

Formation of Highly Active Ziegler-Natta Catalysts Clarified by a Multifaceted Characterization Approach

*Original*

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1 On the formation of highly active Ziegler-Natta  
2 catalysts clarified by a multifaceted  
3 characterization approach

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15  
16 **KEYWORDS:** Ziegler-Natta catalysts, electronic properties, morphology, IR spectroscopy,  
17 synchrotron, total scattering, XRD, pair distribution function

## 18 ABSTRACT

19 Although the formation of nanosized and defective  $\delta$ - $\text{MgCl}_2$  is essential for the performance of  
20 Ziegler-Natta catalysts, the process has not sufficiently been elucidated due to certain  
21 limitations in characterization. Here, the formation of nanostructures and active surfaces of  
22 Ziegler-Natta catalysts were investigated in detail based on a multifaceted set of  
23 characterization techniques represented by X-ray total scattering and various spectroscopies,  
24 in correlation with chemical composition analysis and polymerization tests. Solid samples were  
25 extracted in the course of the catalyst preparation from  $\text{Mg}(\text{OEt})_2$ , and subjected to the analysis.  
26 Several interesting results were found. The addition of  $\text{TiCl}_4$  almost spontaneously converts  
27  $\text{Mg}(\text{OEt})_2$  into  $\text{MgCl}_2$  seeds mainly exposing the  $\{001\}$  basal surface, whose dimensions are  
28 below 2 nm; a large Ti amount stays on the material as physisorbed 4-fold coordinated  
29  $\text{TiCl}_x(\text{OEt})_{4-x}$  species. The heating treatment removes the physisorbed  $\text{TiCl}_x(\text{OEt})_{4-x}$  and/or  
30 convert them into chemisorbed 6-fold coordinated  $\text{TiCl}_x(\text{OEt})_{4-x}$ , while the subsequent addition  
31 of an internal donor (here dibutyl phthalate, DBP) promotes a substantial reconstruction and  
32 growth of  $\text{MgCl}_2$  seeds to almost the same size as the final catalyst (ca. 6 nm), with the exposure  
33 of the more catalytically relevant lateral surfaces. DBP is in one part adsorbed on  $\text{MgCl}_2$   
34 surfaces and in the other part complexed with Ti sites. This complex is only partially removed  
35 in the following steps of the synthesis. The second  $\text{TiCl}_4$  addition replaces the chemisorbed  
36  $\text{TiCl}_x(\text{OEt})_{4-x}$  with 6-fold coordinated  $\text{TiCl}_4$  species, but it also causes side reactions with DBP,  
37 as testified by the formation of phthaloyl chloride (POC). After activation by triethylaluminum  
38 (TEAl), the activity per Ti for ethylene was almost constant throughout the whole preparation  
39 process after the initial  $\text{TiCl}_4$  addition, whereas the activity for propylene was negligible before  
40 the addition of the donor and increased dramatically in the subsequent steps of the preparation.  
41 This was further investigated based on spectroscopies for TEAl-activated samples, in order to  
42 individuate the active Ti species responsible for the catalysis and to monitor the fate of DBP

43 upon TEAl reaction. The multifaceted characterization approach allowed us to integrate  
44 information on the formation of  $\delta$ -MgCl<sub>2</sub>, their surfaces, and adsorbed species, providing us  
45 with deep insights into the meaning of each step within an industrial catalyst preparation  
46 method that has been empirically refined over a long history.

47

## 48 **1. INTRODCUTION**

49 After almost seventy years since Karl Ziegler and Giulio Natta broke the monopoly of Nature  
50 on the synthesis of stereoregular polymers, Ziegler-Natta (ZN) catalysts are nowadays  
51 responsible for 99% of the world polypropylene (PP) production as well as one fourth of that  
52 of high-density polyethylene (HDPE).<sup>1</sup> The economic turnover of this industrial process  
53 brushes the verge of 300 billion dollars in 2020 and is forecasted to still grow at a compound  
54 annual growth rate of 6 % in the next decade.<sup>2</sup>

55 From their original and quite simple composition, ZN catalysts have evolved along several  
56 generations characterized by a gradually improved activity and stereoselectivity, up to the  
57 current multi-component composition: TiCl<sub>4</sub> (the active phase) is dispersed with organic Lewis  
58 bases (the internal donors) on MgCl<sub>2</sub> (the support material) and activated by AlR<sub>3</sub> (the co-  
59 catalyst), together with other organic Lewis bases (the external donors).<sup>3-6</sup> The internal/external  
60 donors are considered to be located at the vicinity of the Ti active species and to improve  
61 stereospecificity through steric hindrance. Such complex composition allows, by means of  
62 catalyst design, finely controlling the structure of the produced polymer across multiple scales,  
63 from the molecular architecture of the polymer chains to its distribution critical for actual  
64 properties, and finally to the morphology of the polymer particles.

65 In industrial practice, two main routes have been developed to integrate  $\text{TiCl}_4$ ,  $\text{MgCl}_2$ , and  
66 an electron donor into a single solid material, usually called pre-catalyst.<sup>3</sup> Note that the electron  
67 donor in the pre-catalyst is termed as internal donor to distinguish it from the external one,  
68 which is added directly in the reactor along with the  $\text{AlR}_3$  activator. The former route  
69 (traditional) is based on the mechanical ball-milling of highly crystalline  $\text{MgCl}_2$  ( $\alpha$  form) with  
70 the internal donor and/or  $\text{TiCl}_4$ .<sup>7-13</sup> The latter route (advanced) employs the chemical  
71 transformation of a  $\text{MgCl}_2$ -precursor into nanostructured and highly defective  $\text{MgCl}_2$  ( $\delta$  form)  
72 by  $\text{TiCl}_4$  itself in the presence of the donor,<sup>14-29</sup> and generally leads to more disordered and  
73 more active nanostructures.<sup>30-32</sup> In a typical chemical preparation route, all the components are  
74 intimately connected to each other.  $\text{TiCl}_4$  promotes the chlorination of the precursor into  $\text{MgCl}_2$   
75 and exerts a capping effect on the newly formed  $\text{MgCl}_2$  nanoparticles.<sup>33</sup> The electron donor not  
76 only influences the  $\text{MgCl}_2$  morphology by stabilizing specific surfaces,<sup>20, 22</sup> but also interacts  
77 with the Ti sites through direct coordination<sup>34-37</sup> or more plausibly through coadsorption.<sup>38</sup> By-  
78 products formed during the chlorination must not be overlooked as these products could adsorb  
79 on  $\text{MgCl}_2$  surfaces, and work as catalytic poisons unless properly removed.<sup>39</sup>

80 All the above-mentioned events parallel in the catalyst preparation to determine the final  
81 structure of ZN catalysts at multiple length scales and, in turn, the catalyst performance.  
82 Therefore, monitoring the evolution of the catalysts along the synthesis is the only way to  
83 elucidate all the inter-connections between their components, laying the groundwork for a  
84 future rational design of new and more efficient catalytic systems. In this work, we focus on  
85 the ZN catalyst obtained from a  $\text{Mg}(\text{OEt})_2$  precursor, using dibutyl phthalate (DBP) as an  
86 internal donor. The  $\text{Mg}(\text{OEt})_2$ -based ZN catalysts are among one of the most employed  
87 catalysts in industrial PP production, because of their high activity and stereoselectivity. The  
88 difficulties of this investigation rely not only on the chemical lability or air sensitivity of  
89 samples, but also on the multi-technique approach needed to face such a multi-scale

90 complexity, ranging from the local structure of the Ti sites to the textural properties of MgCl<sub>2</sub>  
91 particles. Only a few pioneering works in the literature dealt with the evolution of the material  
92 during the ZN catalyst synthesis from Mg(OEt)<sub>2</sub>, where a series of samples were extracted from  
93 the reactor, and characterized for their chemical composition, structure, and activity.<sup>40-42</sup>  
94 According to Jeong et al., the activity towards propylene polymerization increases linearly with  
95 the increase in the number of TiCl<sub>4</sub> addition, while the presence of an internal donor affects  
96 drastically the stereospecificity of the catalyst (enhancing the isotacticity of the produced PP  
97 from less than 50 % up to 95 % in *mmmm*).<sup>40</sup> More in details, Chumachenko et al. found out  
98 that the reaction at early stages between Mg(OEt)<sub>2</sub> and TiCl<sub>4</sub> leads to a mixture of MgCl<sub>2</sub> and  
99 TiCl<sub>3</sub>(OEt) with very high surface area (415 m<sup>2</sup>/g) but low activity and stereospecificity, while  
100 the subsequent addition of DBP causes the removal of inactive TiCl<sub>3</sub>(OEt), the growth of  
101 MgCl<sub>2</sub> crystallites (the surface area decreases to 211 m<sup>2</sup>/g), and a significant increase of the  
102 overall activity and stereospecificity.<sup>42</sup> Finally, Kim et al. mostly focused on the mutual  
103 reactions between Mg(OEt)<sub>2</sub>, TiCl<sub>4</sub> and the benzoyl chloride (BzCl) used as an electron donor  
104 or its precursor, demonstrating the high interchangeability of (OEt)<sup>-</sup> and Cl<sup>-</sup> anionic ligands.<sup>41</sup>

105 Recently, we proposed a combination of cutting-edge characterization techniques to clarify  
106 the identity of δ-MgCl<sub>2</sub>, which includes X-ray total scattering for defining the nano-sized and  
107 disordered structure,<sup>30</sup> and vibrational spectroscopies for determining the exposed surfaces and  
108 their relative extension.<sup>43</sup> In this study, the same approach has been adopted, but complemented  
109 by chemical analysis, polymerization tests and UV-Vis spectroscopy, in order to elucidate the  
110 chemical reactions and structural evolution taking place during the ZN catalyst preparation.

111

## 112 **2. EXPERIMENTAL**

### 113 **2.1. Reagents**

114 Mg powder was purchased from Merck, KGaA. Ethanol (purity > 99.5%, Kanto Chemical)  
115 was dried over 3A molecular sieve with N<sub>2</sub> bubbling. Iodine (I<sub>2</sub>, purity > 99.999%, FUJIFILM  
116 Wako Pure Chemical) was used as a halide initiator. *n*-Heptane (purity > 99.5%, ), toluene  
117 (purity > 99.5%), and di-*n*-butylphthalate (DBP, purity > 98%) were purchased from  
118 FUJIFILM Wako Pure Chemical and dried over 4A molecular sieve with N<sub>2</sub> bubbling.  
119 Triethylaluminium (TEAl) was donated by Tosoh Finechem.  
120 Cyclohexylmethyldimethoxysilane (CMDMS) was purchased from Sigma-Aldrich and  
121 purified by vacuum distillation. Propylene was donated by Japan Polychem Corp., and ethylene  
122 was purchased from Sumitomo Seika Chemicals Co., Ltd.

123

## 124 **2.2. Catalyst Synthesis**

125 All the manipulations and storage were performed under a N<sub>2</sub> atmosphere to prevent moisture  
126 contamination. The starting material, Mg(OEt)<sub>2</sub>, was synthesized according to a previously  
127 reported method.<sup>44-46</sup> Briefly, 2.64 mmol of I<sub>2</sub> and 25.0 g of ethanol were introduced to a 500  
128 mL jacket-type flask equipped with a mechanical stirrer rotating at 180 rpm. After dissolving  
129 I<sub>2</sub> in ethanol at 75 °C, 2.5 g of Mg powder and 25.0 g of ethanol were added. The same amount  
130 of Mg powder and ethanol were repeatedly added with sufficient intervals between individual  
131 additions. The total amount of Mg powder and ethanol were 25.0 g and 125 g. The resultant  
132 solid product was recovered by washing with 200 mL of ethanol and dried in vacuo at below  
133 40 °C.

