

UCLA

UCLA Previously Published Works

Title

Structural Characterization of the EtOH-TiCl₄-MgCl₂ Ziegler-Natta Precatalyst

Permalink

<https://escholarship.org/uc/item/5vz2s4z0>

Journal

The Journal of Physical Chemistry C, 120(32)

ISSN

1932-7447

Authors

D'Anna, V
Norsic, S
Gajan, D
et al.

Publication Date

2016-08-18

DOI

10.1021/acs.jpcc.6b05313

Peer reviewed

Structural Characterization of the EtOH–TiCl₄–MgCl₂ Ziegler-Natta Pre-catalyst

V. D'Anna,[†] S. Norsic,[‡] D. Gajan,[¶] K. Sanders,[¶] A. J. Pell,[¶] A. Lesage,[¶] V.
Monteil,[‡] C. Copéret,[§] G. Pintacuda,[¶] and P. Sautet^{*,†,||}

*CNRS, ENS Lyon, Université Lyon 1, Laboratory of Chemistry, 46, Allée d'Italie, 69364
Lyon 07, France., Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, Chimie Catalyse
Polymères et Procédés (C2P2), LCPP team, 43 Bd du 11 novembre 1918, 69616
Villeurbanne, France., Université de Lyon, Institut des Sciences Analytiques, UMR 5280,
CNRS, Université Lyon 1, ENS Lyon - 5, rue de la Doua, F-69100 Villeurbanne, France.,
Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir-Prelog-Weg 15,
8093 Zürich, Switzerland., and Department of Chemical and Biomolecular engineering,
University of California, Los Angeles, Los Angeles, CA 90095, United States.*

E-mail: Philippe.Sautet@ens-lyon.fr

Phone: (1)310-825-8485.

*To whom correspondence should be addressed

[†]ENS-Lyon

[‡]uni-lyon-pol

[¶]uni-lyon

[§]ETH-Zurich

^{||}UCLA

Abstract

The Ziegler-Natta polymerization is one major example of application of catalysis in industry. Since the first discovery of the Ziegler and Natta, several modifications of the catalyst have been developed, in order to improve its performances. Nowadays, a typical Ziegler-Natta catalyst for polyethylene synthesis consists of a precatalyst, composed by TiCl_4 supported on MgCl_2 in presence of a Lewis base, activated by organoaluminium.

The atomic-scale characterization of the Ziegler-Natta catalyst is crucial for further improvement of the catalyst. Here, the precatalyst $\text{TiCl}_4\text{-MgCl}_2$ with EtOH as internal Lewis base is characterized combining solid-state NMR spectroscopy and periodic density functional theory calculations. From total energy and NMR spectra, 8 surface species were proposed showing EtO^- ligands on the Ti and EtOH/ EtO^- on the surface Mg species. These species lead to a complete interpretation of the NMR 2D spectra. Hence a detailed molecular scale description of the pre-catalyst was obtained.

Introduction

The discovery of the olefin polymerization catalysts achieved by Ziegler and Natta¹⁻⁵ in the 1950th was a worldwide breakthrough. This discovery has allowed the introduction of plastics in everyday life. Indeed polyolefins such as polyethylene and polypropylene represent in 2015 almost half of the 300 million tons of global plastics production in 2015.⁶ Catalysts based on the Ziegler-Natta (ZN) concept are still massively used in the industrial production of plastics, and this puts the ZN catalysts among the most advanced industrial applications of catalysis.^{7,8}

Since the discoveries of Ziegler and Natta, numerous studies were devoted to the improvement of the activity (for ethylene and propylene homo- and co-polymerizations) and the selectivity (in particular the stereoselective polymerization of propylene) of the catalysts, leading to the modern ZN-catalysts.

The last generations of heterogeneous ZN catalytic systems are typically based on titanium tetrachloride, TiCl_4 , supported on magnesium dichloride in presence of Lewis bases (monodentate such as e.g. alcohols or ethers and/or bidentate, referred as “internal” Lewis base). The thus-generated ZN precatalysts are subsequently activated by alkylaluminium. In addition, a bidentate base, so-called external Lewis base, is added in the specific case of stereoselective polymerization of propylene.⁹

The choice of MgCl_2 as support is a consequence of its structural similarities with that of the “violet” TiCl_3 .^{10,11} Among the possible terminations of MgCl_2 , the (110) was found to preferentially interact with TiCl_4 .^{12–15} In the preparation of highly active ZN precatalysts for polyethylene synthesis one of the key steps is the introduction of a monodentate Lewis base, typically an alcohol^{16–21} or an ether,^{22–28} during the preparation of MgCl_2 and its contact with TiCl_4 .

A considerable effort has been devoted to the characterization of the catalyst from a molecular point of view; this is an important task for both fundamental interest and for the possibility to gain some insights that could be very valuable for further improvements of the catalyst. For this purpose, several experimental^{29–35} and computational^{13,15,36–46} studies were performed. Many features of the catalyst, as the structure of the precatalyst, the activation process, the oxidation state(s) of the active titanium species during the polymerization process were investigated; notwithstanding, there are still several open questions.

It was recently shown, by combining solid state NMR and DFT calculations, that THF used as internal Lewis basis was a non-innocent ligand and underwent reaction with TiCl_4 upon adsorption of the latter on the $\text{MgCl}_2\text{-THF}_{1.5}$ support, yielding surface alkoxide species.²² Here we investigate the fate of EtOH in $\text{MgCl}_2\text{-EtOH}_{1.5}$ upon the reaction of TiCl_4 with the latter support by combining solid state NMR and DFT calculations.

Experimental

Synthesis

All chemicals were handled using standard Schlenk procedures under argon atmosphere. Solvents were distilled from drying agents. Pure triethylaluminium (TEA) was purchased from Wacko chemical. Ethylene (purity 99.95%) was purchased from Air Liquide and used without any further purification.

Titanium, Magnesium, Carbon, Hydrogen contents of precatalysts were determined by elemental analysis, performed at the CNRS SCA (Service Central d'Analyse) laboratory in Solaize (France).

Molecular weights of polyethylene samples were determined by size exclusion chromatography (SEC) using a Viscotek Malvern HT-GPC module 350A equipped with three mixed bed columns (300 × 7.8 mm from Malvern Instrument) and a guard column (75 × 7.5 mm). Dry polymer samples were dissolved at 150° C in 1,2,4-trichlorobenzene (stabilized with 2,6-di(tert-butyl)-4-methylphenol), at a 3 mg mL⁻¹ concentration. The system was calibrated with polyethylene standards. Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC1 at a heating rate of 5 K/min. Two successive heating and cooling of the samples were performed. We have considered data (T_m values) obtained during the second heats.

Synthesis of pre-catalysts

The Ziegler-Natta pre-catalyst (MgCl₂/EtOH/TiCl₄) was prepared as follows: first MgCl₂ was stirred in boiling EtOH or 1-¹³C-labeled EtOH (1 g of MgCl₂ for 10 mL of EtOH) for 4 h. After cooling down the suspension, heptane was added dropwise. After decantation, the filtrate was removed and the remaining solid was washed 4 times with heptane. A white

powder of $\text{MgCl}_2(\text{EtOH})_x$ with $x \approx 2$ was obtained. The compound was then treated with an excess of liquid TiCl_4 (1 g of $\text{MgCl}_2(\text{EtOH})_x$ for 10 mL of TiCl_4) at 90° C for 2 h. Toluene was added dropwise, and the mixture cooled down. After decantation, the solid was washed 3 times with hot toluene and 4 times with heptane yielding a yellow powder.

Standard polymerization procedure of ethylene

Ethylene polymerizations were carried out in a 1 L stainless steel autoclave (equipped with safety valves, stirrer, oven) from Sotalem Co. Before each polymerization, the reactor was washed using a millimolar solution of TEA in heptane. A suspension of few milligrams of pre-catalyst was then prepared in 250 mL of a 3 mM solution of TEA in heptane in a Schlenk tube under argon. The mixture was introduced through cannula into the cooled reactor. Then 1 bar of H_2 was introduced with 7 bars of ethylene. The mixture was heated at 80° C under stirring (500 rpm). During the polymerization the total pressure was maintained constant. After 1 hour of polymerization the reactor was slowly cooled down and degassed. The slurry of polymer was then filtrated, washed with ethanol and dried under vacuum at 90° C.

NMR

The solid-state NMR spectra were acquired on a Bruker Avance III 800 spectrometer operating at a magnetic field of 18.8 T (Larmor frequencies of 800.146 MHz for ^1H and 201.205 MHz for ^{13}C), using either a 3.2 mm Bruker HCN standard-bore magic-angle-spinning (MAS) probe or a 1.3 mm Bruker HCN standard-bore MAS probe.

The one-dimensional (1D) ^{13}C cross-polarization (CP)-MAS spectrum⁴⁷ was acquired using the 3.2 mm probe at 18 kHz MAS, with a 1 ms CP contact time using a constant amplitude spin-lock frequency of 50 kHz on ^{13}C , and a linear ramp from 53.5 kHz to 107 kHz on ^1H . The 90-degree ^1H excitation pulse and the SPINAL-64 decoupling⁴⁸ were calibrated at 96 kHz of radio-frequency (RF) field amplitude. In total 512 scans were acquired using a recycle delay

of 2 seconds, resulting in a total experiment time of 17.5 minutes.

The 1D ^1H MAS spectrum was acquired with a spin-echo experiment at 60 kHz MAS using a 1.3 mm probe. The 90° and 180° pulses were calibrated at 100 kHz of RF field amplitude and an echo-shift period of six rotor periods ($100\ \mu\text{s}$) was used. The resulting free-induction decay (FID) was collected starting at the peak of the shifted echo. A total of 128 scans were acquired using a 10 s recycle delay, giving a total experiment time of 21.5 minutes.

The 2D magic-angle-turning (MAT)⁴⁹ experiment was achieved by first cross polarizing from protons using identical conditions as the CP-MAS experiment. The MAT recoupling time was 20 rotor periods (4 ms) and 150 increments were acquired using the echo/anti-echo scheme, using 180° refocusing pulses of 52.6 kHz of RF field amplitude. A recycle delay of 2 s was employed to collect 384 scans per increment, giving a total experiment time of two days, 17 hours, and 17 minutes. The individual CSA sideband patterns were analyzed using the dmfit software.⁵⁰

The ^1H - ^1H double quantum (DQ)-single quantum (SQ) correlation spectrum was acquired using the back-to-back (BABA) sequence⁵¹ at 60 kHz MAS. The double-quantum creation and reconversion recoupling times were both one rotor period ($16.67\ \mu\text{s}$). A total of 128 rotor-synchronized increments in the indirect dimension were acquired using the States-TPPI acquisition mode,⁵² for a total acquisition time of 1.067 ms in the indirect double quantum dimension. A 2-ms z-filter was applied immediately prior to acquisition and 256 scans were acquired per increment using a 2 s recycle delay, giving a total experiment time of 18.5 hours.

The ^1H - ^{13}C heteronuclear correlation (HETCOR) spectrum was acquired using identical CP RF field amplitudes as the CP-MAS spectrum, but with a shorter contact time of $250\ \mu\text{s}$ in order to minimize long-range correlations. Homonuclear decoupling in the ^1H indirect dimension was achieved using the eDUMBO-122 sequence⁵³ at 100 kHz field amplitude and a cycle time of $32\ \mu\text{s}$. The direct dimension was acquired under SPINAL-64 heteronuclear ^1H decoupling using a 96 kHz RF field amplitude. In total 96 increments were acquired with

384 scans per increment using the States-Haberkorn-Ruben acquisition mode,⁵⁴ resulting in an experiment time of 20.5 hours.

