g_y	g_z	%ab
MgCl ₂ /TiCl ₄	A	1.977(3)	1.971(8)	1.936(0)	14.10
	B	1.88(0)	1.89(9)	1.954(4)	84.70
	R	2.003(4)	2.003(4)	2.003(4)	1.20
MgCl ₂ /TiCl ₄	A	1.977(3)	1.977(3)	1.936(0)	8.30
aliphatic	A'	1.969(3)	1.966(0)	1.946(3)	41.50
monoether	C	1.8(7)	1.8(7)	1.8(7)	49.80
	R	2.003(7)	2.003(7)	2.003(7)	0.40
MgCl ₂ /TiCl ₄	A	1.977(3)	1.977(3)	1.936(0)	0.40
aliphatic	B	1.88(0)	1.89(9)	1.954(4)	94.20
diester	D	1.954(5)	1.925(8)	1.849(0)	3.00
	R	2.003(4)	2.003(4)	2.003(4)	2.40

To obtain more information on the nature of these species, the binary sample was treated intentionally with TiCl₃, added during the synthesis of the pre-catalyst. Our interest in performing this experiment, was to identify whether the added Ti(III) species before activation would lead to the formation of Ti(III) species with the same nature as those we observed. The added amount of TiCl₃ was set to a molar ratio Mg/Ti(III) = 40:1 and Mg/Ti(III) = 20:1. In the X-band CW-EPR spectra we observe an increase in the intensity

of the Ti(III) spectra, being the highest for the sample with molar ratio $\text{Mg}/\text{Ti(III)}=20:1$ (Figure 4.6). The intensity of the radical species remained unchanged in both cases.

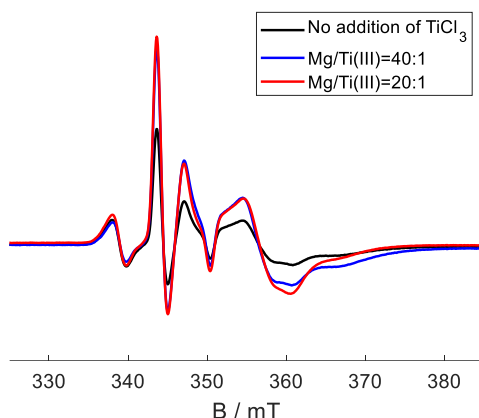


Figure 4.6 CW-EPR spectra of the binary system $\text{MgCl}_2/\text{TiCl}_4$ without the addition of TiCl_3 (black spectra), with the addition of TiCl_3 in ratio $\text{Mg}/\text{Ti(III)}=40:1$ (blue spectra) and ratio $\text{Mg}/\text{Ti(III)}=20:1$ (red spectra). All spectra were recorded with the same spectrometer settings at 50 K and X-band frequency ($\nu_{\text{mw}} = 9.44$ GHz)

Moreover, we performed EPR quantification and compared these results with the “wet chemistry” results obtained in the BPI laboratories (Table 4.4). The addition of TiCl_3 in the binary system in a molar ratio $\text{Mg}:\text{Ti(III)}=40:1$, shows an increase in the amount of EPR-active Ti(III) species from 0.426%, for the system without intentionally added Ti(III), to 0.971%. The addition of a higher amount of TiCl_3 , in molar ratio $\text{Mg}:\text{Ti(III)}=20:1$, leads to an increase of the Ti(III) amount to 0.729%. Nevertheless, this amount is smaller than in the case of the lower added amount of TiCl_3 ($\text{Mg}:\text{Ti(III)}=40:1$). The same behaviour is observed from the “wet chemistry” results of BPI shown in Table 4.4.

In order to investigate in more detail the nature of the Ti(III) species, ESEEM and HYSCORE experiments were performed. A first hint about the magnetic nuclei surrounding the Ti(III) is obtained from Q-band field-dependent three-pulse ESEEM (Figure 4.7).

Table 4.4 Quantification results from EPR spectroscopy and comparison with the chemical analysis data obtained from the BPI laboratories. Ti(Tot.) %wt represents the total amount of Ti (Ti(IV) and Ti(III)) added to the system during synthesis, Ti(III) %wt from BPI results represents the amount from wet chemistry results (isolated and non-isolated Ti(III)), and EPR Ti(III) %wt represents the amount of EPR active Ti(III) species.

Sample composition	Results from BPI			EPR results		
	Ti(Tot.) %wt	Ti(III) %wt	Ti(III)/Ti(Tot.)	Ti(III) %wt	EPR Ti(III)/Ti(Tot.) from BPI	EPR Ti(III)/Ti(III) from BP
MgCl ₂ /TiCl ₄	4.6	0.8	0.17	2×10^{-2}	4.26×10^{-1}	2.45×10^{-2}
MgCl ₂ /TiCl ₄ + added Ti(III) {Mg/Ti(III) = 40 mol/mol}	4.8	0.7	0.14	4.7×10^{-2}	9.71×10^{-1}	7.25×10^{-2}
TiCl ₄ /MgCl ₂ + added Ti(III) {Mg/Ti(III) = 20 mol/mol}	4.9	0.5	0.10	3.6×10^{-2}	7.29×10^{-1}	7.15×10^{-2}

The spectrum shows a rich ESEEM pattern with features in the range from zero to about 10-15 MHz, across the entire spectrum, indicating the presence of hyperfine interactions. The only magnetically active nuclei in the sample are ¹H and ^{35,37}Cl, all other nuclei having too low natural abundance. Given that the ¹H Larmor frequency at the operational field is in the range of 51-54 MHz, the complex spectral pattern is due to the interaction of the unpaired electron with ^{35,37}Cl nuclei ($I=3/2$). The three-pulse ESEEM spectra were recorded as a function of the inter-pulse distance τ as shown in Figure 4.7b for an example taken at a field position corresponding to the narrowest feature of the ESE-detected EPR spectrum ($B_0 = 1227.4$ mT). The sum projected three-pulse ESEEM spectrum (bottom Figure 4.7b) presents three series of peaks with different amplitudes and widths. The narrow peak at $\nu = 4.2$ MHz corresponds to the Larmor frequency of ³⁷Cl and is due to coupling with remote (matrix) Cl nuclei. The remaining peaks at 7.1 MHz and 13.3 MHz must arise from the interaction between the unpaired electron and chlorines directly coordinated to Ti(III). To further elucidate the nature of these transitions, HYSORE experiments were performed at this field and at another field position ($B_0 = 1246.0$ mT).

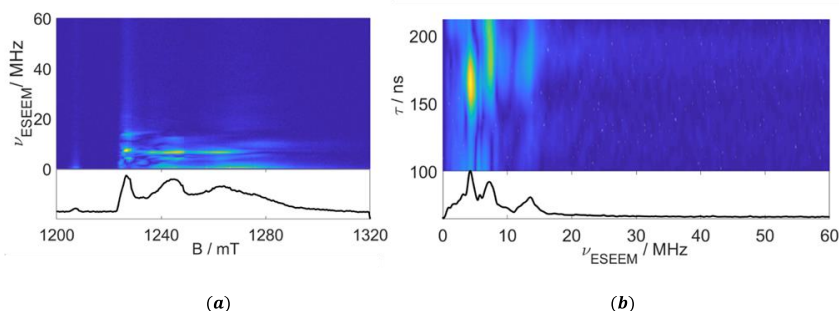


Figure 4.7 a) Three-pulse ESEEM spectrum plotted in the frequency domain versus the resonant magnetic field, b) Three pulse ESEEM vs the interpulse delay τ taken at $B_0 = 1227.4$ mT. The spectra were recorded at 10 K and Q-band frequency ($\nu = 33.8$ GHz).

The HYSCORE spectra recorded at two different magnetic field settings are shown in Figure 4.8. The magnetic fields at which the two HYSCORE experiments were performed are shown in the insets of Figure 4.8. Based on the three-pulse ESEEM vs τ experiment (Figure 4.7b) the spectra were recorded with an interpulse delay $\tau = 188$ ns which limits suppression effects of the relevant ESEEM frequencies. The spectrum recorded at a field position coinciding with that of the ESEEM spectrum of Figure 4.7 b ($B_0 = 1227.4$ mT, corresponding to the g_x, g_y components of species Ti(III)-A), shows a complex set of cross peaks in the (+,+) quadrant, arising from the interaction of $^{37,35}\text{Cl}$ nuclei. A series of peaks appearing at frequencies (1.9, 13.3) MHz (13.3, 1.9) MHz and (7.1, 13.3) MHz and (13.3, 7.1) MHz in the bi-dimensional spectrum of Figure 4.8a (indicated by arrows) is assigned to cross peaks between single and double-quantum transitions.

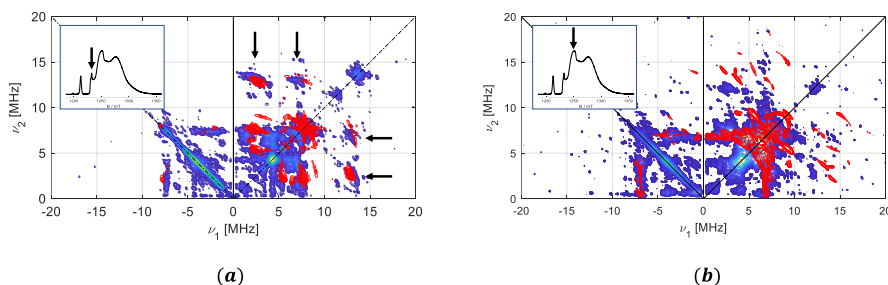


Figure 4.8 Q-band ($\nu = 33.8$ GHz) HYSCORE spectrum recorded at a) $B_0 = 1227.4$ mT and b) $B_0 = 1246.0$ mT. Spectra were recorded at 10 K and an interpulse delay $\tau = 188$ ns. The simulations were obtained with the following parameters $\mathbf{A} = [-5 \ -5 \ 8.5]$ MHz, $[\alpha, \beta, \gamma] = [0 \ 10 \ 0]$, $e^2qQ/h = 8.8$ MHz, $\eta = 0$, $[\alpha, \beta, \gamma] = [0 \ 20 \ 0]$, where α, β, γ are the Euler angles in degree, relating the orientation of the $\mathbf{A}$ and $\mathbf{Q}$ tensor axes with respect to the $\mathbf{g}$ -tensor frame. The signal at 5 MHz is attributed to remote $^{35,37}\text{Cl}$. The arrows in Figure 4.8a indicate the cross peaks between single and double quantum transitions.

The narrow peaks and high resolution of the spectra points to well defined species, reminiscent of molecular systems in solution.

The HYSCORE spectrum in Figure 4.8b was recorded at $B_0 = 1246.0$ mT, corresponding to the g_z component of species Ti(III)-**A**, partially overlapped with that of Ti(III)-**B**, leading to the particularly complex situation where contributions from both species are simultaneously present. Despite the resolution, the extraction of the spin Hamiltonian parameters is not an easy task in light of the significant anisotropic hyperfine interaction and fairly large nuclear quadrupole couplings expected for Ti-Cl species, [183,227]. Our approach to the analysis, therefore, was to simulate the HYSCORE spectra, taking reliable data previously obtained by some of us in the case of TiCl_3 molecular complexes and validated by DFT calculations [183,227] as an initial approximation and trying to reach an agreement between the simulated and experimental spectra. The nuclear quadrupole interaction parameters were varied in broad limits to obtain an understanding of the strength of this interaction. Obviously, given all the above considerations, we did not aspire to really fit the experimental HYSCORE spectra, but rather, to achieve a qualitative resemblance between the simulations and experiments. We find that the experimental spectra taken at the two observer positions can be reasonably simulated with a single set of hyperfine and quadrupole values, corresponding to values determined for TiCl_3 molecular species and Ti(III) in ZN catalysts previously studied by some of us [183,227]. An example of a tentative simulation is shown in red in Figure 4.8, superimposed to the experimental spectra. The simulation was obtained introducing a ^{35}Cl hyperfine-interaction tensor characterized by a large dipolar component and relatively small Fermi contact contribution ($\mathbf{A} = [-5 \ -5 \ +8.5]$ MHz), and using nuclear quadrupole interaction value (e^2qQ/h) of 8.8 MHz. Satisfactory simulations could also be obtained when varying the latter parameter in the range 7–12 MHz. These values are lower than those recently reported in a detailed NMR study for TiCl_3 ($e^2qQ/h = 14.5$ MHz) [275], but are consistent with values obtained for an activated ZNC [227].

To monitor the ^1H nuclear transitions, not observable in the recorded HYSCORE spectra at Q-band, two-pulse ESEEM spectra (Figure 4.9) were recorded at X-band at different field positions corresponding to the spectral contributions of the organic radical and the Ti(III) species present in the binary system. The spectra show a series of peaks between 0-5 MHz indicating an interaction of the Ti(III) species with $^{35,37}\text{Cl}$, already observed in the three-pulse ESEEM and HYSCORE spectra at Q-band. The peak at 15 MHz at the magnetic field position of the radical ($B_0 = 347.3$ mT) correlates to the Larmor frequency of ^1H nuclei (Figure 4.9a). The sum frequencies ($\nu_+ \approx 2 \nu_{\text{H}}$) are also detectable along with the Larmor frequency of the proton. No observation could be made for the interaction of Ti(III) species with ^1H nuclei (Figure 4.9b), indicating that the organic molecules remain

far from the Ti(III)-A species in this sample. At higher field settings (Figure 4.9c,d) a signal is observed at ν_H , although it is not unambiguously clear whether this is due to an interaction of Ti(III)-B with a proton or whether the signals are due to the $^{35,37}\text{Cl}$ nuclear transitions that accidentally match the proton Larmor frequency.

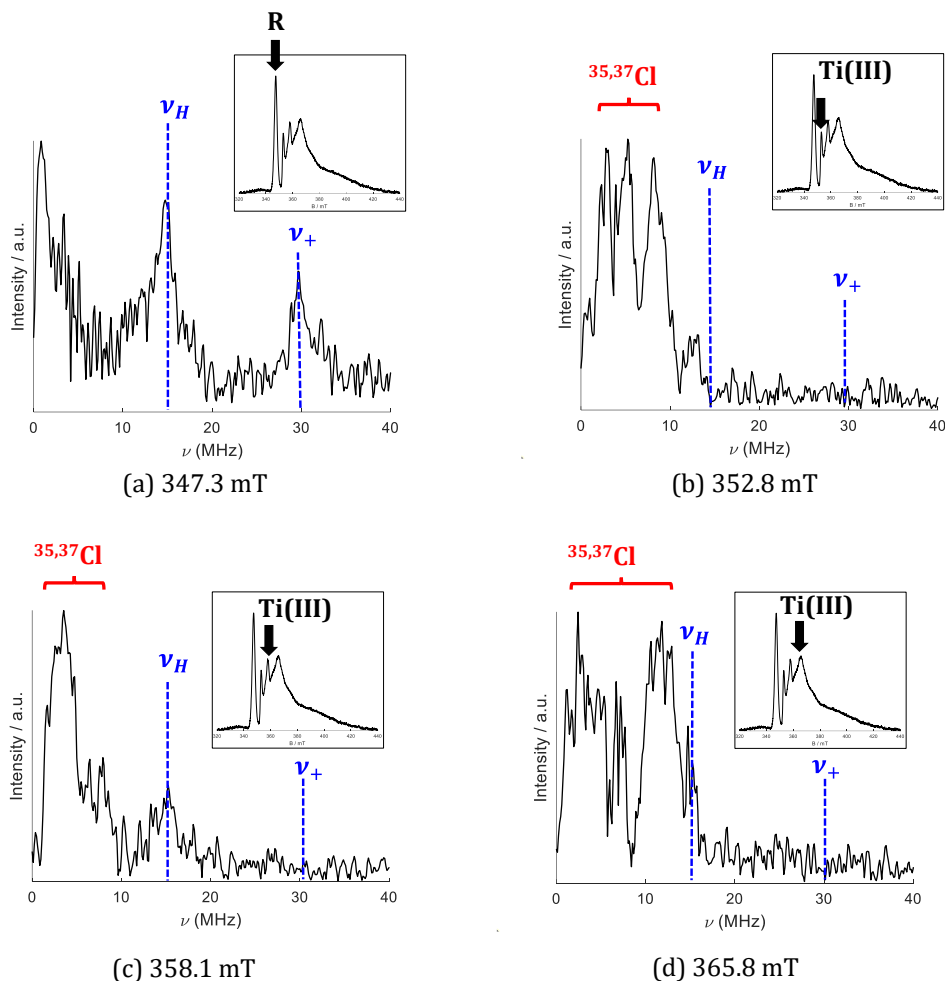


Figure 4.9 Two-pulse ESEEM spectra taken at different magnetic field positions (a) $B_0 = 347.3$ mT corresponding to an organic radical species, and (b) $B_0 = 352.8$ mT ($g = 1.976$), (c) $B_0 = 358.1$ mT ($g = 1.947$) and (d) $B_0 = 365.8$ mT ($g = 1.902$) corresponding to Ti(III) species. The spectra were recorded at 10 K at X-band frequency ($\nu = 9.76$ GHz). The proton Larmor frequency (ν_H) and the sum frequency $\nu_+ (\approx 2\nu_H)$ are represented in blue, while peaks arising from interaction with chlorine nuclei are represented in red.

In summary, the following conclusions can be drawn for the hyperfine and nuclear quadrupole interactions of Ti(III)-Cl species in the $\text{MgCl}_2/\text{TiCl}_4$ binary system. The anisotropic hyperfine tensor is similar to that estimated and computed for molecular TiCl_3

species in solution [183], with a dipolar component T of the order of 5 MHz and small a_{iso} of less than 1 MHz. The nuclear quadrupole interaction tensor is close to axial and the coupling constant e^2qQ/h is of the order of 9 ± 2 MHz with its main axis nearly parallel to the main axis of the anisotropic hyperfine tensor. No interaction of Ti(III) species with ^1H nuclei has been observed for Ti(III)-**A**, but a weak 3-pulse ESEEM signal around the ^1H Larmor at higher field setting may point to an interaction with a ^1H nucleus in Ti(III)-**B**.

4.2.1.2. $\text{MgCl}_2/\text{TiCl}_4/\text{monoether}$ ternary system

In the case of ternary system $\text{MgCl}_2/\text{TiCl}_4/\text{aliphatic monoether}$, the presence of the Lewis base, induces a significant change in the EPR spectrum. The simulation of the X-band CW-EPR and Q-band ESE-EPR spectra are shown in Figure 4.10 and indicate a substantial suppression of the Ti(III)-**B** species and appearance of a new and relatively broad signal centered at $g = 1.87$ and indicated as Ti(III)-**C** in Figure 4.10. Given the broad linewidth of this signal no significant details can be extracted from the simulation and this species will not be discussed further.