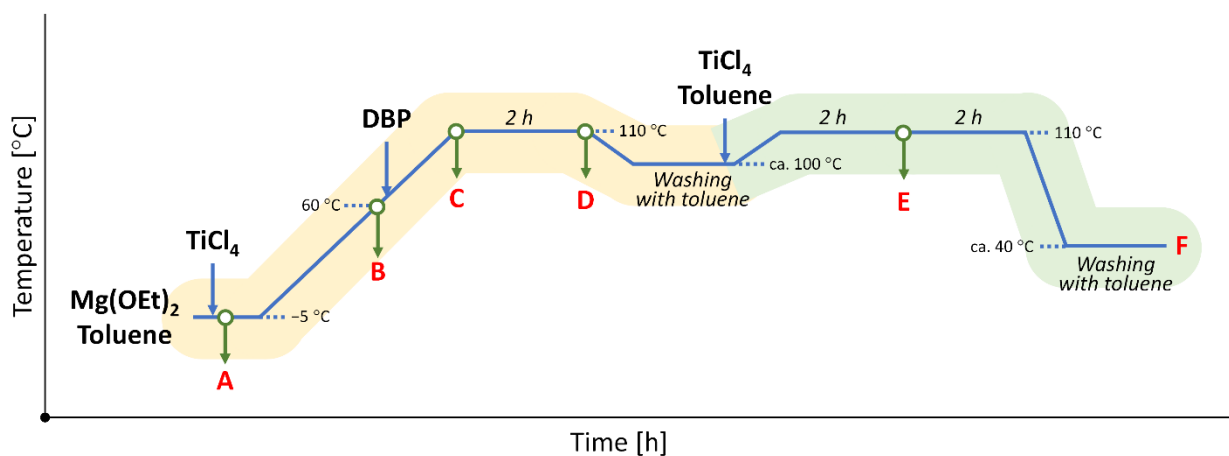
134 The procedures for catalyst preparation and sampling are shown in Scheme 1. A three-necked  
135 flask (500 mL) equipped with a mechanical stirrer and purged with N<sub>2</sub> was charged with 20 g  
136 of Mg(OEt)<sub>2</sub> powder and 136 mL of toluene. 20 mL of TiCl<sub>4</sub> was dropwise introduced by  
137 keeping the temperature of the mixture below -5 °C. The mixture was gradually heated, and  
138 when the temperature reached 60 °C, 4.3 mL of DBP was dropped in the flask. The mixture

139 was further heated, and kept at 110 °C for 2 hours. The solid product in the flask was washed  
140 with toluene twice by a decantation method, and then 16 mL of TiCl<sub>4</sub> and 68 mL of toluene  
141 were introduced. The mixture was heated and aged at 110 °C for 4 hours. Note that the aging  
142 time after the second addition of TiCl<sub>4</sub> is usually set to 2 hours, while the duration was extended  
143 to 4 hours in this study for the sake of characterization. Finally the mixture was sufficiently  
144 washed with toluene and *n*-heptane to obtain the catalyst. At several key points in the above  
145 preparation, samples were extracted from the flask using a syringe. The amount of each  
146 extraction corresponded to ca. 3 g of solid. The extracted solid was washed thoroughly with *n*-  
147 heptane, dried in vacuum at 80 °C, and stored under N<sub>2</sub> for characterization. The timing of the  
148 extraction and the corresponding sample codes are as follows: **(A)** after the first TiCl<sub>4</sub> addition,  
149 **(B)** immediately before the addition of DBP, **(C)** when the temperature of the mixture reached  
150 110 °C, **(D)** after being kept at 110 °C for 2 hours, **(E)** after 2 hours of the aging, and **(F)** the  
151 final catalyst. All the extracted samples were adequately washed with dehydrated *n*-heptane  
152 and then dried in vacuum at 80 °C.

153

154

155 **Scheme 1.** Schematic description of the main steps upon ZN catalyst preparation, with  
156 indication of sampling points.



157

158

### 159 2.3. Ethylene and Propylene Polymerization

160 Polymerization tests were carried out in semi-batch mode. A mechanically stirred 1 L  
 161 autoclave reactor was charged with 300 mL of heptane and 3.0 mmol of TEAl for ethylene  
 162 polymerization, or with 300 mL of heptane, 3.0 mmol of TEAl, and 0.30 mmol of CMDMS  
 163 for propylene polymerization. Either ethylene or propylene was introduced to the reactor and  
 164 saturated at 0.4 MPa and 70 °C. The polymerization was initiated by the injection of a catalyst  
 165 (10–50 mg) into the reactor and continued for 30 minutes, where the temperature, the monomer  
 166 pressure, and the stirring speed were maintained at 70 °C, 0.4 MPa, and 500 rpm, respectively.  
 167 The obtained polymer powder was recovered by filtration and vacuum drying at 60 °C for 6  
 168 hours.

169

### 170 2.4. Catalysts Activation by TEAl

171 In order to investigate the activation process, some selected samples (A, B, C, and F) were  
 172 separately reacted with TEAl. The activation of the catalysts was carried out in glove-box by  
 173 impregnating at room temperature the powders with TEAl (diluted 10 v/v % in hexane) at an  
 174 Al:Ti ratio of 2:1. Afterwards, the solvent was removed by degassing under vacuum.

175

### 176 2.5. Characterization

### 177 **2.5.1. Chemical Composition**

178 The chemical composition of the samples was analyzed as follows. The Ti content was  
179 measured by a colorimetric method, where ca. 50 mg of a sample was dissolved in an aqueous  
180 solution of HCl/H<sub>2</sub>SO<sub>4</sub>, and then H<sub>2</sub>O<sub>2</sub> solution was added to develop the color. The absorption  
181 intensity of the band at 410 nm was recorded on a UV–vis spectrometer (V-670 JASCO), which  
182 was used to calculate the titanium content based on external calibration.<sup>44</sup> Organic contents  
183 were analyzed by <sup>1</sup>H NMR on a Bruker AVANCE III 400 MHz spectrometer according to our  
184 previous study.<sup>39</sup> 10–30 mg of a sample was dissolved in 0.7 mL of DMSO-*d*<sub>6</sub> with 40 μg of  
185 1,1,2,2-tetrachloroethane as an internal standard. The morphology of the catalyst particles was  
186 observed by scanning electron microscopy (SEM, Hitachi Ltd., S-4500). In order to minimize  
187 the risk of moisture contamination during sample transfer, sputter coating was omitted. The  
188 acceleration voltage was set to 1 kV to suppress a charge-up effect.

189

### 190 **2.5.2. Polymer Characterization**

191 The obtained polymers were subjected to differential scanning calorimetry (DSC, Mettler  
192 Toledo DSC 822) under a nitrogen atmosphere. About 8 mg of polymer in an aluminum pan  
193 were heated to 230 °C and then cooled down to 25 °C (20 °C min<sup>-1</sup>). The cooled sample was  
194 then heated up to 230 °C at a heating rate of 20 °C min<sup>-1</sup> to determine the melting temperature  
195 ( $T_m$ ) and the crystallinity ( $X_c$ ) from the melting endotherm.

196 Gel permeation chromatography (GPC, Tosoh Co., HLC-8321GPC/HT) measurements were  
197 performed at 140 °C using *o*-dichlorobenzene as a mobile phase. Polystyrene standards were  
198 used for calibration.

199

### 200 **2.5.3. X-ray Total Scattering**

201 X-ray total scattering data were acquired at the BL04B2 of SPring-8 (Hyogo, Japan). Each  
202 sample in the powder form was filled in a quartz glass capillary with a diameter of 2 mm and  
203 a wall thickness of 0.01 mm, placed in a vacuum chamber, and irradiated with the X-ray beam  
204 at an energy of 61.4 keV ( $\lambda=0.202 \text{ \AA}$ ). The diffraction patterns were recorded in transmission  
205 mode and in the horizontal scattering plane by using solid-state array detectors. The upper limit  
206 of the scattering vector ( $Q$ ) was  $25.7 \text{ \AA}^{-1}$ . The measured X-ray scattering data were corrected  
207 for polarization, absorption, and background. The contribution of Compton scattering was  
208 subtracted using standard analysis procedures.<sup>47</sup> The calculated total structure factor  $S(Q)$  was  
209 converted into reduced pair distribution function (PDF)  $G(r)$  via Fourier transformation with a  
210 Lorch modification function.<sup>48</sup>

211

#### 212 **2.5.4. IR Spectroscopy**

213 IR spectra were collected with a Bruker Vertex70 FT-IR spectrophotometer, equipped with  
214 a DTGS detector for the Far-IR region and a MCT detector for the Mid-IR region (hereafter  
215 generically referred to as IR).

216 For the Far-IR measurements, the samples were prepared directly inside a N<sub>2</sub>-filled glove-  
217 box as thin layers deposited on a highly pure Si wafer (from a suspension in hexane), and placed  
218 inside a quartz cell with PE windows, allowing to measure the spectra without exposing the  
219 samples to air. Far-IR spectra were acquired at a resolution of  $4 \text{ cm}^{-1}$ , and are shown after  
220 subtracting the weak contributions of both the Si wafer and the PE windows.

221 For the IR measurements, the samples were diluted in anhydrous KBr, compressed in the  
222 form of thin self-supporting pellets (with a resulting density of 10 mg of sample per  $\text{cm}^2$ ) inside  
223 the glove-box, and placed inside a quartz cell with KBr windows. The IR spectra were acquired  
224 at a resolution of  $2 \text{ cm}^{-1}$ . The curve fitting of the spectra in the  $\nu(\text{C}=\text{O})$  region was carried out  
225 by OPUS software (Bruker), imposing the Gaussian shape to the contributions.

226

### 227 **2.5.5. DR UV-Vis Spectroscopy**

228 UV-Vis spectra were collected in diffuse reflectance mode (DR), with a Varian Cary5000  
229 spectrophotometer, equipped with a reflectance sphere. The powder samples were directly  
230 placed inside a bulb-shaped cell made of optical quartz (Suprasil) within the glove-box, and  
231 successively measured in N<sub>2</sub> atmosphere. The spectra have been collected in reflectance mode  
232 and then converted in the Kubelka-Munk function.

233

## 234 **3. RESULTS AND DISCUSSION**

235 In this study, we performed a multi-faceted characterization of solid samples extracted at  
236 different steps of catalyst preparation for addressing two key questions: 1) how catalyst  
237 nanostructures are generated and shaped during the preparation, and 2) which are the mutual  
238 interactions between all the catalyst components. The structure of the Section is as follows: in  
239 Section **3.1** the chemical composition of all the samples is discussed; Section **3.2** describes the  
240 performances of each intermediate as well as of the final catalyst in olefin polymerization after  
241 activation by TEAL; then the results of individual characterization methods are explained and  
242 discussed in Sections **3.3-3.6**, and finally all the results are combined to give a conclusive  
243 picture in Section **4**.

244

### 245 **3.1. Chemical Composition**

246 The evolution of the chemical composition along the ZN catalyst synthesis is summarized in  
247 Table 1. In general, it has been reported that Mg(OEt)<sub>2</sub> is chlorinated by TiCl<sub>4</sub> to produce  
248 MgCl<sub>2</sub> and TiCl<sub>x</sub>(OEt)<sub>4-x</sub>. The OEt group remains in the catalyst to a greater or lower extent  
249 due to both/either incomplete chlorination of Mg(OEt)<sub>2</sub> and/or persistence of surface  
250 TiCl<sub>x</sub>(OEt)<sub>4-x</sub> species, which greatly reduces the activity and stereospecificity of the catalyst.