Computational details

The periodic calculations were performed at the Density Functional Theory (DFT) level, using the VASP^{55,56} code. The General Gradient Approximation (GGA) was chosen with the PBE functional;^{57,58} the atomic cores were described using the Projector-Augmented Wave (PAW) method.^{59,60} A plane waves basis set with an kinetic energy cutoff of 400 eV was used. The van der Waals interactions were taken into account with the Grimme-D2 method.⁶¹ The MgCl_2 surface was modeled by the (110) termination, since it yields much more favorable adsorption energy of TiCl_4 compared to the (001) and (104) surfaces.²² The MgCl_2 solid is formed by the repetition of Cl-Mg-Cl two-dimensional sheets, bound by van der Waals forces. These sheets are perpendicular to the (110) surface and their terminations form one-dimensional rows (Figure 1). Two model systems were exploited to reproduce the reaction environment. The first one, denoted as *extended*, consists of a 3×3 supercell of the (110) surface of MgCl_2 , hence including 3 rows, each containing 3 surface Mg atoms, where a unit of TiCl_4 is anchored. It is composed by ten layers of MgCl_2 with nine Mg atoms per layer. During the geometrical optimizations, the bottom five layers were kept frozen in the geometry of the bulk, while the others and the adsorbed species were relaxed. A large portion of vacuum (~ 20 Å) was used, in order to minimize the vertical interactions between the cells, since they are physical meaningless. In this regard, the dipolar correction along the C axis was also applied. The optimization of this system was performed at the Gamma point, which is sufficient considering the large unit cell.

The second model system is shown in the Figure S1 of the Supporting Information and will be called *compact* in the following. It contains the same number of frozen and relaxed layers and the same vacuum of the *extended* one. In the *compact* system only one MgCl_2 sheet is

considered with a 1×3 unit cell, and hence it is 3 times smaller than the extended model. There are 3 Mg per surface plane instead of 9 previously. Each vertical layer contains one TiCl_4 unit; that leads to an increase of the TiCl_4 coverage, compared with the *extended* model system. The *compact* cell was optimized using a $2 \times 1 \times 1$ Monkhorst-Pack grid. The same cells without the TiCl_4 unit were used to represent the bare MgCl_2 surface. All the molecular calculations were performed inserting the species in a $20 \times 20 \times 20 \text{ \AA}^3$ box. Temperature and entropy effects are not included. While the temperature will affect the values of the free energy of formation of the surface species, it should not significantly affect the relative energy values between the various considered surface species. Indeed the species are immobilized on the surface, so that translational and rotational contributions are zero. The main contribution will arise from the free reactants, affecting in an identical way all the free energy of formation for the surface species.

The NMR calculations were performed using the VASP package. For both model systems, the number of layers of the cell were reduced from ten to four, while the vacuum thickness was lowered to $\sim 14 \text{ \AA}$. All the chemical shifts values of ^{13}C and ^1H were referred to the ones of TMS. TMS was considered in isolated form; the optimization and NMR calculations were performed on a TMS molecule inside a $20 \times 20 \times 20 \text{ \AA}^3$ box.

Results and discussion

Experimental investigations

Elemental analysis of ZN-precatalyst obtained from the synthesis shows the presence of 7.5 %wt of Ti, 16.7 %wt of Mg and 13.5 %wt of EtOH, thus giving an average molecular formula $\text{MgCl}_2(\text{EtOH})_{0.42}(\text{TiCl}_4)_{0.23}$ and a ratio EtOH/Ti close to 2.

Upon activation with triethylaluminium (TEA) ($\text{Al/Ti} \approx 100$), the ZN pre-catalyst provides a highly active catalyst for homopolymerization of ethylene under standard conditions (7 bars of ethylene and 1 bar of H_2 at 80°C) with an activity of $24700 \text{ gPE} \cdot \text{gcat}^{-1} \cdot \text{h}^{-1}$. The

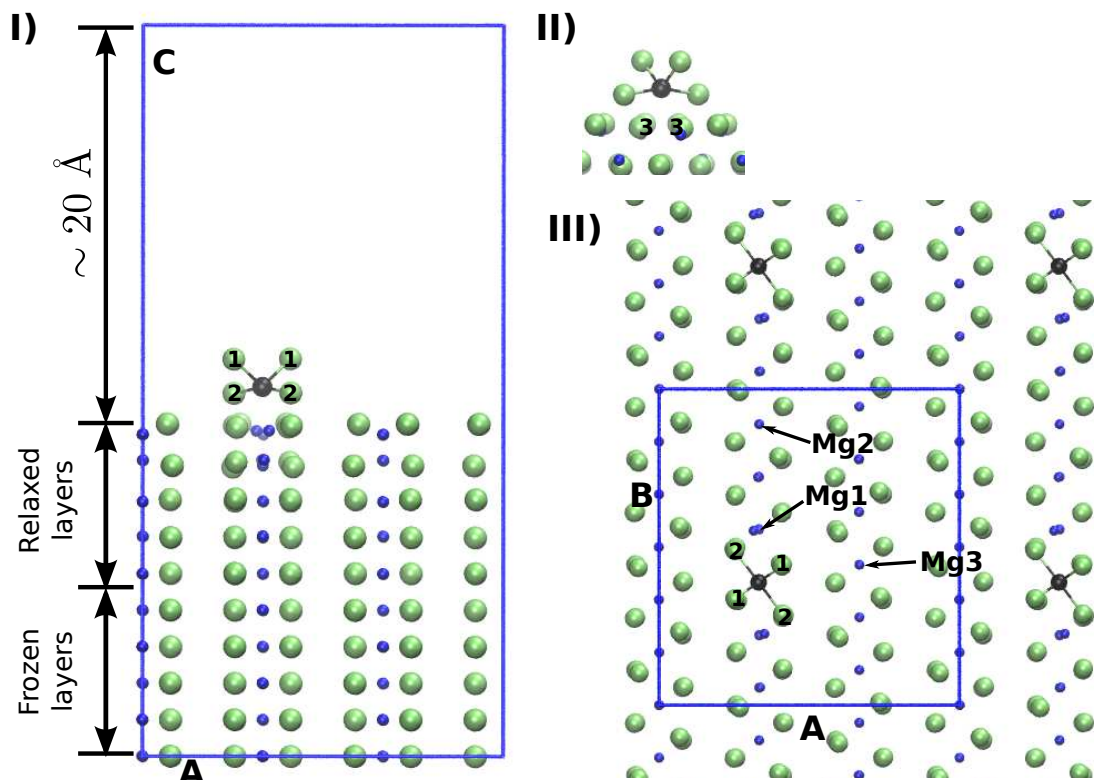


Figure 1: *Extended* cell representing the TiCl_4 anchored on a (110) MgCl_2 surface. Three different directions of observation are shown. Part III (top view) shows the repetition of the cell in the surface plane. The Cl, Mg and Ti species are represented in lime, blue and black, respectively.

polyethylene exhibits expected properties with such type of catalysts: $M_n=35650 \text{ g}\cdot\text{mol}^{-1}$, $\text{PDI}=7.4$ and a melting temperature of 135.3° C .

The structure of the pre-catalyst was then investigated by solid-state NMR spectroscopy through selective ^{13}C -labeling strategies. Figure 2 shows a set of NMR experiments recorded on $\text{EtOH-TiCl}_4\text{-MgCl}_2$ prepared from 1- ^{13}C labeled ethanol. In the 1D ^{13}C spectrum (Figure 2a), the most intense peaks between 60-100 ppm are assigned to resonances arising from the ^{13}C -labelled CH_2 groups in different environments. Four distinct resonances are observed at chemical shifts of 91.1 (A), 85.0 (B), 69.1 (C) and 60.1 (D) ppm for these methylene carbons. For each of these 4 isotropic resonances, the parameters of the chemical shift

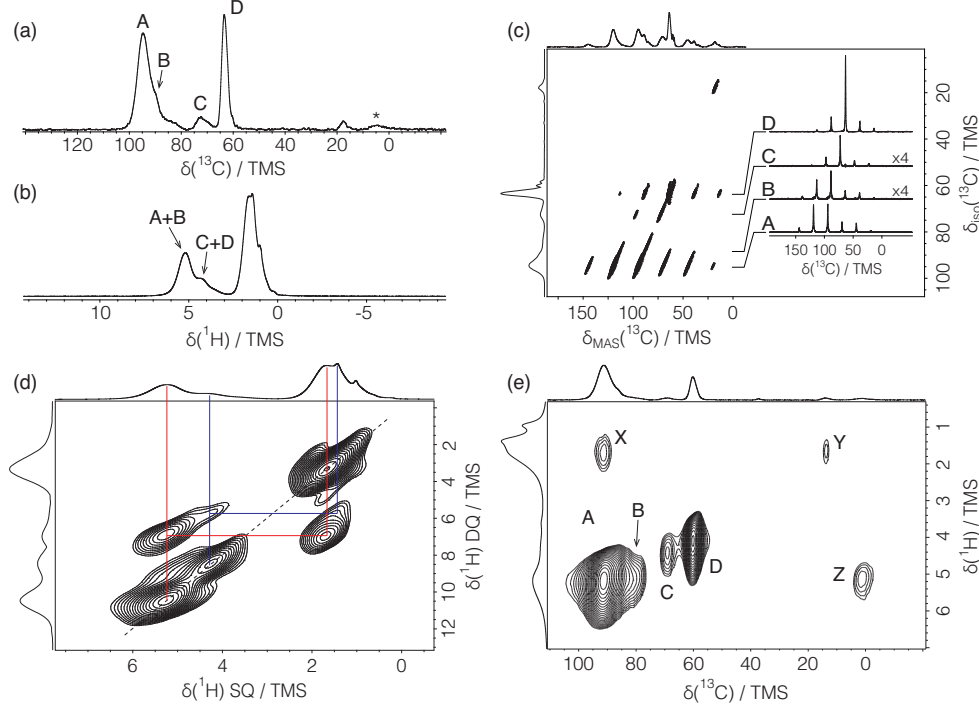


Figure 2: Experimental solid-state MAS NMR spectra of the $\text{MgCl}_2\text{-CH}_3^{13}\text{CH}_2\text{OH-TiCl}_4$ Ziegler-Natta precatalyst measured at an external magnetic field strength of 18.8 T (nominal ^1H Larmor frequency of 800 MHz). Parts (a) and (b) are the one-dimensional MAS spectra of ^{13}C and ^1H , respectively. The MAT spectrum shown in (c) displays the sideband pattern for each carbon environment, resolved isotropically; a zoom on the CSA of the four signals is shown in the insert. The BABA double quantum ^1H - ^1H correlation is shown in (d). The blue and red lines indicate the two correlations found. The ^1H - ^{13}C HETCOR is displayed in (e); the peaks are named with the letters A-D and X-Z.

anisotropy (CSA) tensor were extracted from a CP-MAT experiment (Figure 2c and Table 1). The ^1H spectrum of $\text{MgCl}_2(\text{CH}_3^{13}\text{CH}_2)_{0.42}(\text{TiCl}_4)_{0.23}$ shown in Figure 2b displays two

Table 1: Experimental ^{13}C chemical shift (ppm), Span (ppm) and Skew of the CH_2 groups. The same labels used in the HETCOR spectrum of Figure 2 (c) are used to identify the ^{13}C chemical shifts.

Label (Figure 2 c)	$\delta_{^{13}\text{C}}$ (ppm)	Span (ppm)	Skew
A	91.1	100.4	1
B	85.0	89.6	1
C	69.1	69.8	0.64
D	60.1	60.4	0.69

main broad resonances centered at around 5 and 2 ppm, and corresponding respectively to the CH₂ and CH₃ groups of the pre-catalyst. The 2D DQ-SQ ¹H-¹H correlation spectrum shown in Figure 2d allows a more detailed analysis of these ¹H chemical shifts. In particular, the autocorrelation peaks along the diagonal reveal two main broad methylene resonances at around 5.2 and 4.2 ppm, which correlate with distinct CH₃ resonances, at 1.7 ppm (red lines) and at 1.4 ppm (blue lines), respectively.

