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## Article

# Activity enhancement of MgCl<sub>2</sub>-supported Ziegler-Natta catalysts by Lewis-Acid pre-treatment for ethylene polymerization

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**Abstract** Ziegler-Natta precatalysts were synthesized from Lewis-base-modified-MgCl<sub>2</sub> supports and treated by various Lewis acids, prior to activation by triethylaluminum, in order to increase their activity in ethylene polymerization. BCl<sub>3</sub> provided the highest increase in activity. Interestingly, polymerization results showed no substantial modification of polymer properties, which is consistent with the Lewis acid only promoting the creation of new active sites, after activation by TEA, possessing very similar features than the original ones achievable with conventional precatalysts (*i.e.* without Lewis-acid treatment).

**Keywords** Ziegler-Natta catalysis, ethylene polymerization, Heterogeneous catalysis, Lewis acids

## INTRODUCTION

Since the 1950s and K. Ziegler's and G. Natta's discovery and improvement of the namesake catalysis for olefin polymerization, plastics have become essential to everyday life: food supplies, transport and infrastructure for instance heavily rely on thermoplastics, principally polyolefins.<sup>[1–3]</sup> Consequently, polyolefins such as polyethylene and polypropylene now represent almost half of the 350 million tons of global plastics production (as of 2018). Ziegler-Natta (ZN) catalysis is still widely used in industrial polyolefin production and is as a result ever evolving; making it one of the most constantly upgraded industrial applications of catalysis.

Heterogeneous ZN catalytic systems for olefin polymerization typically rely on an inorganic recipe comprised of Ti, Mg, Cl and selected organic molecules as additional ligands. Ti-based precatalysts can be obtained from several processes, such as co-precipitation and impregnation for instance, aiming at generating the correct electronics and sterics for the Ti atoms that will further evolve into active polymerization sites after trialkylaluminum treatment. Impregnation-derived precatalysts are usually obtained from titanium tetrachloride (TiCl<sub>4</sub>), supported on magnesium dichloride (MgCl<sub>2</sub>) and, thereafter, activated by a cocatalyst, systematically alkylaluminum-based.<sup>[4]</sup> The use of various Lewis bases, usually monodentate oxygen-based ligands, as key ingredients, makes up for geometry selection for the Mg and Ti atoms, imparted by the crystallographic phases and faces selected during the precatalyst synthesis. MgCl<sub>2</sub> is widely considered the optimal support and was chosen for its structural similarities with  $\delta$ -TiCl<sub>3</sub>,<sup>[5,6]</sup> and its (110) face for preferentially interacting with TiCl<sub>4</sub>. (110) being inexistent in MgCl<sub>2</sub> crystallite, monodentate Lewis bases, generally ethers<sup>[7–13]</sup> or alcohols,<sup>[14–20]</sup> are used for MgCl<sub>2</sub> “activation” by creating (110) step-defect (more stable than only (110) surface), which, after TiCl<sub>4</sub> addition, further leads to a highly active ZN precatalyst for ethylene polymerization.<sup>[21]</sup>

Understanding the recipe/activity/polymer-properties relationship is thus essential and has led to interesting discoveries,<sup>[22,23]</sup> including in our research group. *Ribour et al.* found that a Lewis-acid treatment on polypropylene precatalysts, featuring conventional bidentate internal and external Lewis bases as ligands, brought about an increase in activity by revealing more catalytically active sites, thereafter capable of inserting propylene in conjunction with trialkylaluminum.<sup>[24–26]</sup>

The purpose of this work is to expand the understanding of the Lewis-acid effect on ZN precatalysts. We elected polyethylene synthesis as a perfect case study. We believed that the “simpler” ethylene polymerization where the role of Lewis bases is less critical would help us better appreciate the lone Lewis-acid effect. We were hoping to decorrelate some of the many reactions,

yielding Lewis adducts potentially formed with the several bidentate Lewis bases essential to the control of isotacticity in the propylene case, and limit the obvious reactivities to formations of simpler Lewis pairs. Industrial mimics of precatalysts were synthesized, using THF and EtOH as Lewis bases for support “activation”, and various Lewis-acid treatments were performed in order to fully apprehend their effects on subsequent ethylene polymerization.

## EXPERIMENTAL

All manipulations (polymerizations, precatalysts’ syntheses and treatments) were performed using standard Schlenk techniques under an argon atmosphere.

### *Materials*

Ethylene (99.95%) and dihydrogen (99.999%) (purchased from Air Liquide) were used with CuO, molecular sieves and aluminum oxide purification columns. Anhydrous MgCl<sub>2</sub> (98%) was purchased from Aldrich and used as received. Tetrahydrofuran was purchased from Aldrich and purified over Na/benzophenone and then distilled. Titanium(IV) tetrachloride (Honeywell Fluka - ≥98.0%) was purchased from Fisher Scientific, BCl<sub>3</sub> (1M in heptane) from Sigma-Aldrich and BCl<sub>3</sub>, SiCl<sub>4</sub> and SnCl<sub>4</sub> in methylene chloride (1M) from Acros Organics. Triethylaluminum (TEA) was purchased neat from Albemarle (Louvain-La-Neuve/Belgium) and used as a heptane solution (1M), after cannula transfer in a Schlenk flask and appropriate dilution Ar. Heptane and Toluene were collected dry from a Solvent Purification System (SPS, MBraun). 1,2-dichloroethane (99.8%) was purchased from Aldrich.