251 Here, the OEt group was quantified by the methylene peak in  $^1\text{H}$  NMR, so the OEt residual can  
 252 be associated to either  $\text{Mg}(\text{OEt})_2$  or  $\text{TiCl}_x(\text{OEt})_{4-x}$ . Initially (**A,B**), the Ti content is pretty high  
 253 (about  $2.5 \text{ mmol g}^{-1}$ ) and the Ti:OEt molar ratio is about 1:1. By introducing DBP and heating  
 254 up to  $110 \text{ }^\circ\text{C}$ , the Ti content is reduced to less than half (**C**), and to a further half by the aging  
 255 (**D**), whereas the Ti:OEt molar ratio is kept almost constant. Hence, it is plausible that in the  
 256 early stages of catalyst preparation, Ti is present almost exclusively as  $\text{TiCl}_3(\text{OEt})$ . Heating  
 257 with DBP causes a reduction in the amount of  $\text{TiCl}_3(\text{OEt})$ . The second  $\text{TiCl}_4$  treatment has  
 258 almost no impact on the Ti content (**E,F**), but the OEt further decreases to below  $0.2 \text{ mmol g}^{-1}$ ,  
 259 suggesting that  $\text{TiCl}_x(\text{OEt})_{4-x}$  species are replaced by  $\text{TiCl}_4$ . Concerning DBP, its content at the  
 260 end of ZN catalyst synthesis (**F**) converges to about  $0.6 \text{ mmol g}^{-1}$ , which corresponds to a  
 261 molar amount comparable to that of Ti. Finally, it is worth noticing that in ZN catalysts  
 262 containing DBP as an internal donor, phthaloyl chlorides (POC) are known as typical by-  
 263 products, which are produced by a reaction of DBP and  $\text{TiCl}_4$  at an elevated temperature. In  
 264 our analysis, POC were not observed during the first  $\text{TiCl}_4$  treatment (**C,D**), but was slightly  
 265 observed (column Cl in Table 1) after the second  $\text{TiCl}_4$  treatment (**E,F**), which suggests that  
 266 the fresh  $\text{TiCl}_4$  is more reactive towards the surface adsorbates.

267

268 **Table 1.** Evolution in the chemical composition along the synthesis steps.

Sample	Ti <sup>a</sup> [mmol g <sup>-1</sup> ]	OEt <sup>b</sup> [mmol g <sup>-1</sup> ]	Pthalate <sup>b,c</sup>			
			<i>n</i> -Bu [mmol g <sup>-1</sup> ]	Et [mmol g <sup>-1</sup> ]	Cl [mmol g <sup>-1</sup> ]	Phthalate (total) [mmol g <sup>-1</sup> ]
<b>A</b>	2.42	2.09				
<b>B</b>	2.53	2.49				
<b>C</b>	1.07	0.89	1.70	0.09	n.d. <sup>d</sup>	0.89
<b>D</b>	0.56	0.47	0.97	0.56	n.d. <sup>d</sup>	0.77

<b>E</b>	0.63	0.18	0.73	0.48	0.03	0.63
<b>F</b>	0.56	0.18	0.68	0.46	0.04	0.61

269 <sup>a</sup> Determined by titration.

270 <sup>b</sup> Determined by <sup>1</sup>H NMR.

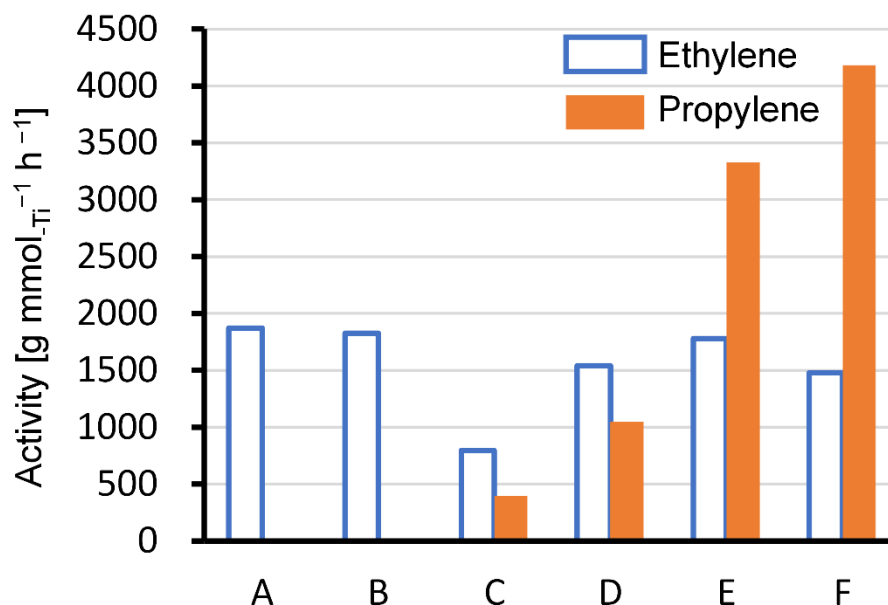
271 <sup>c</sup> The *n*-Butoxy groups of DBP is known to be substituted by ethoxy groups as well as  
 272 chlorine atoms during catalyst preparation. The total phthalate amount was calculated as half  
 273 of the total amount of possible substitutional groups: (*n*-Bu + Et + Cl)/2.

274 <sup>d</sup> Not detected.

275

### 276 **3.2. Performance in Olefin Polymerization**

277 Samples **A–F** have been used as catalysts for ethylene and propylene homopolymerization  
 278 after activation by TEAL. Table 2 summarizes the activity data, while Figure 1 shows the  
 279 activity normalized per Ti-mol. The reactivity is completely different for the two monomers,  
 280 suggesting that the composition and structural features required for ethylene and propylene  
 281 polymerization are completely different. The ethylene polymerization activity (per Ti-mol) was  
 282 almost constant throughout the catalyst synthesis, i.e. insensitive to the composition and  
 283 structural features. In contrast, propylene polymerization was found to be sensitive to the stage  
 284 of the catalyst preparation: no polymer was obtained before DBP was added and heated up to  
 285 110 °C (**A,B**), but then the activity increased significantly along with the synthesis. The  
 286 characterization of all the produced polymers is summarized in Table S1 and Figure S1.



287

288 **Figure 1.** Ethylene and propylene polymerization activity of the samples extracted at different  
 289 stages in the course of catalyst preparation. Reaction conditions: monomer pressure = 0.4 MPa,  
 290 catalyst = 10–50 mg, *n*-heptane = 300 mL, TEAl = 3.0 mmol, 70 °C, 30 min, CMDMS (for  
 291 propylene polymerization) = 0.30 mmol.

292

293 **Table 2.** Evolution of the activity towards ethylene and propylene polymerization.

Sample	Activity in ethylene polym.		Activity in propylene polym. <sup>a</sup>	
	[g-PE g-cat <sup>-1</sup> h <sup>-1</sup> ]	[g-PE mmol-Ti <sup>-1</sup> h <sup>-1</sup> ]	[g-PP g-cat <sup>-1</sup> h <sup>-1</sup> ]	[g-PP mmol-Ti <sup>-1</sup> h <sup>-1</sup> ]
<b>A</b>	4300	1900	n.d.	n.d.
<b>B</b>	4800	1800	n.d.	n.d.
<b>C</b>	840	800	420	400
<b>D</b>	880	1500	600	1000
<b>E</b>	1100	1800	2100	3300
<b>F</b>	820	1500	2300	4200

294 <sup>a</sup> No polymer was obtained when **A** or **B** was used as the catalyst.

295

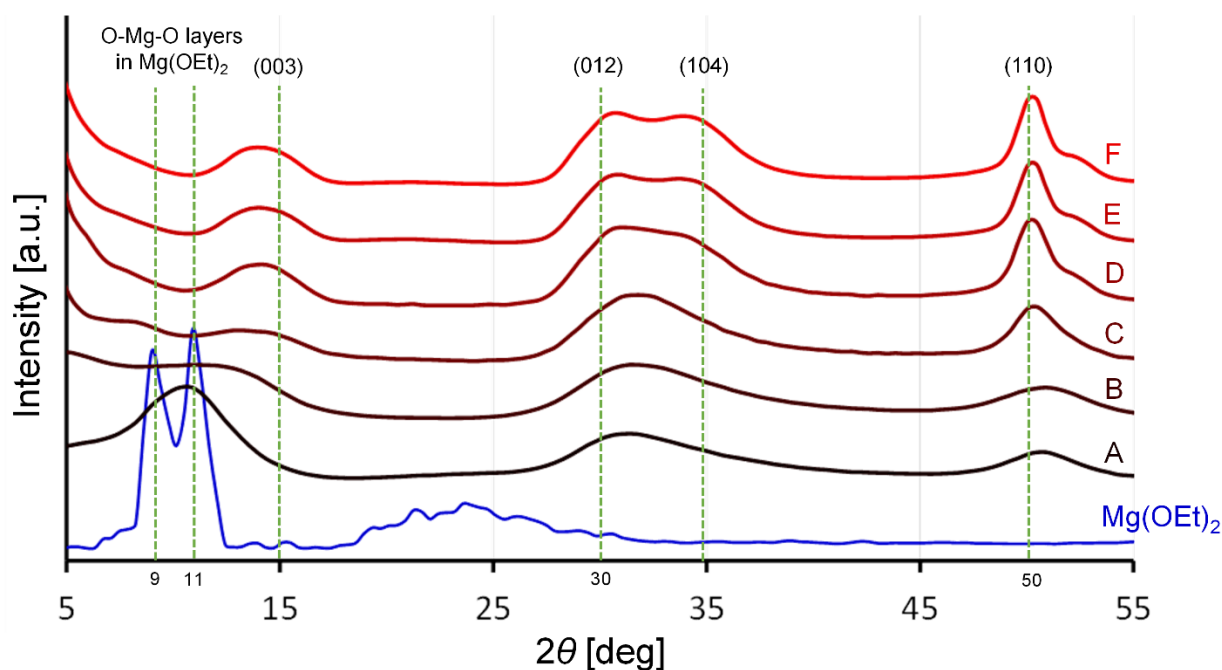
### 296 3.3. Formation of Nanostructure Along the Synthetic Steps