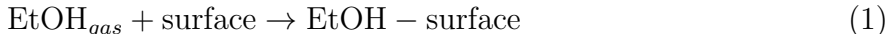
The 2D ¹H,¹³C HETCOR in Figure 2e shows four intense C/H correlations, labelled A, B, C and D in the Figure, at 91.1/5.1 ppm, 85.0/5.1 ppm, 69.1/4.4 ppm and 60.1/4.0 ppm, respectively, corresponding to the four distinct CH₂ groups. The use of a short CP contact time (250 μs) allows for the observation of mainly one-bond correlations. While the peaks C and D fall in the range of standard ethoxy derivatives, the downfield shift and the larger CSA observed for peaks A and B are more consistent with ethoxy groups bound to a highly electrophilic transition metal, like Ti.^{22,62} The ¹H chemical shifts of these correlation peaks are centered at around 5.1 ppm (for peaks A and B) and at around 4.2 ppm (for peaks C and D) in agreement with what was observed in the proton DQ-SQ spectra. In addition to these intense correlations, three additional correlations, named X, Y and Z in Figure 2e, are also observed at 91.1/1.5 ppm, 20.0/1.5 ppm and 2.0/5.1 ppm, respectively. X is a long-range correlation between the methyl protons and the methylene carbons; Y is a one-bond correlation resulting from the natural abundance CH₃ groups, and Z is a long-range correlation between the methyl carbons at natural abundance and the methylene protons.

The observation of the four distinct methylene resonances and thereby of four different -OCH₂-CH₃ moieties indicates that upon addition of TiCl₄ to the MgCl₂/EtOH support EtOH is converted to four different entities. We therefore investigated the potential surface species by DFT calculation, considering first the adsorption of EtOH on TiCl₄/MgCl₂ with various coverage levels. Following, the possibilities of alcoholysis of one M-Cl (M= Mg, Ti) bond were described. Finally, the potential double alcoholysis reaction on one metal was

analyzed. In the following, these three different types of interactions of the EtOH ligand will be discussed both from the total energy aspect and from the simulated ^{13}C and ^1H chemical shifts.

Adsorption of EtOH molecules on $\text{TiCl}_4\text{--MgCl}_2$

At first the interaction of one EtOH molecule with the bare MgCl_2 surface was analyzed (EtOH-bareMgCl_2) using the *extended* cell. If one expresses the coverage, θ_{EtOH} , as monolayer (ML= number of EtOH molecules per surface Mg atom), this case corresponds to $\theta_{\text{EtOH}} = 1/9$ ML. The optimized structure shows that EtOH binds with the O atom interacting with a surface Mg atom (Mg-O distance of 2.05 Å) in a Lewis base-Lewis acid type interaction with an adsorption energy of -118 kJ/mol, according to Equation 1 (with surface= MgCl_2).



Upon adsorption of TiCl_4 on MgCl_2 , the surface Mg atoms are not equivalent anymore. Consequently, the study of the interaction of EtOH with surface Mg was expanded by considering three different Mg interaction sites, indicated as Mg1, Mg2 and Mg3 in the part III of Figure 1. In particular, Mg1, Mg2 and Mg3 represent a Mg surface atom close to TiCl_4 , a Mg atom “far” from the TiCl_4 but belonging to the same row, and a Mg atom of a row different from the one of TiCl_4 , respectively. In the following, the structures representing the interaction between the EtOH and the different Mg atoms will be referred as EtOH-Mg1, EtOH-Mg2 and EtOH-Mg3. In order to complete the description of the system, also the direct interaction between EtOH and TiCl_4 (EtOH-TiCl_4) was considered. The obtained structures are shown in Figure S2 of the Supporting information.

Analogously to the case of the EtOH-bare-MgCl_2 system, the adsorption energy ΔE_{ads} of each structure was calculated according to Equation 1, with surface= $\text{TiCl}_4\text{--MgCl}_2$ (using the *extended* cell). The obtained energies are collected in Table 2, where also ΔE_{ads} for

EtOH-bare-MgCl₂ is shown for comparison. Table 2 shows that the three structures, where

Table 2: Adsorption energy (ΔE_{ads}) of EtOH with TiCl₄-MgCl₂. The ΔE_{ads} for EtOH on the bare MgCl₂ is also shown. The relative stability (ΔE_{rel}) of the isomeric structures is reported. All the values are expressed in kJ/mol.

Structure	ΔE_{ads} (kJ/mol)	ΔE_{rel} (kJ/mol)
EtOH-Mg1	-118	+1
EtOH-Mg2	-116	+3
EtOH-Mg3	-119	0
EtOH-TiCl ₄	-17	+101
EtOH-bareMgCl ₂	-118	

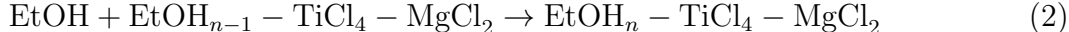
EtOH is linked to a Mg atom, have almost the same energy (within 3 kJ/mol), with values similar to what was obtained on pure MgCl₂ (within 2 kJ/mol). The calculated Mg-O distances are 2.04-2.05 Å for all the structures, as found on EtOH-bare-MgCl₂. These results show that the presence of the TiCl₄ at the surface of MgCl₂ does not affect the interaction of EtOH with the MgCl₂ surface. No significant lateral interaction is seen between EtOH and TiCl₄, even for the closer Mg1 position. A particularly weak adsorption energy was found when EtOH is positioned on the octahedral TiCl₄ unit, since the binding is only due to the interaction between the H of hydroxyl and a Cl of TiCl₄. That position will hence not be occupied.

The increase of EtOH coverage on TiCl₄-MgCl₂ was studied using the *compact* cell; in particular, the coverages of 1/3, 2/3, 1, 4/3, 5/3 and 2 ML were considered, that correspond to 1, 2, 3, 4, 5 and 6 molecules per 3 surface Mg within the *compact* cell. In this case all the Mg atoms were considered equivalent, since within the *extended* system the lateral interactions between EtOH and TiCl₄ were observed to be negligible. The obtained structures, denoted as 1EtOH, 2EtOH, 3EtOH, 4EtOH, 5EtOH and 6EtOH, are shown in Figure S3 of the Supporting information. While the elemental analysis gave EtOH/Ti= 2/1, θ_{EtOH} = 2/3 ML in the *compact* cell, values of θ_{EtOH} > 2/3 ML were also taken into account. This quantifies

the effect of EtOH on the energetic of the system and, then, gives an idea of the importance of the EtOH coverage on the description of the system. Also, a sampling of the disposition of the EtOH molecules on the surface is provided, and, from this, representation of local portions of the pre-catalyst could be obtained.

For the cases of $\theta = 2/3$ ML and $\theta = 1$ ML, two different isomers were considered, indicated as 2EtOH-1 and 2EtOH-2 for $2/3$ ML, 3EtOH-1 and 3EtOH-2 for 1 ML. In 2EtOH-1 and 3EtOH-1 two EtOH molecules interact with one Mg atom, while in 2EtOH-2 and 3EtOH-2 each EtOH interacts with a different Mg atom.

The differential adsorption energies were calculated according to the reaction shown in Equation 2; these values are indicative of the presence of the EtOH molecules on the adsorption of a further one.



The results are summarized in Table 3, where the average adsorption energies are also shown.

Table 3: Differential (ΔE_{dif}) and average (ΔE_{av}) adsorption energies of EtOH with $\text{TiCl}_4\text{--MgCl}_2$ (*compact* model system). The relative stabilities (ΔE_{rel}) of the isomeric structures are also shown. All the values are expressed in kJ/mol. The coverage, θ , defined as number of molecules per surface Mg atom is also shown.

Structure	θ ML	ΔE_{dif} (kJ/mol)	ΔE_{av} (kJ/mol)	ΔE_{rel} (kJ/mol)
1EtOH	1/3	-119	-119	
2EtOH-1	2/3	-86	-103	+36
2EtOH-2	2/3	-123	-121	0
3EtOH-1 ^a	1	-99	-113	+6
3EtOH-2 ^a	1	-104	-115	0
4EtOH ^b	4/3	-100	-111	
5EtOH	5/3	-72	-104	
6EtOH	2	-31	-92	

^a For the calculation of ΔE_{dif} 2EtOH-2 was considered.

^b For the calculation of ΔE_{dif} 3EtOH-2 was considered.

The interaction energy relative to the adsorption of one EtOH molecule on the *compact* cell is similar to the ones obtained in the case of the *extended* one.

Table 3 shows that placing two ethanol molecules on the same surface Mg atom (2EtOH-1) is 36 kJ/mol less stable than distributing them on two different Mg centers (2EtOH-2). The adsorption energy of the second EtOH molecule is then equivalent to that of the first one. Also in the case of the 3EtOH the adsorption on different Mg atoms is energetically favoured, while the difference in energy between the two isomers is less important than the case of the adsorption of two EtOH molecules. For the third and fourth EtOH molecules (coverage of 1 and 4/3 ML) the differential adsorption energy is decreased by 15–20 kJ/mol. A markedly weaker adsorption is found at higher coverage.

The calculated ^{13}C and ^1H chemical shifts of EtOH interacting with $\text{TiCl}_4\text{--MgCl}_2$ are shown

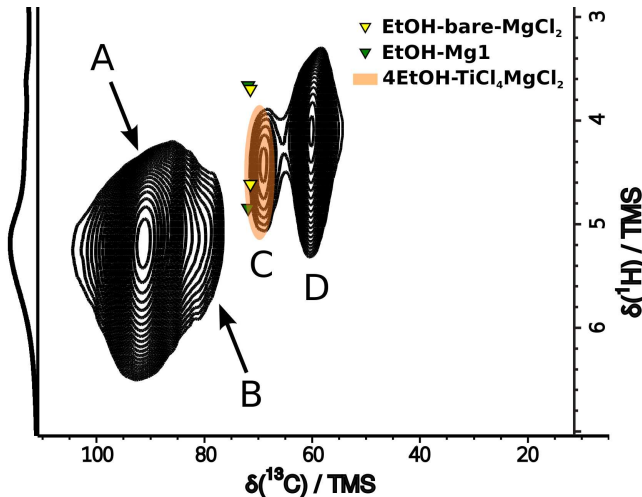


Figure 3: Graphical comparison between the experimental 2D-HETCOR spectrum and the calculated ^{13}C and ^1H correlations. The CH_2 groups of EtOH adsorbed on $\text{TiCl}_4\text{--MgCl}_2$ are shown. To indicate the position of one EtOH molecule on $\text{TiCl}_4\text{--MgCl}_2$, the nomenclature given in Table 2 was used.

in Table S1, while their position with respect to the experimental 2D-HETCOR spectrum is indicated by the green and yellow inverted triangles in Figure 3. The values inherent to the CH_2 group are 71-73 ppm for ^{13}C and 4-5 ppm for ^1H ; these values are in accordance with the experimental signal C.

The CH_2 chemical shifts obtained for one EtOH interacting with different Mg atoms (Mg1, Mg2 and Mg3) of the $\text{TiCl}_4\text{--MgCl}_2$ system do not significantly differ from these obtained for EtOH on the bare MgCl_2 (maximum $\Delta(\delta^{13}\text{C}) \approx 1$ ppm and maximum $\Delta(\delta^1\text{H}) \approx 0.3$ ppm). This suggests that the presence of the TiCl_4 unit does not affect significantly the values of the chemical shifts of the EtOH interacting with the Mg, analogously to what was seen for the energies. The CH_3 group appears at 19-23 ppm for ^{13}C and at 1 ppm for ^1H , while the proton chemical shift (OH group) is more dependent on the structure (2-4 ppm). The differences in chemical shifts for $1\text{EtOH--TiCl}_4\text{--MgCl}_2$ described with the *extended* and with the *compact* systems ($\Delta(\delta) \approx 0.1$ ppm for both ^{13}C and ^1H) show that the change of Ti coverage does not affect the EtOH signal.

In order to evaluate the influence of the EtOH coverage, the NMR spectra were calculated also for the $\text{TiCl}_4\text{--MgCl}_2$ system with four EtOH molecules co-adsorbed ($\theta_{\text{EtOH}} = 4/3$ ML); the obtained values are shown in Table S2 of the Supporting Information, while their position with respect to the experimental spectrum is indicated by the orange region in Figure 3. Figure 3 shows that the coverage has only a minor effect on the chemical shifts and confirms the identification of the signal C as the signal of the EtOH molecules on the surface.