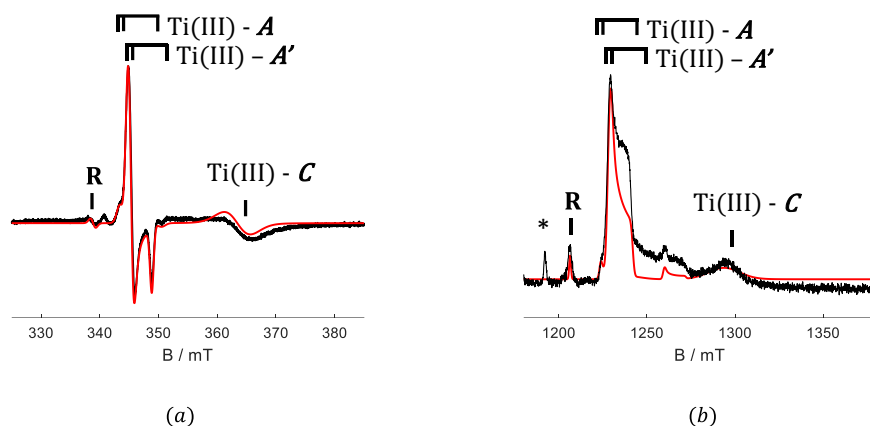


Figure 4.10 Experimental (black) and computer-simulated (red) EPR spectra of Ti(III) species in the $\text{MgCl}_2/\text{TiCl}_4/\text{monoether}$ ternary system. A) X-band ($\nu = 9.5$ GHz) CW-EPR recorded at 77 K; b) Q-band ($\nu = 33.8$ GHz) ESE detected EPR recorded at 50 K. The stick diagrams indicate the two Ti species, **R** the organic radical and ***** a spurious signal of the Q-band cavity. The g -values for species Ti(III)-**A**, Ti(III)-**A'** and Ti(III)-**C** are reported in Table 4.3

Moreover, the principal g values (listed in Table 4.3) of species Ti(III)-**A'** are slightly different from Ti(III)-**A** indicating a slight modification in the local coordination environment. The g -tensor components of these two species are indicated in Figure 4.10 by a stick diagram.

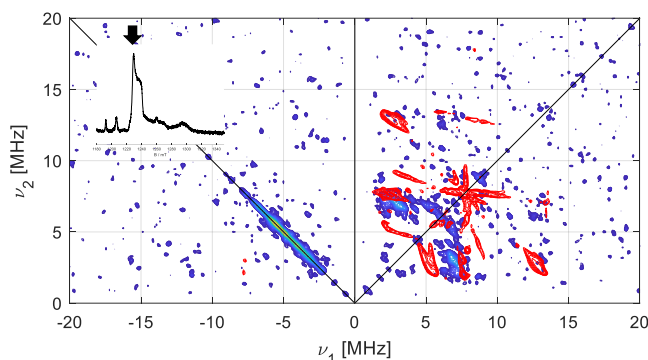


Figure 4.11 HYSORE spectrum of the ternary system $\text{MgCl}_2/\text{TiCl}_4/\text{monoether}$ recorded at $B_0 = 1227.4$ mT and with an interpulse delay $\tau = 200$ ns. Due to the low signal intensity, the spectrum was symmetrized to better identify the correlation peaks. The simulation was obtained using the same parameters reported in Figure 4.8, with the intensity adjusted to match that of the experimental spectrum. The spectra were recorded at 10 K and Q-band frequency ($\nu = 33.8$ GHz).

The Q-band HYSORE spectrum recorded at the maximum echo intensity (corresponding to the $g_{\perp}$ component of the EPR spectrum of species Ti(III)-A') is shown in Figure 4.11. At variance with the case of the binary system, the spectrum is characterized by a pair of relatively weak cross peaks at (3, 7.1) MHz and (7.1, 3) MHz, which correspond to cross-peaks between single-quantum frequencies observed in the spectrum of the binary system. The overall intensity of the HYSORE spectrum is lower than the one observed for the binary system and the presence of correlation peaks between the single and double-quantum frequencies are barely observable. The lower intensity of the $^{35,37}\text{Cl}$ cross peaks may be ascribed to a reduced number of coordinated chlorine to the Ti(III) ion, which may be an indication of the presence of the Lewis base in the first coordination sphere of Ti(III) . This would concur with the slight g -shift observed in the EPR spectrum. Indeed the two-pulse ESEEM spectra (Figure 4.12), recorded at X-band, now reveal unambiguously an interaction with ^1H nuclei for all magnetic field settings corresponding to contributions of Ti(III) species, which contrasts the case of the binary system $\text{MgCl}_2/\text{TiCl}_4$. This may be linked to the decrease in the peak intensity of the $^{35,37}\text{Cl}$ HYSORE peaks (Figure 4.11). It also confirms that the change in the EPR features between Ti(III)-A and Ti(III)-A' is due to ligation of the Lewis base, since Ti(III)-A does not interact with a proton (Figure 4.9b).

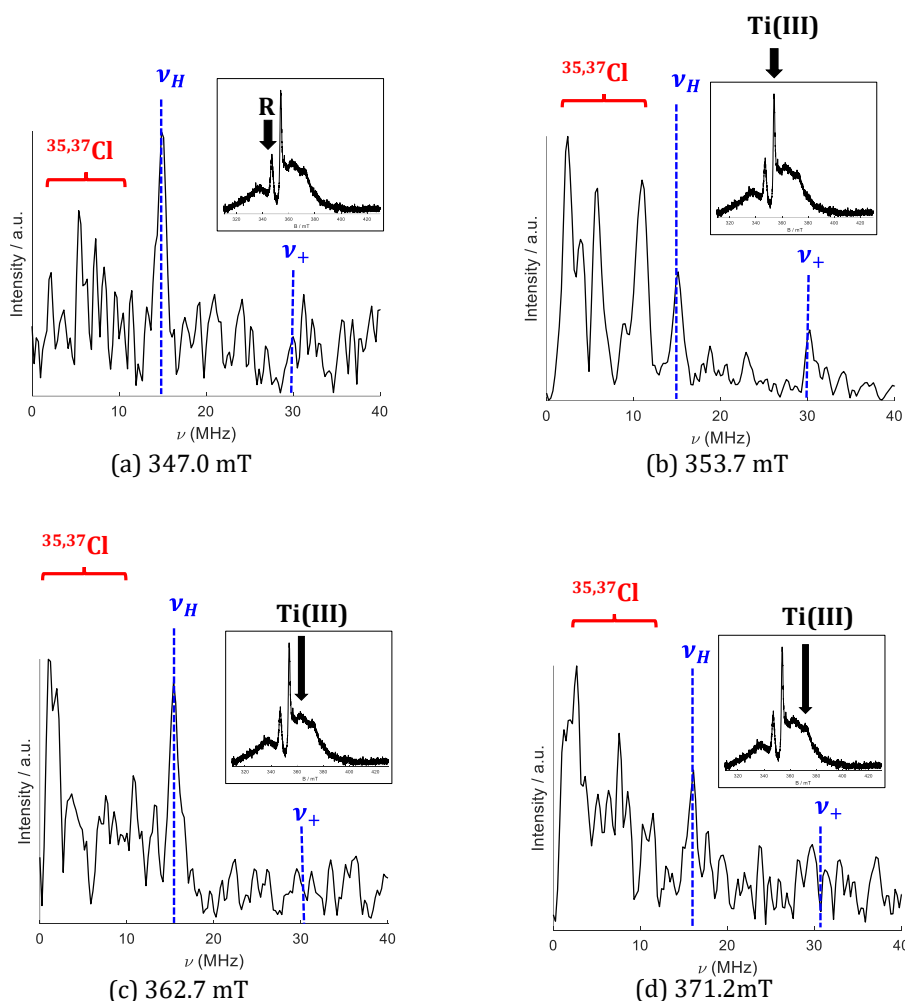


Figure 4.12 Two-pulse ESEEM spectrum taken at different magnetic field positions: (a) $B_0 = 347.0$ mT corresponding to an organic radical species, and (b) $B_0 = 353.7$ mT ($g = 1.971$), (c) $B_0 = 362.7$ mT ($g = 1.922$) and (d) $B_0 = 371.2$ mT ($g = 1.878$) corresponding to Ti(III) species. The spectra were recorded at 10 K at X-band frequency ($\nu = 9.76$ GHz). The proton Larmor frequency (ν_H) and the sum peaks $\nu_+ (\approx 2\nu_H)$ are represented in blue, while peaks arising from interaction with chlorine nuclei are represented in red.

Two-pulse-ESEEM experiments taken at observer positions corresponding to the spectral contributions of the radical and the Ti(III) species (Figure 4.12) show the presence of signals at the ^1H Larmor frequency. The observation of ^1H signals at magnetic field settings corresponding to the Ti(III) resonance, indicate that, at variance with the previous case, the Lewis base (monoether) remains in the proximity of the Ti(III) for all Ti(III) species, in agreement with the modified g -tensor of Ti(III)-A' compared to Ti(III)-A.

4.2.1.3. $\text{MgCl}_2/\text{TiCl}_4/\text{diester}$ ternary system

Finally, in the case of the ternary system $\text{MgCl}_2/\text{TiCl}_4/\text{diester}$, the EPR spectra presented in Figure 4.13, gives evidence of the selective suppression of the Ti(III)-A species. The spectrum is dominated by the broad resonances of the quasi-axial species Ti(III)-B , which accounts for the 94% of the total spectral intensity. The simulation of the spectrum also indicates the presence of additional species, with abundance of the order of 3% (species Ti(III)-D). The spin-Hamiltonian parameters and the relative abundance of the species obtained from the simulation are collected in Table 4.3.

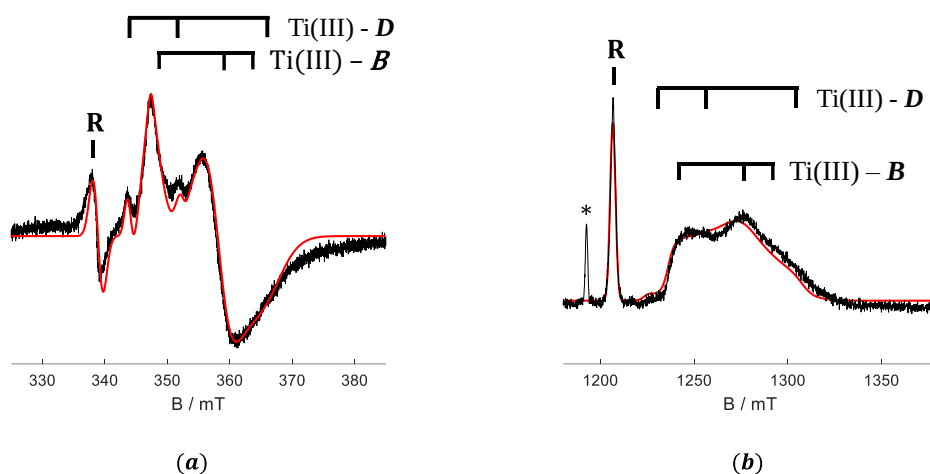


Figure 4.13 Experimental (black) and computer-simulated (red) EPR spectra of Ti(III) species in the $\text{MgCl}_2/\text{TiCl}_4/\text{diester}$ ternary system. (a) X-band ($\nu = 9.5$ GHz) CW-EPR recorded at 77 K; (b) Q-band ($\nu = 33.8$ GHz) ESE-detected EPR recorded at 50 K. The stick diagrams indicate the two Ti species, R the organic radical and * a spurious signal of the Q-band cavity. The g -values for species Ti(III)-A , Ti(III)-A' and Ti(III)-C are reported in Table 4.3

The addition of TiCl_3 during the synthesis of the ternary system with a diester in molar ratio $\text{Mg}:\text{Ti(III)}=50:1$ led to an increase in the intensity for the same Ti(III) species, present in the system before any treatment with TiCl_3 or co-catalyst. The intensity for the radical species remained unchanged (Figure 4.14). The EPR quantification results reveal an increase of the Ti(III) amount from 0.84% to 2.06% upon the addition of TiCl_3 . Same behavior is observed from the “wet chemistry” results from the BPI laboratories (Table 4.5).

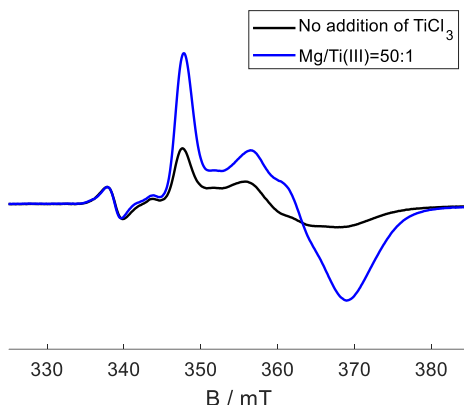


Figure 4.14 X-band CW-EPR spectra of the ternary system $\text{MgCl}_2/\text{TiCl}_4/\text{diester}$ without the addition of TiCl_3 (black spectra), with the addition of TiCl_3 in ratio $\text{Mg}/\text{Ti(III)}=50:1$ (blue spectra). All spectra were recorded with the same spectrometer settings at 50 K and X-band frequency ($\nu = 9.44$ GHz).

Table 4.5 Quantification results from EPR spectroscopy and comparison with the chemical analysis data obtained from the BPI laboratories. Ti(Tot.) %wt represents the total amount of Ti (Ti(IV) and Ti(III)) added to the system during synthesis, Ti(III) %wt from BPI results represents the amount from wet chemistry results (isolated and non-isolated Ti(III)), and EPR Ti(III) %wt represents the amount of EPR active Ti(III) species

$\text{MgCl}_2/\text{TiCl}_4/\text{diester}$	Results from BPI			EPR results		
	Ti(Tot.) %wt	Ti(III) %wt	$\text{Ti(III)}/\text{Ti(Tot.)}$	Ti(III) %wt	EPR $\text{Ti(III)}/\text{Ti(Tot.)}$ from BPI	EPR $\text{Ti(III)}/\text{Ti(III)}$ from BPI
$\text{MgCl}_2/\text{TiCl}_4/\text{diester}$	3.1	0.4	0.12	2.6×10^{-2}	8.4×10^{-3}	6.51×10^{-2}
$\text{MgCl}_2/\text{TiCl}_4/\text{diester} +$ added Ti(III) { $\text{Mg}/\text{Ti(III)} = 50$ mol/mol}	3.4	0.4	0.11	7×10^{-2}	2.06×10^{-2}	17.5×10^{-2}

The Q-band ESE-detected EPR spectrum (Figure 4.13) has a relatively low intensity (weak spin echo signal) so that the HYSCORE spectra in this case were non-informative. Attempts to extract information from two-pulse ESEEM spectra, (Figure 4.15) were also frustrated by the observation of very weakly modulated echo decays and correspondingly weak and non-informative frequency-domain spectra. The high peaks at very low frequency may be a result of poor background removal. An example of the a time-domain spectrum recorded at $B_0 = 371.2$ mT is given in Figure 4.16.

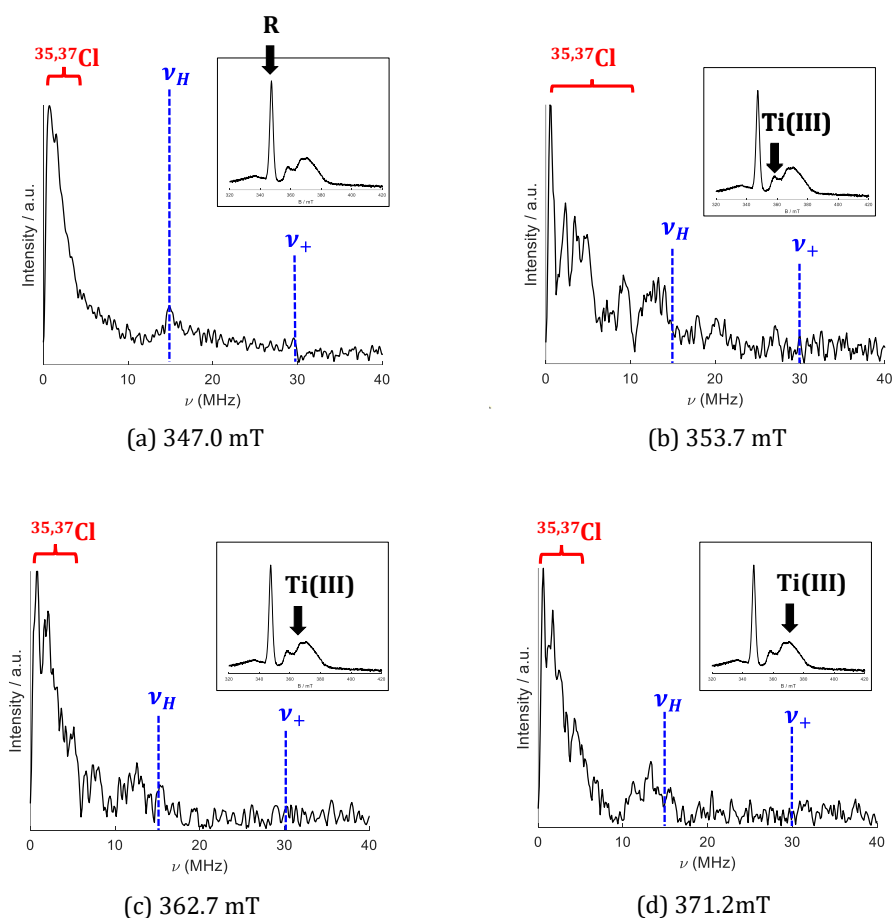


Figure 4.15 Two-pulse ESEEM spectrum plotted in the frequency domain taken at different magnetic field positions corresponding to (a) $B_0 = 347.0$ mT corresponding to radical species, and (b) $B_0 = 353.7$ mT ($g = 1.971$), (c) $B_0 = 362.7$ mT ($g = 1.911$) and (d) $B_0 = 371.2$ mT ($g = 1.878$) corresponding to Ti(III) species. The spectra were recorded at 10 K and X-band frequency ($\nu = 9.76$ GHz). The proton Larmor frequency (ν_H) and the sum peaks $\nu_+ (\approx 2\nu_H)$ are represented in blue, while peaks arising from chlorine interaction are represented in red.

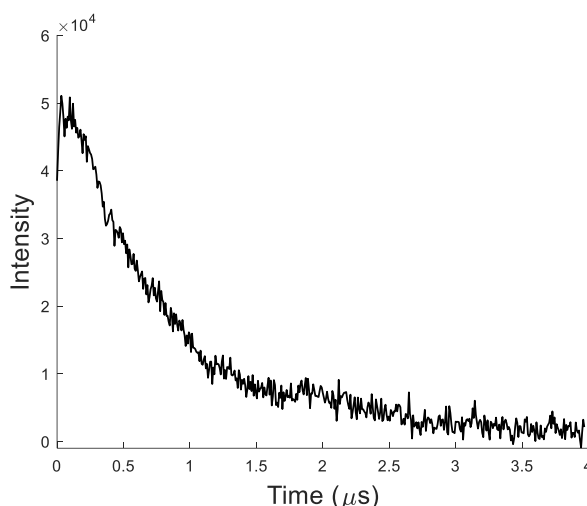


Figure 4.16 The two-pulse ESEEM spectrum plotted in the time domain taken at $B_0 = 371.2$ mT. The spectrum was recorded at 10 K and X-band frequency ($\nu = 9.7$ GHz).

4.2.2. Ziegler-Natta pre-catalyst systems containing a diether as an internal Lewis base

In section 4.2.1 we demonstrated how different Lewis bases, containing different functional groups (monoether and diester), influence the coordination of Ti(III) species on the surface of a highly active MgCl_2 support in pre-active ZNCs. In this section we extend our study to two pre-catalysts of the so-called "fifth generation" of Ziegler-Natta systems (named **A1** and **B1**), both containing a diether as an internal Lewis base ($\text{MgCl}_2/\text{TiCl}_4/\text{diether}$). The only difference between the two pre-catalysts is the diether's structure (structural information is confidential). The influence of different substituent groups, ring size, and steric effects of Lewis bases containing the same functional group has already attracted attention in the industrial sector. Cavallo *et al.* [276] have reported that the formation enthalpies and entropies in a series of diether complexes are influenced by structural factors like the length of the chain between the two oxygens. Little is known, however, on how these factors affect the distribution of surface paramagnetic species.