### *Sample Preparation*

#### *TiCl<sub>4</sub>/MgCl<sub>2</sub>/THF precatalyst*

Firstly, MgCl<sub>2</sub> was stirred in boiling THF with a ratio of 1g per 7mL of solvent for 4 hours at 90°C, washed with heptane three times and dried under vacuum at 90°C for 1h to yield a white solid corresponding to MgCl<sub>2</sub>(THF)<sub>1.5</sub> (“activated support”). Secondly, the latter compound was immersed in pure TiCl<sub>4</sub> for 4h at 90°C and washed with hot toluene three times, hot 1,2-dichloroethane once and cold heptane once. A solution of TiCl<sub>4</sub> in heptane (5mL/20mL) was then added and the mixture stirred for 2h at 90°C and washed again by heptane until no trace of soluble TiCl<sub>4</sub> remained (characteristic HCl smokes upon air contact). Finally, the TiCl<sub>4</sub>/MgCl<sub>2</sub>/THF precatalyst (“Reference” precatalyst) powder was obtained after drying under high vacuum.

#### *TiCl<sub>4</sub>/MgCl<sub>2</sub>/EtOH precatalyst*

MgCl<sub>2</sub> was solubilized in ethanol by heating at reflux (78°C). The solution was then cooled by addition of room-temperature heptane. Two subsequent heptane washes were required before drying under vacuum at 90°C in order to obtain the MgCl<sub>2</sub>(EtOH)<sub>2</sub> support. TiCl<sub>4</sub> was added identically to the THF-support procedure and only heptane washes were consequently realized. TiCl<sub>4</sub> was subsequently added again during 2h at room temperature. Heptane washes before drying under high vacuum were necessary to yield the Reference-EtOH precatalyst.

#### *MCl<sub>x</sub> treatment*

“V” mL of MCl<sub>x</sub> (M=B, Sn or Si; X = 3 or 4; 1M in heptane or methylene chloride) was generally added to 1g of Reference precatalyst in 10mL of heptane or 1,2-dichloroethane and the mixture heated to 90°C for 2h, washed with heptane and then dried under high-vacuum.

#### *Ethylene polymerization*

5-10 mg of precatalyst (precise mass was monitored) was added to a 1L flask containing a 400mL volume of a 3 mmol·L<sup>-1</sup> TEA solution in heptane under Ar atmosphere and the mixture was then transferred to a 1L-autoclave reactor. The ratio Al/Ti varied between 300 and 700 in these experiments. After that, 1 bar of dihydrogen and then 6 bar of ethylene were subsequently added in the reactor and the polymerization was performed at 80°C. Polymerizations were stopped after a 5-bar consumption of ethylene from the 2L ballast that feeds the reactor corresponding to about 30 g of polyethylene, which we consistently verified gravimetrically. The obtained polymer, already

precipitated after the dispersion polymerization, was washed with methanol and filtered through sintered glass.

### **Characterization**

Molar masses of the polyethylenes were determined by size exclusion chromatography (SEC) with a Viscotek system (Malvern Instruments, Malvern, UK) equipped with three columns (Polefin 300mm×8mm I. D. from Polymer Standards Service, porosity of 1 000, 100 000 and 1 000 000 Å). Sample solutions of 1 mg·mL<sup>-1</sup> were eluted in 1,2,4-trichlorobenzene using a flow rate of 1 mL·min<sup>-1</sup> at 150 °C. The mobile phase was stabilized with 2,6-di(tert-butyl)-4-methylphenol. Three detectors were used: viscosimeter, refractometer and Light Scattering detector. The system was calibrated with polystyrene standards using triple calibration.

Differential scanning calorimetry (DSC) was performed on a Mettler-Toledo DSC 3+ at a heating and cooling rate of 10 K·min<sup>-1</sup>. Around 3mg of polymer were precisely weight in a 40µL-aluminum crucible. DSC data reported ( $T_m$  values) are collected from second heating segments to erase the thermal history of the sample.

Ti, Mg, B, Sn, Si and C contents (wt %) of precatalysts were determined by elemental analysis (Atomic Absorption Spectroscopy), performed at Mikroanalytischen Laboratorium Kolbe in Oberhausen (Germany).

## **RESULTS AND DISCUSSION**

A homemade Ziegler-Natta precatalyst was used as reference obtained by the addition of TiCl<sub>4</sub> on a MgCl<sub>2</sub>(THF)<sub>x</sub> complex ( $x \approx 1.5$ ), well representative of industrial precatalysts in ethylene polymerization and highly active (in combination with triethylaluminum as cocatalyst).