For $\theta_{\text{EtOH}} = 1/9$ ML and $\theta_{\text{EtOH}} = 4/3$ ML the average ^1H chemical shifts are collected in Table S1 and S2, respectively. Their position with respect to the experimental $^1\text{H}\text{--}^1\text{H}$ DQ-SQ correlation spectrum is shown in Figure 4. For both θ_{EtOH} values considered, the calculated $^1\text{H}(\text{CH}_2)\text{--}^1\text{H}(\text{CH}_3)$ correlations identify the experimental correlation indicated with the blue line of Figure 2 (d) to EtOH molecules adsorbed on Mg.

Finally, the Span and the Skew were considered for the ^{13}C signal of the CH_2 group. For both $\theta_{\text{EtOH}} = 1/9$ ML and $\theta_{\text{EtOH}} = 4/3$ ML, the calculated values are shown in Table S3 of the Supporting information. The span depends more on the coverage than the chemical shift, with 90 ppm at $1/9$ ML and 79 ppm at $4/3$ ML (average value). The comparison of the calculated values with the experimental ones relative to the C signal ($\delta_{13\text{C}} = 69.1$ ppm)

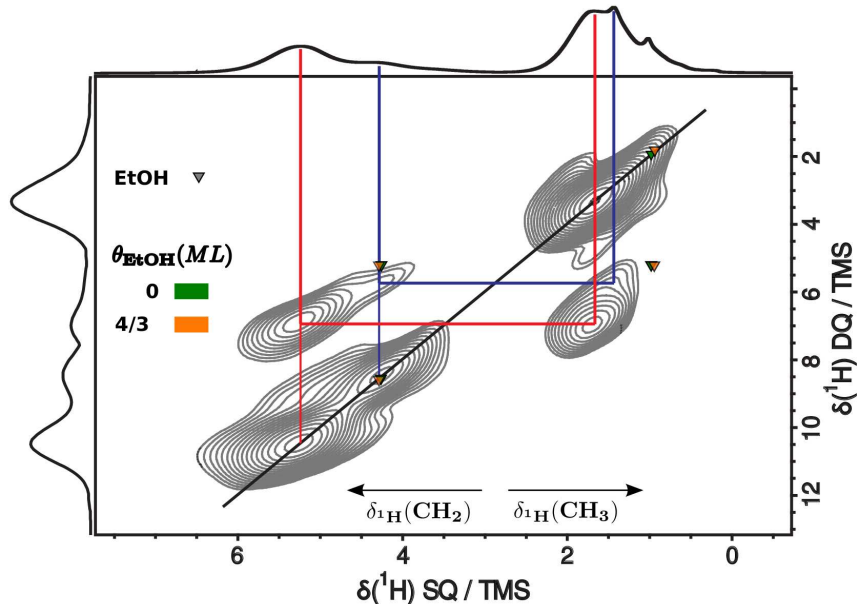


Figure 4: Graphical comparison of calculated and experimental ^1H - ^1H correlations. The correlations inherent to the EtOH molecules adsorbed on $\text{TiCl}_4\text{-MgCl}_2$ are shown. The values inherent to the two conditions of EtOH coverages $\theta_{\text{EtOH}} = 1/9$ ML (green symbols) and $\theta_{\text{EtOH}} = 4/3$ ML (orange symbols) are shown. The calculated ^1H - ^1H correlations were obtained considering the average chemical shifts of the CH_2 and CH_3 groups.

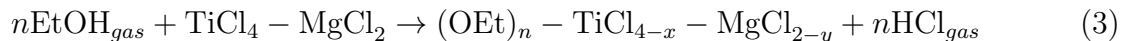
in Table 1 shows a slight overestimation of the calculated Span. The Skew is 0.4-0.5 but comparison with experiment should be considered with care, because experimental errors for this parameter can be important.

Alcoholysis of Ti-Cl or Mg-Cl by EtOH with formation of one EtO group

Following the interaction between the EtOH molecules with the $\text{TiCl}_4\text{-MgCl}_2$ system, alcoholysis of Ti-Cl by EtOH may occur leading to the formation of Ti-OEt groups.

In this regard, Figure 1 shows that the Cl species are not all equivalent. In particular, part I of the Figure shows that there are two different kinds of Cl bound to the Ti at different z coordinate with respect to the surface, labelled 1 and 2. Cl1 is terminal on the Ti,

while Cl2 is bridging Ti and Mg. Part II of Figure 1 points the two Cl^- ions (labelled Cl3) belonging to the MgCl_2 surface that show a weak interaction with the Ti. A final group of Cl^- ions consists of those on the MgCl_2 surface far from the Ti. Based on the results obtained for the adsorption of EtOH on $\text{TiCl}_4\text{--MgCl}_2$, where TiCl_4 appears to have only a short range influence on the MgCl_2 surface, all these Cl^- were considered equivalent. For sake of completeness, the alcoholysis of Mg-Cl bonds in the bulk was also considered. The possible structures obtained after alcoholysis of M-Cl (M=Ti, Mg) are labeled EtO-1, EtO-2, EtO-3, EtO-surface and EtO-bulk according to the type of Cl atom reacted. They are shown in Figure 5. These structures were studied using both the *extended* and *compact* cells; the formation energies, ΔE_{form} , were calculated according to the reaction shown in equation 3, with $n = 1$.

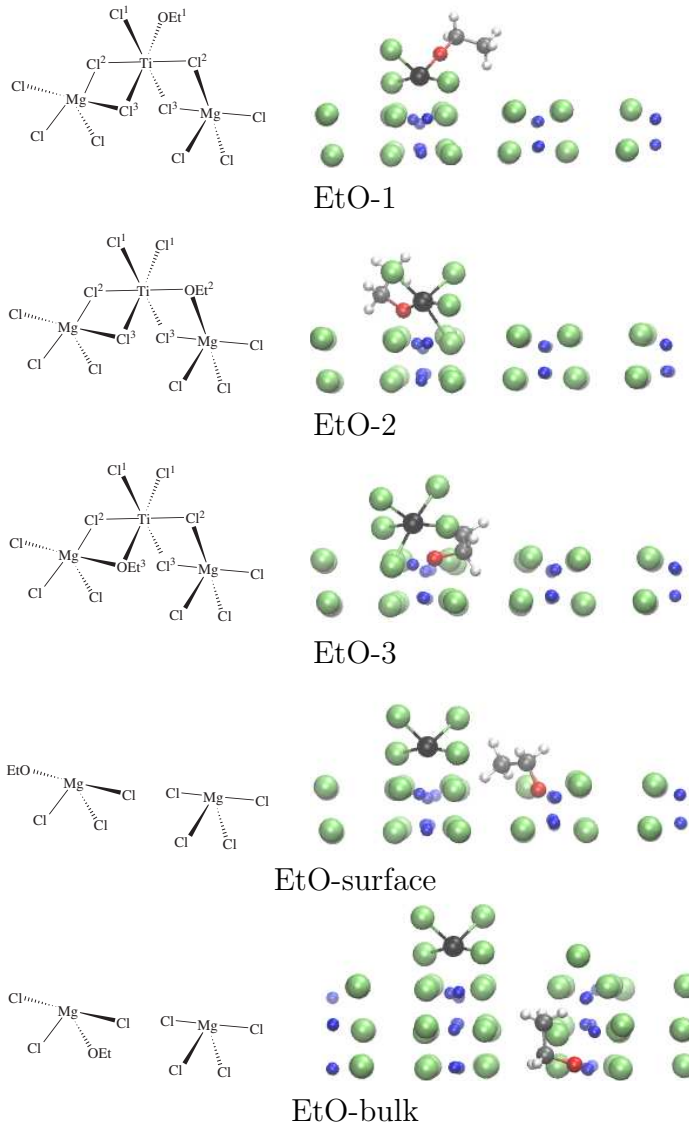


with $x + y = n$. The values of ΔE_{form} and the relative stability, ΔE_{rel} are summarized in Table 4.

Table 4 shows that both surface models (and Ti coverages) give the same relative stability order and very similar values of ΔE_{form} . The most significant variation in stability with the change of the model system is for the alcoholysis of Ti-Cl2 giving EtO-2, resulting in a destabilization of 7 kJ/mol when the *compact* cell is used. Besides the variation of TiCl_4 coverage, going from the *extended* to the *compact* cell does not significantly influence the energetic of the considered structures. Table 4 shows that the alcoholysis of Ti-Cl bonds is more favorable than that of Mg-Cl bonds (the case of bulk Cl being very endothermic). However, we will also consider here the alcoholysis of Mg-Cl at the surface of MgCl_2 since the calculated values of ΔE_{int} is not highly endothermic and this species could be representative of the real surface of MgCl_2 , if defects, such as Cl^- vacancies, were present.

Among the isomers where EtO^- is close to Ti, EtO-3 is the less stable. Considering the

Figure 5: Possible structures obtained from the alcoholysis of one M-Cl (M= Ti, Mg) bond. The structure obtained using the *extended* model system are shown.



synthesis procedure of the pre-catalyst, EtO-3 can be assumed to be irrelevant for the description of the real system. The exothermic formation of the Ti–O bond is in agreement with the theoretical descriptions of the nature of the Ti–O and Ti–Cl bonds.⁶³ The alcoholysis of M-Cl was also studied starting at higher EtOH coverage on the MgCl_2 support, $\theta_{\text{EtOH}} = 4/3$ ML. Note that alcoholysis is performed by a 5th molecule in the cell, so that the final coverage of EtOH+EtO is $5/3$ ML. The same four positions as for $\theta_{\text{EtOH}} = 0$ ML

Table 4: Energy of formation, ΔE_{form} and relative stability, ΔE_{rel} for the alcoholysis of one M-Cl bond. The values obtained within the *extended* and the *compact* cells are shown. All the values are expressed in kJ/mol. Structure names refer to Figure 5.

Structure	<i>Extended</i>		<i>Compact</i>	
	ΔE_{form} (kJ/mol)	ΔE_{rel} (kJ/mol)	ΔE_{form} (kJ/mol)	ΔE_{rel} (kJ/mol)
EtO-1	-38	0	-40	0
EtO-2	-37	+1	-30	+10
EtO-3	+11	+49	+11	+51
EtO-surface	+20	+58	+20	+60
EtO-bulk	+69	+107		

were considered (the bulk Cl atom was excluded); the structures obtained in high coverage condition are shown in Figure S4 of the Supporting information. The obtained formation energies are summarized in Table 5, where the relative stabilities are also given. Table 5 shows

Table 5: Formation energy, ΔE_{form} and relative stability, ΔE_{rel} for the alcoholysis of one M-Cl bond in presence of other EtOH molecules on the MgCl_2 support ($\theta_{EtOH} = 4/3$ ML). All the values are expressed in kJ/mol.

Structure	ΔE_{form} (kJ/mol)	ΔE_{rel} (kJ/mol)
4EtOH-EtO-1	-19	0
4EtOH-EtO-2	-19	0.3
4EtOH-EtO-3	+60	+79
4EtOH-EtO-surface	+83	+102

that, in all the cases, alcoholysis becomes less favored at high EtOH coverage. Reactions at Cl1 and Cl2 are still exoenergetic, while the ones involving the Cl^- of the MgCl_2 support became more endoenergetic. This general decrease in stability can be simply attributed to the steric hindrance exerted on the EtOH performing the alcoholysis by those chemisorbed on MgCl_2 at proximity of the Ti center.

Globally, going from $\theta_{EtOH} = 0$ ML to $\theta_{EtOH} = 4/3$ ML does not influence the order of

stability of the different isomers.

The ^{13}C and ^1H chemical shifts calculated for the EtO^- groups of these structures are collected in Tables S4 and S5, while the chemical shifts of the EtOH molecules present in the high coverage condition are shown in Table S6 of the Supporting information. The graphical representation of these chemical shifts on top of the experimental 2D-HETCOR spectrum is shown in Figure 6.