The X-band CW-EPR spectra show a complex powder pattern indicating the presence of at least two Ti(III) species and a radical species before any activation in both systems (**A1** and **B1**, Figure 4.17). The main difference between the two spectra is the presence of an abundant radical species in pre-catalyst **A1**, while in pre-catalyst **B1**, this is practically undetectable. The spectral shape for the Ti(III) species is similar for the two

samples pointing to a similar local environment of the Ti(III) species. The spin Hamiltonian parameters extracted from the simulation of the EPR spectra taken at X- and Q-band frequencies are listed in Table 4.6.

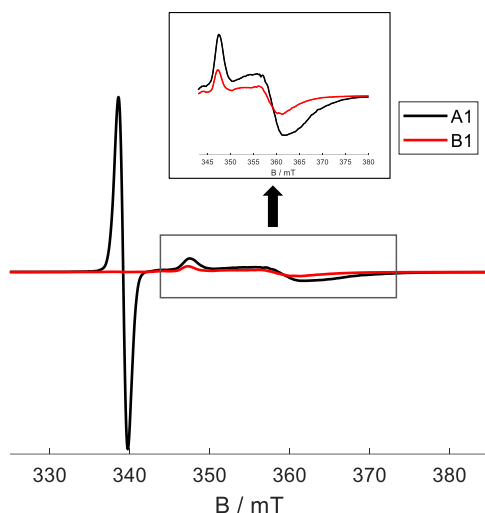


Figure 4.17 CW-EPR spectra of samples **A1** (black) and **B1** (red) before activation. All spectra are measured with the same spectrometer settings, at 77 K (liquid nitrogen) and X-band frequency ($\nu = 9.76$ GHz). The spectra are not normalized.

The X-band CW-EPR spectrum of sample **A1** is again presented in Figure 4.18a, with the corresponding Q-band ESE-detected EPR spectrum in Figure 4.18b. The experimental spectra are presented in black, while simulations are in red. The most abundant species (**S1**) is characterized by a nearly axial g -tensor ($g_x = 1.862(5)$, $g_y = 1.888(4)$, and $g_z = 1.950(1)$). These values are typical for Ti(III) species in these systems and similar to those reported in section 4.2.1.1 and to those observed by Morra *et al.* for an activated catalyst [235]. Inspection of Table 6 shows that species Ti(III)-**S1** are characterized by $g_{\perp} < g_{\parallel}$ indicative of a d_{xy} ground state associated to distorted octahedral coordination. Species Ti(III)-**S2** is present in the sample as minority species and is characterized by a rhombic g -tensor ($g_x = 1.972(1)$, $g_y = 1.943(5)$, $g_z = 1.880(1)$) suggesting a less symmetric environment. A very intense signal at $g = 2.002(3)$ is also present, related to an abundant organic radical species.

In order to extract the principal g -values for the radical and the Ti(III) species two spectra have been recorded at X-band and two ESE-detected EPR spectra at Q-band frequency at different powers. The EPR signal of the radical species saturates at microwave powers higher than 0.01084 mW, while the EPR signal of the Ti(III) species are far less visible at this power. Therefore, the X-band spectra have been measured at 1.084 mW, used to

extract the g -values for Ti(III) species (the scaled spectra in Figure 4.18a), and at 0.01084 mW (the spectra in Figure 4.18a), used to obtain the g -values for the radical species. The X-band spectra have been measured at 77 K. The ESE-detected EPR spectra have been measured at 10 K, to obtain the g -values for Ti(III) species (the scaled spectra in Figure 4.18b), and at 50 K (the spectra in Figure 4.18b), to obtain the g -values for the radical species.

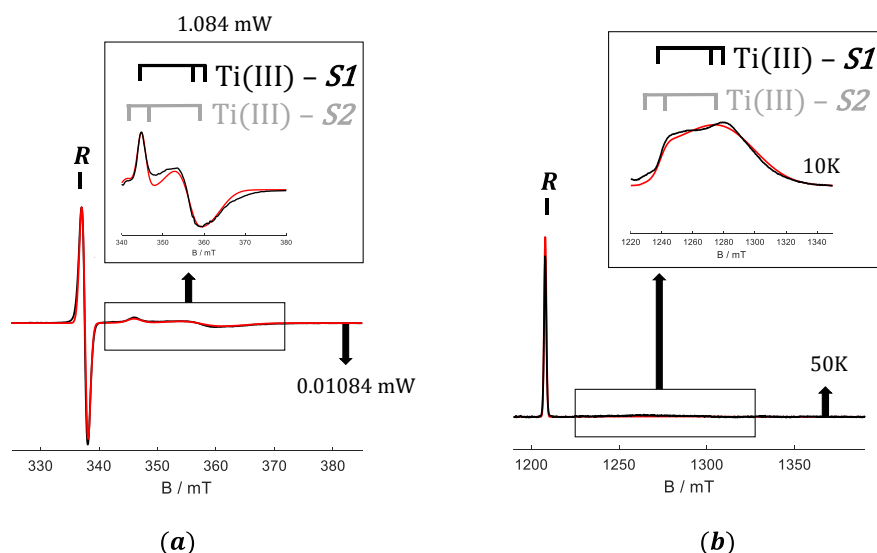


Figure 4.18 Experimental (black) and simulated (red) spectra of sample **A1**. (a) CW-EPR spectra at X-band frequency ($\nu = 9.7$ GHz), measured and simulated at two powers at 77 K, at 1.084 mW to obtain the spin Hamiltonian parameters for Ti(III), and at 0.01084 mW for the radical, and (b) ESE-detected EPR spectra at Q-band frequency ($\nu = 33.8$ GHz) recorded at 10 K for the Ti(III) species and 50 K for the radical. The stick diagrams indicate the two Ti species, and R the organic radical.

The spectrum of pre-catalyst **B1** (Figure 4.19), is also characterized by the presence of two Ti(III) species with different g -tensors (Table 4.6). One of the two species corresponds to species **S1** observed in pre-catalyst **A1**, while the second Ti(III) species (Ti(III)-**S3**) is characterized by a pseudo axial g -tensor with $g_{\parallel} < g_{\perp}$, which is opposite to what observed in sample **A1**. Interestingly, the radical signal ($g = 2.002(3)$) is barely detected in this sample.

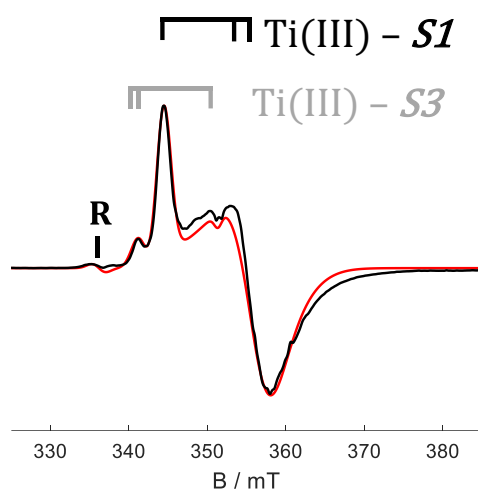


Figure 4.19 Experimental (black) and simulated (red) spectra of pre-catalyst **B1** at X-band frequency ($\nu = 9.7$ GHz) at 77 K. The spectra are normalized.

Table 4.6 Spin Hamiltonian parameters extracted from computer simulation of the experimental spectra for pre-catalyst **A1** and **B1**. The relative abundance of the different species refers to the X-band ($\nu = 9.76$ GHz) CW-EPR experiments recorded at 77 K.

Sample	Species	g_x	g_y	g_z	%ab
Pre-catalyst A1 MgCl ₂ /TiCl ₄ /diether	S1	1.859(5)	1.891(4)	1.952(3)	67.25
	Ti(III) S2	1.972(1)	1.943(5)	1.880(0)	3.5
	R	2.002(3)	2.002(3)	2.002(3)	29.24
Pre-catalyst B1 MgCl ₂ /TiCl ₄ /diether	S1	1.883(2)	1.888(4)	1.952(3)	96,7
	S3	1.972(1)	1.969(2)	1.916(3)	3.14
	Ti(III) R	2.002(3)	2.002(3)	2.002(3)	0.14

To obtain information about the surrounding environment of the paramagnetic species present in the two samples, advanced pulse EPR experiments at X- and Q-band have been performed. An intense spin echo signal was observed for the radical species in sample **A1**, while no echo was detected for Ti(III) species. Pre-catalyst **B1**, did not present any echo signal, indicating that fast relaxation mechanisms, possibly related to a high local concentration of Ti(III), are present. Advanced pulse EPR experiments were thus performed on pre-catalyst **A1**, in an effort to elicit more information about the local environment of the radical species.

The only magnetic nuclei present in the sample before any activation with TEA are ^1H , ^{13}C , and $^{35,37}\text{Cl}$. Six-pulse HYSCORE, Mims and Davies ENDOR at Q-band frequency,

and four-pulse HYSCORE and matched HYSCORE experiments at X-band frequency have been performed on sample **A1** to extract the spin-Hamiltonian information for the interaction with these surrounding magnetic nuclei.

Given the long relaxation time of the organic radical species, X-band HYSCORE experiments could be performed at room temperature. A representative X-band ^1H HYSCORE spectrum is reported in Figure 4.20a. The spectrum is dominated by an extended ridge centered at the ^1H nuclear Larmor frequency (14.75 MHz), with a maximum width of approximately 12 MHz. The spectrum was analyzed using an approach proposed by Dikanov *et al* [219,277]. Assuming an axial hyperfine interaction with isotropic component a and anisotropic tensor $(-T, -T, 2T)$, in the powder ^1H HYSCORE spectrum can be described as follows by [278]:

$$\nu_{\beta} = \{Q_{\beta} \nu_{\alpha}^2 + G_{\beta}\}^{1/2} \quad (4.1)$$

where:

$$Q_{\beta} = \frac{T + 2a + 4\nu_1}{T + 2a - 4\nu_1} \quad (4.2)$$

and:

$$G_{\beta} = -2\nu_1 \left(\frac{4\nu_1^2 - a^2 + 2T^2 - aT}{T + 2a - 4\nu_1} \right) \quad (4.3)$$

where ν_1 is the nuclear Zeeman frequency. When the square of each pair of cross-peak frequencies is plotted as ν_{β}^2 vs. ν_{α}^2 (Figure 4.20b), the contour line shape is transformed into a straight line whose slope and intercept are given by Q_{β} and G_{β} , respectively.

Using the Dikanov analysis two possible sets of (a_{iso}, T) were calculated, (9 MHz, 3 MHz) and (12 MHz, -3 MHz). These were used to simulate the HYSCORE spectra recorded at room temperature (Figure 4.20a) and the matched HYSCORE spectra at 80 K (Figure 4.21a), both recorded at X-band. The best fitting was achieved for the values of the set (9 MHz, 3 MHz) refined to $a_{\text{iso}} = 8$ MHz and $T = 3$ MHz.

A more detailed analysis of ^1H hyperfine interactions was obtained by low temperature Davies and Mims-ENDOR experiments performed at Q-band frequency. The spectra recorded at 30 K and the corresponding simulations are reported in Figure 4.21.

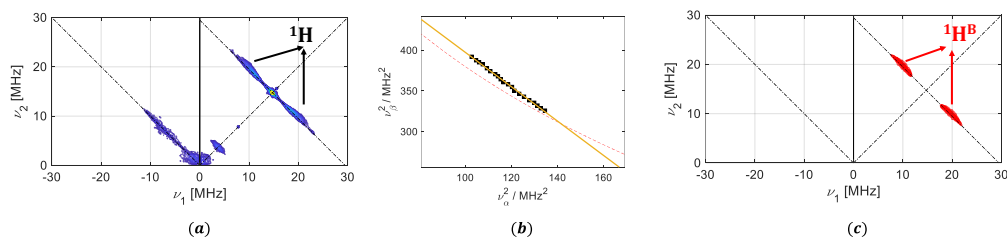


Figure 4.20 (a) X-band ($\nu = 9.5$ GHz) ^1H HYSCORE spectrum of pre-catalyst **A1** measured at room temperature at $B_0 = 346.3$ mT. The spectrum is the sum of individual spectra recorded with different τ values ($\tau = 96, 120, 136, 160$, and 184 ns) and summed after the Fourier transform. The ^1H Larmor frequency ($\nu = 14.75$ MHz) is represented by the anti-diagonal line, (b) Points of cross-peaks in the ν_β^2 vs ν_α^2 representation, taken from the experimental spectrum (black dots) and the corresponding fits (solid curves) obtained through the Dikanov analysis. The dashed line is defined by the equation $|\nu_\alpha + \nu_\beta| = 2\nu_{\text{HB}}$, (c) Simulation of the HYSCORE spectra at (a) using the hyperfine coupling parameters $a_{\text{iso}} = 9$ MHz and $T = 3$ MHz obtained from Dikanov analysis.

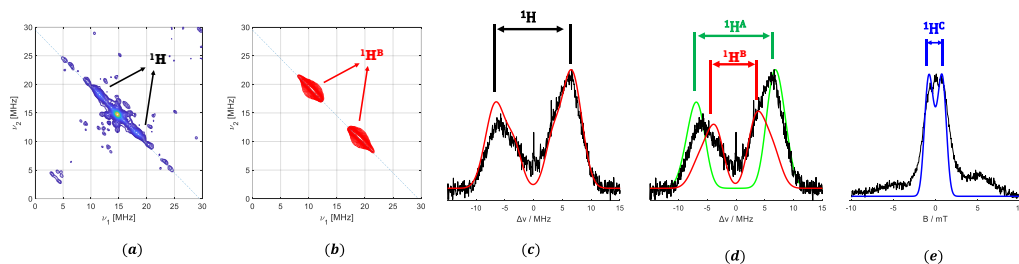


Figure 4.21 (a) X-band ($\nu = 9.76$ GHz) ^1H matched HYSCORE spectrum for pre-catalyst **A1** at X-band measured at 80 K at $B_0 = 346.5$ mT with $\tau = 102$ ns. (b) The simulated ^1H matched HYSCORE spectra using the parameters from the Dikanov analysis. (c,d) ^1H Davies ENDOR spectra (black spectra) recorded at Q-band frequency ($\nu = 33.8$ GHz) at $B_0 = 1208$ mT. Experimental parameters: temperature 30 K, $\pi/2$ pulse 16 ns, π pulse 32 ns, $\tau = 150$ ns, RF pulse 14 μs , with (c) full spectrum simulation (red) of the two overlapped inequivalent protons, (d) separate simulations of the two inequivalent protons indicated as $^1\text{H}^{\text{A}}$ and $^1\text{H}^{\text{B}}$ (green and red simulation), (e) ^1H Mims ENDOR experimental spectra (black) for pre-catalyst **A1** recorded at Q-band frequency ($\nu = 33.8$ GHz) at the magnetic field position corresponding to the contribution of the organic radical and the corresponding simulations (blue for $^1\text{H}^{\text{C}}$). Experimental parameters: temperature 30 K, $\pi/2$ pulse 16 ns, $\tau = 150$ ns, RF pulse 14 μs . The Davies and Mims ENDOR spectra were simulated using the spin-Hamiltonian parameters in Table 4.7.

The Davies-ENDOR spectrum (Figure 4.21c) is characterized by a pair of broad and asymmetric lines centered at the ^1H Larmor frequency and separated by about 20 MHz. Attempts to simulate the spectrum using only the values derived from the analysis of the room temperature HYSCORE spectrum (Figure 4.20) and the matched HYSCORE spectrum (Figure 4.21, a and b) were unsuccessful as clearly in this case a much larger coupling is detected. The spectral shape could be reproduced satisfactorily assuming the

presence of two different protons (H^A and H^B in Figure 4.21d) characterized by different couplings (Table 4.7). The reason for not observing the coupling for proton H^A in the HYSCORE spectra (Figure 4.20) and the matched HYSCORE spectra (Figure 4.21a) will be due to the difference in temperature in which the experiments were performed and the fact that the hyperfine coupling of $^1H^A$ is mainly dominated by the (large) Fermi contact part and will thus give rise to very shallow spin-echo modulations in comparison to the contributions of $^1H^B$ and $^1H^C$. Davies ENDOR experiments are much more ideal to detect these large proton hyperfine couplings.

Table 4.7 Hyperfine interaction of ^1H , ^{13}C , and $^{35,37}Cl$ nuclei with the unpaired electron of the radical species in pre-catalyst **A1**. Hyperfine and quadrupole values are given in MHz and Euler angles α , β , γ are given in degrees. Only the ^{35}Cl values are given, but simulations included both $^{35,37}Cl$ isotopes.

Nuclei	a_{iso}	T_x	T_y	T_z	α, β, γ	e^2qQ/h	η	α, β, γ
^{35}Cl	3.9±0.6	-0.5±0.3	-0.5±0.3	1.0±0.7	0,15,0 ±10	13 ±1.5	0.45 ±0.2	0,60,0 ±10
^{13}C	4.0±0.7	-2.3±0.7	-2.3±0.7	4.6±1.2	0,70,0 ±10			
$^1H^A$	18.0±4.0	-2.0±0.6	-2.0±0.6	4.0±1.2				
$^1H^B$	8.0±1.0	-3.0±1.0	-3.0±1.0	6.0±2.2				
$^1H^C$	0.8±0.2	-1.8±0.5	-1.8±0.5	3.6±1.0				

Moreover, Mims-ENDOR experiments highlighted the presence of a third ^1H coupling (H^C , Figure 4.21e) characterized by a small hyperfine interaction of the order of 4 MHz, which agree with literature data for radical species in organic compounds [279,280] and fits the signals observed in the HYSCORE spectra (Figure 4.20) and the matched HYSCORE spectra (Figure 4.21, a and b). Mims ENDOR is ideally suited to determine the weak proton hyperfine couplings.

To further characterize the radical species, Q-band 6-pulse HYSCORE experiments (Figure 4.22) were performed to obtain enhanced intensity signals of weakly coupled nuclei, which are usually suppressed in the standard HYSCORE spectra in the presence of strongly modulating nuclei [223].

The spectrum clearly shows the presence of two cross peaks centered at the ^{13}C nuclear Larmor frequency. The maximum coupling extracted from the spectrum is of the order

of 8 MHz (Table 4.7). It corroborates the assignment of the EPR signal to an organic radical. In the spectrum additional cross peaks in the low frequency region are observed in both HYSCORE quadrants, which are assigned to the hyperfine interaction with $^{35,37}\text{Cl}$ nuclei. This is an important observation as it demonstrates that the radical is in close contact with the MgCl_2 surface.

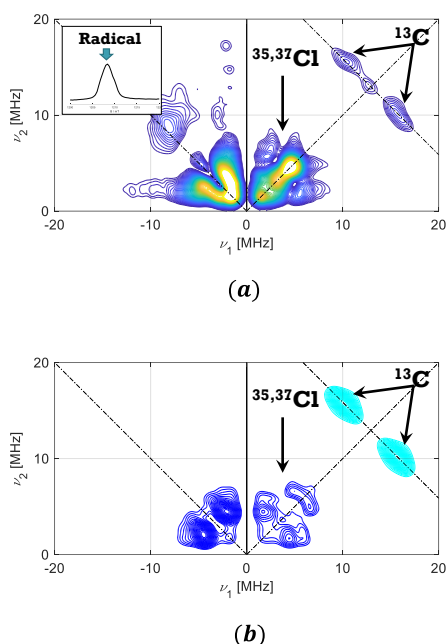


Figure 4.22 (a) Six-pulse HYSCORE spectrum of pre-catalyst **A1** recorded at Q-band frequency ($\nu = 33.8$ GHz), at a magnetic field $B_0 = 1208$ mT corresponding to the maximum echo intensity for the radical species and $T = 50$ K. The spectrum is measured with τ value of 150 ns. (b) Simulation of the experimental six-pulse HYSCORE spectrum using the spin Hamiltonian parameters listed in Table 4.7. The simulation in dark blue corresponds to $^{35,37}\text{Cl}$ and the one in light blue to ^{13}C .