Lewis acids were selected among halogenated derivatives according to the following criteria: (1) solubility in hydrocarbon solvents (or chlorinated hydrocarbons) without introducing any additional polar solvents; (2) inability to lead by itself to polymerization active species when AlEt<sub>3</sub> is added. Based on these criteria, BCl<sub>3</sub>, SnCl<sub>4</sub> and SiCl<sub>4</sub>, varying by the oxidation state and the Lewis acidity of the central ion (M) in the chloride-containing molecule MCl<sub>x</sub>, were selected. In a previous work on precatalyst for isotactic polypropylene synthesis, the optimal treatment was performed at 90°C during 2h,<sup>[25]</sup> which we held constant for all the study.

### **Effect of Lewis Acid and Treatment Solvent on Reference precatalyst**

SiCl<sub>4</sub> is not soluble in hydrocarbons, hence we resorted to a chlorinated hydrocarbon, 1,2-dichloroethane (1,2-DCE), as reaction solvent which conveniently solubilizes all studied Lewis acids, in order to only observe the Lewis-acid effect during precatalyst treatments. Elemental analyses were performed on the “activated” support and the corresponding precatalysts and the results are shown in Table 1.

TiCl<sub>4</sub> addition lead to a large decrease in THF content (C/Mg = 5.4 for the activated support; C/Mg = 1.1 after TiCl<sub>4</sub> addition). It is well reported that TiCl<sub>4</sub>(THF)<sub>2</sub> formation occurs under these conditions and was in our case likely removed with hot-toluene washes. After Lewis-acid treatment, THF species were slightly (BCl<sub>3</sub> and SnCl<sub>4</sub>) to barely (SiCl<sub>4</sub>) altered/removed. It is likely that the formation of Lewis adducts leads to the depletion of THF in the precatalysts. Since SiCl<sub>4</sub> has a lower Lewis acidity as compared to its counterparts, it could explain why its effect is less drastic.<sup>[27,28]</sup>

1,2-DCE is generally used in “Reference” precatalyst synthesis as hot-washing solvent in order to remove free or weakly adsorbed TiCl<sub>4</sub> from the support surface, therefore the Ti amount after treatment was reduced accordingly (Table 1 - Ti/Mg = 0.4-0.6 for 1, 2 and 3; Ti/Mg = 0.12 for Reference). We replaced 1,2-DCE with heptane, a less polar solvent but still capable of solubilizing TiCl<sub>4</sub>, only for BCl<sub>3</sub> treatment as it presents a higher Lewis acidity (Table 1 – Precatalyst 4), thus maximizing the possibility to evidence any washing-solvent effect. THF species were still removed in the same quantities as with 1,2-DCE (C/Mg = 0.9 with heptane and C/Mg = 0.8 with 1,2-DCE). The effect of the solvent was nonetheless observed for the Ti content which was less removed using

heptane rather than when 1,2-DCE was employed, as expected ( $Ti/Mg = 0.10$  with heptane and  $Ti/Mg = 0.06$  in 1,2-DCE) even if the original  $BCl_3$  amount added to the “Reference” precatalyst ( $B/Ti = 3$ ) was higher in heptane than in 1,2-DCE.

We noticed a higher adsorption (likely chemisorption) of  $BCl_3$  and  $SiCl_4$  on the surface ( $M/Mg = 0.12$  and  $0.09$ ) than  $SnCl_4$  ( $M/Mg = 0.01$ ). This could either be due to geometrical constraints limiting the adsorption of  $SnCl_4$  or more physisorption rather than chemisorption, when compared to the other Lewis acids, which could explain the lower Sn amount observed after washing. Solvent effect was not substantial in  $MCl_x$  fixation on the surface ( $B/Mg = 0.13$  in heptane instead of  $B/Mg = 0.12$  in 1,2-DCE). We thus elected to work with heptane solutions for further investigations, to minimize the use of chlorinated solvents.

**Table 1** Effect of Lewis acids and solvents on Reference precatalyst

Precatalyst	$MCl_x$	Solvent	Ti / Mg / M / C <sup>(c)</sup> wt %	C/Mg	Ti/Mg	M/Mg	M/Ti
Support	-	-	- / 12.1 / - / 32.2	5.4	-	-	-
Reference	-	-	4.5 / 19.1 / 0.0 / 10.5	1.1	0.12	-	-
1	$BCl_3^{(a)}$	1,2-DCE	1.8 / 18.1 / 1.0 / 6.9	0.8	0.06	0.12	2.45
2	$SnCl_4^{(a)}$	1,2-DCE	2.2 / 22.3 / 0.9 / 11.1	1.0	0.05	0.01	0.17
3	$SiCl_4^{(a)}$	1,2-DCE	1.9 / 20.3 / 2.0 / 13.5	1.3	0.04	0.09	1.81
4	$BCl_3^{(b)}$	heptane	3.7 / 19.5 / 1.1 / 8.4	0.9	0.10	0.13	1.35

(a) Solution 1M in DCM with a ratio  $B/Ti = 1.6$ ;

(b) Solution 1M in heptane with a ratio  $B/Ti = 3.0$ ;

(c) Obtained from Elemental Analysis (Ti: titanium; Mg: magnesium; M: boron or tin or silicon; C: carbon).