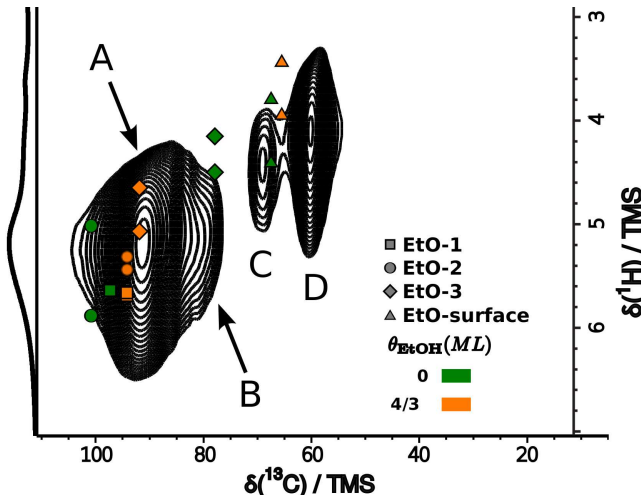


Figure 6: Graphical comparison between the experimental 2D-HETCOR spectrum and the calculated ^{13}C and ^1H correlations. The CH_2 groups of the alcoholysis products, $\text{EtO}-\text{TiCl}_{4-x}-\text{MgCl}_{2-y}$ with $x + y = 1$, are shown. The nomenclature given in Table 4 is used.

For $\theta_{\text{EtOH}} = 0$ ML, the calculated NMR results on the CH_2 group of EtO^- define three regions of ^{13}C and ^1H chemical shifts. The first group (~ 100 ppm for ^{13}C and 5.5 ppm for ^1H , green squares and green circles in Figure 6) corresponds to the signals of EtO-1 and EtO-2; the second group (~ 80 ppm for ^{13}C and 4.2 for ^1H green diamonds) is inherent to EtO-3. Finally, the third group (~ 69 ppm (^{13}C) and 4.0 ppm (^1H), green triangles) coincides with the signal of ethoxy on the MgCl_2 surface.

Within the uncertainty of the calculations, the peak A in the experimental spectrum can

be clearly associated to the terminal EtO-1 and bridging EtO-2 species, resulting from the alcoholysis of the Ti-Cl bond. Peak D could be attributed to the ethoxy groups obtained by alcoholysis of the Mg-Cl bond “far” from the TiCl_4 unit. This latter assignment is supported by the ^{13}C chemical shifts of ethoxy groups in solid $\text{ClMg}(\text{OEt})$ and $\text{Cl}_3\text{Mg}_2\text{OEt}$ well-defined species.⁶⁴ It should be however noted that the reaction of EtOH with Mg-Cl is not observed in the case of the bare support $\text{MgCl}_2(\text{EtOH})_2$, implying that Ti would play a role for that reaction on the pre-catalyst. In addition, the DFT calculations give an endoenergetic nature for this reaction by 20 kJ/mol, so that more reactive defects sites might be required on MgCl_2 for that reaction. Alternatively, HCl could also be scavenged by the large excess of TiCl_4 .

A general overestimation of the calculated ^{13}C chemical shifts can be noted (by 5 – 10 ppm). Figure 6 shows that, in principle, the chemical shifts of EtO-3 (green diamonds) could be associated to the B peak. However, this assignment is not conclusive, since it is the only case where the experimental ^{13}C chemical shift is underestimated. Moreover, EtO-3 was above classified from its energy as not representative of the real system, consequently the B peak still remains unassigned.

The chemical shifts calculated for structures resulting from alcoholysis of M-Cl with spectator additional chemisorbed EtOH molecules on the support ($\theta_{\text{EtOH}} = 4/3 \text{ ML}$) are indicated with orange symbols in Figure 6. A slight shift to lower value ($\sim 3 \text{ ppm}$) of the ^{13}C chemical shift with respect to the case of $\theta_{\text{EtOH}} = 0 \text{ ML}$ can be noted. The only exception is the ^{13}C chemical shift of EtO-3, that is, now, closer to the ones of EtO-1 and EtO-2. Globally, the results obtained for $\theta_{\text{EtOH}} = 4/3 \text{ ML}$ are similar to the ones of $\theta_{\text{EtOH}} = 0 \text{ ML}$.

The assignments of the HETCOR spectrum were verified considering the ^1H correlations between the CH_2 and the CH_3 groups, using the average values of ^1H chemical shifts for these groups shown in Table S5 of the Supporting information; a graphical comparison with the experimental ^1H - ^1H DQ-SQ correlations spectrum is provided in Figure 7. The $^1\text{H}(\text{CH}_2)$ - $^1\text{H}(\text{CH}_3)$ correlation calculated for EtO-1 and EtO-2 on Ti, indicated in Figure 7 with green

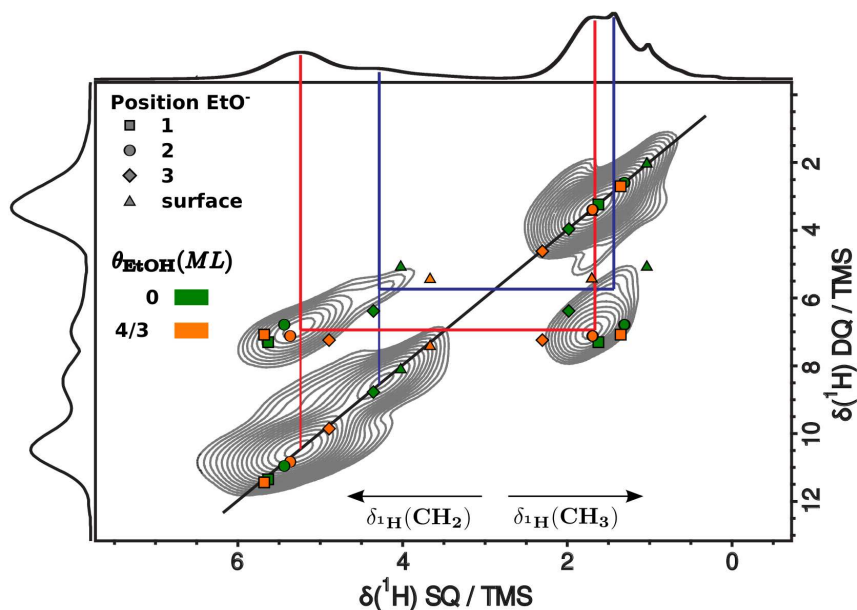


Figure 7: Graphical comparison of calculated and experimental ^1H - ^1H correlations. The correlations inherent to the first alcoholysis products are shown. The positions of the EtO^- groups are labelled according to Figure 1. For each structure, the calculated ^1H - ^1H correlations were obtained considering the average chemical shifts of the CH_2 and CH_3 groups. The values inherent to the two conditions of EtOH coverages $\theta_{\text{EtOH}} = 0$ ML (green symbols) and $\theta_{\text{EtOH}} = 4/3$ ML (orange symbols) are shown.

squares and circles, are 5.6-1.6 ppm and 5.4-1.3 ppm, respectively; these values can be associated to the experimental correlation 5.2-1.7 ppm (red line). Quite similar results were obtained for EtO-1 and EtO-2 for $\theta_{\text{EtOH}} = 4/3$ ML (orange squares and circles of Figure 7). For EtO^- replacing one surface Cl^- , within $\theta_{\text{EtOH}} = 0$ ML, a $^1\text{H}(\text{CH}_2)$ - $^1\text{H}(\text{CH}_3)$ correlation of 4.0-1.0 ppm was obtained, (green triangles in Figure 7). This reproduces the experimental correlation 4.2-1.4 ppm (blue line). For $\theta_{\text{EtOH}} = 4/3$ ML, the values are slightly shifted; a correlation 3.7-1.7 ppm was found in less good agreement with the experimental spectrum (orange triangles in Figure 7). This could indicate that the coverage in the structure 4EtOH-EtO-surface is too high with respect to the experimental situation. Indeed the elemental analysis indicates 2 EtOH/EtO per Ti atom.

Finally, for both θ_{EtOH} values considered here, the $^1\text{H}(\text{CH}_2)$ - $^1\text{H}(\text{CH}_3)$ correlation found for EtO-3 does not reproduce any experimental signal. This corroborates the choice above to

not assign the ^{13}C chemical shift of 85.0 ppm to EtO-3 and, consequently, the EtO-3 species is confirmed as not relevant for the description of the pre-catalyst.

The comparison of the calculated values of Span with the experimental ones (values relative to A and D in Table 1) shows a general reasonable overestimation of the Spam, as seen for the cases describing the interaction of EtOH with the surface.

Alcoholysis of Ti-Cl or Mg-Cl by EtOH with formation of two EtO groups

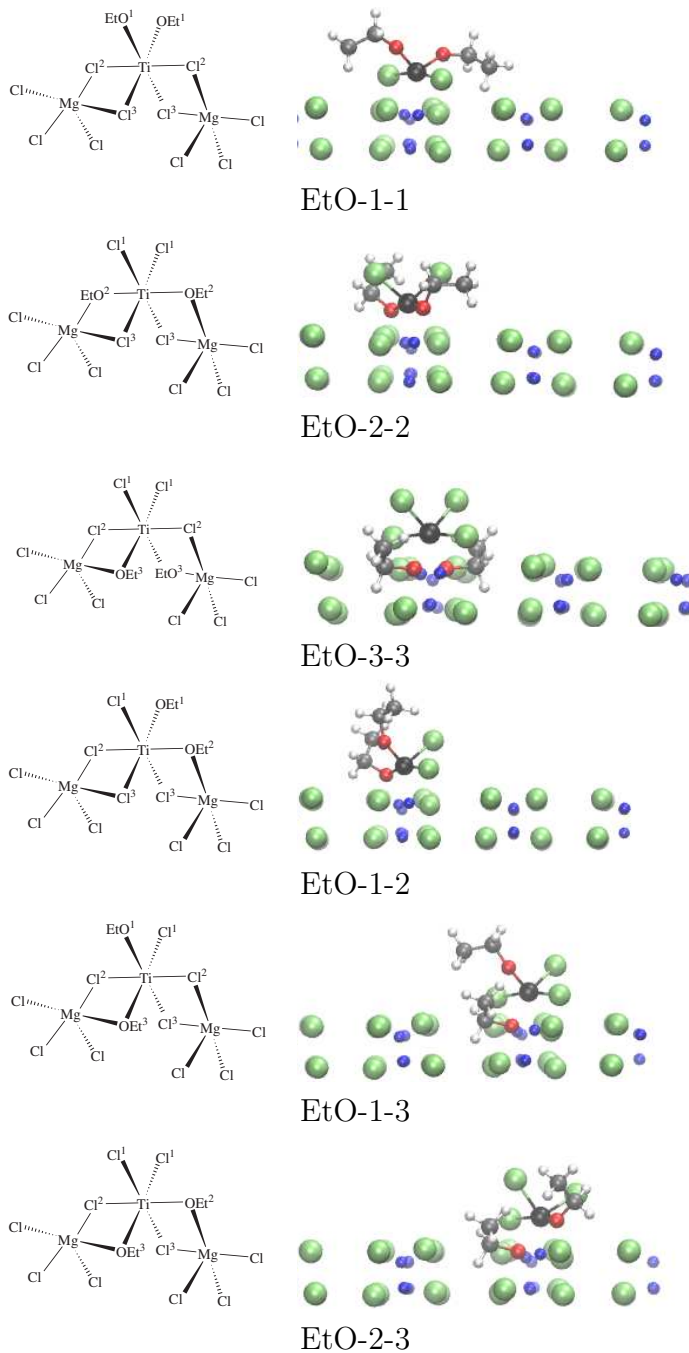
The case of a second alcoholysis of M-Cl leading to two EtO^- groups around Ti was also analyzed. In this case Cl^- in positions 1, 2 and 3 were considered; consequently, there are six structures possible, shown in Figure 8. Also in this case, both the *extended* and the *compact* cells were considered. The energies of formations, ΔE_{form} , calculated according to equation 3 with $n = 2$, are shown in Table 6, where also the relative stability is reported. Considering the results obtained with the *extended* cell, Table 6 shows that all the ΔE_{form}

Table 6: Energies of formation (ΔE_{form}) and relative stability (ΔE_{rel}) inherent to the alcoholysis of two M-Cl bonds within $\theta_{\text{EtOH}} = 0$ ML. All the values are expressed in kJ/mol.