4.2.3. Conclusion

Overall, this detailed analysis shows that prior to activation different paramagnetic species are present in ZN pre-catalysts, whose characteristics depend on the presence and nature of the added Lewis bases.

For the binary system $\text{MgCl}_2/\text{TiCl}_4$, we observe two dominant Ti(III) species, characterized by distinctively different EPR spectra. Species Ti(III)-A characterized by a

pseudo-axial EPR spectrum with $g_{\perp} > g_{\parallel}$, and species Ti(III)-**B** characterized by a reversed g -tensor symmetry with $g_{\perp} < g_{\parallel}$. Both species are characterized by a Cl-rich environment revealed by Q-Band HYSCORE spectra. Two-pulse ESEEM reveals that the unpaired electron of Ti(III)-**A** is not interacting with a nearby proton, while a ^1H hyperfine coupling cannot be entirely ruled out for Ti(III)-**B** in the binary system.

Addition of an aliphatic monoether (ternary system) reveals two new Ti(III) species. Ti(III)-**A'** has slightly changed principal g values compared to Ti(III)-**A**, while the dominant species Ti(III)-**C** has very different EPR parameters. In the two pulse ESEEM spectra of both species, signals at the ^1H Larmor frequency were detected, indicating that both species remain in close contact with the monoether Lewis base. No evidence of such a proximity was obtained when a diester was used as a donor additive, however, the two-pulse ESEEM spectra were of poor quality. Next to the two Ti(III) centers present in the binary system (Ti(III)-**A** and Ti(III)-**B**), the ternary system with the aliphatic diester showed a small contribution of a third Ti(III) center (Ti(III)-**D**). Analysis of the g -tensor indicates that Ti(III)-**B** can only be associated with a pseudo-octahedral coordination, while Ti(III)-**A** may be related to both octahedral or tetrahedral coordination. These differences point thus to the localization of the Ti(III) species at different terminations of the MgCl_2 substrate. Remarkably, these two species are selectively suppressed by the presence of different Lewis bases. When a monoether is present, species Ti(III)-**B** is suppressed, while the opposite happens in the presence of a diester. This observation is important as directly reveals a preferential adsorption of different Lewis bases in ZN catalysts, which, in turn, directly influences the nature of Ti(III) species.

The influence of the nature of the added Lewis bases on the nature of the paramagnetic species formed at the surface of ZN pre-catalysts was further confirmed by the study of "fifth generation" ZN pre-catalysts (**A1** and **B1**), containing diethers of different nature. While the native Ti(III) species have similar structure, in one case (sample **A1**) the EPR-spectral contribution of an intense carbon-based radical is found. Hyperfine spectroscopy was used to characterize the local environment of the radical, recovering the interactions with protons ^{13}C and $^{35,37}\text{Cl}$ nuclei, which demonstrate an intimate contact with the MgCl_2 matrix. It appears therefore that internal Lewis bases of the same family, with a diether functional group but with different structures, cause a different distribution of the paramagnetic species on the surface of MgCl_2 support. This may be related to the bulkiness of the diethers used (structural information is confidential).

Investigation of Ti(III) species on activated Ziegler – Natta catalysts

The pre-catalysts analyzed and discussed in Chapter 4 have been activated with TEA using the standard activation procedure in liquid phase and also via a solid-gas reaction contacting the pre-catalyst with TEA vapors. The EPR characterization of these activated samples is reported in this chapter. Moreover, the evolution of the EPR signal of Ti(III) species during the polymerization process has been followed by recording EPR spectra at different stages of the polymerization reaction.

The activation of the pre-catalyst is a key step enabling the conversion of potential active sites into actual catalytic active sites [281]. One of the most significant and influential parameters in olefin polymerization is thus the choice of a proper co-catalyst and that of internal and external Lewis bases added prior or during the activation. According to the literature, various co-catalysts result in different stability and reactivity of the active centers with varying performances, which consequently affect the polymer's ultimate qualities, including physical and chemical properties [151,282–284]. Masoori *et al.* showed that TEA demonstrated the highest activity among 14 different co-catalyst compounds [85]. It also represents one of the most used co-catalysts together with TIBA and DEAC.

5.1. Isolated Ti(III) Species on the Surface of Activated Ziegler – Natta Catalysts Containing Different Lewis Bases

The impact of the chemical structure of Lewis bases on the nature of EPR-active Ti(III) species in ZNC systems is still not fully explored. In Chapter 4.2 it has been shown that Lewis bases of different nature influence the local coordination environment of native Ti(III) species. The amount of these species is significantly increased upon contacting the pre-catalyst with the co-catalyst, due to the reduction of EPR-silent Ti(IV) species to Ti(III). Figure 5.1 depicts the CW-EPR spectra recorded at X-band of the binary and ternary systems ($\text{MgCl}_2/\text{TiCl}_4$, $\text{MgCl}_2/\text{TiCl}_4/\text{monoether}$ and $\text{MgCl}_2/\text{TiCl}_4/\text{diester}$)

activated with TEA in the gas phase following the method outlined in Chapter 3.2.1, and compares these with the EPR spectra of the corresponding pre-catalyst (see chapter 4.2.1). After the reaction with TEA the intensity of the EPR spectrum of all three samples increases by about one order of magnitude. Moreover, in the case of the ternary systems (Figure 5.1b, c) the spectrum shows a significant change with respect to the one recorded for the pre-catalyst. This suggests that, while in the case of the binary system the reductive activation does not alter significantly the local environment of the Ti(III) species, when Lewis bases are present, a significant change of the Ti(III) ligand field occurs. A detailed analysis of each system is provided in the following.

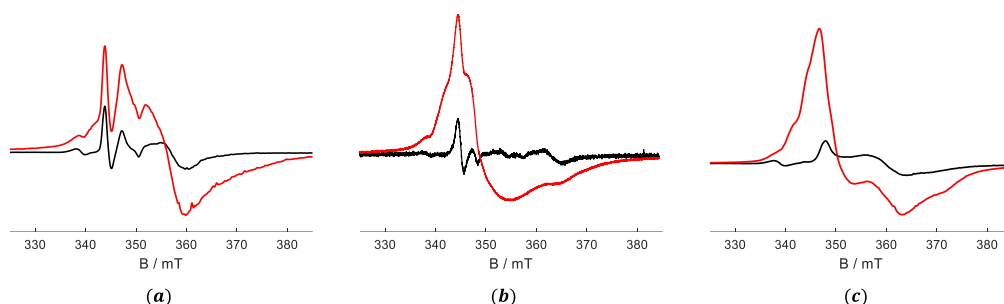


Figure 5.1 Activation with TEA vapors of: (a) the binary system $\text{MgCl}_2/\text{TiCl}_4$, (b) the ternary system $\text{MgCl}_2/\text{TiCl}_4/\text{monoether}$, and (c) the ternary system $\text{MgCl}_2/\text{TiCl}_4/\text{diester}$. Spectra in black represent the corresponding pre-catalyst systems before activation, while the red spectra represent the activated sample. All spectra have been recorded at liquid nitrogen temperature (77 K) at X-band frequency ($\nu = 9.7$ GHz).

5.1.1. Activation of the $\text{MgCl}_2/\text{TiCl}_4$ pre-catalyst

The experimental and simulated EPR spectra recorded upon activation of the pre-catalyst are shown in Figure 5.2 and the corresponding spin-Hamiltonian parameters are listed in Table 5.1 together with those obtained before activation. The simulations show that upon activation with TEA, species Ti(III)-**A** remain almost unvaried, while species Ti(III)-**B** changes and are therefore named as Ti(III)-**B'** (Table 5.1). After activation, however, a decrease of the abundance is observed for species Ti(III)-**A** and Ti(III)-**B** as a new Ti(III) species, named Ti(III)-**E**, is formed. This new species is characterized by a rhombic g -tensor typical of activated Ziegler-Natta systems [184,241,245].

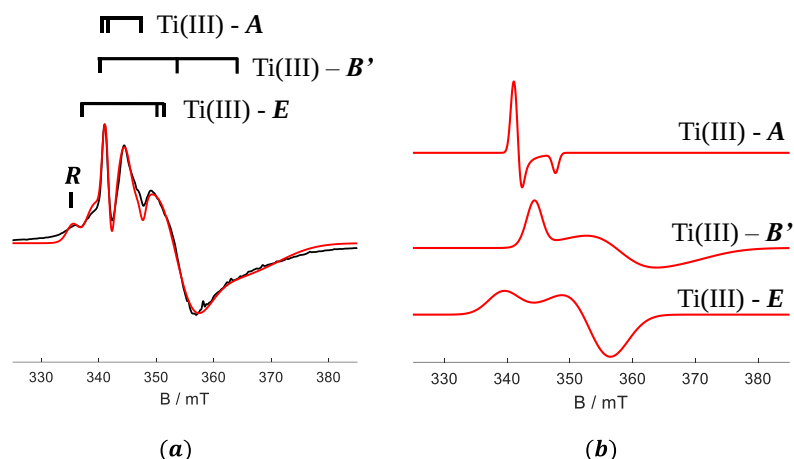


Figure 5.2 (a) Experimental (black) and computer simulated (red) CW-EPR spectra of Ti(III) species in the activated $\text{MgCl}_2/\text{TiCl}_4$ binary system upon TEA vapors. All spectra were recorded at liquid nitrogen temperature (77 K) at X-band frequency ($\nu = 9.7$ GHz). (b) Separate simulations of species Ti(III)-A, Ti(III)-B', and Ti(III)-E.

Table 5.1 Spin Hamiltonian parameters obtained from the simulation of the EPR spectra of Ti(III) in the binary system $\text{MgCl}_2/\text{TiCl}_4$ before and after activation with TEA vapors. The relative abundance (ab) of the different species refers to the CW-EPR experiments at X-band at 77 K.

Sample	Species	g_x	g_y	g_z	%ab
$\text{MgCl}_2/\text{TiCl}_4$	A	1.977(3)	1.971(8)	1.936(0)	14.10
	Ti(III) B	1.88(0)	1.89(9)	1.954(4)	84.70
	R	2.003(4)	2.003(4)	2.003(4)	1.20
$\text{MgCl}_2/\text{TiCl}_4$ + TEA	A	1.976(4)	1.971(6)	1.937(5)	2.06
	B'	1.830(3)	1.880(2)	1.954(4)	54.80
	Ti(III) E	1.889(3)	1.909(7)	1.985(2)	42.82
	R	2.003(4)	2.003(4)	2.003(4)	0.32

5.1.2. Activation of the $\text{MgCl}_2/\text{TiCl}_4$ /monoether pre-catalyst

In the case of the ternary system containing a monoether as internal donor, the experimental and simulated X-band CW-EPR spectra recorded upon activation are shown in Figure 5.3. The corresponding spin Hamiltonian parameters are listed in Table 5.2 together with those obtained before activation. Inspection of Table 5.2 and Figure 5.3b, show that, at variance with the previous case, the activation process leads to the

formation of a new set of Ti(III) species. The simulation reveals the presence of at least three species (named **F**, **G** and **H**) with roughly similar abundance. Species Ti(III)-**G** is characterized by a pseudo-axial **g**-tensor ($g_{\perp} > g_{\parallel}$) while species Ti(III)-**F** feature a different **g** structure with $g_{\perp} < g_{\parallel}$, revealing a different local coordination symmetry. On the other hand, species Ti(III)-**H** is characterized by a rhombic **g**-tensor, similar to what is reported by reference [245] for an activated high-yield Ziegler–Natta catalyst. Several studies show that Ti(III) species characterized by a chlorine environment display principal *g*-values not exceeding the value of 1.95 [242,274,285,286]. On the other hand, Ti(III) species with a *g*-value ≥ 1.95 have been tentatively assigned to surface-alkylated Ti(III) species [241,274]. In order to investigate in more detail the nature of the Ti(III) species formed after activation with TEA, 3-pulse ESEEM and HYSCORE experiments were performed at Q-band and compared with those recorded before activation. A first hint of the magnetic nuclei surrounding the Ti(III) species was obtained from 3-pulse ESEEM experiments. The spectrum was recorded at Q-band frequency and at a magnetic field position ($B_0 = 1228.2$ mT, $g=1.996$) corresponding to the most intense feature of the ESE spectrum (Figure 5.4). In order to avoid blind spot effects, the 3-pulse ESEEM experiment was taken as a function of the interpulse delay τ and the sum projection of the different spectra after Fourier transformation is shown in Figure 5.4.

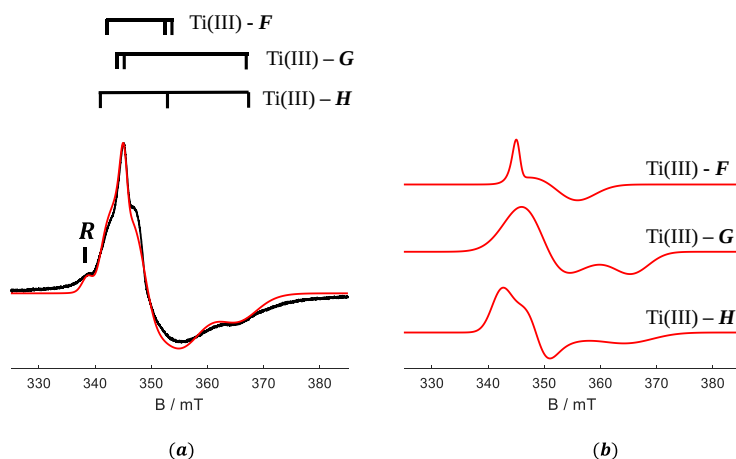


Figure 5.3 (a) Experimental (black) and computer simulated (red) CW- EPR spectra of Ti(III) species in the $\text{MgCl}_2/\text{TiCl}_4/\text{monoether}$ ternary system after activation with TEA vapors, recorded at 77 K at X-band frequency ($\nu = 9.7$ GHz). The stick diagrams indicate the three Ti-species and R the radical. (b) Separate simulations of species Ti(III)-**F**, Ti(III)-**G**, and Ti(III)-**H**.

The frequency-domain ESEEM spectrum shows peaks at 5 MHz, 7.1 MHz and 8.6 MHz amenable to the hyperfine interaction of Ti(III) species with $^{35,37}\text{Cl}$ ($I = 3/2$) nuclei. A peak at ≈ 13.6 MHz, which is peculiar to this sample, corresponds to the nuclear frequency

of ^{27}Al at this field, indicating a small hyperfine interaction with nearby Al nuclei. This result is important as it implies a close proximity of co-catalyst residues with the Ti(III) species [245].

Table 5.2 Spin Hamiltonian parameters obtained from the simulation of the EPR spectra of Ti(III) in the ternary system $\text{MgCl}_2/\text{TiCl}_4/\text{monoether}$ before and after activation with TEA vapors. The relative abundance (ab) of the different species refers to the CW-EPR experiments at X-band performed at 77 K.

Sample	Species	g_x	g_y	g_z	% ab
$\text{MgCl}_2/\text{TiCl}_4$ aliphatic monoether	A	1.977(3)	1.977(3)	1.936(0)	8.30
	A'	1.969(3)	1.966(0)	1.946(3)	41.50
	C	1.8(7)	1.8(7)	1.8(7)	49.80
	R	2.003(7)	2.003(7)	2.003(7)	0.40
$\text{MgCl}_2/\text{TiCl}_4$ aliphatic monoether + TEA	F	1.912(2)	1.928(4)	1.968(5)	25.00
	G	1.959(3)	1.950(2)	1.860(4)	31.99
	H	1.985(0)	1.949(3)	1.860(1)	46.60
	R	2.003(7)	2.003(7)	2.003(7)	0.41

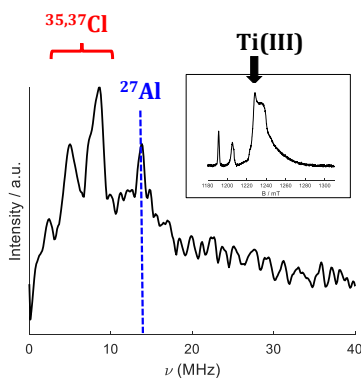


Figure 5.4 Three pulse ESEEM spectrum taken at $B_0 = 1228.2$ mT. The spectrum is the sum projection of different ESEEM spectra recorded as a function of the interpulse delay τ , which was varied from 100 ns to 324 ns in steps of 8 ns. The spectra were recorded at 30 K at Q-band frequency ($\nu = 33.8$ GHz).

5.1.3. Activation of the $\text{MgCl}_2/\text{TiCl}_4/\text{diester}$ pre-catalyst

The activation of a $\text{MgCl}_2/\text{TiCl}_4/\text{diester}$ pre-catalyst with TEA, performed in the gas phase, leads to the EPR spectrum shown in Figure 5.5. The spin Hamiltonian parameters obtained from computer simulation of this spectrum are collected in Table 5.3, where comparison is set with data obtained for Ti(III) species in the pre-catalyst. Three Ti(III) species are identified (Ti(III)-*I*, Ti(III)-*D'* and Ti(III)-*J*) which are highlighted in Figure 5.5 by a stick diagram. While before activation the spectrum was dominated by species Ti(III)-*B*, characterized by a pseudo-axial *g*-tensor with $g_{\perp} < g_{\parallel}$, after activation the most abundant species (Ti(III)-*D'*) shows a reversed *g*-tensor symmetry ($g_{\perp} > g_{\parallel}$). The principal *g* values extracted from the simulation are very similar to those observed for species Ti(III)-*D*, which was a minor species in the pre-catalyst.

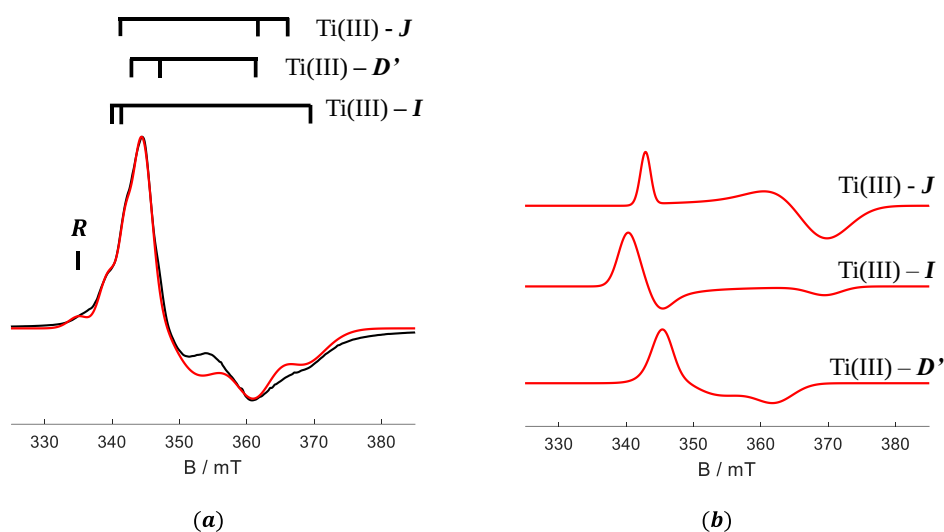


Figure 5.5 (a) Experimental (black) and computer simulated (red) CW-EPR spectra of Ti(III) species in the $\text{MgCl}_2/\text{TiCl}_4/\text{diester}$ ternary system after activation with TEA vapors, recorded at 77 K at X-band frequency ($\nu = 9.7$ GHz). The stick diagrams indicate the three Ti species and R the radical. (b) Separate simulations of species Ti(III)-*D'*, Ti(III)-*I*, and Ti(III)-*J*.

Table 5.3 Spin Hamiltonian parameters obtained from the simulation of the EPR spectra of Ti(III) in ternary system $\text{MgCl}_2/\text{TiCl}_4/\text{diester}$ before and after activation with TEA vapors. The relative abundance (ab) of the different species refers to the X-band CW EPR experiments at 77 K.