### ***Use of modified precatalysts in Ethylene Polymerization***

The Reference and modified precatalysts were used for the polymerization of ethylene with triethylaluminum as cocatalyst and the results are summarized in Table 2. The Reference precatalyst provided a highly active catalyst ( $12 \text{ kg}_{PE} \cdot \text{g}_{cat}^{-1} \cdot \text{h}^{-1}$  measured with 6 bar of ethylene and 1 bar of  $H_2$  at  $80^\circ\text{C}$ ) and the polymer exhibited expected properties ( $M_n = 54 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\bar{D} = 3.5$  and a melting temperature of  $135.0^\circ\text{C}$ ) of high-density polyethylene made by Ziegler-Natta catalysis.

An increase in polymerization activity was observed for all modified precatalysts except with  $SiCl_4$  treatment ( $10 \text{ kg}_{PE} \cdot \text{g}_{cat}^{-1} \cdot \text{h}^{-1}$ ). We observed an increase of activity that could be correlated to the Lewis acidity ( $BCl_3 > SnCl_4 > SiCl_4$ ;  $18 \text{ kg}_{PE} \cdot \text{g}_{cat}^{-1} \cdot \text{h}^{-1}$  after  $BCl_3$  treatment and  $16 \text{ kg}_{PE} \cdot \text{g}_{cat}^{-1} \cdot \text{h}^{-1}$  after  $SnCl_4$  treatment). We speculate that, in the case of  $SiCl_4$  treatment, the decrease of activity is mostly due to Ti removal, including Ti that could promote some potential active species (with TEA addition) by 1,2-DCE as we concluded earlier. However, when normalized to the Ti amount, one can realize that the activity in fact nearly doubled (entry 3 compared to Reference, Table 2), even when the less Lewis-acidic Si-based chloride was used for treatment.

Polymers obtained from modified precatalysts displayed similar properties ( $M_n$ ,  $M_w$ ,  $\bar{D}$  and  $T_m$ ) as the Reference polymer. This observation led us to believe that very similar if not identical active species were involved in the polymerization process: *i.e.* the same propagation step (behavior in presence of ethylene) and the same chain transfer step (behavior in presence of  $H_2$ ) occurred during polymerization.

Postulating that transfer to dihydrogen is highly preponderant when compared to transfer to alkylaluminum, to monomer and  $\beta$ -hydride/elimination reaction in those cases, Equation (1) can represent the polymerization rate,  $R_p$  as function of  $k_p$  the propagation rate constant,  $k_{tH}$  the  $H_2$ -transfer rate constant,  $C^*$  the number of active sites and  $C_M$  and  $C_{H_2}$  the concentration of monomer

and dihydrogen respectively, and  $k_{tH}$  the rate of initiation of polymerization from the newly generated hydride species after  $H_2$ -transfer.<sup>[29]</sup>

$$R_p = \frac{k_{tH} \cdot C_M}{\frac{k_{tH}}{k_p} + \frac{k_{tH} \cdot C_{H_2}}{k_p \cdot C_M}} \cdot C^* \quad (1)$$

Ziegler-Natta catalysis gives high molar masses polymers meaning that the transfer frequency is much smaller than the propagation frequency, hence, the second term in denominator is much smaller than 1. Assuming that  $k_{tH}$  is comparable to  $k_p$ , it gives us the following Equation (2), after simplification:<sup>[29]</sup>

$$R_p = k_p \cdot C^* \cdot C_M \quad (2)$$

Polymerization degree  $r_n$  can also be represented by Equation (3) using the same assumption concerning transfer reactions, where  $R_t$  and  $R_{tH}$  are the global and the Hydrogen transfer rates.<sup>[30]</sup>

$$\frac{1}{r_n} = \frac{\sum R_t}{R_p} = \frac{R_{tH}}{R_p} = \frac{k_{tH} \cdot C_{H_2}^n}{k_p \cdot C_M} \quad (3)$$

As molar masses of polymers are similar (Figure 1-a), the ratio  $R_{tH}/R_p$  is equal before and after Lewis-acid treatments. As we worked under the same polymerization conditions, ( $C_M$  and  $C_{H_2}$  remained equal for all polymerizations), ratio  $k_p/k_{tH}$  does not change. We then face two possibilities: either  $k_p$  and  $k_{tH}$  vary exactly similarly to explain how the molar masses remain constant with and without Lewis-acid treatment or they both remain the same. We can safely assume that these rate constants are not modified, since a modification of the active site would certainly affect differently the propagation and the transfer to dihydrogen. Thus,  $k_p$  is invariable with and without Lewis-acid treatment. Therefore, only an increase in the number of active sites (Equation 2) can explain the increase in activity observed for Lewis-acid-treated precatalysts.