Structure	<i>Extended</i>		<i>Compact</i>	
	ΔE_{form} (kJ/mol)	ΔE_{rel} (kJ/mol)	ΔE_{form} (kJ/mol)	ΔE_{rel} (kJ/mol)
EtO-1-1	-60	+5	-56	+2
EtO-2-2	-48	+16	-47	+11
EtO-1-2	-65	0	-58	0
EtO-1-3	-32	+33	-24	+34
EtO-2-3	-30	+35	-25	+33
EtO-3-3	+25	+90	—	—

are exoenergetic except the one relative to the structure EtO-3-3. Also, this structure is +90 kJ/mol higher in energy than the most stable one, EtO-1-2, and hence strongly improb-

Figure 8: Possible structures obtained from the alcoholysis of two M-Cl bonds and their relative nomenclature.



able; for these reasons EtO-3-3 was not studied using the *compact* cell and for $\theta_{EtOH} = 4/3$ ML. The most stable structure, EtO-1-2, combines a terminal EtO group on Ti and a bridge

one between Ti and Mg.

The energy values obtained using the *compact* cell reproduce quite well the ones obtained with the *extended* cell. The only significant difference is seen for the formation energy of EtO-1-2 (7 kJ/mol less exothermic in the *compact* cell). Hence, also in the case of two alcoholysis steps, the increase of Ti coverage going from the *extended* to the *compact* cell does not significantly affect the description of the precatalytic system.

Table 7 shows the energy of the second alcoholysis for both cells, considering EtO-1 and EtO-2 as starting structures. EtO-3 was not taken into account since we shown that it was not representative of the experimental pre-catalyst. Comparing the obtained data with the

Table 7: Energies of the second alcoholysis (ΔE_{form}) starting, when possible, from EtO-1 and EtO-2. A coverage of $\theta_{EtOH} = 0$ ML is considered. All the values are expressed in kJ/mol.

		Reagent			
		<i>Extended</i>		<i>Compact</i>	
		EtO-1	EtO-2	EtO-1	EtO-2
Product	EtO-1-1	-22	–	-16	–
	EtO-2-2	–	-11	–	-17
	EtO-3-3	–	–	–	–
	EtO-1-2	-27	-28	-18	-28
	EtO-1-3	+6	–	+16	–
	EtO-2-3	–	+7	–	+5

energy values of the first substitution (Table 4) it appears that, when one EtO[–] group is already present in a position 1 or 2, a second replacement in position 1 or 2 is less favorable by 10 to 26 kJ/mol, while a substitution in position 3 is slightly less endoenergetic. One exception is seen in the case of EtO-1-3 within the *compact* cell, where the substitution of Cl[–] in position 3 is slightly more endoenergetic (5 kJ/mol).

Clearly, a second alcoholysis is plausible, and a replacement of a Cl[–] in position 1 and 2 is favored compared to a Cl[–] in position 3. Consequently, the structures EtO-1-1, EtO-2-2 and EtO-1-2 are expected to be representative of the experimental system. The second alcoholy-

Table 8: Energies of formation (ΔE_{form}) and relative stability (ΔE_{rel}) inherent the alcoholysis of two M-Cl bonds, with co-adsorbed EtOH molecules ($\theta_{EtOH} = 4/3$ ML). All the values are expressed in kJ/mol.

Structure	ΔE_{form} (kJ/mol)	ΔE_{rel} (kJ/mol)
4EtOH-EtO-1-1	-36	0
4EtOH-EtO-2-2	+17	+53
4EtOH-EtO-1-2	+10	+46
4EtOH-EtO-1-3 I	+50	+86
4EtOH-EtO-1-3 II	+40	+75
4EtOH-EtO-2-3	+26	+61

sis was also studied in the presence of co-adsorbed EtOH molecules ($\theta_{EtOH} = 4/3$ ML). The structures obtained are shown in Figure S5 of the Supporting information. In this condition two conformations of EtO-1-3 were taken into account: EtO-1-3-I, where the two EtO⁻ are “eclipsed”, and EtO-1-3-II, where the two EtO⁻ are “staggered”. The values of formation energies and the relative stability are summarized in Table 8.

Clearly, the double alcoholysis becomes less favorable when the MgCl₂ rows are already populated by EtOH molecules. Adsorbed EtOH molecules close to the Ti center exert significant steric repulsion with the two EtO⁻ groups on Ti due to the close distance. Only the double alcoholysis of the top Ti-Cl bonds for which the created Ti-OEt groups point away from the surface (EtO-1-1) remains exothermic in these conditions. All other formation energies are positive, hence not favorable. Considering that the ratio EtOH/Ti obtained from the elemental analysis is 2/1, the pre-catalyst is expected to correspond to low coverage of EtOH. The ¹³C and ¹H chemical shifts of the EtO⁻ groups calculated for this class of structures are shown on Figure 9, together with the range for the EtOH molecules present for $\theta_{EtOH} = 4/3$ ML (green region). Numerical values are collected in Tables S8 and S9, while the chemical shifts of the EtOH molecules present for $\theta_{EtOH} = 4/3$ ML are summarized in Table S11 of the Supporting information. The ¹H and ¹³C chemical shifts of the three most stable geometries, EtO-1-1 (dark green squares in Figure 9), EtO-2-2 (dark green circles)

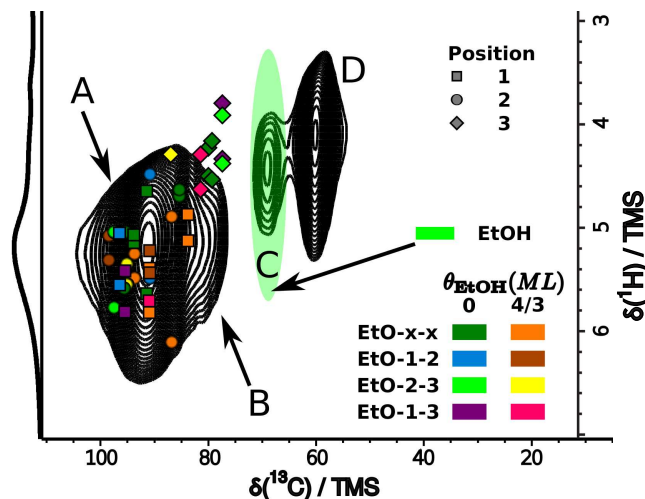


Figure 9: Graphical comparison between the experimental 2D-HETCOR spectrum and the calculated ^{13}C and ^1H correlations for the structures resulting from the alcoholysis of two M-Cl bonds. EtO-x-x indicates the structures resulting from the alcoholysis of two equivalent M-Cl bonds (EtO-1-1, EtO-2-2 and EtO-3-3). The results in absence of co-adsorbed EtOH molecules ($\theta_{\text{EtOH}} = 0$ ML) and in their presence ($\theta_{\text{EtOH}} = 4/3$ ML) are shown. For $\theta_{\text{EtOH}} = 4/3$ ML, the calculated chemical shifts of the EtOH molecules adsorbed on the surface are also shown (green region of the Figure).

and EtO-1-2 (blue symbols) are between 4.4 and 5.6 ppm and 85 and 97 ppm, respectively. The values obtained cover both the peaks A and B of the experimental HETCOR spectrum. More specifically, peak B can be attributed to one of the EtO group in the EtO-2-2 species resulting from double alcoholysis of Ti-Mg bridging Cl atoms (that species is only 16 kJ/mol less stable than the most stable species from double alcoholysis which contribute to peak A). Another possibility for peak B could be the EtO-1-1 species perturbed by a neighboring EtOH molecule (orange squares in Figure 9), but this configuration appears unlikely considering the low EtOH coverage seen experimentally.

The HETCOR assignments were verified considering the $^1\text{H}(\text{CH}_2)$ - $^1\text{H}(\text{CH}_3)$ correlation calculated using the average values of the CH_2 and CH_3 groups (see Table S10 of the Supporting information). A graphical comparison between the calculated correlations and the experimental $^1\text{H}^1\text{H}$ SQ-DQ correlation spectrum is shown in Figure 10. Within the incertitude of the calculation, the $^1\text{H}(\text{CH}_2)$ - $^1\text{H}(\text{CH}_3)$ correlations obtained reproduce the experimental

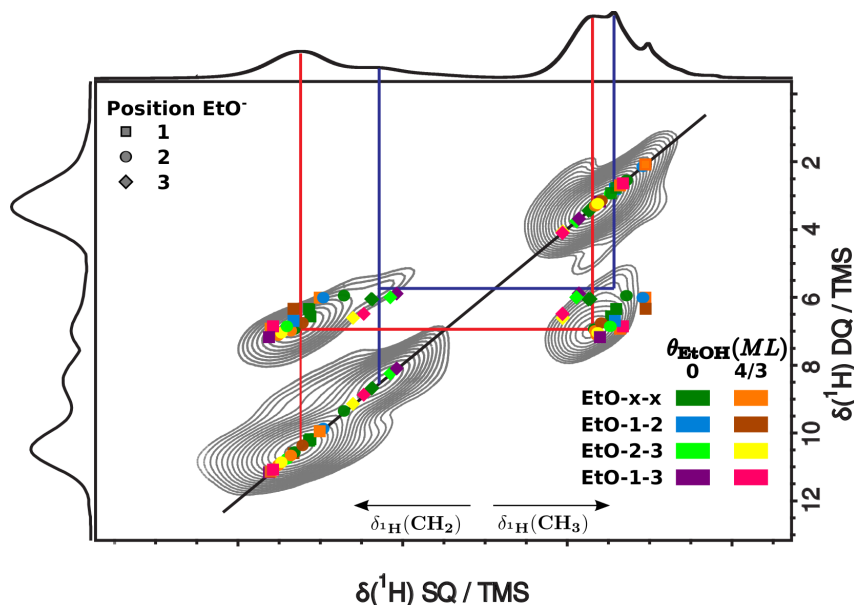


Figure 10: Graphical comparison of calculated and experimental ^1H - ^1H correlations. The correlations inherent to the alcoholysis of two M-Cl bonds are shown. The positions of the EtO^- groups are named according to Figure 1. EtO-x-x indicates the structures resulting from the alcoholysis of two equivalent M-Cl bonds (EtO-1-1, EtO-2-2 and EtO-3-3). For each structure, the calculated ^1H - ^1H correlations were obtained considering the average chemical shifts of the CH_2 and CH_3 groups. The values inherent to the two conditions of co-adsorbed EtOH coverages $\theta_{\text{EtOH}} = 0$ ML and $\theta_{\text{EtOH}} = 4/3$ ML are shown.

correlation indicated with the red line. It should be noticed that the ^1H - ^1H correlation alone could not be considered as conclusive, since the small difference of the ^1H chemical shifts of the CH_3 groups (≈ 0.3 ppm) makes the assignment difficult.

The span of the CSA tensors were analyzed; Table S12 collects all the values calculated, within the $\theta_{\text{EtOH}} = 0$ ML and $4/3$ ML. The comparison of the calculated data with the experimental ones (see the values relative to A and B signal of Table 1) gives a general overestimation of the calculated Span, similarly to what seen previously. However, among the values of θ_{EtOH} considered, the values obtained at $\theta_{\text{EtOH}} = 0$ ML are the ones closer to the experimental ones in agreement with the low observed EtOH/EtO coverage in the experiment.

Conclusion

The Ziegler-Natta pre-catalyst composed of TiCl_4 chemisorbed on MgCl_2 modified by EtOH as Lewis base was characterized by combining solid-state NMR and periodic-DFT calculations. The experimental ^{13}C and ^1H NMR spectra show that at least four different surface ethoxy species are present. The model chosen to represent the experimental pre-catalyst is constituted with a TiCl_4 complex chemisorbed on the (110) MgCl_2 surface.