Sample	Species	g_x	g_y	g_z	% ab
$\text{MgCl}_2/\text{TiCl}_4$	A	1.977(3)	1.977(3)	1.936(0)	0.40
aliphatic	B	1.88(0)	1.89(9)	1.954(4)	94.20
diester	Ti(III) D	1.954(5)	1.925(8)	1.849(0)	3.00
	R	2.003(4)	2.003(4)	2.003(4)	2.40
$\text{MgCl}_2/\text{TiCl}_4$	I	1.989(2)	1.970(3)	1.830(3)	15.29
aliphatic	J	1.830(4)	1.850(4)	1.972(4)	19.94
diester	Ti(III) D'	1.956(5)	1.932(3)	1.868(0)	63.97
+ TEA	R	2.003(4)	2.003(4)	2.003(4)	0.78

5.2. Activation of a Ziegler-Natta catalyst containing a diether as internal donor

Two fifth-generation pre-catalysts (**A1** and **B1**, described in Chapter 4.2.2) were activated with TEA following two different procedures. In one case the pre-catalyst was contacted with TEA vapors as previously described, while a second batch of the same sample was activated using an excess of 8% TEA solution in isohexane (Al/Ti around 1000 mol/mol) in the presence of methyl-cyclohexyl-dimethoxy silane (MCDMS) as an external donor (MCDMS/TEA = 20 mol/mol, samples **A3** and **B3**), thus following the industrial practice at BPI. The pre-contact time of the pre-catalyst and co-catalyst was 30 min. Of particular interest here was to understand the differences in the distribution and nature of Ti(III) species in the system **A3** and **B3**. A quantitative EPR assessment was also made to understand how the quantity of the paramagnetic Ti(III) species present in the samples is related to the results obtained in the pilot plants in BPI site. These results are discussed in more detail in chapter 5.2.2.

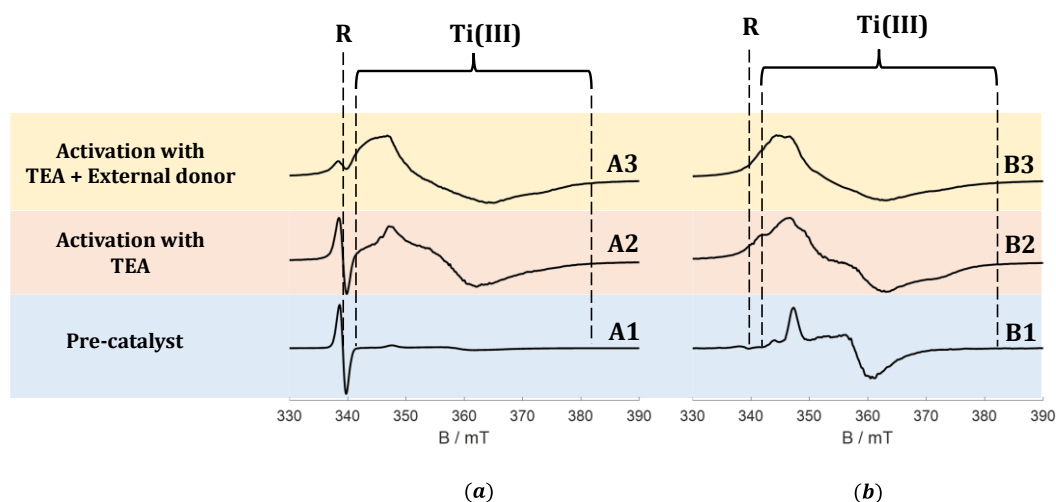


Figure 5.6 Experimental CW-EPR spectra at X-band frequency ($\nu = 9.7$ GHz) for (a) system A (**A1**, **A2**, and **A3**), and (b) system B (**B1**, **B2**, and **B3**). All spectra were recorded at 77 K (liquid nitrogen temperature).

From the CW-EPR experiments at X-band (Figure 5.6), recorded at 77 K, spectra with distinct spectral patterns were obtained for samples **A2**, **A3**, **B2** and **B3**. The Ti(III) spectral features are significantly different from those observed for Ti(III) impurities in the pre-catalysts (samples **A1** and **B1**, Chapter 4.2.2), indicating a change in the distribution of the paramagnetic species upon the reductive activation.

In the following, the nature of Ti(III) species formed after activation with TEA vapors, without external donor (sample **A2** and **B2**) is discussed first, followed by the case of the liquid phase activation (samples **A3** and **B3**).

5.2.1. Activation in gas phase

The activation with TEA vapors was performed in situ in the EPR tube by using the system shown in Figure 3.2b (Chapter 3.2.1). The corresponding activated samples of pre-catalyst **A1** and **B1**, activated with TEA in the gas phase in the absence of external donor, are named **A2** and **B2**. The CW-EPR spectra recorded at X-band frequency for sample **A1** and **A2** are shown in Figure 5.7a and for sample **B1** and **B2** in Figure 5.7b. From the spectrum in Figure 5.7a it is observed that after activation the spectrum is still characterized by the presence of an intense radical signal, while, as observed in all cases, an increase in the intensity of Ti(III) species is observed as a function of exposure to the TEA vapors (red spectra). The spectral intensity further increases upon heating the

system at 80 °C for one hour, likely due to a better diffusion of the co-catalyst under these conditions. This is shown in Figure 5.9 for sample **A2**.

The activation of pre-catalyst **B1** was performed under the same conditions and the reaction with TEA vapors is accompanied by visual changes in color and major changes in the X-band CW-EPR spectra. The sample before activation had a yellow color, that turned black immediately after contact with the TEA vapors. This is accompanied by the onset of a new intense EPR spectrum, shown in Figure 5.7b. The quantitative evaluation obtained by double integration of the spectra is shown in Figure 5.8.

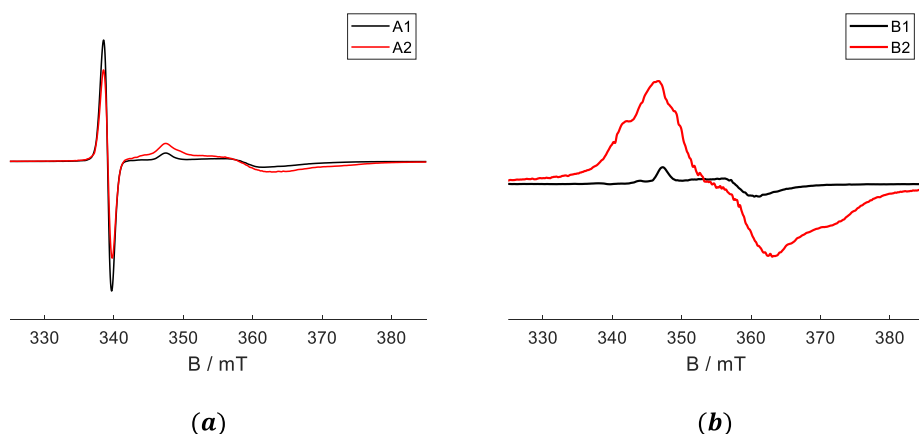


Figure 5.7 CW-EPR spectra of (a) pre-catalyst **A1** and (b) pre-catalyst **B1**. The spectra were recorded before activation (black spectra, **A1** and **B1**), after activation with TEA (red spectra, **A2** and **B2**). All the spectra have been measured with the same EPR spectrometer settings at X-band frequency ($\nu = 9.7$ GHz) at 77 K (liquid nitrogen). The spectra are shown not normalized.

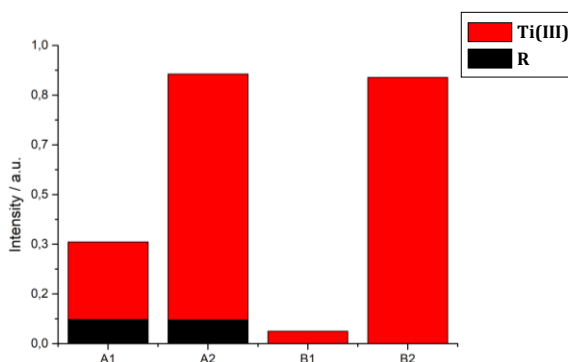


Figure 5.8 The intensity of the active species in sample **A1**, **A2**, **B1** and **B2** presented in arbitrary units derived from the double integration of the spectra recorded at 77 K (Figure 5.7).

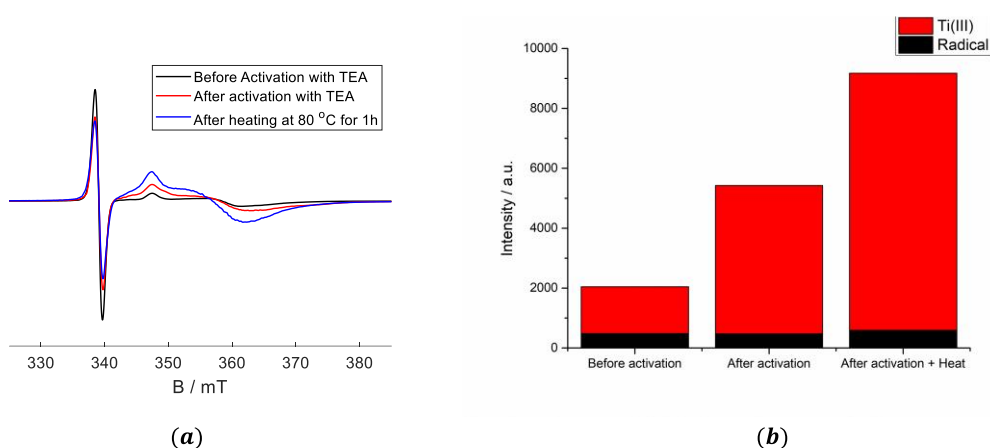


Figure 5.9 (a) CW-EPR spectra of pre-catalyst **A1**, before activation (black spectra), after activation with TEA (red spectra), and after activation and heating for one hour at 80 °C (blue spectra). All the spectra have been measured with the same EPR parameters at X-band frequency ($\nu = 9.7$ GHz) at 77 K (liquid nitrogen). The spectra are not normalized. (b) The intensity of the active species presented in arbitrary units from the double integration of the spectra recorded at 77 K.

Computer simulation of the spectra obtained after activation are shown in Figure 5.10 and were obtained based on the presence of different species, characterized by distinctively different spin-Hamiltonian parameters, listed in Table 5.4. Sample **A2** could be simulated considering two slightly different species (**S1** and **S4** in Table 5.4). The Ti(III) species **S1** is observed also in the pre-catalyst (see also Chapter 4.2.2) and is the dominant species, while species **S4** has a similar g -tensor as species **S2** (observed in the pre-catalyst in Chapter 4.2.2) with slight changes. Sample **B2** is characterized by a more complex spectrum, which could be simulated considering at least 3 different species, one of which (**S6**) shows considerable g rhombicity.

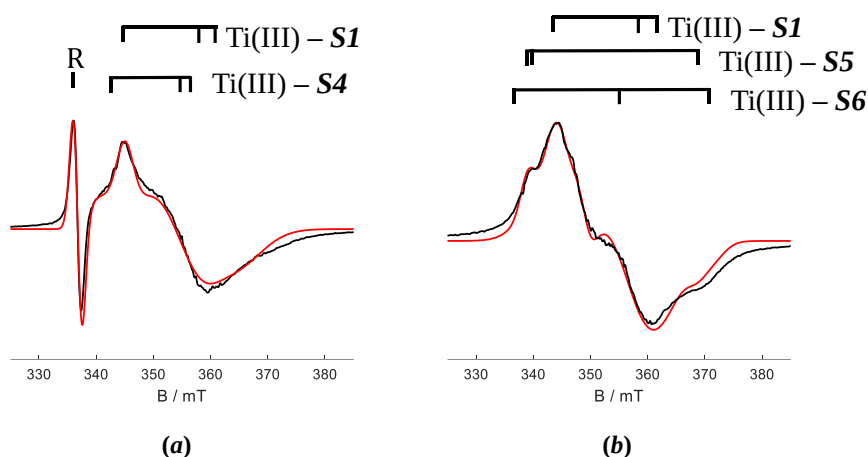


Figure 5.10 Experimental (black) and simulated (red) CW-EPR spectra for (a) sample **A2**, and (b) sample **B2**. The spectra were recorded at X-band frequency ($\nu = 9.7$ GHz) at 77 K. All spectra are normalized.

Table 5.4 Experimental (black) and simulated (red) spectra for (a) sample **A2**, and (b) sample **B2**. The spectra were recorded at X-band frequency at 77 K. The relative abundance (ab) of the different species refers to the X-band CW-EPR spectra recorded at 77 K

Sample	Species	g_x	g_y	g_z	% ab
Catalyst A2 MgCl ₂ /TiCl ₄ /diether activated with TEA vapors	S1	1.855(0)	1.884(5)	1.951(4)	68.85
	Ti(III) S4	1.981(5)	1.910(0)	1.880(0)	28.67
	R	2.003(4)	2.003(4)	2.003(4)	2.48
Catalyst B2 MgCl ₂ /TiCl ₄ /diether activated with TEA vapors	S1	1.879(5)	1.879(3)	1.955(8)	63.56
	S5	1.978(1)	1.970(2)	1.830(1)	17.37
	Ti(III) S6	1.989(0)	1.932(3)	1.815(2)	19.07
	R	-	-	-	-

5.2.2. Activation in liquid phase

Pre-catalysts **A1** and **B1** were activated in liquid phase, in the presence of MCDMS as an external Lewis base, following standard protocols (see Chapter 3.2.1) developed at BPI laboratories. A third activated sample, named **AC**, with the same composition of **A1**, but synthesized following a different procedure, was provided by BPI and represents a third set of industrial catalysts all activated in liquid phase. The activated samples are named **A3**, **AC** and **B3** and the corresponding EPR spectra recorded at X and Q-band frequencies are shown in Figure 5.11 and Figure 5.12 respectively. The CW-EPR spectrum at X-band

of sample **A3**, shown in Figure 5.11a, is characterized by a broad and ill-defined powder pattern. To increase the spectral resolution, ESE-detected EPR experiments were carried out at Q-band frequency (Figure 5.12) and the simulation was performed by simultaneously fitting the spectra recorded at two frequencies (X- and Q-band) using the same set of spin-Hamiltonian parameters (Table 5.5). The presence of the external donors during the activation leads to the formation of a new Ti(III) species (**S7**), which is not present in the gas-phase activated sample. A similar *g*-tensor was reported previously by our group in activated Ziegler-Natta catalysts [245]. The catalyst **AC** is characterized by a X-band CW EPR spectrum (Figure 5.11b) dominated by the presence of the radical and showing a weak, but well-defined Ti(III) signal. The Ti(III) spectrum could be simulated assuming the contribution of species **S1'**, similar to **S1** identified for all activated samples and a second species (**S3**, Table 5.5) peculiar to this sample. Moreover, there is no contribution from **S7** for this sample (unlike **A3**), despite same precursors. This observation indicates that despite the two samples share the same composition, slightly different synthetic routes, based on different industrial “recipe”, affect the distribution and nature of the Ti(III) species in the system.

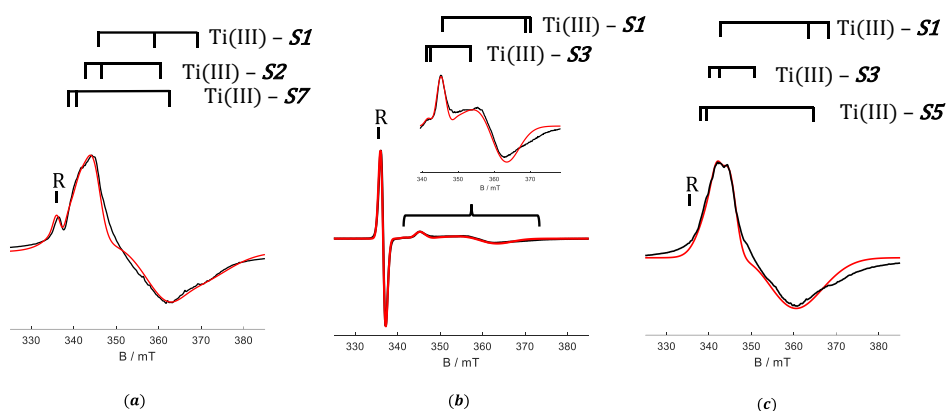


Figure 5.11 Experimental (black) and simulated (red) CW-EPR spectra of catalysts (a) A3, (b) AC, and (c) B3, recorded at X-band frequency ($\nu = 9.7$ GHz) at 77 K. all spectra are normalized.

The spectrum of the activated sample **B3** is shown in Figure 5.11c and Figure 5.12c, and the corresponding spin-Hamiltonian parameters are listed in Table 5.5. Similarly, to what is observed for sample **A3**, after activation the spectrum becomes broader, and several different components are identified by means of computer simulation. In particular the spectrum could be simulated assuming three different species (Table 5.5). Species **S1''**, similar to species **S1**, and **S3** concur with those observed in samples **A3** and **AC**, while a new species named **S5** is peculiar to sample **B3**.

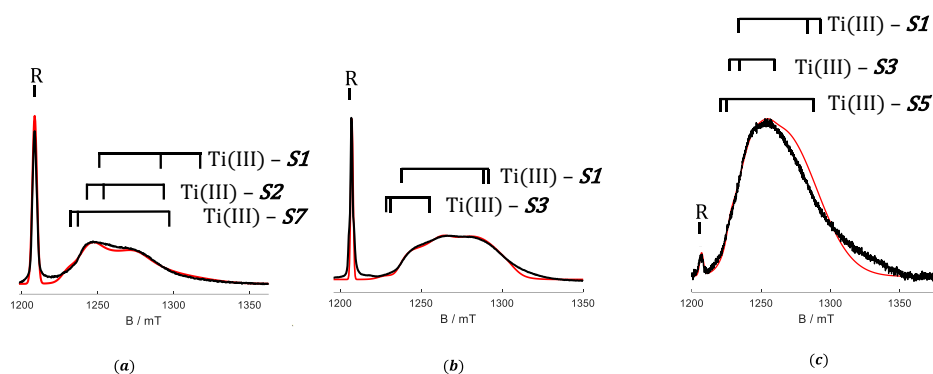


Figure 5.12 Experimental (black) and simulated (red) ESE-detected EPR spectra of sample (a) **A3**, (b) **AC**, and (c) **B3** recorded at Q-band frequency ($\nu = 33.8$ GHz) at 10 K (sample **A3** and **B3**) and at 35K (sample **AC**).

Pulse EPR experiments were attempted on all samples, however, only samples **A3** and **AC** gave a sufficiently intense electron spin echo to allow for pulse EPR experiments. HYSCORE experiments were performed for sample **A3** at different magnetic field positions, in order to characterize the local environment of both the radical and the Ti(III) species.

Table 5.5 Spin Hamiltonian parameters extracted from computer simulation of the experimental spectra for activated catalysts **A3**, **AC**, **B3**. The relative abundance (ab) of the different species refers to the X-band EPR CW-EPR spectra recorded at 77 K.