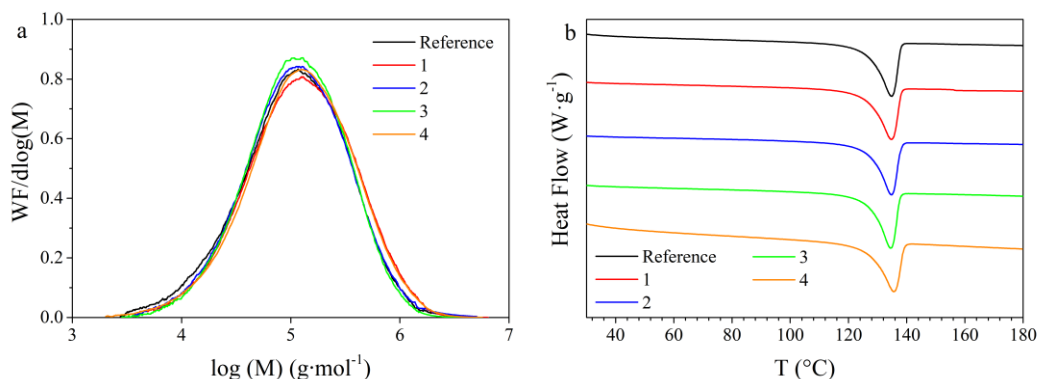
Treatment with  $BCl_3$  in heptane resulted in a strong activation of the precatalyst ( $33 \text{ kg}_{PE} \cdot \text{g}_{cat}^{-1} \cdot \text{h}^{-1}$ ) and no substantial modification of polymer properties when compared to polymer from Reference precatalyst (entry 4, Table 2). As the only difference with  $BCl_3$  treatment in 1,2-DCE was the substantial decrease of Ti content, we can thus conclude that 1,2-DCE removed Ti species which were capable of being active after Lewis-acid addition. Indeed, when Ti-normalized, the activities of both of these  $BCl_3$ -modified precatalysts are comparable but the nominal activity of the 1,2-DCE-treated precatalyst is lower by almost a factor of 2, which matches the removal of Ti mentioned in Table 1 (entry 1 vs. entry 4). Treatment with  $BCl_3$  in heptane was therefore chosen for precatalyst modification for the rest of the study in order to observe clearly the Lewis-acid effect. This choice is supported by the fact that heptane is chemically inert, and cannot account for any extra chlorination effects that could arise from the mere reactivity of chlorinated solvents with Lewis-acidic surfaces, and that  $BCl_3$  presented the strongest precatalyst activation, as evidenced in Table 1 and Table 2.

**Table 2** Polymerization results of Reference and treated precatalysts.<sup>(a)</sup>

	Activity		$M_n^{(b)}$	$M_w^{(b)}$	$\mathcal{D}^{(b)}$	$T_m^{(c)}$
	$\text{kg}_{PE} \cdot (\text{g}_{cat} \cdot \text{h})^{-1}$	$\text{kg}_{PE} \cdot (\text{mol}_{Ti} \cdot \text{h})^{-1}$				
<b>Reference</b>	12	13000	54	190	3.5	135.0
<b>1</b>	18	48000	66	220	3,3	134.9
<b>2</b>	16	34000	61	200	3,3	134.7
<b>3</b>	10	26000	65	184	2,8	134.6

4	33	42000	62	220	3.5	135.6
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- (a) Polymerization at 80°C, C<sub>2</sub>H<sub>4</sub> pressure = 6 bar, solvent (heptane): 400 mL, TEA: 3 mM, H<sub>2</sub> pressure 1 bar;  
 (b) Obtained from HT-SEC;  
 (c) Obtained from DSC.



**Figure 1** Molecular weights (a) and melting temperatures (b) profiles of polyethylenes

### *BCl<sub>3</sub> Effect with MgCl<sub>2</sub>(EtOH)<sub>x</sub> Activated Support*

The precatalyst modified by BCl<sub>3</sub> in heptane from the previous section was taken as the Reference precatalyst (Table 1 and Table 2 – precatalysts “Reference” and 4) and renamed Reference-THF for clarity. A new precatalyst was synthesized with a MgCl<sub>2</sub>-support activated this time with Ethanol (EtOH) as Lewis base or complexing solvent and was called “Reference-EtOH”. A BCl<sub>3</sub> treatment (in heptane) was done on this latter precatalyst.

The washes during the Reference-EtOH precatalyst synthesis were only realized using heptane repeatedly in order to remove the TiCl<sub>4</sub> excess and most of the corresponding EtOH-derived adducts. Hence, the Ti amount in Reference-EtOH precatalyst was significantly higher than for Reference-THF, although most of Ti species were weakly anchored to the MgCl<sub>2</sub>(EtOH)<sub>x</sub> surface (Table 3). Subsequently, BCl<sub>3</sub> treatment removed a large amount of Ti contrary to Reference-THF precatalyst, in which more washing steps were performed and, thus, a majority of the Ti species are strongly chemisorbed on the MgCl<sub>2</sub>(THF)<sub>x</sub> surface.

Reference-EtOH precatalyst presented a higher activity (38 kg<sub>PE</sub>·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>) than Reference-THF precatalyst (12 kg<sub>PE</sub>·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>), which could be explained by its higher Ti content. However, even with a strong removal of Ti by BCl<sub>3</sub> treatment, an increase of activity was again observed for the BCl<sub>3</sub>-modified precatalyst (53 kg<sub>PE</sub>·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>), which prompted us to hypothesize a similar activation phenomenon in both Lewis-base treated-MgCl<sub>2</sub> cases (EtOH and THF).