#### 297 3.3.1. PXRD

298 The solid samples extracted in the course of catalyst preparation (**A** to **F**), as well as the  
299  $\text{Mg}(\text{OEt})_2$  starting material, were subjected to X-ray total scattering measurements. The X-ray  
300 diffraction patterns are shown in Figure 2. The pattern of  $\text{Mg}(\text{OEt})_2$  exhibits two strong peaks  
301 at  $2\theta = 9$  and  $11^\circ$ . The structure of  $\text{Mg}(\text{OEt})_2$  has not been clearly identified yet, but it is  
302 believed that it resembles that of  $\text{Mg}(\text{OH})_2$  (Brucite,  $P\bar{3}m1$ ), where the H atoms are substituted  
303 with ethyl groups, and the split peaks correspond to (001) reflection.<sup>27, 49, 50</sup> That is, the O-Mg-  
304 O layers are stacked across a layer of  $-\text{C}_2\text{H}_5$  groups, and hence the peaks at  $2\theta = 9$  and  $11^\circ$  are  
305 most likely originated from the stacking of the O-Mg-O layers. A broad peak centered at  $2\theta =$   
306  $10^\circ$  is also observed in the pattern of **A** (right after the first  $\text{TiCl}_4$  addition), which suggests that  
307 the structure of **A** memorizes the layered structure of  $\text{Mg}(\text{OEt})_2$  to some extent. The same  
308 pattern, however, also contains weak reflections at  $2\theta = 27\text{--}40^\circ$  and  $50^\circ$ , which correspond to  
309 the (012)/(104) and (110) reflections of  $\text{MgCl}_2$ , and indicate that the  $\text{MgCl}_2$  seeds are already  
310 formed at the very initial stage of the synthesis. The peak at  $2\theta = 10^\circ$  becomes weaker when  
311 the temperature is increased up to  $60^\circ\text{C}$  (**B**), and eventually disappears after the addition of  
312 DBP and heating up to  $110^\circ\text{C}$  (**C**). Instead, the peak corresponding to the Cl-Mg-Cl stacking  
313 along the  $c$ -axis emerges at  $15^\circ$ . In the following steps of the preparation (from **D** to **F**), the  
314 broad peak in the  $27\text{--}40^\circ$  range becomes stronger, reflecting the growth of the  $\text{MgCl}_2$   
315 crystallites both in the lateral and vertical directions. The patterns of **C**–**F** are typical for  $\delta$ -  
316  $\text{MgCl}_2$ : three broad peaks are observed at around  $15^\circ$ ,  $27\text{--}40^\circ$ , and  $50^\circ$ , which correspond to  
317 (003), (012)/(104), and (110) reflections. The broadness of the peaks indicates the nano size of  
318  $\text{MgCl}_2$  in all the dimensions, while the merge of the (012) and (104) reflections into a single  
319 broad peak (in particular for **C**) dictates the total lack of periodicity in the stacking of Cl-Mg-  
320 Cl layers.<sup>8</sup> Hence, PXRD measurements clearly indicate that the  $\text{MgCl}_2$  crystallites or their

321 seeds are formed just after the first  $\text{TiCl}_4$  addition, and they gradually grew through the  
322 subsequent steps of preparation, maintaining a disordered structure along the Cl-Mg-Cl  
323 stacking direction.

324



325

326 **Figure 2.** Powder X-ray diffraction (PXRD) patterns of the samples extracted at different steps  
327 of the synthesis and of the  $\text{Mg}(\text{OEt})_2$  starting material. The X-axis was scaled with the  
328 wavelength of  $\text{Cu K}\alpha$  ( $\lambda=1.5418 \text{ \AA}$ ) for comparison with the literature. The typical diffraction  
329 peaks of  $\alpha\text{-MgCl}_2$  are denoted by dotted lines. The patterns are vertically shifted for clarity.

330

331 The SEM images of the catalyst samples are shown in Figure S2. The spherical  $\text{Mg}(\text{OEt})_2$  is  
332 an aggregate of plate-like particles with a length of several micrometers.<sup>51</sup> The surface of **A**,  
333 just after contact with  $\text{TiCl}_4$ , is notably rough since the plate-like particles partially retain their  
334 shape. In **B**, the macroparticles became smoother and more spherical due to the fusion of plate-  
335 like particles. After adding the donor (**C**), the surface became even smoother, and the plate-  
336 like particles were completely fused. From **C** to **F**, no significant changes were observed. In

337 addition, the macroparticles seem to grow slightly from **A** to **C**, which is probably due to the  
338 fusion of small  $\text{Mg}(\text{OEt})_2$  macroparticles or the growth of the catalyst primary particles. Such  
339 ripening phenomenon has been reported previously, where the resultant catalyst particles were  
340 about 10% bigger in diameter than the original  $\text{Mg}(\text{OEt})_2$  particles.<sup>44, 52</sup>

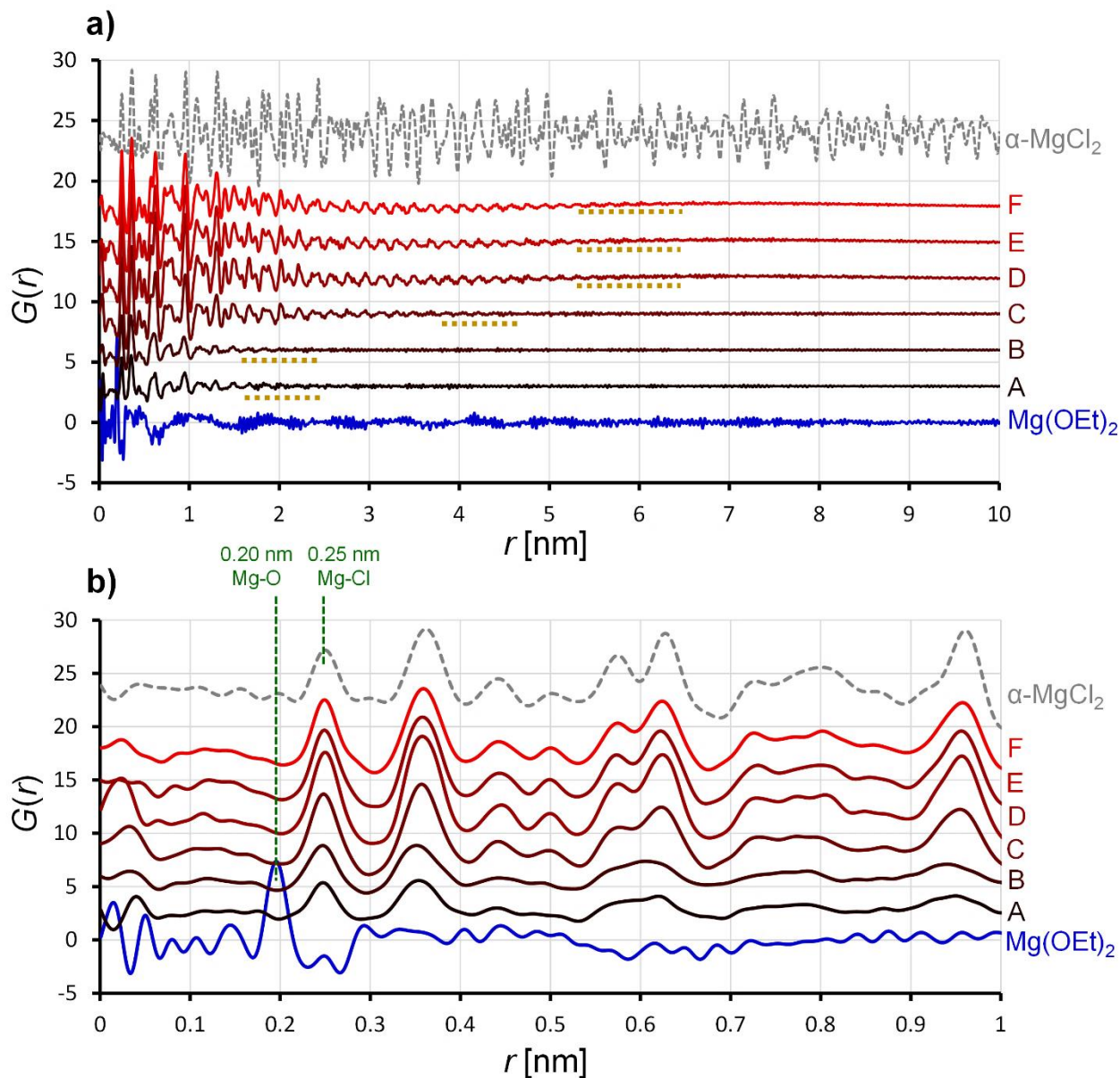
341

### 342 3.3.2. PDF

343 The total scattering data were converted into PDFs. Figure 3 shows PDFs of the extracted  
344 samples (**A–F**) as well as of  $\text{Mg}(\text{OEt})_2$  and  $\alpha\text{-MgCl}_2$  in the long-range (part a) and short-range  
345 (part b) regions. PDFs directly correlate with the atomic configuration in the real space: i) peak  
346 positions correspond to atomic distances; ii) the broadness represents their distribution,  
347 including the thermal vibration effect; iii) the relative abundance of the atomic pairs can be  
348 estimated by the intensity of the peaks; therefore, the distance at which the amplitude becomes  
349 completely negligible corresponds to the crystalline dimensions.<sup>53</sup> For  $\text{Mg}(\text{OEt})_2$ , a weak  
350 oscillation can be observed from around 0.5 to 6 nm; however, this is not due to the local atomic  
351 configuration, but to density fluctuation originated from a nanostructure, that is most plausibly  
352 caused by O-Mg-O layers.<sup>54</sup> The fact that limiting the  $Q_{\min}$  to  $1.0 \text{ \AA}^{-1}$  completely diminishes  
353 the fluctuation also supports this hypothesis (Figure S3). From **A** to **F**, the distance at which  
354 the amplitude disappears gradually increases (as marked in yellow in Figure 3a), from  $r = \text{ca.}$   
355 2 nm (**A,B**) to ca. 4-5 nm (**C**) and to ca. 5.5-6.5 nm (**D,F**), suggesting that the  $\text{MgCl}_2$  crystallites  
356 slowly grow during the synthesis.

357 In the shorter region (Figure 3b), the pattern of  $\text{Mg}(\text{OEt})_2$  shows a prominent peak at 0.20  
358 nm, which is attributed to the Mg-O atomic pair. For comparison, the distance between Mg and  
359 O in  $\text{Mg}(\text{OH})_2$  is estimated at a very close value, ca. 0.21 nm. The PDF pattern of **A** does not  
360 exhibit such peak, providing evidence that the Mg-O bond is immediately converted to Mg-Cl  
361 by contacting  $\text{Mg}(\text{OEt})_2$  with  $\text{TiCl}_4$ . Although there is no traceable Mg-O in the PDF, there is

362 a remnant of the periodic structure formed by  $\text{Mg}(\text{OEt})_2$  in the PXRD. Such a memory of the  
363 precursor structure on PXRD has also been reported in the formation of  $\delta\text{-MgCl}_2$  from  
364  $\text{MgCl}_2$ /Lewis base adducts.<sup>55,56</sup> The positions of the most relevant peaks in the patterns of the  
365 extracted samples are similar to those of  $\alpha\text{-MgCl}_2$ , for example, the peaks at 0.25, 0.35, 0.58,  
366 0.63, and 0.97 nm. This fact indicates that the local structures of the extracted samples were  
367 almost identical to that of the  $\alpha\text{-MgCl}_2$  even at the stage of seeds formation (**A**). The relatively  
368 weak peak intensity of **A** and **B** over  $r = 0.5\text{--}1.0$  nm is due to its finite crystal dimension (<2  
369 nm).  
370  
371



372

373 **Figure 3.** Part a) Atomic pair distribution functions (PDFs) of the extracted samples in the  
 374 long-range region. Part b) Those in the short-range (part b) region.  $Q_{\min}$  was set as  $0.1 \text{ \AA}^{-1}$ . The  
 375 PDFs of Mg(OEt)<sub>2</sub> and highly crystalline  $\alpha$ -MgCl<sub>2</sub> (acquired at AichiSR,  $Q_{\max}=15 \text{ \AA}^{-1}$ . See  
 376 ref<sup>30</sup>) are also provided for comparison purpose. The patterns are vertically shifted for clarity.

377

### 378 3.3.3. Quantitative Structural Determination

379 The structure of  $\delta$ -MgCl<sub>2</sub> in the extracted samples was quantitatively determined by PXRD  
 380 fitting and cross-validated by PDF fitting, following the same approach discussed in our

381 previous work.<sup>30</sup> Table 3 summarizes the structural parameters of MgCl<sub>2</sub> nanoparticle models  
382 as determined by PXRD fitting, where  $L_a=L_b$  correspond to the lateral size in the  $ab$  plane,  $L_c$   
383 is the crystallite dimension in the basal direction, and  $P_c$  is the probability of finding  $\alpha$ -MgCl<sub>2</sub>  
384 sequences as an indicator of the amount of stacking disorders ranging from 25 to 100%; the  
385 accuracy of the fit is also provided in terms of  $R_w$ , defined as the residual between the  
386 experimental and the simulated patterns. A typical fitting pattern is shown in Figure S4a.