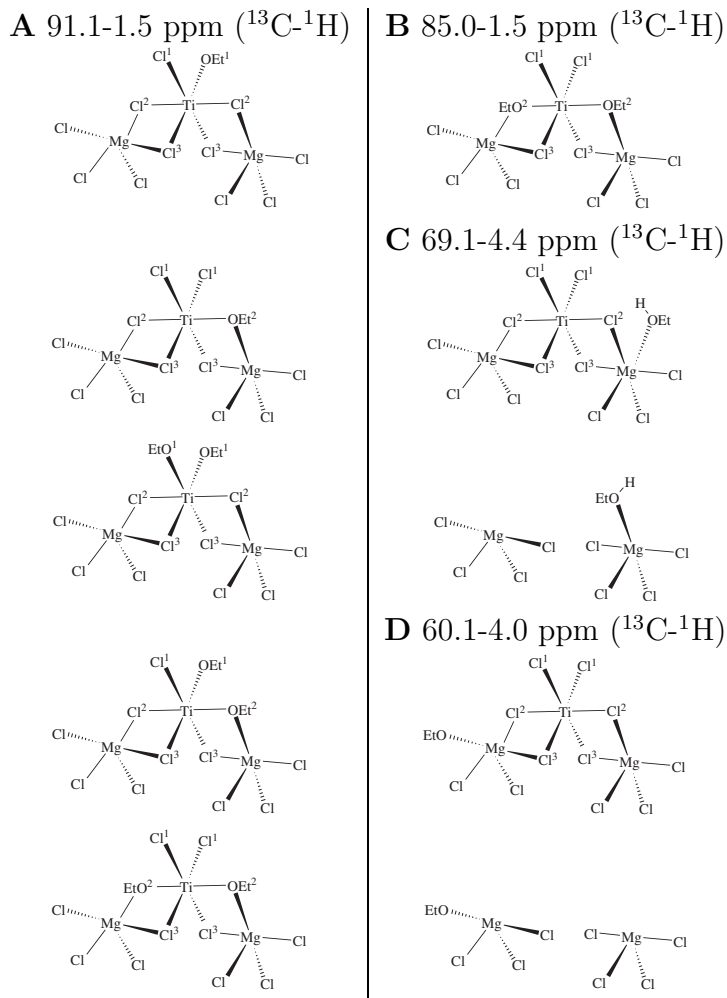
Figure 11 summarizes the results and shows all the species favorable from their total energy, realistic for their coverage and hence representative of the experimental system. The values of ^1H and ^{13}C chemical shifts are recalled for each structure and they are assigned to the features in the 2D-HETCOR spectrum.

At first the adsorption of EtOH on the surface was analysed. Calculations show that molecular adsorption in an associative manner can only happen on the surface Mg Lewis centers and not on the Ti. Several molecules were co-adsorbed, reaching a θ_{EtOH} of 2 ML. For $\theta > 4/3$ ML the values of differential adsorption energy remarkably decreased (in absolute value); consequently, the highest coverage considered was for $\theta_{\text{EtOH}} = 4/3$ ML. The ^1H and ^{13}C chemical shifts calculated for this class of structures (see Figure 11) reproduce the peak C of the 2D-HETCOR spectrum (Figure 2e).

Alcoholysis of M-Cl bonds was then considered, and reaction at the Ti center was shown to be exothermic, while that at Mg-Cl bond is weakly endothermic. Various coverage values of spectator EtOH groups on the surface were considered. These spectator molecules do not affect the stability order of the isomers resulting from alcoholysis, but a high coverage of EtOH makes the alcoholysis more difficult. Ethoxy species formed by the alcoholysis of Ti-Cl bonds (see Figure 11) explain the peak A in the experimental ^1H - ^{13}C HETCOR spectrum (Figure 2 e).

The presence of the peak D in this HETCOR spectrum was attributed to the alcoholysis of Mg-Cl bonds. The calculated NMR parameters sustain this assignment, however the slight

Figure 11: Summary of the calculated structures representative of the pre-catalyst and assignment of the experimental 2D-HETCOR spectrum.



endothermic character if this reaction of the perfect (110) surface suggest that it requires more defective sites.

Double alcoholysis at the same Ti center was calculated to be an energy favorable possibility, but that reaction is more sensitive to the presence of a large coverage (higher than 1ML) of spectator EtOH groups on the surface.

These Ti-OEt species EtO-1-1, EtO-1-2 and EtO-2-2 (see Figure 11) resulting from double alcoholysis of Ti-Cl bonds match peak A of the HETCOR spectrum. The specific case resulting from double alcoholysis of the bridging Ti-Cl-Mg bonds (EtO-2-2) provides one

ethoxy group at lower ^{13}C chemical shift and can explain the B shoulder in the spectrum. As a summary the HETCOR spectrum can be fully interpreted. The large A peak is attributed to single or double ethoxy species on Ti, and its B shoulder is associated to the Mg-EtO-Ti-OEt-Mg species. Peak C at lower ^{13}C chemical shift is explained by chemisorbed EtOH molecules on the Mg surface atoms, and the D feature can only be attributed to ethoxy groups on Mg, resulting from alcoholysis. The proposed species also explain the correlations seen in the BABA ^1H - ^1H correlation spectrum. Hence, from the combined NMR and theory approach, it is clear that ethoxy ligands are present of surface Ti atoms as a major species since this explains the presence of the peaks A and B in the 2D-CPMAS NMR spectra. Ethoxy or EtOH ligands are also present on surface Mg atoms, yielding peaks C and D. Unfortunately, intensities are not quantitative under these NMR conditions. It is thus not possible to provide an accurate relative ratio of EtO^-/EtOH ligands present on Ti vs Mg atoms. The values of $2\text{EtOH}(\text{EtO}^-)/\text{Ti}$ determined by elemental analysis is an upper bound for the number of EtO^- ligands per Ti. While it is not possible to determine the exact ratio of Ti centers that bear EtO^- ligands, NMR data suggest that this fraction is important.

The situation of the precatalyst prepared with EtOH can be compared to the case where THF is used as a Lewis base, which was studied before. Molecular chemisorption of THF on the Mg surface site and opening of THF on Ti forming an alkoxy-chloro compound was observed. The ethoxy formed here is reminiscent of the alkoxy-chloro formed with THF. The case of EtOH shows however two important differences: double alcoholysis was shown to occur, explaining the B shoulder in the spectrum, and the amount of ethoxy species versus the remaining ethanol appears much larger than that of opened THF versus molecular intact one. The combination of NMR and DFT calculations hence allowed a detailed characterization of the structure of $\text{TiCl}_4\text{-MgCl}_2\text{-EtOH}$. Even if the structures model here can fully explain the main features of the NMR spectra, it cannot be excluded that Ti and EtO^- co-adsorption structures on other surfaces (such as the (104) surface) could also contribute in a minor way to the measured broad spectra. The study of the pre-catalyst structure will be the starting

point in the atomic-level study of the activation process when aluminum alkyl co-catalysts will be contacted with precatalysts to form titanium-carbon bonds at their surface. In this regard, it is expected that the EtO^- groups linked to the Ti centers influence the interaction of the Ti complex with AlEt_3 during the activation of the catalysts as well as the relative stability of the possible products resulting from that interaction.

Acknowledgement

The authors thank the PSMN, CINES and IDRIS for the computational resources. V. D’Anna acknowledges the Swiss National Science Foundation (Early Post-Doc mobility).

Supporting Information Available

The images of the structures obtained for $\theta_{\text{EtOH}} = 4/3$ ML and the ^{13}C and ^1H chemical shifts calculated for all the structure shown are collected in the Supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

References

- (1) Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H. Polymerisation von Äthylen und anderen Olefinen. *Angewandte Chemie* **1955**, *67*, 426–426.
- (2) Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H. *German Patent* **1953**, 973626.
- (3) Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H. *British Patent* **1953**, 799392.
- (4) Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H. *British Patent* 799823.
- (5) Natta, G. Macromolecular Chemistry: From the Stereospecific Polymerization to the Asymmetric Autocatalytic Synthesis of Macromolecules. *Science* **1965**, *147*, 261–272.

- (6) Stürzel, M.; Mihan, S.; Mülhaupt, R. From Multisite Polymerization Catalysis to Sustainable Materials and All-Polyolefin Composites. *Chem. Rev.* **2015**, *113*, 1397–1433.
- (7) Lloyd, L. *Handbook of Industrial Catalysts*; Fundamental and Applied Catalysis; Springer, 2011; Chapter 8.
- (8) Mülhaupt, R, Catalytic Polymerization and Post Polymerization Catalysis Fifty Years After the Discovery of Ziegler’s Catalysts. *Macromol. Chem. Phys.* **2003**, *204*, 289–327.
- (9) Albizzati, E.; Giannini, U.; G., C.; Noristi, L.; Resconi, L. In *Polypropylene Handbook: Polymerization, Characterization, Properties, Processing, Applications*; Moore, E., Ed.; Hanser Publishers, 1996.
- (10) Busico, V. In *Polyolefins: 50 years after Ziegler and Natta I*; Kaminsky, W., Ed.; Advances in Polymer Science; Springer Berlin Heidelberg, 2013; Vol. 257; pp 37–57.
- (11) Moore, E. *Polypropylene Handbook: Polymerization, Characterization, Properties, Processing, Applications*; Hanser Publishers, 1996.
- (12) Boero, M.; Parrinello, M.; Weiss, H.; Huffer, S. A First Principles Exploration of a Variety of Active Surfaces and Catalytic Sites in Ziegler-Natta Heterogeneous Catalysis. *J. Phys. Chem. A* **2001**, *105*, 5096–5105.
- (13) Seth, M.; Ziegler, T. Theoretical Study of the Copolymerization of Ethylene and Propylene by a Heterogeneous Ziegler-Natta Catalyst. *Macromolecules* **2004**, *37*, 9191–9200.
- (14) Brambilla, L.; Zerbi, G.; Piemontesi, F.; Nascetti, S.; Morini, G. Structure of $\text{MgCl}_2\text{-TiCl}_4$ Complex in Co-Milled Ziegler-Natta Catalyst Precursors with Different TiCl_4 Content: Experimental and Theoretical Vibrational Spectra. *J. Mol. Catal. A: Chem.* **2007**, *263*, 103 – 111.

- (15) Credendino, R.; Liguori, D.; Fan, Z.; Morini, G.; Cavallo, L. Toward a Unified Model Explaining Heterogeneous Ziegler-Natta Catalysis. *ACS Catal.* **2015**, *5*, 5431–5435.
- (16) Di Noto, V.; Marigo, A.; Viviani, M.; Marega, C.; Bresadola, S.; Zannetti, R. MgCl₂-Supported Ziegler-Natta Catalysts: Synthesis and X-ray Diffraction Characterization of some MgCl₂-Lewis Base Adducts. *Makromol. Chem.* **1992**, *193*, 123–131.
- (17) Forte, M. C.; Coutinho, F. M. Highly Active Magnesium Chloride Supported Ziegler-Natta Catalysts with Controlled Morphology. *Eur. Polym. J.* **1996**, *32*, 223 – 231.
- (18) Sozzani, P.; Bracco, S.; Comotti, A.; Simonutti, R.; ; Camurati, I. Stoichiometric Compounds of Magnesium Dichloride with Ethanol for the Supported Ziegler-Natta Catalysis: First Recognition and Multidimensional MAS NMR Study. *J. Am. Chem. Soc.* **2003**, *125*, 12881–12893, PMID: 14558837.
- (19) Thushara, K. S.; Mathew, R.; Ajithkumar, T. G.; Rajamohanan, P. R.; Bhaduri, S.; Gopinath, C. S. MgCl₂·4(CH₃)₂CHOH: A New Molecular Adduct and Super Active Polymerization Catalyst Support. *J. Phys. Chem. C* **2009**, *113*, 8556–8559.
- (20) Malizia, F.; Fait, A.; Cruciani, G. Crystal Structures of Ziegler-Natta Catalyst Supports. *Chem. Eur. J.* **2011**, *17*, 13892–13897.
- (21) Thushara, K. S.; Gnanakumar, E. S.; Mathew, R.; Ajithkumar, T. G.; Rajamohanan, P. R.; Bhaduri, S.; Gopinath, C. S. MgCl₂·4((CH₃)₂CHCH₂OH): A New Molecular Adduct for the Preparation of TiCl_x/MgCl₂ Catalyst for Olefin Polymerization. *Dalton Trans.* **2012**, *41*, 11311–11318.
- (22) Grau, E.; Lesage, A.; Norsic, S.; Copéret, C.; Monteil, V.; Sautet, P. Tetrahydrofuran in TiCl₄/THF/MgCl₂: a Non-Innocent Ligand for Supported ZieglerNatta Polymerization Catalysts. *ACS Catalysis* **2013**, *3*, 52–56.