Polymer properties remained constant, independently of the Lewis base used (THF or EtOH), which means that the same Ti-active species (after TEA addition) were present on both precatalysts (Reference-THF and -EtOH). Moreover, BCl<sub>3</sub> treatment did not modify any polymer properties in the Reference-EtOH, but again only increased the potential of Ti species to become active polymerization species after reduction/alkylation by TEA.

**Table 3** Comparison between THF- and EtOH-activated precatalysts.<sup>(a)</sup>

	Ti/Mg <sup>(b)</sup>	B/Mg <sup>(b)</sup>	Activity		M <sub>n</sub> <sup>(c)</sup>	M <sub>w</sub> <sup>(c)</sup>	D <sup>(c)</sup>	T <sub>m</sub> <sup>(d)</sup>
			kg <sub>PE</sub> ·(g <sub>cat</sub> ·h) <sup>-1</sup>	kg <sub>PE</sub> ·(mol <sub>Ti</sub> ·h) <sup>-1</sup>				
<b>Reference-THF</b>	0.12	-	12	13000	54	190	3.5	135.0
<b>4 (+BCl<sub>3</sub>)</b>	0.10	0.13	33	42000	62	220	3.5	135.6
<b>Reference-EtOH</b>	0.52	-	38	16000	56	193	3.4	134.6

+BCl <sub>3</sub>	0.12	0.17	53	56000	62	193	3.1	135.0
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(a) Polymerization at 80°C, C<sub>2</sub>H<sub>4</sub> pressure = 6 bar, solvent (heptane): 400 mL, TEA: 3 mM, H<sub>2</sub> pressure 1 bar;

(b) Obtained from Elemental Analysis;

(c) Obtained from HT-SEC;

(d) Obtained from DSC.

The choice of Lewis base for support “activation” is therefore not critical in our model systems because in our two chosen examples of representative Lewis bases (THF or EtOH) an increase of activity was observed after BCl<sub>3</sub> treatment.

#### ***Effect of the Ratio B/Ti on Catalytic Performance***

Various B/Ti ratios (from 0.12 to 2.62) were obtained from Reference precatalyst with the corresponding ethylene polymerization results being summarized in Table 4. As observed in the previous sections, for all B/Ti ratios, a drop of an increase in activity for ethylene polymerization with no substantial modification of polymer properties was noticed. The activity seems proportional to the B/Ti ratio up to a B/Ti = 1 and decreased for higher ratios, as Figure 2 clearly shows.

This second phenomena could be explain by an excess of BCl<sub>3</sub> that covered the MgCl<sub>2</sub> surface and inhibited some Ti-active sites, however this needs to be assessed with the help of computational investigations.

While activity increases, molar masses remain constant implying that the ratio  $k_p/k_{th}$  does not vary for every B/Ti ratio (Equation (3)).

**Table 4** Effect of B/Ti ratio on Reference precatalyst in Ethylene Polymerization.<sup>(a)</sup>

B/Ti <sup>(b)</sup>	Activity		M <sub>n</sub> <sup>(c)</sup>	M <sub>w</sub> <sup>(c)</sup>	Đ <sup>(c)</sup>	T <sub>m</sub> <sup>(d)</sup>
	kgPE·(g <sub>cat</sub> ·h) <sup>-1</sup>	kgPE·(mol <sub>Ti</sub> ·h) <sup>-1</sup>				
0	12	13000	54	190	3.5	135.0
0.12	15	15000	63	230	3.6	134.4
0.28	16	22000	65	240	3.6	134.9
0.31	17	22000	69	250	3.6	134.6
0.42	20	27000	60	210	3.5	134.6
0.45	30	31000	60	220	3.7	134.6
1.04	29	45000	63	230	3.7	135.6
1.35	33	42000	62	220	3.5	135.6
2.11	26	36000	59	240	4.0	135.5
2.62	13	23000	65	240	3.7	135.0

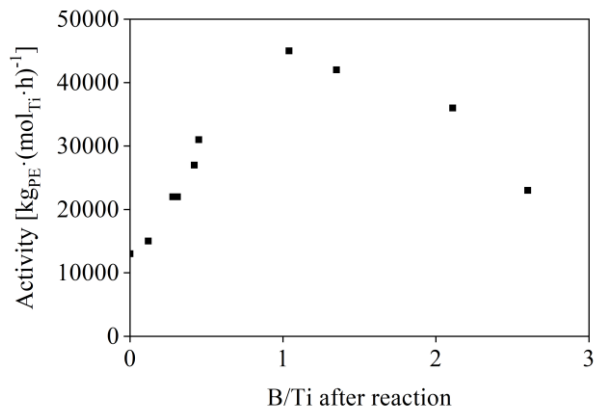
(a) Polymerization at 80°C, C<sub>2</sub>H<sub>4</sub> pressure = 6 bar, solvent (heptane): 400 mL, TEA: 3 mM, H<sub>2</sub> pressure 1 bar;

(b) Obtained from Elemental Analysis;

(c) Obtained from HT-SEC;

(d) Obtained from DSC.





**Figure 2** Activity of pre-catalysts according to B/Ti ratio

### ***Hydrogen Response of the Precatalysts***

In order to assess the H<sub>2</sub> response of our pre-catalysts with and without Lewis-acid treatment, we varied the H<sub>2</sub> pressure during ethylene polymerization from 0 to 2.5 bar while keeping the overall pressure constant (7 bar). The polymerization results for different H<sub>2</sub> concentrations are displayed in Table 5.