387 In **A**, obtained just after contacting Mg(OEt)<sub>2</sub> with TiCl<sub>4</sub>, the MgCl<sub>2</sub> seeds have a lateral  
388 dimension of 1.8 nm and a vertical dimension of 0.3 nm, corresponding to a single Cl-Mg-Cl  
389 layer. Heating up to 60 °C (**B**) brings no significant change in the structure of MgCl<sub>2</sub> seeds.  
390 The addition of donor and heating up to 110 °C (**C**) significantly promotes the growth of the  
391 MgCl<sub>2</sub> seeds both in the lateral and vertical directions (4.0 nm and 1.4 nm, respectively).  
392 Further heating for 2 hours (**D**) induces further growth in the lateral direction (from 4.0 nm to  
393 5.5 nm) as well as a decrease in the stacking disorder ( $P_c$  increases from 25% to 40%). The  
394 second TiCl<sub>4</sub> addition and further aging (**E,F**) do not cause a significant structural change,  
395 which is consistent with the fact that the amount of Ti and phthalate on MgCl<sub>2</sub> is almost kept  
396 constant from **D** to **F** (Table 1). It is likely that the presence of DBP (only in the first TiCl<sub>4</sub>  
397 treatment) is a primary factor to promote the growth of MgCl<sub>2</sub>.

398 The obtained MgCl<sub>2</sub> nanoparticle models were cross-validated using PDF fitting. Simulated  
399 patterns and fitting parameters therein are shown in Figure S4b and Table S2. All the PDF  
400 patterns are reasonably fitted with the PXRD-determined nanoparticle models. The fitting  
401 accuracy for **A** and **B** was relatively poor ( $R_{w,PDF} = 0.374$  and  $0.377$ ), which is likely attributed  
402 to the relatively low periodicity (i.e. weaker signals).

403

404 **Table 3.** MgCl<sub>2</sub> nanoparticle models derived via PXRD fitting and cross-validated by PDF  
405 fitting with the aid of software, DISCUS,<sup>57</sup> PDFgui,<sup>58</sup> and DShaper.<sup>59</sup>  $L_a = L_b$ : lateral size in  $ab$

406 plane;  $L_c$ : crystallite dimension in the basal direction;  $P_c$ : indicator of stacking disorder;  $R_w$ :  
 407 indicator of the fitting accuracy.

Sample Name	$L_a = L_b$ [nm]	$L_c$ [nm]	$P_c$ [%]	$R_{w,PXRD}$	$R_{w,PDF}$
A	1.8	0.3	n.a. <sup>a</sup>	0.162	0.374
B	1.8	0.3	n.a. <sup>a</sup>	0.106	0.377
C	4.0	1.4	25	0.151	0.318
D	5.5	1.4	40	0.115	0.278
E	5.8	1.4	46	0.165	0.270
F	6.1	1.4	49	0.143	0.221

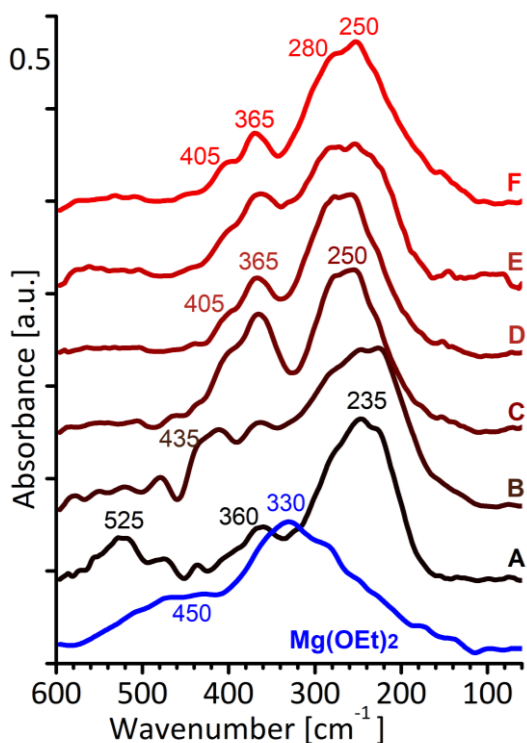
408 <sup>a</sup>  $P_c$  was not specified as the particle model is composed of a single Cl-Mg-Cl layer.

409

### 410 3.4. Morphology of MgCl<sub>2</sub> Nanoparticles Along the Synthetic Steps

411 Far-IR spectroscopy has been applied to all the extracted samples to retrieve information on  
 412 the morphology of the MgCl<sub>2</sub> nanoparticles. As a matter of fact, we have previously  
 413 demonstrated that the vibrations in the region of 600 – 100 cm<sup>-1</sup>, which are due to both intra-  
 414 layer displacement of the atoms in the *ab* plane and inter-layer displacement along *c* axis, are  
 415 sensitive to the relative extension of the different MgCl<sub>2</sub> surfaces.<sup>43</sup> Moreover, vibrations  
 416 involving Ti-Cl, Ti-O and Mg-O also fall in this spectral range, so that Far-IR can provide  
 417 information also on the adsorbates at MgCl<sub>2</sub> surfaces, including the Ti species.

418 Figure 4 displays the evolution of the Far-IR spectra along the synthetic steps, together with  
 419 the spectrum of the Mg(OEt)<sub>2</sub> starting material.



420

421 **Figure 4.** Far-IR spectra of the extracted samples and of the  $\text{Mg}(\text{OEt})_2$  precursor. The spectra  
 422 are vertically stacked for clarity.

423

424 The Far-IR spectrum of  $\text{Mg}(\text{OEt})_2$  is characterized by two main absorptions centered at 330  
 425 and  $450\text{ cm}^{-1}$ , very broad and overlapping to each other. Similar bands have been already  
 426 observed in the past for different  $\text{MgCl}_2$  adducts with alcoholates and alkoxides, and assigned  
 427 to the vibrations of Mg-O bonds.<sup>60-62</sup> As observed in the PDF analysis for the same sample,  
 428 these bands are no more observed already at the first step of the synthesis, while they are  
 429 replaced by the vibrational modes characteristic of  $\text{MgCl}_2$ . The spectrum of **A** shows a main  
 430 absorption band centered at  $235\text{ cm}^{-1}$ , together with two weaker bands at 525 and  $360\text{ cm}^{-1}$ .  
 431 The sharp band at  $235\text{ cm}^{-1}$  is assigned to the basal (001) surface,<sup>43</sup> in well agreement with the  
 432 PXRD analysis according to which the first  $\text{MgCl}_2$  seeds are mostly formed as monolayers.  
 433 The band at  $525\text{ cm}^{-1}$ , instead, is attributed to the  $\nu(\text{Ti-O})$  vibrations of 4-fold coordinated  
 434  $\text{Ti}(\text{OEt})_x\text{Cl}_{4-x}$  species (vide infra).<sup>63</sup> The relatively high intensity of this band is in well

435 agreement with the high and nearly equimolar Ti and OEt percentages in **A** (2.42 and 2.09  
436 mmol g<sup>-1</sup>, respectively). Finally, the band at 360 cm<sup>-1</sup> is attributed to a few ethoxide residues  
437 on the MgCl<sub>2</sub> seeds.

438 In the spectrum of **B**, the main absorption band is still located at 235 cm<sup>-1</sup>, indicating that  
439 even after heating at 60 °C MgCl<sub>2</sub> particles mainly expose the basal surface (001). The band at  
440 525 cm<sup>-1</sup> is no more observed, while a new band with similar intensity is present at 435 cm<sup>-1</sup>.  
441 This band is assigned to  $\nu(\text{Ti-Cl})$  of 6-fold coordinated Ti species,<sup>11</sup> and indicates that a fraction  
442 of the Ti ethoxy chloride complexes are chemisorbed on the MgCl<sub>2</sub> seeds during the warm-up  
443 process up to 60 °C. Unfortunately, the destiny of this band in the following steps of the  
444 synthesis cannot be further investigated because of the drastic decrease of the Ti loading (to  
445 0.56 mmol g<sup>-1</sup> in **F**), which makes the band too weak in intensity.

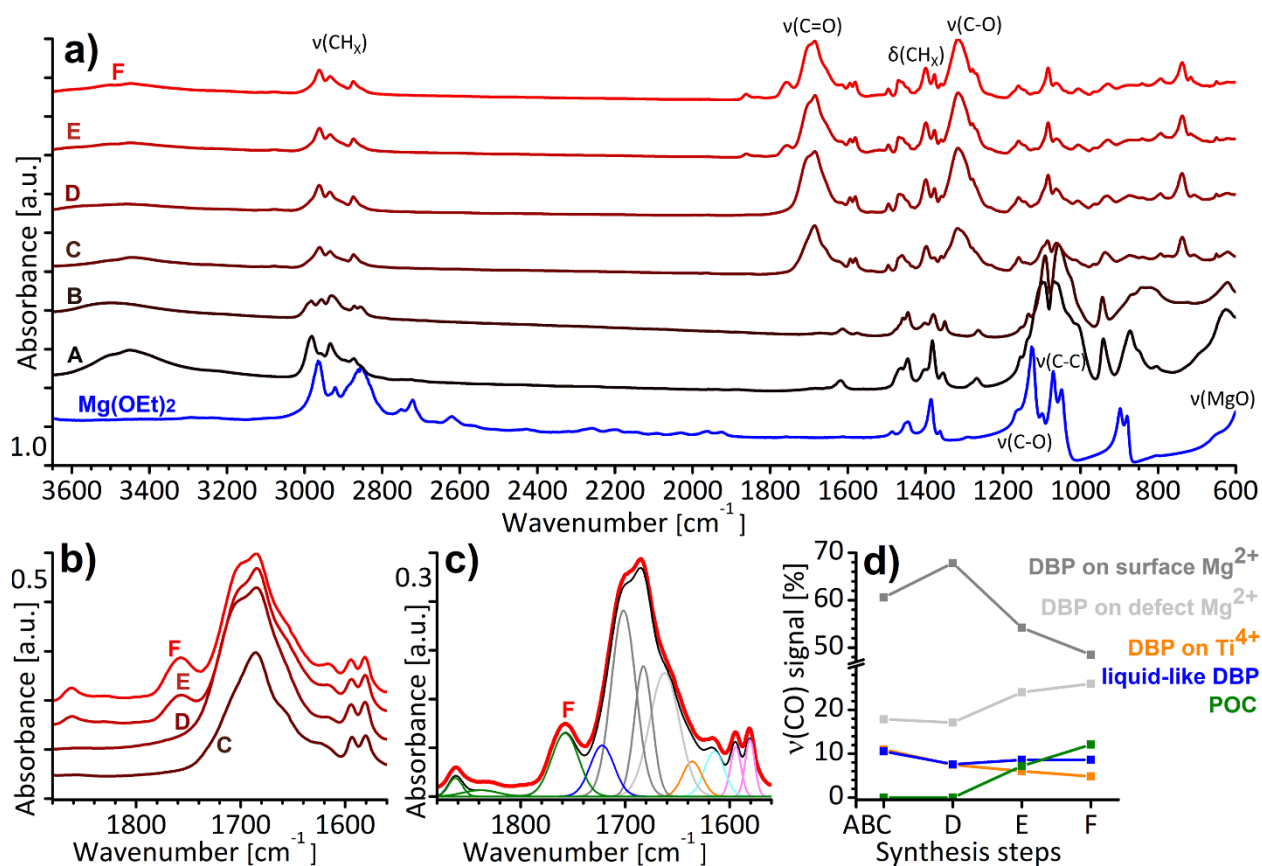
446 The addition of DBP (**C**) causes a significant change in the Far-IR spectrum: the main  
447 absorption band upward shifts to 250 cm<sup>-1</sup> (with a shoulder at 280 cm<sup>-1</sup>) and a sharp and intense  
448 band appears at 365 cm<sup>-1</sup> (with a pronounced hump at 405 cm<sup>-1</sup>). According to previous  
449 calculations, both manifestations can be associated to a morphological reconstruction of the  
450 MgCl<sub>2</sub> crystallites, which now do not expose anymore exclusively the basal (001) surface. In  
451 particular, the (110) surface is the principal responsible for the main signals at 250 and 365 cm<sup>-1</sup>  
452 <sup>1</sup>, while both the (012) and (015) surfaces significantly contribute at 280 and 405 cm<sup>-1</sup>.<sup>43</sup>