Sample	Species	g_x	g_y	g_z	% ab
Activated catalyst A3 MgCl ₂ /TiCl ₄ /diether + TEA + Silane	Ti(III) S1	1.819(2)	1.890(1)	1.953(2)	70.9
	Ti(III) S2	1.972(1)	1.943(5)	1.880(1)	8.6
	Ti(III) S7	1.984(2)	1.976(1)	1.860(2)	20.3
	R	2.003(4)	2.003(4)	2.003(4)	0.17
Activated catalyst AC MgCl ₂ /TiCl ₄ /diether	Ti(III) S1'	1.865(2)	1.864(3)	1.951(2)	80.93
	Ti(III) S3	1.970(1)	1.970(1)	1.935(4)	17.98
	R	2.003(4)	2.003(4)	2.003(4)	1.08
Activated catalyst B3 MgCl ₂ /TiCl ₄ /diether + TEA + Silane	Ti(III) S1''	1.883(2)	1.890(1)	1.951(2)	75.86
	Ti(III) S3	1.970(1)	1.969(1)	1.920(1)	6.90
	Ti(III) S5	1.981(2)	1.971(2)	1.831(3)	17.24
	R	-	-	-	-

The local environment of the radical species was investigated by performing matched HYSCORE experiments (Figure 5.13a) at X-band frequency, and four-pulse HYSCORE (Figure 5.14a), six-pulse HYSCORE (Figure 5.14c) and Davies and Mims ENDOR (Figure 5.13c and Figure 5.13e) at Q-band frequency. The ^1H matched HYSCORE spectrum (Figure 5.13a and Figure 5.13b) shows the presence of a series of cross peaks centered at the ^1H nuclear Larmor frequency, which are confirmed by Davies and Mims ENDOR experiments (Figure 5.13c and Figure 5.13e). Interactions with three different sets of protons are identified, which are highlighted in Figure 5.13b, d, and e and in Table 5.6. Standard HYSCORE experiments (Figure 5.14a) are characterized by a rich set of cross peaks, amenable to the interaction of the radical species with $^{35,37}\text{Cl}$ nuclei, while 6-pulse HYSCORE experiments (Figure 5.14c) highlight the presence of a set of cross peaks centered at the ^{13}C nuclear Larmor frequency. All spectra are consistent with those observed on the pre-catalyst before activation, indicating that activation does not significantly perturb the local environment of the radical species (Figure 4.21, Chapter 4.2.2).

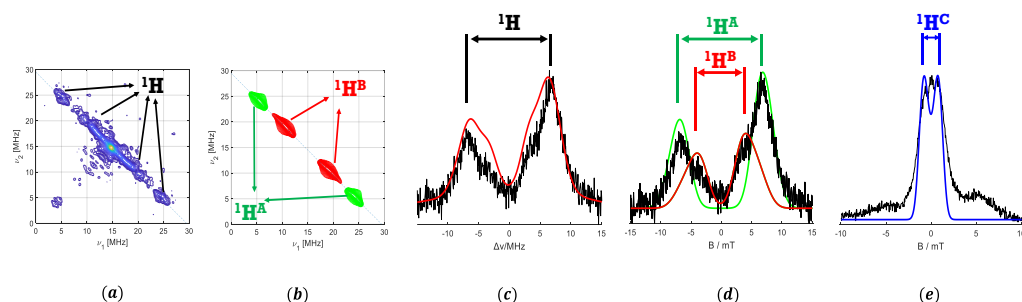


Figure 5.13 Pulse experiments for activated catalyst **A3** recorded at the radical position. (a) ^1H Matched HYSCORE spectrum measured at X-band frequency ($\nu = 9.76$ GHz) at 5K at $B_0 = 346.3$ mT with two different τ values ($\tau = 102$ and $\tau = 118$ ns). The spectra were summed after the Fourier transformation; (b) The simulated ^1H Matched HYSCORE spectra; (c)(d) ^1H Davies ENDOR spectra (black spectra) recorded at Q-band frequency ($\nu = 33.8$ GHz) at $B_0 = 1208$ mT. Experimental parameters: temperature 10 K, $\pi/2$ pulse 16 ns, π pulse 32 ns, $\tau = 150$ ns, RF pulse 14 μs , (c) full spectrum simulation (in red) of the two overlapped inequivalent protons, (d) separate simulations of the two inequivalent protons indicated as $^1\text{H}^A$ and $^1\text{H}^B$ (green and red simulation), (e) ^1H Mims ENDOR experimental spectra (black) recorded at Q-band frequency ($\nu = 33.8$ GHz) and simulated spectra (blue simulation, $^1\text{H}^C$). Experimental parameters: temperature 10 K, $\pi/2$ pulse 16 ns, $\tau = 120$ ns, RF pulse 14 μs . The spectra were simulated using the spin-Hamiltonian parameters in Table 5.6.

To characterize the environment of Ti(III) species in sample **A3**, HYSCORE spectra at Q-band frequency were also recorded at $B_0 = 1245$ mT corresponding to the g_x component of Ti(III)-**S2** species (Figure 5.15). The spectrum shows a series of cross peaks amenable to the interaction with Cl nuclei. A tentative simulation was attempted based on the

hyperfine interactions detected in Ti(III)-Cl containing systems analyzed in this thesis and reported in literature on Ziegler-Natta catalyst systems [183,227,272]. The Cl hyperfine interaction, represented as the sum of Fermi and dipolar terms, is dominated by the isotropic term with a value of $a_{\text{iso}} = 3.9$ MHz and an anisotropic coupling -tensor $\mathbf{T} = [-0.5 \pm 0.2 \ -0.5 \pm 0.2 \ +1.0 \pm 0.5]$ MHz. The nuclear quadrupole interaction values (e^2qQ/h) is in the range 5–7 MHz. These values are somewhat lower than those recently reported by us in pre-activated Ziegler-Natta systems [287] and those found for TiCl_3 [241].

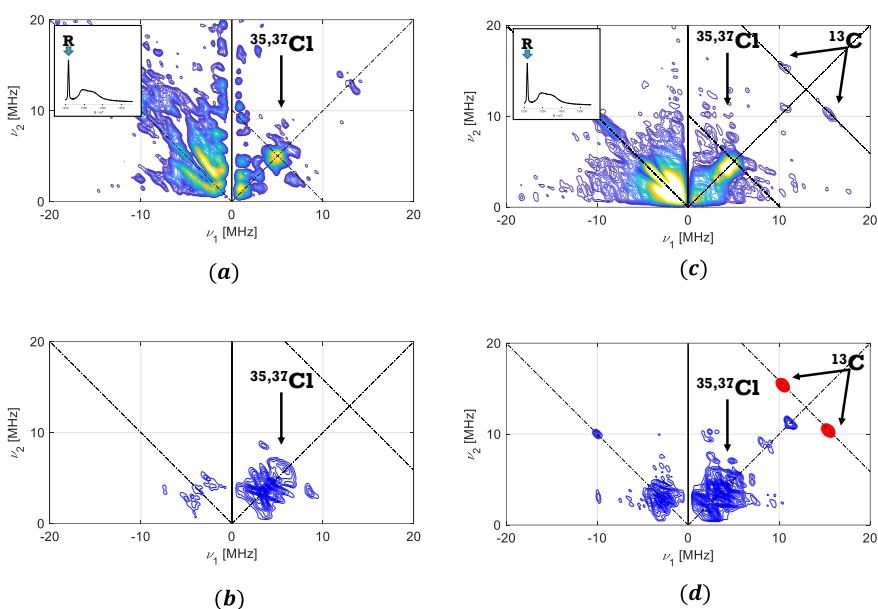


Figure 5.14 HYSCORE and six-pulse HYSCORE spectra recorded at 10 K in Q-band frequency ($\nu = 33.8$ GHz), at field position ($B_0 = 1208$ mT) corresponding to the maximum echo intensity for the radical species. (a) Experimental HYSCORE spectrum recorded with a single τ value of 112 ns, and (b) the corresponding simulation. (c) Experimental six-pulse HYSCORE spectrum, represented as the sum of two individual spectra recorded with two different τ values ($\tau = 112$ and $\tau = 150$ ns), and (d) the corresponding simulation. The spin Hamiltonian parameters used in the simulations are reported in Table 5.6. The simulation in blue corresponds to $^{35,37}\text{Cl}$ and the one in red to ^{13}C .

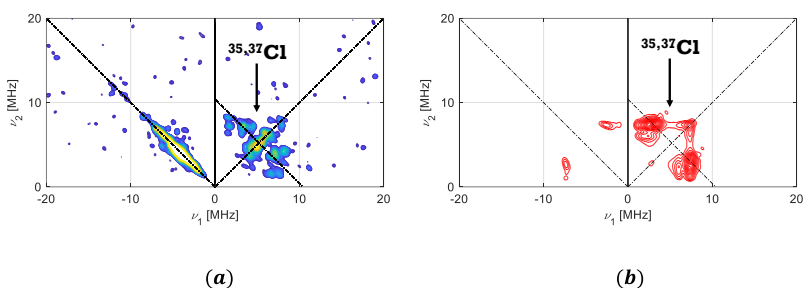


Figure 5.15 (a) HSCORE spectrum recorded Q-band frequency ($\nu = 33.8$ GHz) at 1245 mT corresponding to the highest intensity for Ti(III) species. The spectrum was recorded at 10 K, and it represents the sum of three individual spectra recorded with two different τ values (one spectrum with $\tau = 116$, and two spectra with $\tau = 144$ ns). The spectra were summed after the Fourier transform. (b) The simulation for $^{35,37}\text{Cl}$ nuclei is represented in red and the simulation parameters are given in Table 5.6.

For sample **AC**, X-band 3-pulse-ESEEM experiments were carried out as a function of the interpulse delay τ at different observer positions (Figure 5.16). The spectrum recorded at the magnetic field setting corresponding with the EPR signal of the radical, Figure 5.16b, is characterized by a strong signal at ~ 15 MHz corresponding to the Larmor frequency of ^1H .

Table 5.6 Spin-Hamiltonian parameters of $^1\text{H}^{\text{A}}$, $^1\text{H}^{\text{B}}$, $^1\text{H}^{\text{C}}$, ^{13}C and $^{35,37}\text{Cl}$ nuclei showing the interaction with radical species after activation with TEA in presence of MCDMS. Hyperfine and quadrupole values are given in MHz and Euler angles α , β , γ are given in degrees. Only the ^{35}Cl values are given, but simulations included both $^{35,37}\text{Cl}$ isotopes.

	Nuclei	a_{iso}	T_x	T_y	T_z	α, β, γ	e^2qQ/h	η	α, β, γ
R	^{35}Cl	3.9 ± 0.6	-0.5 ± 0.3	-0.5 ± 0.3	1.0 ± 0.7	$0, 15, 0$ ± 10	13 ± 1.5	0.45 ± 0.2	$0, 60, 0$ ± 10
	^{13}C	4.8 ± 0.7	-0.7 ± 0.2	-0.7 ± 0.2	1.4 ± 0.4	$0, 70, 0$ ± 10			
	$^1\text{H}^{\text{A}}$	18.0 ± 4.0	-2.0 ± 0.6	-2.0 ± 0.6	4.0 ± 1.2				
	$^1\text{H}^{\text{B}}$	9.0 ± 0.5	-3.0 ± 0.3	-3.0 ± 0.3	6.0 ± 0.3				
	$^1\text{H}^{\text{C}}$	0.3 ± 0.2	-1.0 ± 0.2	-1.0 ± 0.2	2.0 ± 0.4				
Ti(III)	^{35}Cl	4.0 ± 0.8	-0.5 ± 0.3	-0.5 ± 0.3	1.0 ± 0.7	$50, 10, 0$ ± 5	8.4 ± 1.5	0.5 ± 0.2	$0, 67, 10$ ± 10

At the field positions corresponding to the Ti(III) species (Figure 5.16b and c) a series of low frequency peaks is observed, assigned to the hyperfine interaction with $^{35,37}\text{Cl}$ nuclei. However, the most relevant feature is represented by the observation of a signal at ~ 15 MHz (proton Larmor frequency) with a maximum width of approximately 2.3 MHz. At this magnetic field position, only Ti(III) species are excited, hence the observation of a signal at the proton Larmor frequency, indicates a proximity between the paramagnetic Ti(III) species and protons. Assuming a pure dipolar interaction, a dipolar tensor of the form $[-1.1 \ -1.1 \ 2.2]$ MHz can be determined, which translates, based on the electron-proton dipolar interaction and assuming the electron to be fully localized on the titanium, in a distance of the order of 0.43 nm between the unpaired electron in the Ti(III) 3d orbitals and the proton. This must be associated to the organic moiety of the co-catalyst or to the Lewis base. The observation of Ti(III)-H interactions were reported in the case of a heterogeneous Ziegler Natta catalyst, in case of a peculiar system containing BCl_3 as a co-activator [272] and in the case of homogeneous catalysts [288]. Here we demonstrate that the typical Ti(III) species obtained on industrial samples and via standard activation, are indeed characterized by a proton-rich environment, *i.e.* they retain some degree of proximity with the organic moiety of the triethyl aluminum co-catalyst or with the Lewis base.

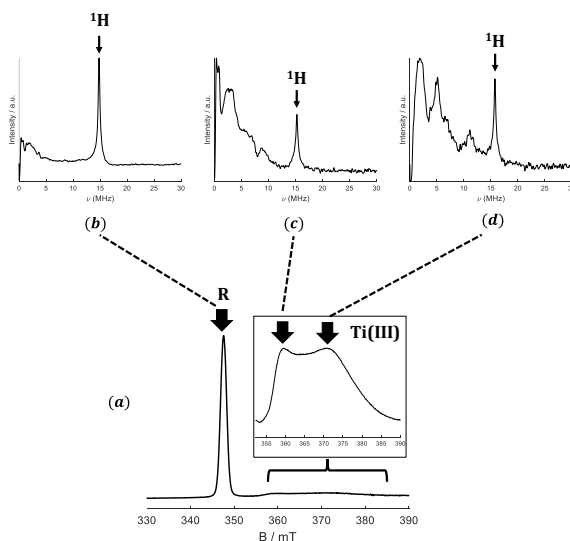


Figure 5.16 Pulse experiments for sample **AC** recorded at X-band frequency ($\nu = 9.76$ GHz) at 10 K, including: (a) ESE-detected EPR spectrum, and three-pulse ESEEM spectra taken at (a) $B_0 = 347.2$ mT corresponding to radical species, (b) $B_0 = 358$ mT corresponding to Ti(III) species, and (c) $B_0 = 370$ mT corresponding to Ti(III) species. The 3-pulse ESEEM spectra were recorded for different τ -values varied from 100 ns to 324 ns in steps of 8 ns and the sum projections is shown.

It is interesting at this stage to compare the two activation methods and in particular the effect on the EPR spectra of the presence of the MCDMS external donor. Comparison of the EPR spectra obtained after activation with the two different procedures is reported in Figure 5.17. The EPR spectrum recorded after activation in the liquid phase **A3** (red line in Figure 5.17) is characterized by a broader spectral envelope and the presence of a new species (**S7**, Table 5.5) that seem to be specifically related to the activation pathway. In a similar way, also the spectrum of sample **B3** displays a broad lineshape and from the simulation analysis a new species was identified (**S5**, Table 5.5), with similar characteristics.

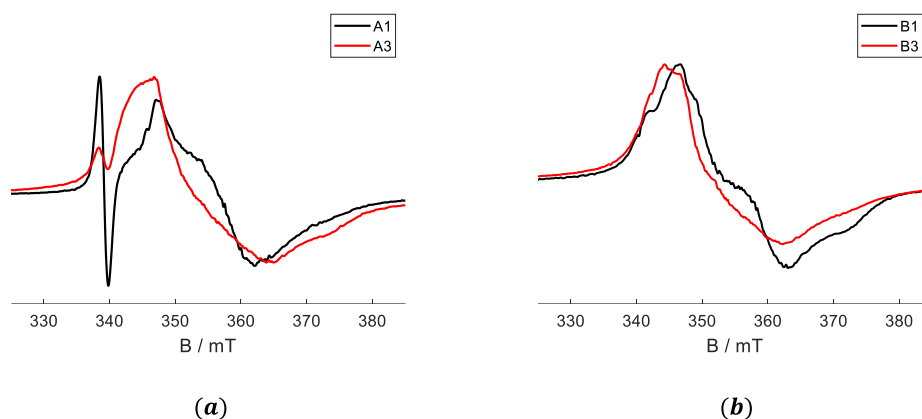


Figure 5.17 X-band EPR spectra showing a comparison of the activated samples by only TEA vapors without external donor (black spectra, Sample **A2** and **B2**) with the activated samples by TEA in presence of MCDMS as external donor (red spectra, sample **A3** and **B3**). (a) The EPR spectra of sample **A2/A3**, (b) the EPR spectra of sample **B2/B3**. All spectra have been measured at X-band frequency ($\nu = 9.7$ GHz) at 77 K and are normalized.

The separate simulations of all the species, present in the pre-catalysts, the activated catalyst in gas phase and liquid phase are shown in Figure 5.18.

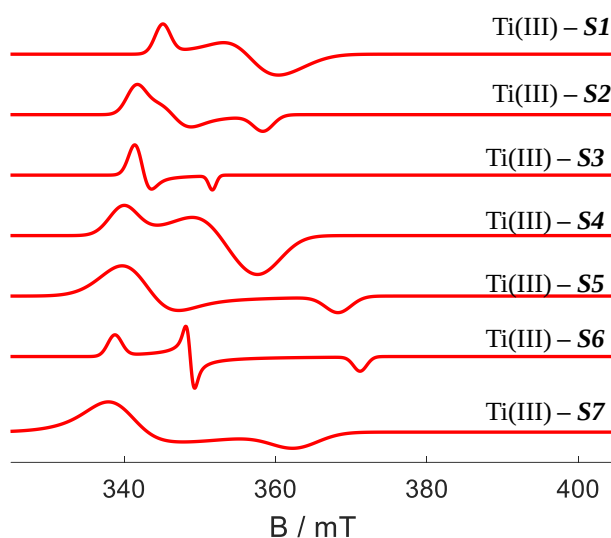


Figure 5.18 Separate simulations of species **S1**, **S2**, **S3**, **S4**, **S5**, **S6**, and **S7**.

Unfortunately, the lack of clear hyperfine interactions (^1H , ^{13}C , ^{29}Si) amenable to the proximity of the MCDMS, prevent to assign this species to specific Ti(III) ions coordinated to the Lewis bases.

The relevance of this comparison is directly linked to their industrial relevance, since differences in their catalytic activity was observed in the pilot plants at the BPI site in Ferrara. In particular, catalyst **B3** showed a strong reduction in productivity when compared to catalyst **A3**. The analysis of the EPR spectra shows some differences in the Ti(III) species present in the two samples.

From the quantitative point of view the EPR quantitation of radical and Ti(III) species in the two samples was obtained using the SpinCount package of Bruker Xenon Software [247]. The results are presented in Table 5.7 and show only a minor difference in spin concentration between the two activated catalytic systems, which can be considered within the error bar of the quantitative determination. As far as the radical species are concerned, pre-catalyst **A1** contains a significantly larger amount of radical species (more than three order of magnitudes) with respect to **B1**.

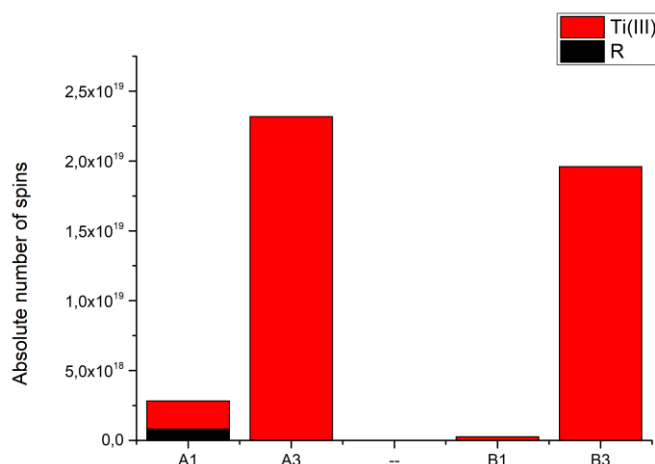


Figure 5.19 Comparison of the absolute number of spins for the radical and Ti(III) species in sample **A1**, **A3**, **B1** and **B3**. The integration window, determined by the linewidth of the signals was set 8 mT for the radical, 40 mT for the Ti(III) species in pre-catalyst A1 and B1, 68 T for Ti(III) in sample A3 and 82 mT for sample B3. See Table 5.7.