- (23) Kim, I.; Kim, J. H.; Choi, H. K.; Chung, M. C.; Woo, S. I. Comonomer Enhancement Effect of 1-Hexene in Ethylene Copolymerization Catalyzed over $\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ Catalysts. *J. Appl. Polym. Sci.* **1993**, *48*, 721–730.
- (24) Czaja, K.; Bialek, M. Microstructure of Ethylene-1-Hexene and Ethylene-1-Octene Copolymers Obtained over Ziegler-Natta Catalysts Supported on $\text{MgCl}_2(\text{THF})_2$. *Polymer* **2001**, *42*, 2289 – 2297.
- (25) Sobota, P. Metal-Assembled Compounds: Precursors of Polymerization Catalysts and New Materials. *Coord. Chem. Rev.* **2004**, *248*, 1047 – 1060.
- (26) Seenivasan, K.; Sommazzi, A.; Bonino, F.; Bordiga, S.; Groppo, E. Spectroscopic Investigation of Heterogeneous Ziegler-Natta Catalysts: Ti and Mg Chloride Tetrahydrofurans, Their Interaction Compound, and the Role of the Activator. *Chem. Eur. J.* **2011**, *17*, 8648–8656.
- (27) Pirinen, S.; Koshevoy, I. O.; Denifl, P.; Pakkanen, T. T. A Single-Crystal Model for MgCl_2 -Electron Donor Support Materials: $[\text{Mg}_3\text{Cl}_5(\text{THF})_4\text{Bu}]_2$ (Bu = n-Butyl). *Organometallics* **2013**, *32*, 4208–4213.
- (28) Pirinen, S.; Jayaratne, K.; Denifl, P.; Pakkanen, T. T. Ziegler-Natta Catalysts Supported on Crystalline and Amorphous MgCl_2/THF Complexes. *J. Mol. Catal. A: Chem.* **2014**, *395*, 434 – 439.
- (29) Garino, C.; Borfecchia, E.; Gobetto, R.; van Bokhoven, J. A.; Lamberti, C. Determination of the Electronic and Structural Configuration of Coordination Compounds by Synchrotron-Radiation Techniques. *Coord. Chem. Rev.* **2014**, *277/278*, 130 – 186, Following Chemical Structures using Synchrotron Radiation.
- (30) Groppo, E.; Gallo, E.; Seenivasan, K.; Lomachenko, K. A.; Sommazzi, A.; Bordiga, S.; Glatzel, P.; vanSijfhout, R.; Kachatkou, A.; Bras, W. et al. XAS and XES Techniques

- Shed Light on the Dark Side of Ziegler-Natta Catalysts: Active-Site Generation. *Chem-CatChem* **2015**, *7*, 1432–1437.
- (31) Groppo, E.; Seenivasan, K.; Barzan, C. The Potential of Spectroscopic Methods Applied to Heterogeneous Catalysts for Olefin Polymerization. *Catal. Sci. Technol.* **2013**, *3*, 858–878.
- (32) Tijssen, K. C.; Blaakmeer, E. M.; Kentgens, A. P. Solid-State NMR Studies of Ziegler-Natta and Metallocene Catalysts. *Solid State Nuclear Magnetic Resonance* **2015**, *6869*, 37 – 56.
- (33) Kim, S. H.; Tewell, C. R.; Somorjai, G. A. Surface Characterization of the $\text{TiCl}_x/\text{MgCl}_2$ Model ZieglerNatta Polymerization Catalysts: Adsorption Site Studies Using Mesitylene Thermal Desorption. *Langmuir* **2000**, *16*, 9414–9420.
- (34) Morra, E.; Giamello, E.; VanDoorslaer, S.; Antinucci, G.; D’Amore, M.; Busico, V.; Chiesa, M. Probing the Coordinative Unsaturation and Local Environment of Ti^{3+} Sites in an Activated High-Yield ZieglerNatta Catalyst. *Angew. Chem. Int. Ed.* **2015**, *54*, 4857–4860.
- (35) Fregonese, D.; Glisenti, A.; Mortara, S.; Rizzi, G. A.; Tondello, E.; Bresadola, S. $\text{MgCl}_2/\text{TiCl}_4/\text{AlEt}_3$ catalytic system for olefin polymerisation: a XPS study. *J. Mol. Catal. A: Chem.* **2002**, *178*, 115 – 123.
- (36) D’Amore, M.; Credendino, R.; Budzelaar, P. H.; Causá, M.; Busico, V. A Periodic Hybrid DFT Approach (Including Dispersion) to MgCl_2 -Supported Ziegler-Natta Catalysts - 1: TiCl_4 Adsorption on MgCl_2 Crystal Surfaces. *J. Catal.* **2012**, *286*, 103 – 110.
- (37) Cavallo, L.; Guerra, G.; Corradini, P. Mechanisms of Propagation and Termination Reactions in Classical Heterogeneous ZieglerNatta Catalytic Systems: A Nonlocal Density Functional Study. *JACS* **1998**, *120*, 2428–2436.

- (38) Bahri-Laleh, N.; Correa, A.; Mehdipour-Ataei, S.; Arabi, H.; Haghighi, M. N.; Zohuri, G.; Cavallo, L. Moving Up and Down the Titanium Oxidation State in Ziegler-Natta Catalysis. *Macromolecules* **2011**, *44*, 778–783.
- (39) Vanka, K.; Singh, G.; Iyer, D.; Gupta, V. K. DFT Study of Lewis Base Interactions with the MgCl_2 Surface in the Ziegler-Natta Catalytic System: Expanding the Role of the Donors. *J. Phys. Chem. C* **2010**, *114*, 15771–15781.
- (40) Stukalov, D. V.; Zilberberg, I. L.; Zakharov, V. A. Surface Species of Titanium(IV) and Titanium(III) in MgCl_2 -Supported Ziegler-Natta Catalysts. A Periodic Density Functional Theory Study. *Macromolecules* **2009**, *42*, 8165–8171.
- (41) Dwivedi, S.; Taniike, T.; Terano, M. Understanding the Chemical and Physical Transformations of a Ziegler-Natta Catalyst at the Initial Stage of Polymerization Kinetics: The Key Role of Alkylaluminum in the Catalyst Activation Process. *Macromol. Chem. Phys.* **2014**, *215*, 1698–1706.
- (42) Costuas, K.; Parrinello, M. Structure and Chemical Activity of Point Defects on MgCl_2 (001) Surface. *J. Phys. Chem. B* **2002**, *106*, 4477–4481.
- (43) Boero, M.; Parrinello, M.; Terakura, K. First Principles Molecular Dynamics Study of Ziegler-Natta Heterogeneous Catalysis. *JACS* **1998**, *120*, 2746–2752.
- (44) Bazhenov, A.; Linnolahti, M.; Pakkanen, T. A.; Denifl, P.; Leinonen, T. Modeling the Stabilization of Surface Defects by Donors in Ziegler-Natta Catalyst Support. *J. Phys. Chem. C* **2014**, *118*, 4791–4796.
- (45) Bazhenov, A. S.; Denifl, P.; Leinonen, T.; Pakkanen, A.; Linnolahti, M.; Pakkanen, T. A. Modeling Coadsorption of Titanium Tetrachloride and Bidentate Electron Donors on Magnesium Dichloride Support Surfaces. *J. Phys. Chem. C* **2014**, *118*, 27878–27883.

- (46) Kuklin, M. S.; Bazhenov, A. S.; Denifl, P.; Leinonen, T.; Linnolahti, M.; Pakkanen, T. A. Stabilization of Magnesium Dichloride Surface Defects by Mono- and Bidentate Donors. *Surf. Sci.* **2015**, *635*, 5 – 10.
- (47) Pines, A.; Gibby, M. G.; Waugh, J. S. Proton-Enhanced Nuclear Induction Spectroscopy ^{13}C Chemical Shielding Anisotropy in Some Organic Solids. *Chem. Phys. Lett.* **1972**, *15*, 373 – 376.
- (48) Fung, B.; Khitrin, A.; Ermolaev, K. An Improved Broadband Decoupling Sequence for Liquid Crystals and Solids. *J. Magn. Reson.* **2000**, *142*, 97 – 101.
- (49) Hu, J.; Alderman, D.; Ye, C.; Pugmire, R.; Grant, D. An Isotropic Chemical Shift-Chemical Shift Anisotropy Magic-Angle Slow-Spinning 2D NMR Experiment. *J. Magn. Reson., Ser. A* **1993**, *105*, 82 – 87.
- (50) Massiot, D.; Fayon, F.; Capron, M.; King, I.; Le Calvé, S.; Alonso, B.; Durand, J.-O.; Bujoli, B.; Gan, Z.; Hoatson, G. Modelling One- and Two-Dimensional Solid-State NMR Spectra. *Magn. Reson. Chem.* **2002**, *40*, 70–76.
- (51) Feike, M.; Demco, D.; Graf, R.; Gottwald, J.; Hafner, S.; Spiess, H. Broadband Multiple-Quantum NMR Spectroscopy. *J. Magn. Reson., Ser. A* **1996**, *122*, 214 – 221.
- (52) Marion, D.; Ikura, M.; Tschudin, R.; Bax, A. Rapid Recording of 2D NMR Spectra Without Phase Cycling. Application to the Study of Hydrogen Exchange in Proteins. *J. Magn. Reson.* **1989**, *85*, 393 – 399.
- (53) Elena, B.; de Paëpe, G.; Emsley, L. Direct Spectral Optimisation of Proton-Proton Homonuclear Dipolar Decoupling in Solid-State NMR. *Chem. Phys. Lett.* **2004**, *398*, 532 – 538.

- (54) States, D.; Haberkorn, R.; Ruben, D. A Two-Dimensional Nuclear Overhauser Experiment with Pure Absorption Phase in Four Quadrants. *J. Magn. Reson. (1969)* **1982**, *48*, 286 – 292.
- (55) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for *Ab Initio* Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169–11186.
- (56) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59*, 1758–1775.
- (57) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (58) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple [Phys. Rev. Lett. 77, 3865 (1996)]. *Phys. Rev. Lett.* **1997**, *78*, 1396–1396.
- (59) Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50*, 17953–17979.
- (60) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59*, 1758–1775.
- (61) Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *Journal of Computational Chemistry* **2006**, *27*, 1787–1799.
- (62) Halbert, S.; Copéret, C.; Raynaud, C.; Eisenstein, O. Elucidating the Link between NMR Chemical Shifts and Electronic Structure in d⁰ Olefin Metathesis Catalysts. *JACS* **2016**, *138*, 2261–2272, PMID: 26787258.
- (63) Dobado, J.; Molina, J.; Ugglá, R.; Sundberg, M. Multiple Bonding in Four-Coordinated Titanium(IV) Compounds. *Inorg. Chem.* **2000**, *39*, 2831–2836.

- (64) Smith, G. M.; Tirendi, C. F.; Amata, R. J.; Band, E. I. Alkoxymagnesium Halide Supports for Heterogeneous Ziegler-Natta Polymerization Catalysts. *Inorg. Chem.* **1993**, *32*, 1161–1166.