453 From **D** on, all the Far-IR spectra are similar to each other and to the spectrum of the final  
454 ZN catalyst (**F**). The features of the spectra are the same as already discussed in our previous  
455 work.<sup>43</sup> Briefly, with respect to the spectrum of **C**, the main absorption band at 250 cm<sup>-1</sup>  
456 undergoes a slight enlargement and the band at 365 cm<sup>-1</sup> slightly decreases in intensity. Overall,  
457 the spectrum indicates that MgCl<sub>2</sub> nanoparticles expose a large variety of surfaces, among  
458 which the relatively most abundant is the (110) one. It is worth noticing that such a surface has  
459 been claimed to be one of the most catalytically relevant ones.<sup>64-67</sup>

460

### 461 3.5. Surface Species Along the Synthetic Steps

462 The evolution of the surface species during ZN catalyst synthesis was investigated by IR  
463 spectroscopy in the Mid-IR region, as reported in Figure 5a. The spectrum of  $\text{Mg}(\text{OEt})_2$  is  
464 analogous to the spectra of Mg alkoxides already reported and described in literature.<sup>68, 69</sup>  
465 Briefly, most of the bands are due to the vibrational modes of the OEt moieties: the  $\nu(\text{CH}_x)$   
466 bands at  $2800\text{-}3000\text{ cm}^{-1}$ , the  $\delta(\text{CH}_2)$  and  $\delta(\text{CH}_3)$  bands at  $1450$  and  $1380\text{ cm}^{-1}$ ,  $\nu(\text{C-O})$  at  $1120$   
467  $\text{cm}^{-1}$ ,  $\nu(\text{C-C})$  at  $1050\text{ cm}^{-1}$  and some rocking modes at  $890\text{ cm}^{-1}$ . Below  $600\text{ cm}^{-1}$  the tail of the  
468 absorption band due to the  $\nu(\text{Mg-O})$  vibrations, contributing in the Far-IR region, is also  
469 observed.



470

471 **Figure 5.** Part a) IR spectra of the extracted samples, normalized to the optical thickness of the  
472 pellets. Part b) Magnification of the C-F spectra in the  $\nu(\text{C=O})$  region. Part c) Curve fitting in  
473 the  $\nu(\text{C=O})$  region for F (the black curve is the sum of all the calculated contributions). Part d)

474 Evolution of individual  $\nu(\text{C}=\text{O})$  components along the synthetic steps. The components are  
475 liquid-like physisorbed DBP, DBP on  $\text{MgCl}_2$  surfaces, DBP on defective  $\text{Mg}^{2+}$  sites, DBP on  
476  $\text{Ti}^{4+}$ , and POC.

477

478 The original bands due to the Mg-ethoxide groups are no more observable in the spectrum  
479 of **A**. Nevertheless, the spectrum still contains intense bands in the  $\nu(\text{CH}_x)$ ,  $\delta(\text{CH}_x)$ ,  $\nu(\text{C}-\text{O})$  and  
480  $\nu(\text{C}-\text{C})$  regions, which correspond well to those observed in the spectra of tetrahedral  
481  $\text{Ti}(\text{OEt})_2\text{Cl}_2$  and  $\text{Ti}(\text{OEt})_3\text{Cl}$  complexes.<sup>63</sup> Hence, at this stage most of the ethoxide groups look  
482 associated into  $\text{TiCl}_x(\text{OEt})_{4-x}$  species rather than incompletely chlorinated  $\text{Mg}(\text{OEt})_x\text{Cl}_{2-x}$ .  
483 Beside the ethoxide bands, the spectrum of **A** displays a weak and broad band in the  $\nu(\text{OH})$   
484 region (around  $3400\text{ cm}^{-1}$ ), which is due to a small amount of moisture contamination. The  
485 spectrum of **B**, obtained after heating **A** up to  $60\text{ }^\circ\text{C}$ , shows only small changes in the position  
486 of the bands ascribed to the ethoxide species, which are compatible with the chemisorption of  
487 the Ti ethoxide chloride complexes and a change in the coordination of the Ti cations from  
488 tetrahedral to octahedral.

489 The IR spectra radically change after the addition of DBP in the reaction mixture (**C**).<sup>70</sup> Most  
490 of the bands associated to the ethoxide groups drastically decrease in intensity after the addition  
491 of DBP (**C**), indicating that the ethoxide groups are mostly removed, in perfect agreement with  
492 the chemical composition of the sample in Table 1. The spectra of **C** to **F** are all dominated by  
493 the vibrational features of DBP, with the characteristic  $\nu(\text{C}=\text{O})$  band around  $1700\text{ cm}^{-1}$  (as  
494 magnified in Figure 5b). The analysis of the  $\nu(\text{C}=\text{O})$  region allows to obtain information on the  
495 coordination modes of DBP at the  $\text{MgCl}_2$  surfaces and hence, indirectly, on the types of  
496 exposed sites. A curve fitting of the  $\nu(\text{C}=\text{O})$  region has been performed for the spectra of **C-F**,  
497 as frequently reported in the literature, where each computed band has been assigned on the  
498 basis of the literature. By way of example, Figure 5c displays the curve fitting of the spectrum

499 of the final catalyst (**F**), which includes all the possible  $\nu(\text{C}=\text{O})$  contributions: for liquid-like  
500 DBP at  $1728\text{ cm}^{-1}$ ,<sup>71, 72</sup> DBP in interaction with different  $\text{Mg}^{2+}$  sites at 1657, 1680 and 1707  
501  $\text{cm}^{-1}$ ,<sup>71-74</sup> DBP in interaction with  $\text{TiCl}_4$  at  $1634\text{ cm}^{-1}$ ,<sup>75, 76</sup> and the POC produced by a side  
502 reaction between DBP and  $\text{TiCl}_4$  at  $110\text{ }^\circ\text{C}$ <sup>42</sup> at 1758, 1836 and  $1862\text{ cm}^{-1}$  (identical bands were  
503 observed by directly co-milling  $\text{MgCl}_2$  and POC).<sup>76, 77</sup> The fit is completed by including the  
504 two ring vibrations of the ortho-disubstituted phenyl ring at 1581 and  $1595\text{ cm}^{-1}$ ,<sup>78</sup> and an  
505 additional band at  $1615\text{ cm}^{-1}$  ascribable to  $\delta(\text{OH})$  of water traces. Focusing on the three bands  
506 due to DBP in interaction with different  $\text{Mg}^{2+}$  sites, the band at  $1707\text{ cm}^{-1}$  can be assigned to  
507 DBP both in a chelate configuration on 4-fold coordinated  $\text{Mg}^{2+}$  sites (the most  
508 thermodynamically favored configuration for DBP on the (110) surface) and monodentate on  
509 5-fold coordinated  $\text{Mg}^{2+}$  sites,<sup>79, 80</sup> the band at  $1680\text{ cm}^{-1}$  is ascribed to monodentate DBP at 4-  
510 fold coordinated  $\text{Mg}^{2+}$  sites,<sup>79, 80</sup> whereas the band at  $1657\text{ cm}^{-1}$  is due to DBP on defect sites.<sup>71,</sup>  
511 <sup>73, 74</sup> It is important to notice that, at a difference than what happens with ethylbenzoate, it is  
512 not possible to quantify the DBP coordinated at 4-fold and 5-fold  $\text{Mg}^{2+}$  sites, but only to  
513 discriminate between DBP adsorbed at  $\text{MgCl}_2$  surfaces and defects.

514 By estimating the integrated areas of each  $\nu(\text{C}=\text{O})$  band in the series of spectra for **C-F**, it  
515 has been possible to estimate in a semi-quantitative way the relative abundances of each species  
516 at the different synthesis steps, as reported in Figure 5d.<sup>81</sup> A few conclusions can be drawn as  
517 follows.

- 518 i. As soon as DBP is added (**C**), some DBP molecules are trapped as liquid-like in the  
519 interparticle pores of the material (blue line). This is compatible with the porosity data  
520 reported by Chumachenko et al.<sup>42</sup> The amount of liquid DBP slightly decreases in the  
521 following steps.
- 522 ii. Moreover, as soon as DBP is added to the reaction mixture (**C**), a non-negligible  
523 amount of a complex with  $\text{TiCl}_4$  (orange line) is formed at  $\text{MgCl}_2$  surfaces. The

524 thermodynamics driving this process was evaluated in the past by experimental  
525 calorimetric measurements<sup>82</sup> and by theoretical calculations.<sup>83</sup> An analogous behavior  
526 has been already observed upon dosing ethyl benzoate (EB) on MgCl<sub>2</sub>/TiCl<sub>4</sub> from the  
527 vapor phase.<sup>84</sup> According to the trend in Figure 5d, some of these complexes are washed  
528 away during the successive steps of the catalyst synthesis, but not all of them.

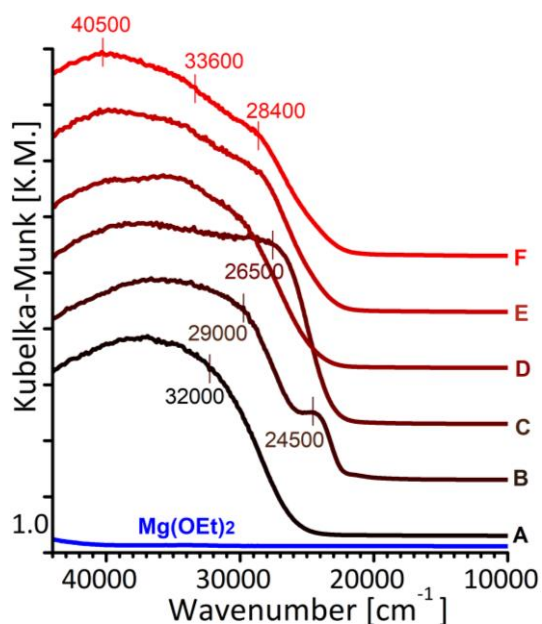
529 iii. DBP on MgCl<sub>2</sub> surfaces (grey line) are the most abundant species in all the samples,  
530 although their amounts slightly decrease along the series in favor of DBP on defective  
531 sites (light grey line), likely because their formation and stabilization is promoted by  
532 DBP itself.<sup>85</sup>

533 iv. Finally, after the second addition of TiCl<sub>4</sub> (E), some DBP molecules are converted into  
534 phthaloyl chloride,<sup>42</sup> which was not present at all upon the first addition of TiCl<sub>4</sub>. This  
535 process increases over time upon aging the sample at 110 °C in the reaction mixture  
536 (F).