Table 5.7 EPR quantitation of number of radical and Ti(III) species in sample **A1**, **A3**, **B1** and **B3**.

Sample	Absolute number of spins	
	R	Ti(III)
A1	8.252×10^{17}	1.997×10^{18}
A3	3.941×10^{16}	2.324×10^{19}
B1	3.645×10^{14}	2.600×10^{17}
B3	-	1.960×10^{19}

Since the radical species in **A1** displays an intense electron spin echo signal, pulse EPR was used to assess the local radical distribution in samples **A1** and **A3**, i.e. before and after the activation of the pre-catalyst. This was done by measuring the contribution of the instantaneous diffusion to the phase memory time T_m , in the two samples, allowing to obtain details on the spatial distribution of the radicals as well as their local concentration.

The local spin concentration (C_{loc}) of radicals in a solid sample can be obtained by measuring the contribution of the instantaneous diffusion to the phase memory time T_m . This is implemented experimentally by measuring the two-pulse electron spin echo (2p-ESE) decays at different B_1 values of the microwave exciting pulses [289–291].

The spin relaxation processes can be intrinsic to the sample, or they can be due to the experiment itself, i.e., due to the perturbing effect of the microwave pulses on the excited spins [292] via the so-called instantaneous diffusion process. Let A and B be the fractions of the total spins that are respectively excited and not excited by the microwave pulses. The fraction of A spins increases, together with the echo intensity, with decreasing pulse length. The spontaneous random spin flips of both A spins and B spins dipolarly coupled to A spins produce a relaxation (*spin diffusion*), which is due to the properties of the sample.

The microwave pulses also cause a change in the orientations of the A spins that modify the local magnetic field acting on any other A spin and therefore produce a relaxation, which is named *instantaneous diffusion*. If the random spin flips due to the intrinsic relaxation processes do not overcome the instantaneous diffusion effect, then both processes contribute additively to the rate of spin dephasing [293].

The relaxation effect of instantaneous diffusion can be changed by varying the microwave power, and this allows us to separate the relative contributions of the two types of relaxation.

By assuming that all the spin packets giving rise to the EPR signal were turned at the same angle of θ_1 by the first pulse and of θ_2 by the second pulse, the echo intensity measured at time τ after the second pulse, with τ the delay time between the pulses, is given by:

$$I_\tau = A_0 \sin \vartheta_1 \sin^2 \left(\frac{\theta_2}{2} \right) e^{-\frac{2\tau}{T_m}} \quad (5.1)$$

whereby A_0 is a constant.

By considering that $\theta_2 = 2 \theta_1$ and assuming that the dephasing was due to the instantaneous diffusion (ID) and to other relaxation processes (SD) in an additive way,

$$\frac{1}{T_m} = A_{SD} + A_{ID} \sin^2 \vartheta_1 \quad (5.2)$$

In a real experiment, not all the spin packets are turned by the same angle by the pulses, therefore the second term is substituted by an average value over the frequency distribution of the spin packets in the EPR spectrum so that:

$$(5.3)$$

A_{SD} accounts for various relaxation processes, including the spin diffusion, while A_{ID} is given by:

$$A_{ID} = \frac{2\pi}{9\sqrt{3}} \gamma^2 h C_A = k C_A \quad (5.4)$$

where γ is the gyromagnetic ratio, h is the Planck constant and C_A is the local concentration of A spins, affected by the pulses in spins/cm³ [294]. k is then 8.2×10^{-13} cm³ s⁻¹. The total local concentration C_{loc} is the sum of the concentration C_A of A spins and concentration C_B of B spins, and it can be obtained through the ratio of the C_A concentration to the fraction of the spectrum excited by the microwave pulses. To reach this target, it is necessary to separate the contribution of the instantaneous diffusion to the echo decay from any other contribution. This can be done by measuring $1/T_m$ as a function of $\langle \sin^2 \theta_1 \rangle$ in (Figure 5.20), which was done by recording a series of echo decays where the microwave power was changed for fixed pulse lengths (Figure 5.21). In fact, the turning angle θ_1 is directly related to the pulse length and the oscillating magnetic-field strength B_1 . The latter is proportional to the square root of the microwave power P sent to the sample ($B_1 \propto \sqrt{P}$), therefore directly related to the microwave attenuation value (dB):

$$\text{dB} = -10 \log_{10} \left(\frac{P}{P_0} \right) = -20 \log_{10} (k B_1) \quad (5.5)$$

in which the constant k can be obtained by correlating the initial intensities of the echo recorded at different microwave powers. One can then plot $1/T_m$ relative to $\langle \sin^2 \theta_1 \rangle$, where θ_1 is the nutation angle of the first pulse. This was done for samples **A1** and **A3** and the result is reported in Figure 5.20. The plots are linear for both samples, but they have different slopes and intercepts. The fitting parameters are reported in Table 5.8 and compared with the average spin concentration (C_{av}) derived from the double integration of the CW-EPR spectra. For a uniform distribution of radicals in the sample, the ratio $R = C_{loc}/C_{av}$ is expected to be 1, whereas $R > 1$ indicates an inhomogeneous distribution resulting in clusters of radicals with average inter-cluster distances larger than the intra-cluster distances. In the case of sample **A3** examination of Table 5.8 shows $R > 1$ indicating that such an inhomogeneous distribution of the carbon radicals is present. In the case of sample **A1** the value $R < 1$ is non-meaningful and further experiments on new batches of samples will be needed in future to understand this discrepancy. Despite this, the method appears to be relevant for understanding the distribution of surface paramagnetic species and it will be particularly interesting for the determination of Ti(III) species as a function of activating treatments.

Table 5.8 The local spin concentration (C_{loc}) for the carbon based radical species in sample **A1** and **A3** derived by the relaxation measurements (left of the table) and compared with the average spin concentration (C_{av}) from the CW-EPR data (right). In the right of the table the average spin concentration from the CW-EPR measurements for Ti(III) species is also given for sample **A1**, **A3**, **B1** and **B3**.

Sample	C_{loc} (cm ⁻³)		C_{av} (cm ⁻³)		R
	Radical	Ti(III)	Radical	Ti(III)	
A1	1.390×10^{18}	-	1.157×10^{19}	2.662×10^{19}	0.120
A3	5.390×10^{18}	-	6.435×10^{17}	3.779×10^{20}	8.376
B1	-	-	6.035×10^{15}	4.305×10^{18}	
B3	-	-	-	3.198×10^{20}	

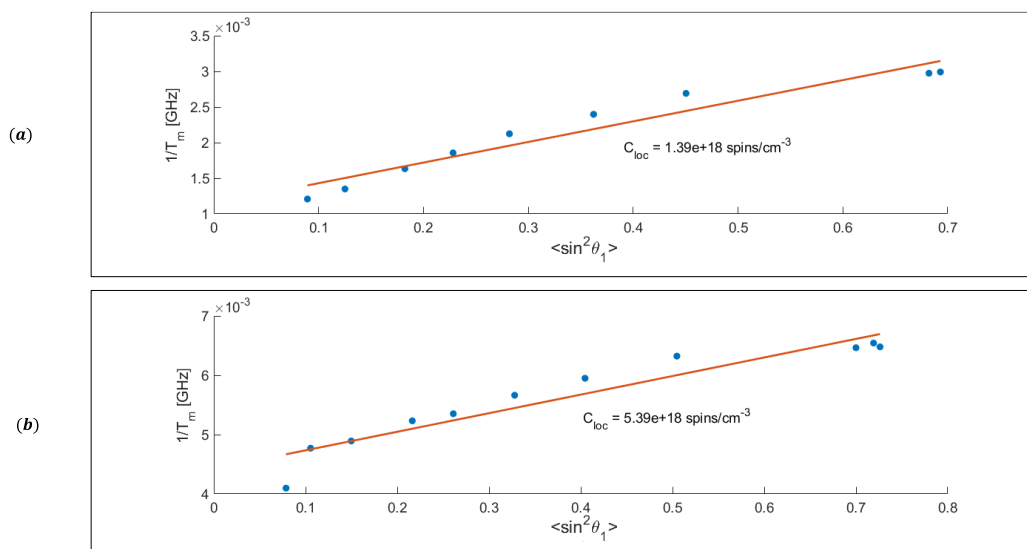


Figure 5.20 Dephasing rate values $1/T_m$ as a function of $\sin^2 \theta_1$ for: (a) pre-catalyst **A1** and (b) activated catalyst **A3**. The experiments were performed at $B_0 = 346.2$ mT, X-band frequency, and a temperature of 5K.

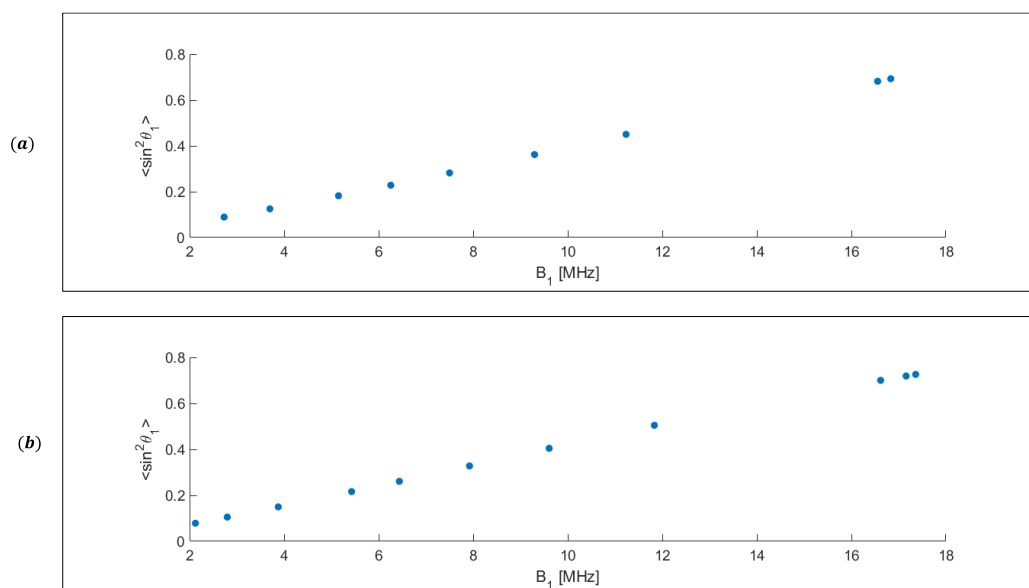


Figure 5.21 The correlation of the B_1 values (in MHz) to the $\sin^2 \theta_1$ tilting angle of the on resonance spins for (a) sample **A1** and (b) sample **A3**. The experiments were performed at $B_0 = 346.2$ mT, X-band frequency, and a temperature of 5K.

5.3. An EPR study of pre-polymerized Ziegler-Natta catalysts

In this chapter, we explore the nature of Ti(III) species in a pre-polymerization step with ethylene by gradually increasing the polymer weight. An EPR study on fully polymerized samples is not possible because of the dilution of the active sites with increasing polymer weight. Therefore, a controlled pre-polymerization step was done. Pre-polymerization uses low concentrations of monomer input, allowing for the examination of the active sites while the polymer weight gradually increases. For this experiment the industrial catalyst based on $\text{MgCl}_2/\text{TiCl}_4$ /diether named **AC** and characterized in paragraph 5.2.2 was used. Six pre-polymerized samples (**AC1-AC6**) with different conversion rates were prepared and scrutinized by EPR.

The pre-polymerization step is often used in industrial polymerization processes for catalytic systems with high activity to control the polymer morphology. In the first step of the polymerization, a small sphere of polymer with an active center in the middle called a "glomerule" is produced. The polymer grows gradually around each active center while preserving the catalyst structure [170]. Afterward, the pre-polymerized particles are fed

to the main reactor and will have approximately the same activity per particle as the bare catalyst [171,174,295] (see also chapter 1.5).

Few EPR studies have reported the coordination of olefin units to open-shell transition-metal ions [235,236]. To the best of our knowledge, no EPR studies have reported the behavior of Ti(III) species during a controlled polymer weight increase. Therefore, this study focuses not only on analyzing the coordination of ethylene monomers, but also how the monomer concentration fed into the reactor affects the paramagnetic species present in system **AC**. The effect of adding ethylene monomers and gradually increasing the polymer weight (**AC1-AC6**) on the EPR spectrum of Ti(III) was investigated by CW-EPR experiments at X-band frequency. The CW-EPR spectrum for the activated catalyst (**AC**) and the pre-polymerized samples (**AC1-AC6**) are shown in Figure 5.22.. Morra *et al.* reported that the adsorption of C₂H₄ to open-shell Ti(III) species in TiAlPO-5 zeotype materials leads to the formation of ethylene-Ti(III) complexes, observed by a modification of the CW-EPR spectral shape after contact with C₂H₄ [235]. However, our study did not detect such changes upon reaction of the activated industrial catalyst (**AC**) with ethylene monomers added to the reactor. Only a dilution of the paramagnetic species was observed. This observation indicates that adding ethylene monomers does not affect the coordination geometry of the Ti(III) species to a significant extent. A quantitative evaluation of the amount of paramagnetic species as a function of polymer growth was performed on the activated catalyst **AC** and the three pre-polymerized samples **AC1**, **AC2**, and **AC3** corresponding to the initial stages of polymerization (Figure 5.23 and Figure 5.24). As expected, the spectra show a decrease in the intensity of the paramagnetic species present in the sample, with an increase in the polymer weight (conversion rate).

Ti(III) species were quantified by comparison to standard solutions of Cu(OTf)₂ in dimethyl sulfoxide (DMSO) with different molar concentrations in the range of 0.1 – 7 mM. To quantify the radical species, a comparison to a standard solution of TEMPO in toluene at different molar concentrations (0.8 - 2 mM) was used. Further experimental details on the EPR quantification are provided in the Methods and Materials chapter (section 3.2.3). The results for the amount of EPR-active Ti(III) are presented in Table 5.9, and the spectra are shown in Figure 5.23. From the quantification results (Table 5.9), we observed that the EPR-active Ti(III) content was 4.54% of the total Ti content in the system. The increase in the amount of polyethylene with an increase in the conversion rate led to a decrease in the amount of Ti(III) species following the order **AC**(Ti(III)) > **AC1**(Ti(III)) > **AC3**(Ti(III)) > **AC2**(Ti(III)), as can be seen in Figure 5.23.

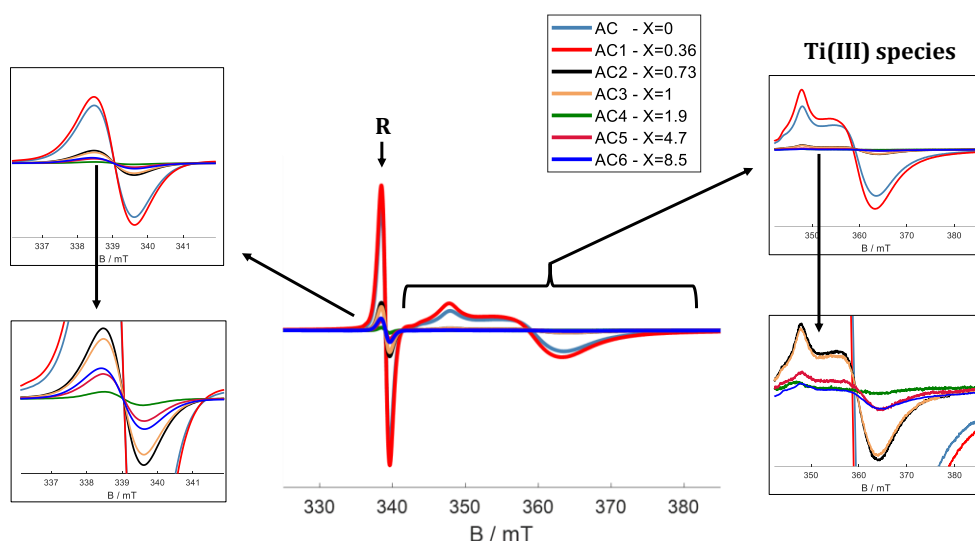


Figure 5.22 CW-EPR spectra of pre-polymerized samples at different conversion rates (X). All the spectra were recorded at room temperature at X-band frequency ($\nu = 9.7$ GHz). The spectra are shown not normalized, and the amount of the sample in the EPR tube was not measured, but was approximately the same for all tubes.

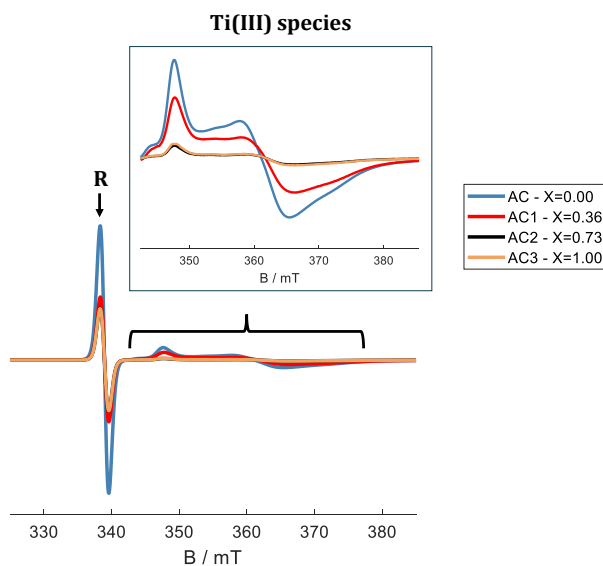


Figure 5.23 CW-EPR spectra of pre-polymerized samples at different conversion rates (X). All spectra were recorded at X-band frequency ($\nu = 9.7$ GHz) at 50 K and a microwave power of 0.063 mW, conditions at which the Ti(III) species did not saturate. The amount of each sample was taken into consideration.

Table 5.9 Quantification results from EPR spectroscopy and comparison with the chemical analysis data obtained from BPI laboratories

Sample code	Sample composition	Results from BPI	EPR results	
		Ti(Total) %wt	Ti(III) %wt	EPR Ti(III)/total Ti from BPI (%)
AC	TiCl ₄ /MgCl ₂ /diether + TEA	2.75	0.125 ± 0.005	4.54 ± 0.12
AC1	TiCl ₄ /MgCl ₂ /diether + TEA + Polyethylene (wt%=26.5)	2.20	0.096 ± 0.004	4.34 ± 0.11
AC2	TiCl ₄ /MgCl ₂ /diether + TEA + Polyethylene (wt%=42.1)	1.80	0.018 ± 0.002	1.01 ± 0.03
AC3	TiCl ₄ /MgCl ₂ /diether + TEA + Polyethylene (wt%=51.1)	1.55	0.0212 ± 0.002	1.37 ± 0.04

A similar trend is observed for the radical species (Figure 5.24, Table 5.10), indicating that an increase in the polymer weight causes dilution of all paramagnetic species. The correlation of this dilution with the increase of PE weight is presented in Figure 5.25a and b.