Since our strategy was to compare Reference pre-catalyst and one BCl<sub>3</sub>-treated pre-catalyst with different H<sub>2</sub> pressures, we selected the highest BCl<sub>3</sub> amount for the treatment with a ratio B/Ti = 2.62 (last entry from Table 4), to maximize the chances to unveil any effect.

For both pre-catalysts, a decrease in activity was observed while increasing the H<sub>2</sub> concentration. We could explain this lower activity by the fact that we reduced monomer concentration; we indeed worked with constant pressure in the reactor. Concerning polymer properties, the same tendency was observed for both pre-catalysts with a decrease in molar masses, with H<sub>2</sub> pressure increasing (Figure 3). Interestingly, in absence of H<sub>2</sub>, molar masses are identical for both pre-catalysts (with and without BCl<sub>3</sub> treatment). Another observation is that melting temperatures decrease slightly when H<sub>2</sub> increases for both pre-catalysts as we can see on Figure 3 (b and d).

In the above-mentioned experiments, we supposed that we only increased C\* since polymer properties ( $k_p/k_{tH}$  keeps constant) and polymerization conditions were not modified, which implicitly means that  $k_p$  and thus  $k_{tH}$  do not vary with or without Lewis-acid treatment. This statement seems acceptable for all the above-mentioned polymerization conditions, namely 80°C, 6 bar of ethylene and 1 bar of H<sub>2</sub>. In these new experiments with varying H<sub>2</sub> pressure, the fact that molar masses evolve very similarly means that the ratio  $k_p/k_{tH}$  is comparable for all pre-catalysts, treated or not. This particularly holds true for higher H<sub>2</sub> pressures, since we do see some variations at very low H<sub>2</sub> pressure. It is unlikely that  $k_p$  and  $k_{tH}$  varied and compensated each other to keep their ratio constant for all experiments. Thus, in this new set of experiments, similar active species are once again present on treated pre-catalysts when compared to the Reference. Moreover, the comparative experiment at 0 bar reinforces this statement. Indeed, under these conditions the main transfer mechanisms is obviously no longer H<sub>2</sub> transfer and polymerization degree  $r_n$  is now represented by Equation (4) using the other chain-transfer-reaction rates ( $R_{tX}$ ) and constants ( $k_{tX}$ ): transfer to monomer ( $X = M$ ), to alkylaluminum ( $X = Al$ ) and the  $\beta$ -hydride/elimination ( $X = \beta$ ). Since molar masses are once again identical for both pre-catalysts (with or without Lewis-acid treatment), it infers that  $k_p$  is not changed by BCl<sub>3</sub> treatment.

$$\frac{1}{r_n} = \frac{\sum R_t}{R_p} = \frac{R_{tM} + R_{t\beta} + R_{tAl}}{R_p} = \frac{k_{tM}}{k_p} + \frac{k_{t\beta}}{k_p \cdot C_M} + \frac{k_{tAl} \cdot C_{Al}^m}{k_p \cdot C_M} \quad (4)$$

We can conclude that propagation rate and chain transfer rate constants are the same for both Reference and treated precatalysts, meaning that the same active species are involved in ethylene polymerization in both cases (in presence of TEA). Overall, in this work, polymerization conditions were varied to evidence that  $k_p/k_{tH}$  ratio and very likely  $k_p$  and consequently all other chain-transfer-rate constants remained equal for all precatalysts, meaning that these results were not a coincidence since they were evidenced in all these sets of conditions.

**Table 5** Polymerization results with modification of H<sub>2</sub> pressure on Reference and treated precatalysts.<sup>(a)</sup>