537

### 538 **3.5. Local Structure of the Ti Centers Along the Synthetic Steps**

539 Finally, DR UV-Vis spectroscopy has been applied to monitor the evolution of the Ti species  
540 from an electronic point of view during the ZN catalyst synthesis (Figure 6). Even though the  
541 oxidation state remains the same (+4), the DR UV-Vis spectra change along the series,  
542 reflecting changes in the titanium coordination sphere.



543

544 **Figure 6.** DR UV-Vis spectra of the extracted samples and of the  $\text{Mg}(\text{OEt})_2$  precursor. The  
 545 spectra are vertically stacked for clarity.

546 Whereas the spectrum of  $\text{Mg}(\text{OEt})_2$  displays no absorption in the whole UV-Vis region, the  
 547 spectra of the extracted samples are dominated by intense absorptions above  $30000\text{ cm}^{-1}$ , due  
 548 to several charge transfer (CT) transitions involving the Ti metal centers and their ligands.  
 549 Since many contributions overlap to each other at high energy and hence cannot be clearly  
 550 identified, the analysis will focus on the absorption band at lower energy, which is more easily  
 551 identifiable and straightforwardly assigned to a  $\text{Cl}(\pi) \rightarrow \text{Ti}(\text{d})$  CT transition.<sup>86, 87</sup> Moreover, on  
 552 this band the Jorgensen semi-empirical rule on the optical electronegativity of transition metals  
 553 and their ligands can be applied.<sup>88</sup>

554 The spectrum of **A** shows the maximum of the first absorption at ca.  $32000\text{ cm}^{-1}$ , which is  
 555 compatible with a charge transfer transition from  $\text{Cl}^-$  ligands to a 4-fold coordinated  $\text{Ti}^{4+}$   
 556 (expected around  $34500\text{ cm}^{-1}$  according to the Jorgensen rule).<sup>88</sup> This indicates that most of the  
 557 Ti in **A** is present as physisorbed 4-fold coordinated  $\text{TiCl}_x(\text{EtO})_{4-x}$  species,<sup>63</sup> in fair agreement  
 558 with both Far-IR and Mid-IR data, and compatibly with the sequence proposed by Brambilla  
 559 et al. for  $\text{TiCl}_4$  chemisorption on  $\text{MgCl}_2$ .<sup>12</sup> Then, after heating at  $60\text{ }^\circ\text{C}$  (**B**), the main absorption

560 downward shifts to ca. 29000  $\text{cm}^{-1}$  and a new sharp band appears at 24500  $\text{cm}^{-1}$ . The downward  
561 shift of these bands is associated to a change in the coordination of the Ti ions from 4-fold to  
562 6-fold (the theoretical value for the CT transition from  $\text{Cl}^-$  ligands to octahedral  $\text{Ti}^{4+}$  is 28200  
563  $\text{cm}^{-1}$ ),<sup>88</sup> indicating that 4-fold coordinated  $\text{TiCl}_x(\text{EtO})_{4-x}$  species at 60 °C have adjusted in the  
564 more stable 6-fold coordinated octahedral configuration on the nascent  $\text{MgCl}_2$  surfaces. This  
565 is again in agreement with the analysis of the Far-IR and Mid-IR spectra. Notably, an analogous  
566 trend was observed during  $\text{TiCl}_4$  chemisorption from the vapor phase onto bare  $\text{MgCl}_2$ .<sup>89</sup> The  
567 two bands, which differ of ca. 4500  $\text{cm}^{-1}$ , might arise from the same  $\text{Cl}(\pi)\rightarrow\text{Ti}(\text{d})$  CT transition  
568 localized on slightly different Ti species (for example with a different number of ethoxide  
569 ligands) and/or from two  $\text{Cl}(\pi)\rightarrow\text{Ti}(\text{d})$  CT transitions on the same Ti cation from two different  
570 Cl species (e.g. axial and equatorial Cl atoms with respect to the ethoxide ligands).<sup>90</sup>

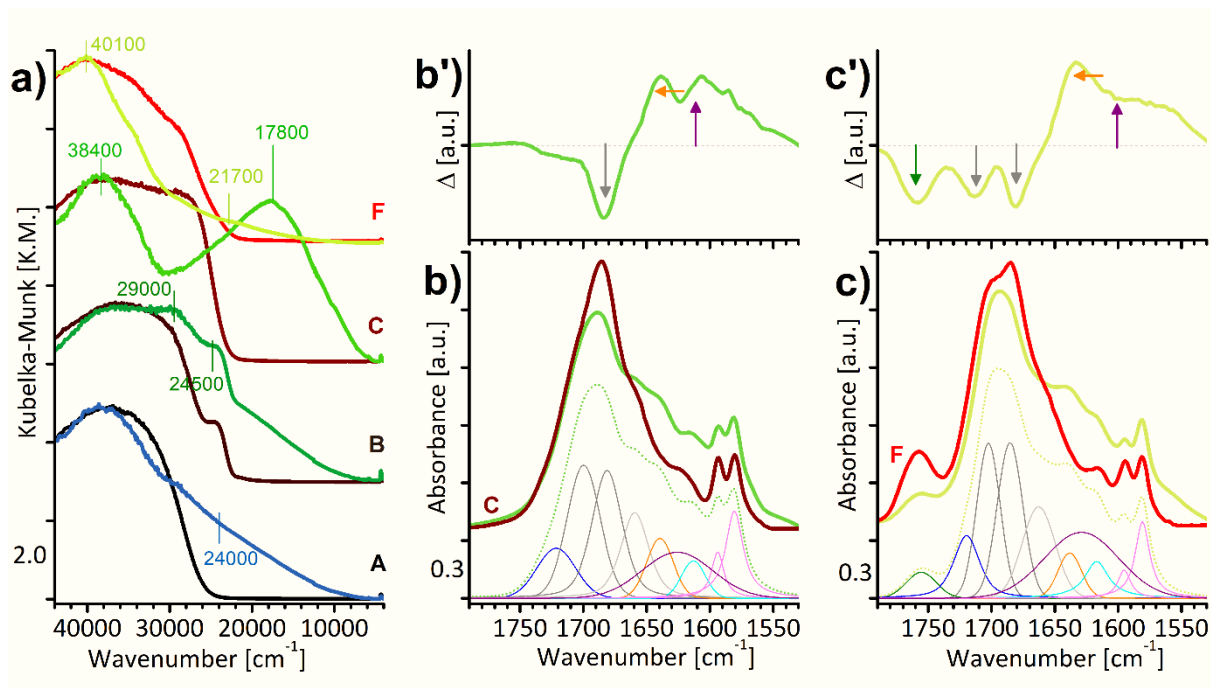
571 The successive synthetic step (C) is dominated by the introduction of DBP, which not only  
572 coordinates to the  $\text{MgCl}_2$  surfaces and defects, but also directly to the Ti centers, as revealed  
573 by the IR spectra in Figure 5c. The corresponding UV-Vis spectrum shows an intense band  
574 peaked at 26500  $\text{cm}^{-1}$ , which is always ascribed to a  $\text{Cl}(\pi)\rightarrow\text{Ti}(\text{d})$  CT transition for 6-fold  
575 coordinated Ti sites, but with a slightly different environment than before. Indeed, IR  
576 spectroscopy revealed that, at this step, most of the ethoxide ligands have been removed, and  
577  $\text{TiCl}_4$ -DBP complexes are formed. Most of the  $\text{TiCl}_4$ -DBP complexes are then removed from  
578  $\text{MgCl}_2$  surfaces in the following steps of ZN catalyst synthesis because of the several washes  
579 with toluene, and that absorption band is almost no more present in the following spectra.  
580 Therefore, spectra of D, E, and F are all dominated by the absorption bands typical of  
581  $\text{Cl}(\pi)\rightarrow\text{Ti}(\text{d})$  CT transitions for  $\text{Ti}^{4+}$  in a 6-fold coordination, with small differences due to  
582 slight distortions in the geometry and minor changes in the effective charge distribution.<sup>86</sup>

583

584 **3.6. Evolution of the samples upon TEAL activation**

585 TEAl activation has been investigated with an Al:Ti ratio of 2:1, in order to simulate the  
 586 excess of activator used in the polymerization tests in Section 3.2. Figure 7 displays some  
 587 significant results obtained by DR UV-Vis and IR spectroscopies.

588



589

590 **Figure 7.** Part a) DR UV-Vis spectra of samples **A**, **B**, **C** and **F**, before and after TEAl  
 591 activation. Part b) Magnification in the  $\nu(\text{C}=\text{O})$  of the IR spectra of **C** before and after TEAl  
 592 activation. Curve fitting is also shown for activated **C**. Part b') Difference spectrum calculated  
 593 by subtracting to the spectrum of activated **C** the spectrum before TEAl activation. Parts c and  
 594 c') same as in parts b and b' for **F**.

595

596 In the UV-Vis spectrum of **A**, the position of the main absorption (that was assigned to a  
 597  $\text{Cl}(\pi) \rightarrow \text{Ti}(d)$  CT transition) upward shifts at  $38400 \text{ cm}^{-1}$ , which is compatible with the  
 598 reduction of the Ti sites from +4 to +3 oxidation state.<sup>88</sup> At the same time, a broad absorption  
 599 grows up centered at about  $24000 \text{ cm}^{-1}$ , whose position corresponds to a  $\text{Ti}^{3+}$  d-d transition, but  
 600 whose intensity is much higher. Similar bands have been already observed in the past for TEAl-

601 activated ZN catalysts and assigned to intersite d-d transition involving two  $Ti^{3+}$  sites bridged  
602 by a  $Cl^-$  ligand, thus assuming a partial charge transfer character,<sup>91</sup> for this reason, they have  
603 been considered as proof of the formation of  $TiCl_3$  clusters. In **A**, the formation of  $TiCl_3$  clusters  
604 is favored by the high mobility of physisorbed  $TiCl_x(OEt)_{4-x}$  species.

605 An analogous trend is observed also in **B**, although in this case the two bands at 29000 and  
606 24500  $cm^{-1}$  remain unaltered, revealing that the fraction of 6-fold coordinated  $TiCl_x(EtO)_{4-x}$   
607 species responsible for those bands are evidently less reactive towards TEAL.

608 The spectrum of activated **C** is characterized by two very intense and well-defined absorption  
609 bands at 38400 and 17800  $cm^{-1}$ . The former is assigned to a  $Cl(\pi) \rightarrow Ti(d)$  CT transition for a  
610 Ti in the +3 oxidation state (as already discussed for **A**), while the latter is very peculiar, quite  
611 different from the fingerprint of the  $TiCl_3$  clusters typically observed in TEAL-activated ZN  
612 catalysts. Instead, that band recalls the UV-Vis spectrum reported in the literature for a  
613  $[TiCl_4(thf)_2]_1[MgCl_2(thf)_{1.5}]_2$  adduct after reaction with an Al-alkyl (trioctyl-aluminum, in that  
614 case).<sup>90</sup> Therefore we can imagine the formation of DBP-bonded  $TiCl_3$ .

615 Finally, the DR UV-Vis spectrum of activated **F** is characterized by the almost complete  
616 erosion of the bands at 33600 and 28400  $cm^{-1}$  that were present before the reaction with TEAL,  
617 leaving the place for an intense CT transition absorption band at 40100  $cm^{-1}$  and a quite weak  
618 band at 21700  $cm^{-1}$ , which is attributed to isolated, 5-fold coordinated and alkylated  $Ti^{3+}$   
619 species (although the broadness of the band reveals a certain heterogeneity of the sites, in terms  
620 of slightly different structural parameters and chemical surroundings).<sup>92</sup> According to the data  
621 of polymerization activity shown in Figure 1, those species are thus the main responsible for  
622 propylene polymerization.