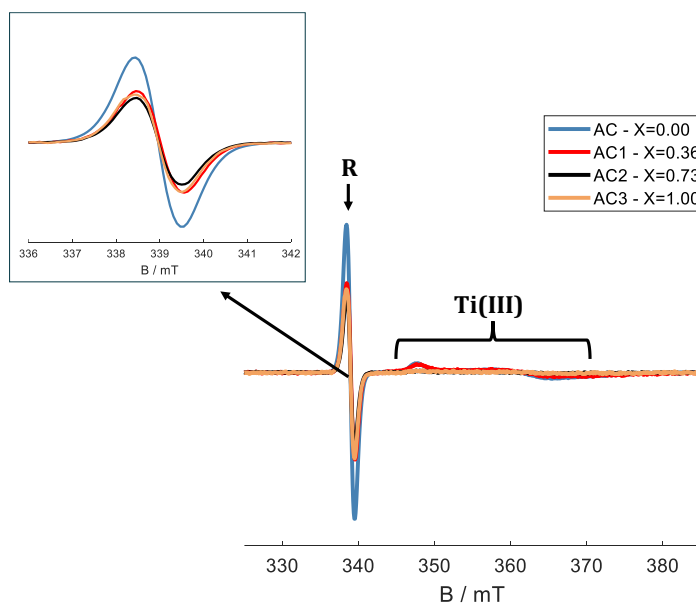


Figure 5.24 CW-EPR spectra of pre-polymerized samples at different conversion rates (X). All spectra were recorded at X-band frequency ($\nu = 9.7$ GHz) at 50 K and a microwave power of 0.0015 mW, conditions at which the radical species did not saturate. The amount of each sample was taken into consideration.

Table 5.10 Correlation between conversion rate and EPR active Ti(III) and radical content

Conversion gPE/gcat	EPR active Ti(III) content gTi(III)/gcat	EPR active Ti(III) content molesTi(III)/gcat	Radical content moles of Radical/gcat
0	$1.25 \times 10^{-3} \pm 3 \times 10^{-5}$	$2.61 \times 10^{-5} \pm 2 \times 10^{-6}$	$6.21 \times 10^{-7} \pm 5 \times 10^{-8}$
0,36	$9.55 \times 10^{-4} \pm 2 \times 10^{-5}$	$1.99 \times 10^{-5} \pm 2 \times 10^{-6}$	$3.17 \times 10^{-7} \pm 3 \times 10^{-8}$
0,73	$1.82 \times 10^{-4} \pm 4 \times 10^{-6}$	$3.81 \times 10^{-6} \pm 3 \times 10^{-7}$	$2.95 \times 10^{-7} \pm 2 \times 10^{-8}$
1	$2.12 \times 10^{-4} \pm 5 \times 10^{-6}$	$4.42 \times 10^{-6} \pm 3 \times 10^{-7}$	$2.97 \times 10^{-7} \pm 2 \times 10^{-8}$

(*) The ethylene was added in the reactor with a flow rate of 135 g/h with an instrument error of 10%

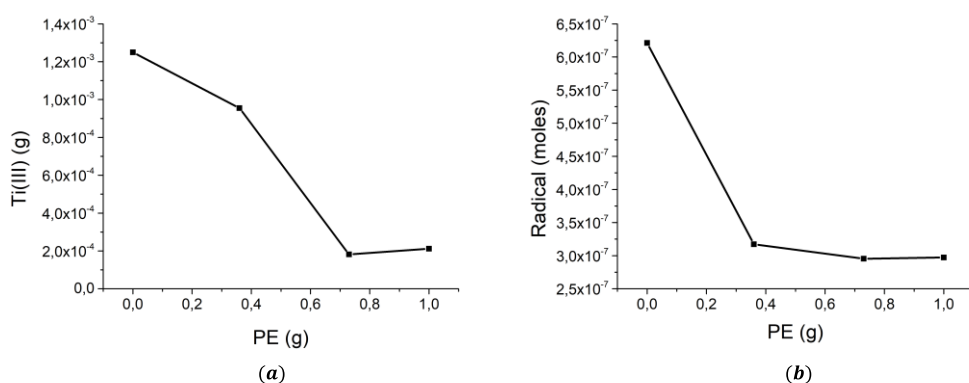


Figure 5.25 Dilution of (a) EPR-active Ti(III), and (b) radical species as determined by EPR plotted as a function of the increasing PE weight

5.4. Conclusion

The activation of the pre-catalyst with triethyl aluminum compounds (TEA), in gas or in liquid phase, leads to the formation of Ti(III) species. In this work we show that the EPR spectroscopic features of these species are influenced by the nature of the pre-catalyst, in particular from the Lewis bases, the synthetic route (recipe) of preparing the pre-catalyst, and by the type of activation with TEA (in liquid or in gas phase).

In binary systems, Ti(III) species **A** and **B** are still present even after activation with TEA in gas phase, and the presence of a new Ti(III) species, named species **E**, is observed, characterized with a pseudo-axial ($g_{\perp} < g_{\parallel}$) geometry. In the presence of Lewis bases, monoether or diester, different Ti(III) species from those observed before activation are formed. Each of these systems consists of two Ti(III) species with pseudo axial geometry, characterized with a reversed geometry between each other, and a Ti(III) species with a

rhombic ***g***-tensor (Ti(III)-***H*** in the system with monoether and Ti(III)-***D'*** in the presence of a diester) being the most abundant species for both systems.

In the ternary system containing a monoether, the 3-pulse ESEEM spectra at Q-band frequency reveal an enrichment of the chlorine signal, which is related to the formation of new Ti(III) species upon activation as observed also in the CW-EPR spectra at X-band. Importantly, a signal at ~13.6 MHz corresponds to the nuclear frequency of ^{27}Al , revealing the close proximity of the co-catalyst to the Ti(III) species after the reaction with TEA.

In two sets of pre-catalyst systems of the “fifth generation” of Ziegler-Natta catalysts containing different diethers as internal Lewis base (sample **A1** and **B1**), the EPR spectra show that the structure of the diether slightly influences the distribution of Ti(III) species. The main difference is the presence of an intense radical signal in sample **A1**. The activation with TEA, was performed in gas phase (samples **A2** and **B2**) and in liquid phase (samples **A3** and **B3**, in presence of MCDMS as external donor). In both cases, the activation with TEA, led to a significant change of the EPR spectrum of the corresponding pre-catalysts (**A1** and **B1**). An increase of the Ti(III) species signal is observed and a change in the spectral shape, confirming the formation of new Ti(III) species. However, in all cases species **S1**, observed before activation (**A1** and **B1**), remains the most abundant species even after activation (**A2**, **A3**, **B2** and **B3**). This indicates that the geometry of these species is not affected by the type of activation used. Interestingly, the geometry of the other Ti(III) species, observed before activation, is here reported to be altered by the type of activation used (in gas or in liquid phase). The activation in liquid phase, led to the formation of an additional Ti(III) species for sample **A3**, not observed in the activation process with TEA performed in gas phase (sample **A2**).

In a third ZNC system activated in liquid phase (named **AC**), whose pre-catalyst contains the same diether as sample **A1** but was prepared using a different recipe, we demonstrate that the synthetic route of preparing the pre-catalyst affects slightly the distribution of Ti(III) species in the CW-EPR spectra when compared to the activated system **A2**. Distinctive from the other analyzed samples, pulse experiments, in particular 3-pulse ESEEM experiments, reveal an interaction of Ti(III) species with ^1H nuclei (ESEEM signal at ~15 MHz) with an estimated inter-nuclear distance of 0.43 nm, when assuming a pure dipolar interaction for the analysis. This interaction must be associated to the moiety of the co-catalyst or to the Lewis base and represents an important observation which is specific to this sample.

The radical species in sample **A1** remains present even after the activation. Advanced EPR measurements reveal that the interaction of the radical species with ^1H , ^{13}C , and

$^{35,37}\text{Cl}$ remains unchanged upon activation. However, the formation of radical clusters upon activation with TEA (in sample **A3**) was observed by measuring the local microscopic average concentration by instantaneous diffusion. These clusters show a larger average intercluster distance than the spin-spin distance within each cluster.

In a last set of experiments, we analyzed pre-polymerized samples of increasing polymer weight, prepared using a $\text{MgCl}_2/\text{TiCl}_4$ /diether activated ZNC system. The insertion of monomer units to the coordination sphere of Ti(III) species did not lead to any modification in the EPR spectra. However, a dilution of paramagnetic species is observed with increasing polymer weight.

Conclusion

Ziegler-Natta catalysis has been extensively studied for many decades, but the atomic-scale structure of the active-sites in these catalysts remains a matter of debate and researchers continue to work on developing new techniques and approaches to better understand the nature of the catalytic centers.

In this PhD thesis Electron Paramagnetic Resonance (EPR) spectroscopy has been used to investigate paramagnetic species in heterogeneous Ziegler-Natta catalyst (ZNC) prepared in the laboratories of Giulio Natta R&D Centre of Basell Poliolefine Italia (BPI) in an effort to couple advanced spectroscopic methods to the characterization of samples of industrial relevance. The thesis project was developed as a joint PhD between the EPR laboratories of the University of Torino and Antwerp and the BPI laboratories, within the frame of the H2020 MSCA-EJD PARACAT project (grant agreement No 813209).

The approach involved the use of hyperfine spectroscopic experiments, namely HYSCORE and ENDOR measurements, benchmarked against a series of systems of increasing complexity. With this approach, it was possible to determine the nature of Ti(III) species introduced in $\text{MgCl}_2/\text{TiCl}_4$ catalyst precursors, in the presence and absence of different Lewis bases, revealing preferential adsorption on different surface terminations of different Lewis bases. In the binary system ($\text{MgCl}_2/\text{TiCl}_4$) two Ti(III) species were observed that were called Ti(III)-**A** and Ti(III)-**B**. The addition of Lewis bases (monoether or diester) led to a selective suppression of these species. In the presence of a monoether ($\text{MgCl}_2/\text{TiCl}_4/\text{monoether}$) species Ti(III)-**A** was found to be dominant, while in the presence of a diester ($\text{MgCl}_2/\text{TiCl}_4/\text{diester}$) species Ti(III)-**B** becomes the dominant species (Chapter 4.2.1).

Moving from this observation, the influence of Lewis bases, having the same functional group but a different structure, was also investigated in two ZN pre-catalyst systems of the "fifth generation" (**A1** and **B1**), containing diethers of different natures (Chapter 4.2.2). A slightly different distribution of Ti(III) species was observed in the two cases with the main difference being the presence of an intense carbon-based radical in sample **A1**, which appears to be related to the bulkiness of the diethers used as a Lewis base.

Additionally, the same pre-catalysts were investigated upon activation with triethylaluminum (TEA), via a solid-gas reaction and liquid phase (following the industrial practice at BPI). As expected, a strong increase in the Ti(III) EPR signal was observed as a result of the reductive activation of the pre-catalysts, revealing the formation of new species characterized by different spin-Hamiltonian parameters. Importantly, 3-pulse ESEEM spectra at Q-band reveal a proximity of the Ti(III) species with ^{27}Al nuclei from the co-catalyst in the system with a monoether as an internal donor, substantiating the formation of bimetallic Ti(III)-Al sites (Chapter 5.1).

In the two ZN pre-catalyst systems of the "fifth generation" (**A1** and **B1**), containing diethers of different natures, a comparison between the activation in gas phase and liquid phase (in presence of methyl-cyclohexyl-dimethoxy silane (MCDMS)) was made, revealing minor differences in the spectroscopic characteristics of the formed Ti(III) species (Chapter 0). The intense radical species observed in one of the two catalysts (**A1**) was exploited to set up a methodology based on the instantaneous diffusion to measure the local microscopic concentration of the radicals. This revealed the formation of local radical clustering, but more importantly, will be the basis for future investigations related to the local concentration, *i.e.* clustering of Ti(III). Future work will involve the use of advanced dipolar spectroscopy techniques, which allow to probe the distances between paramagnetic sites. Although well-known in EPR studies of proteins, these methods have not been exploited in the study of ZNC.

In the polymerization of ethylene and propylene, one of the most crucial steps involves the coordination of ethylene and propylene monomers to the transition-metal ions of ZNC systems. Previously our group investigated the formation of a $\pi\{\text{Ti(III)-ethylene}\}$ bond in TiAlPO-5 zeotype materials, believed to be involved as intermediates in polymerization, and probed the metal-to- substrate π^* back-donation [235]. In this thesis, pre-polymerized samples of increasing polymer weight, representing the most complex composition of ZNC, were analyzed using an activated $\text{MgCl}_2/\text{TiCl}_4/\text{diether}$ ZNC system (Chapter 5.3). This step is crucial in industrial practice when using highly active ZNC systems, to control the morphology of the polymer particles. The insertion of ethylene monomer units to the coordination sphere of Ti(III) species, did not lead to any modification in the EPR spectra as observed before by our group. Only a dilution of paramagnetic species is observed with increasing polymer weight, with no changes in the coordination geometry of Ti(III) species.

Overall, the current work has shown that different EPR techniques, including hyperfine spectroscopy, are promising tools to study ZNC systems prepared under industrial relevant conditions. However, the interpretation of the complex EPR data is not always straightforward, and the here presented study should be extended in future. In order to

better understand the inner working of ZNC systems, it will be interesting to involve the use of isotopically enriched probe molecules like ^{13}C -enriched CO for monitoring the local environment of Ti(III) species and ^{13}C -enriched TEA to verify the formation of the Ti- ^{13}C bond. In the polyolefin industry CO is used to temporarily quench the polymerization reaction by interacting with the Ti-alkyl bonds and generating carbonyl groups. However, no information about the direct bond between Ti and CO was achieved so far, and the combination of EPR spectroscopy with the use of ^{13}C -enriched CO could promise a breakthrough in understanding this mechanism and the nature of the active sites. Also, an extension to a wider pallet of Lewis bases, will allow to understand in more detail the influence of these electron donors on the catalytic process.

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Appendix

Publications

1. **Podvorica, L.**; Salvadori, E.; Piemontesi, F.; Vitale, G.; Morini, G.; Chiesa, M. Isolated Ti(III) Species on the Surface of a Pre-active Ziegler Natta Catalyst. *Appl. Magn. Reson.* **2020**, 51, 1515–1528. DOI: 10.1007/s00723-020-01266-2.
2. Bracci, M.; Bruzzese P. C.; Famulari, A.; Fioco, D.; Guidetti, A.; Liao Y.- K.; **Podvorica, L.**; Rezayi, S. F.; Serra, I.; Thangavel, K. Paramagnetic Species in Catalysis Research: A Unified Approach Towards (the role of EPR in) Heterogeneous, Homogeneous and Enzyme Catalysis. In *Electron Paramagnetic Resonance: Volume 27*; Chechik, Victor; Murphy, D. M.; Bode, Bela E, Ed.; Royal Society of Chemistry: London, 2020; pp. 1 – 46. DOI: 10.1039/9781839162534-00001

Oral Presentations

1. Leonora Podvorica, “*Scientific Integrity*“ at 1st PARACAT Training School on “Basics of Electron Paramagnetic Resonance (EPR) for applications in (bio)catalysis”, Antwerp, Belgium, 15/07/2019.
2. L. Podvorica, M. Chiesa, F. Piemontesi, S. Van Doorslaer, “*Paramagnetic active sites in Ziegler-Natta Catalysts*” at 1st PARACAT Training School (Antwerp Summer School) on “Basics of Electron Paramagnetic Resonance (EPR) for applications in (bio)catalysis”, Antwerp, Belgium, 16/07/2019.
3. L. Podvorica, M. Chiesa, E. Salvadori, F. Piemontesi, S. Van Doorslaer, “*EPR Characterization of Ti (III) Species in Heterogeneous Ziegler-Natta Catalysts*” at 2nd PARACAT Training School (Cardiff Winter School) focused on Catalysis, in Cardiff, UK, 13/01/2020.
4. L. Podvorica, E. Salvadori, H. Y. V. Ching, F. Piemontesi, G. Vitale, G. Morini, S. Van Doorslaer, M. Chiesa, “*Multifrequency EPR investigation on isolated Ti(III) Species on the Surface of Pre-active Ziegler Natta Catalysts*”, at PARACAT Satellite Meeting of the ESR Spectroscopy Group and the Royal Society of Chemistry, Online, Cardiff, UK, 15/04/2021.

5. L. Podvorica, “*The Application of X-Ray Absorption and X-Ray Emission Spectroscopy to Study Ziegler-Natta Catalysts*” at PARACAT Summer School 2021 - Spectroscopic and computational methods towards molecular structure and reactivity, Zaragoza, Spain, 21/07/2021.
6. L. Podvorica, E. Salvadori, H. Y. V. Ching, F. Piemontesi, G. Vitale, G. Morini, S. Van Doorslaer, M. Chiesa, “*Isolated Ti(III) Species on the Surface of a Pre-Active Ziegler - Natta Catalysts*.”, at the 4th PARACAT Training School On “Chemistry at the Surface Key Aspects in Materials Design and Catalysis. An International Workshop in Honor of Gaetano Granozzi and Elio Giamello, Baveno, Italy, 26/11/2021.
7. L. Podvorica, E. Salvadori, F. Piemontesi, G. Vitale, G. Morini, S. Van Doorslaer, M. Chiesa, “*Isolated Ti(III) Species on the Surface of a Pre-Active Ziegler - Natta Catalysts*”, at 1st International School of Inorganic Materials, Brdonecchia, Italy, 17/12/2021.
8. L. Podvorica, E. Salvadori, H. Y. V. Ching, F. Piemontesi, G. Vitale, G. Morini, S. Van Doorslaer, M. Chiesa, “*Multifrequency EPR investigation on Industrial Ziegler Natta Catalysts*”, at EPR Catalysis Workshop, in Athens, Greece, 22/09/2022.

Poster presentations

1. L. Podvorica, E. Salvadori, H. Y. V. Ching, F. Piemontesi, G. Vitale, G. Morini, S. Van Doorslaer, M. Chiesa, “*EPR Characterization of Ti (III) Species in Heterogeneous Ziegler-Natta Catalysts*”, at the 11th Conference of European Federation of EPR Groups, Bratislava, Slovakia, 02/09/2019.
2. L. Podvorica, E. Salvadori, H. Y. V. Ching, F. Piemontesi, G. Vitale, G. Morini, S. Van Doorslaer, M. Chiesa, “*EPR Characterization of Ti (III) Species in Heterogeneous Ziegler-Natta Catalysts*”, at the 8th School of the European Federation of EPR groups on “Advanced EPR”, Brno, Czech Republic, 20/11/2019.
3. L. Podvorica, E. Salvadori, H. Y. V. Ching, F. Piemontesi, G. Vitale, G. Morini, S. Van Doorslaer, M. Chiesa, “*EPR Characterization of Ti (III) Species in Heterogeneous Ziegler-Natta Catalysts*”, at the 7th Annual Cardiff Catalysis Institute Conference, Cardiff, UK, 16/01/2020.

4. L. Podvorica, E. Salvadori, H. Y. V. Ching, F. Piemontesi, G. Vitale, G. Morini, S. Van Doorslaer, M. Chiesa, “*Multifrequency EPR investigation on isolated Ti(III) Species on the Surface of Pre-active Ziegler Natta Catalysts*”, at the 54th International Meeting of the ESR Spectroscopy Group of the Royal Society of Chemistry, Remote, UK, 16/04/2021.
5. L. Podvorica, E. Salvadori, H. Y. V. Ching, F. Piemontesi, G. Vitale, G. Morini, S. Van Doorslaer, M. Chiesa, “*EPR Investigation on Isolated Ti(III) Species on the Surface of Pre-active Ziegler Natta Catalysts*”, at the 28th Benelux EPR Society Meeting, Remote, Belgium, 28/06/2021.
6. L. Podvorica, E. Salvadori, H. Y. V. Ching, F. Piemontesi, G. Vitale, G. Morini, S. Van Doorslaer, M. Chiesa, “*EPR Investigation of an Industrial Ziegler-Natta Catalyst*”, at the XLVIII Italian Conference of Inorganic Chemistry, Pisa, Italy, 09/09/2022.

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