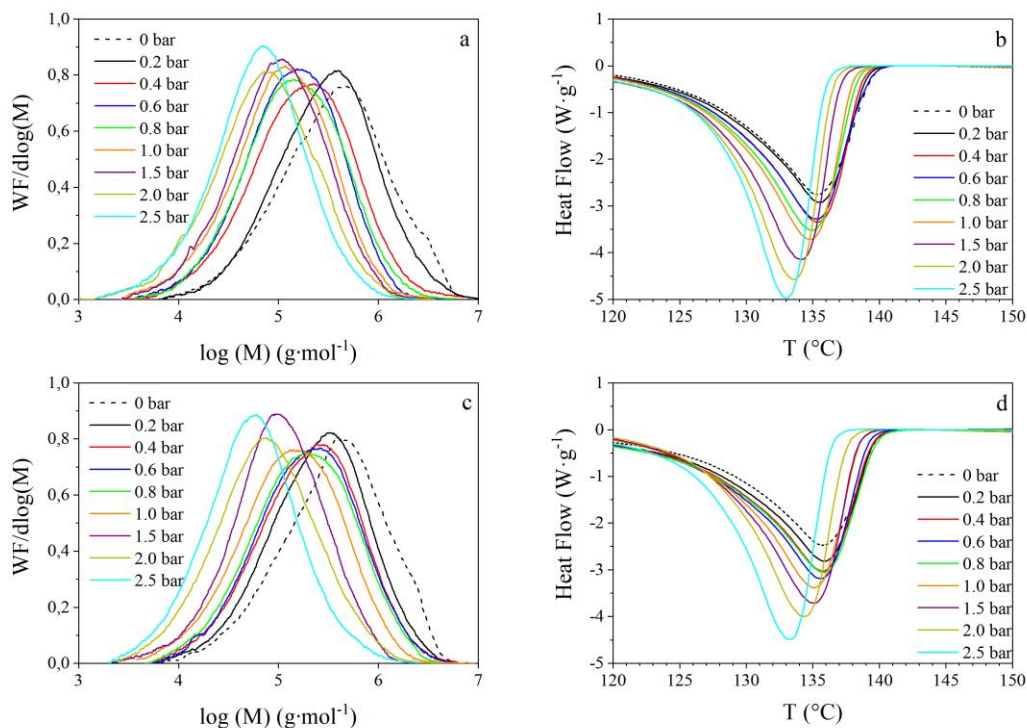
Precatalyst	P (H <sub>2</sub> ) <i>bar</i>	Activity		M <sub>n</sub> <sup>(c)</sup> <i>kg·mol<sup>-1</sup></i>	M <sub>w</sub> <sup>(c)</sup> <i>kg·mol<sup>-1</sup></i>	Đ <sup>(c)</sup>	T <sub>m</sub> <sup>(d)</sup> °C
		<i>kgPE·(g<sub>cata</sub>·h)<sup>-1</sup></i>	<i>kgPE·(mol<sub>Ti</sub>·h)<sup>-1</sup></i>				
Reference	0	37	40000	163	699	4.3	135.4
	0.2	23	25000	160	570	3.6	135.7
	0.4	18	19000	86	340	3.9	135.3
	0.6	17	18000	73	230	3.2	135.3
	0.8	15	16000	75	260	3.5	135.0
	1.0	12	13000	54	190	3.5	135.0
	1.5	10	11000	53	168	3.2	134.1
	2.0	6.6	7100	35	134	3.8	133.6
	2.5	4.8	5100	32	109	3.3	133.0
+ BCl <sub>3</sub> <sup>(b)</sup>	0	33	58000	163	636	3.9	135.8
	0.2	26	46000	120	440	3.5	135.8
	0.4	21	37000	100	370	3.7	135.7
	0.6	17	30000	100	360	3.6	135.6
	0.8	14	25000	89	320	3.7	135.8
	1.0	13	23000	65	240	3.7	135.0
	1.5	11	19000	52	165	3.2	135.1
	2.0	7.0	12000	38	145	3.8	134.8
	2.5	6.7	12000	30	99	3.3	133.2

(a) Polymerization at 80°C, solvent (heptane): 400 mL, TEA: 3 mM, total pressure in the reactor: 7 bar (“N” bar H<sub>2</sub> + “7-N” bar C<sub>2</sub>H<sub>4</sub>);

(b) BCl<sub>3</sub> (1M in heptane) added as explained in experimental section with a ratio B/Ti = 2, elemental analysis gave us a ratio of B/Ti = 2.62 in the treated precatalyst;

(c) Obtained from HT-SEC;

(d) Obtained from DSC.



**Figure 3** Hydrogen effect on molar masses and melting temperatures of Reference and treated precatalysts. a) SEC profiles of Reference and b) its DSC curves. c) and d) are respectively the SEC and the DSC profiles for treated precatalyst.

## CONCLUSION

Industrial Ziegler-Natta precatalysts were synthesized from Lewis-base-modified-MgCl<sub>2</sub> supports and treated by various Lewis acids, prior to activation by triethylaluminum, in order to increase their activity in ethylene polymerization. BCl<sub>3</sub> provided the highest increase in activity and heptane was the synthesis/washing solvent of choice with the best compromise between active-species' creation and non-removal of Ti-based species. Polymerization results showed no substantial modification of polymer properties, which is consistent with the Lewis acid only promoting the creation of an increased concentration of active sites after reduction/alkylation by TEA, independently from the original Lewis base chosen for the preparation of the MgCl<sub>2</sub> support. The H<sub>2</sub> response for Reference and treated precatalysts were the same. These combined experiments prompt us to hypothesize that Lewis acids revealed new “pre-active” sites very similar if not identical to other pre-active sites (which evolve into active sites after triethylaluminum addition). An optimal B/Ti ratio was found to be close to 1 Boron per Titanium chemisorbed on the surface, as if to statistically maximize the amount of active Ti species (involving correct geometry and electronics).

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*Graphical abstract*

**Activity enhancement of MgCl<sub>2</sub>-supported Ziegler-Natta catalysts by Lewis-Acid pre-treatment for ethylene polymerization**

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Adding a Lewis acid such as BCl<sub>3</sub>, SnCl<sub>4</sub> or SiCl<sub>4</sub> to a Lewis-based-modified-MgCl<sub>2</sub>/TiCl<sub>4</sub> Ziegler-Natta precatalyst increases activity in polymerization without any substantial modification of the polymer properties in ethylene polymerization meaning that their role is to reveal new active sites which was “dormant”.