623 On the contrary, IR spectroscopy provides new insights on the fate of the donor after TEAL  
624 activation, which is one of main open questions in ZN catalysis. As a matter of fact, depending  
625 on the temperature a more or less large fraction of DBP is known to be cleaned up by TEAL (a

626 minimal fraction at room temperature, almost the totality at about 100 °C),<sup>93</sup> but the state of  
627 the molecules remaining on the catalyst surfaces is still unclear. Figure 7b and **Figure 7c**  
628 display the magnification of the  $\nu(\text{C}=\text{O})$  region for **C** and **F** before and after TEAl activation  
629 at room temperature, revealing an analogous trend for the samples corresponding to the initial  
630 DBP addition and to the sample at the end of the synthesis (the quantification of the integrated  
631 areas for all the individual  $\nu(\text{C}=\text{O})$  components are reported in Table S3).

632 The fraction of liquid-like DBP is roughly constant, indicating that DBP molecules trapped  
633 within the pores during ZN catalyst synthesis are not washable and not accessible even for  
634 TEAl. The fraction of DBP adsorbed on  $\text{Mg}^{2+}$  sites drops down (especially for surface  $\text{Mg}^{2+}$   
635 sites), together with the fraction of POC in **F**, in the face of the appearance of a new component  
636 at ca.  $1625\text{ cm}^{-1}$ , which can be reasonably assigned to DBP in interaction with the  $\text{Al}^{3+}$  centers,  
637 coming from both the TEAl molecules in excess and the  $\text{AlCl}_x\text{Et}_{3-x}$  by-products adsorbed on  
638 the catalyst. Finally, the fraction of DBP in interaction with the Ti centers is almost constant,  
639 but the position of the band shifts at higher frequencies (from  $1634$  to  $1640\text{ cm}^{-1}$ ), likely  
640 because of the reduction from  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$ . This suggests that the  $\text{TiCl}_4$ -DBP complexes that  
641 are formed on the catalyst surface and remain after the following thermal and chemical  
642 treatments, they do remain even after TEAl activation and are actually activated, so that a  
643 possible role in the overall catalytic process cannot be discarded.

644

#### 645 **4. Conclusions**

646 The multi-technique investigation presented in this work sheds light on the chemical  
647 reactions and structural evolution taking place during the formation of an industrial-like  
648 Ziegler-Natta pre-catalyst, starting from the  $\text{Mg}(\text{OEt})_2$  precursor and in the presence of DBP  
649 as an internal donor. Five intermediate samples have been extracted from the glass reactor at  
650 different stages, plus the final catalyst, and analyzed in terms of structure, morphology, and

651 surface species. All the techniques converge in demonstrating that as soon as  $\text{Mg}(\text{OEt})_2$  is  
652 contacted with  $\text{TiCl}_4$ , all Mg-O bonds are converted into Mg-Cl ones, forming the first seeds  
653 of  $\text{MgCl}_2$ , which appear as Cl-Mg-Cl monolayers with a lateral dimension of below 2 nm, and  
654 releasing  $\text{TiCl}_x(\text{OEt})_{4-x}$  as by-products (first physisorbed as 4-fold coordinated, and then  
655 chemisorbed as 6-fold coordinated). Those species efficiently polymerize ethylene but not  
656 propylene.

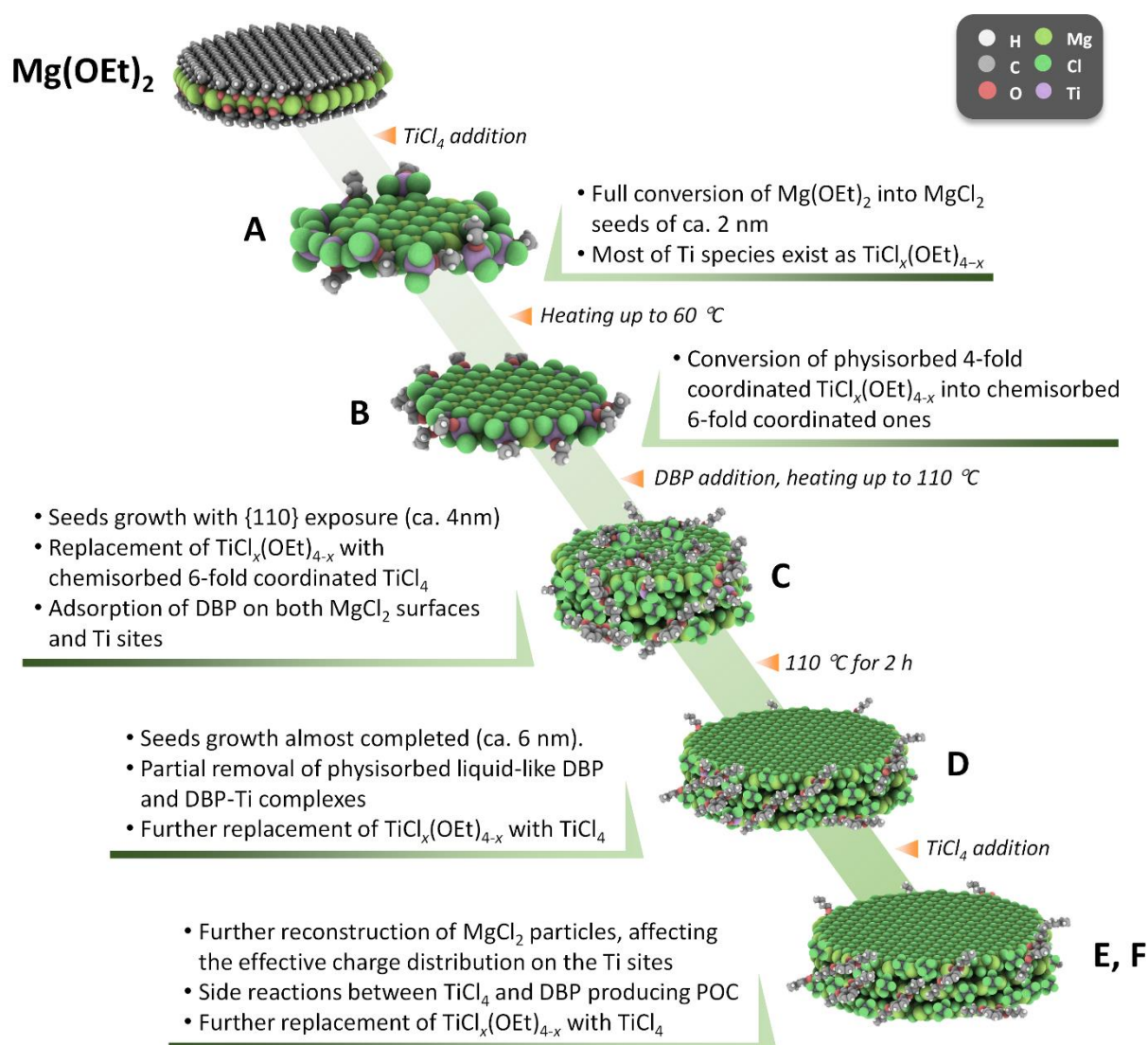
657 The addition of the DBP electron donor significantly promotes the growth of  $\text{MgCl}_2$  seeds  
658 with the preferential exposure of lateral surfaces, including those relevant for the catalysis; as  
659 a matter of fact, only after the DBP addition the catalyst becomes active in propylene  
660 polymerization. Most of DBP is coordinated to  $\text{MgCl}_2$  surfaces, corroborating the hypothesis  
661 that the influence of the electron donors on the stereoselectivity of ZN catalysts is mostly due  
662 to a steric modulation of the Ti surroundings. However, a non-negligible fraction of DBP is  
663 actually complexed to the Ti ions, and some of these species remain in ZN catalyst even at the  
664 end of the synthesis and can be effectively activated by TEAl (at least at room temperature,  
665 further investigation will be needed to monitor the activation process at higher temperatures).

666 Finally, the second addition of  $\text{TiCl}_4$  is mostly chemisorbed as 6-fold coordinated on  $\text{MgCl}_2$   
667 surface largely replacing the  $\text{TiCl}_x(\text{OEt})_{4-x}$  species, although a fraction of  $\text{TiCl}_4$  is also  
668 consumed in a side reaction with DBP, as testified by the formation of phthaloyl chlorides. The  
669 newly formed Ti species are remarkably more active in propylene polymerization (the  
670 production of polypropylene per hour per Ti mole almost triples at this step). It is worth  
671 noticing that the aging at 110 °C allows a further rearrangement of the species in the material  
672 (both in  $\text{MgCl}_2$  morphology, and in DBP disposition, and in the local structure of the Ti sites),  
673 further increasing the activity towards propylene polymerization, which is attributed to  
674 isolated, 5-fold coordinated and alkylated  $\text{Ti}^{3+}$  species. This demonstrates the positive effect of

675 the final thermal treatment to afford truly performant ZN catalysts. All these findings are  
 676 schematically summarized in Figure 8.

677 More in general, this unprecedented knowledge of all the chemical reactions and structural  
 678 evolution at each step of ZN catalyst synthesis will drive the choices of the researchers from  
 679 both academia and companies that aim at the optimization of this complex multicomponent  
 680 material.

681



682

683 **Figure 8.** Schematic representation of catalyst formation from  $\text{Mg}(\text{OEt})_2$ . The  $\text{MgCl}_2$

684 nanoparticle models were drawn by atomistic system rendering software Speck with the aid of

685 Vesta.<sup>94</sup>

686

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691

### 692 **Author Contributions**

693 A.P.<sup>†</sup> and T.W.<sup>†</sup> wrote the manuscript. A.P.<sup>†</sup> and A.A. acquired and analyzed the vibrational  
694 and electronic spectroscopies. T.W.<sup>†</sup> performed sample preparation, chemical analysis, and the  
695 synchrotron X-ray total scattering experiments. G.T. created some nanoparticle models and  
696 helped computational simulation. T.I. acquired SEM observation and interpreted the results.  
697 Z.D. performed DSC measurement and analysis. M.T. contributed to finalize the manuscript.  
698 P.C. designed and performed the polymerization tests. E.G. and T.T. conceived the concept  
699 and supervised the entire research.

700 <sup>†</sup>These authors contributed equally.

701

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705

### 706 **Notes**

707 The authors declare no competing financial interest.

708

## 709 **Supporting Information**

710 The polymer characterization results, the SEM images of the extracted samples (A–F), the  
711 PDFs of the samples where  $Q_{\min}$  was intentionally increased to  $1.0 \text{ \AA}^{-1}$ , typical PXRD and  
712 PDF fitting results, the fitting parameters obtained by PDFgui, and the contributions of  
713 individual  $\nu(\text{C=O})$  components for the IR spectra of C and F, before and after TEAl activation  
714 are available. This information is available free of charge on the ACS Publications website.

715

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723

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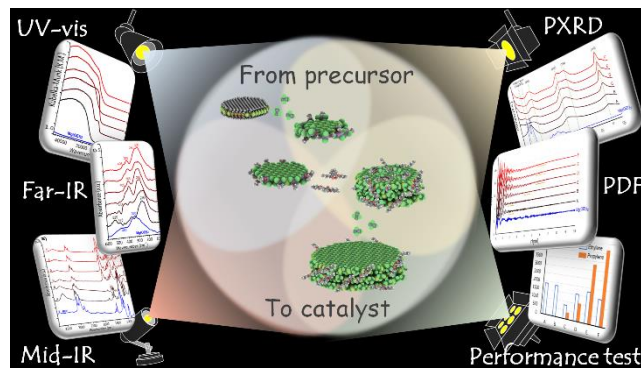
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