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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 δ -MgCl₂ 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 Mg(OEt)₂, and subjected to the analysis.
26 Several interesting results were found. The addition of TiCl₄ almost spontaneously converts
27 Mg(OEt)₂ into MgCl₂ 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 TiCl_x(OEt)_{4-x} species. The heating treatment removes the physisorbed TiCl_x(OEt)_{4-x} and/or
30 convert them into chemisorbed 6-fold coordinated TiCl_x(OEt)_{4-x}, while the subsequent addition
31 of an internal donor (here dibutyl phthalate, DBP) promotes a substantial reconstruction and
32 growth of MgCl₂ 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 MgCl₂
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 TiCl₄ addition replaces the chemisorbed
36 TiCl_x(OEt)_{4-x} with 6-fold coordinated TiCl₄ 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 TiCl₄ 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 δ -MgCl₂, 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).¹ 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.²

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: TiCl₄ (the active phase) is dispersed with organic Lewis
58 bases (the internal donors) on MgCl₂ (the support material) and activated by AlR₃ (the co-
59 catalyst), together with other organic Lewis bases (the external donors).³⁻⁶ 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 TiCl_4 , MgCl_2 , and
66 an electron donor into a single solid material, usually called pre-catalyst.³ 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 AlR_3 activator. The former route
69 (traditional) is based on the mechanical ball-milling of highly crystalline MgCl_2 (α form) with
70 the internal donor and/or TiCl_4 .⁷⁻¹³ The latter route (advanced) employs the chemical
71 transformation of a MgCl_2 -precursor into nanostructured and highly defective MgCl_2 (δ form)
72 by TiCl_4 itself in the presence of the donor,¹⁴⁻²⁹ and generally leads to more disordered and
73 more active nanostructures.³⁰⁻³² In a typical chemical preparation route, all the components are
74 intimately connected to each other. TiCl_4 promotes the chlorination of the precursor into MgCl_2
75 and exerts a capping effect on the newly formed MgCl_2 nanoparticles.³³ The electron donor not
76 only influences the MgCl_2 morphology by stabilizing specific surfaces,^{20, 22} but also interacts
77 with the Ti sites through direct coordination³⁴⁻³⁷ or more plausibly through coadsorption.³⁸ By-
78 products formed during the chlorination must not be overlooked as these products could adsorb
79 on MgCl_2 surfaces, and work as catalytic poisons unless properly removed.³⁹

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 MgCl₂
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)₂, where a series of samples were extracted from
93 the reactor, and characterized for their chemical composition, structure, and activity.⁴⁰⁻⁴²
94 According to Jeong et al., the activity towards propylene polymerization increases linearly with
95 the increase in the number of TiCl₄ 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*).⁴⁰ More in details, Chumachenko et al. found out
98 that the reaction at early stages between Mg(OEt)₂ and TiCl₄ leads to a mixture of MgCl₂ and
99 TiCl₃(OEt) with very high surface area (415 m²/g) but low activity and stereospecificity, while
100 the subsequent addition of DBP causes the removal of inactive TiCl₃(OEt), the growth of
101 MgCl₂ crystallites (the surface area decreases to 211 m²/g), and a significant increase of the
102 overall activity and stereospecificity.⁴² Finally, Kim et al. mostly focused on the mutual
103 reactions between Mg(OEt)₂, TiCl₄ and the benzoyl chloride (BzCl) used as an electron donor
104 or its precursor, demonstrating the high interchangeability of (OEt)⁻ and Cl⁻ anionic ligands.⁴¹

105 Recently, we proposed a combination of cutting-edge characterization techniques to clarify
106 the identity of δ-MgCl₂, which includes X-ray total scattering for defining the nano-sized and
107 disordered structure,³⁰ and vibrational spectroscopies for determining the exposed surfaces and
108 their relative extension.⁴³ 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 N₂ bubbling. Iodine (I₂, 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 N₂ 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 N₂ atmosphere to prevent moisture
126 contamination. The starting material, Mg(OEt)₂, was synthesized according to a previously
127 reported method.⁴⁴⁻⁴⁶ Briefly, 2.64 mmol of I₂ 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 I₂ 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.

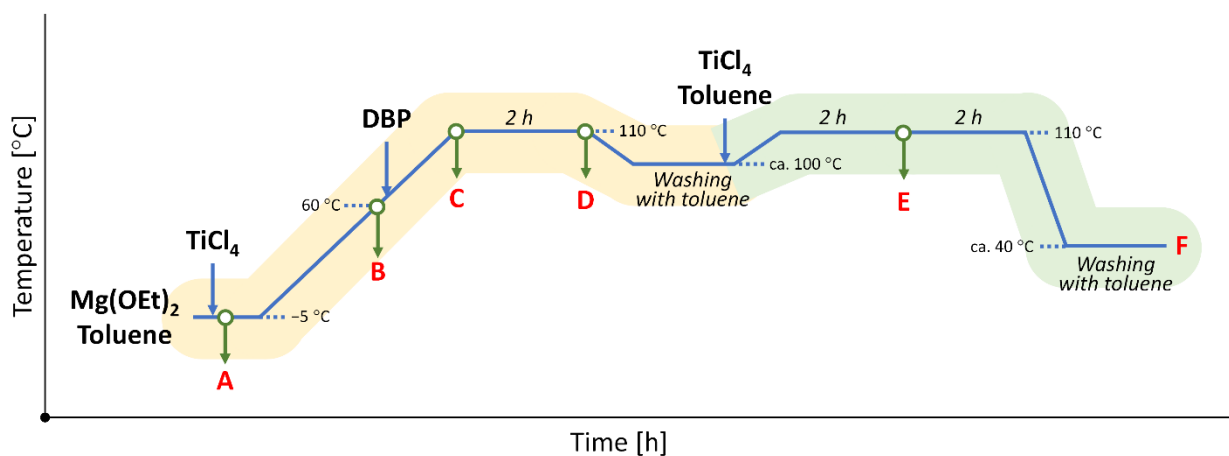
134 The procedures for catalyst preparation and sampling are shown in Scheme 1. A three-necked
135 flask (500 mL) equipped with a mechanical stirrer and purged with N₂ was charged with 20 g
136 of Mg(OEt)₂ powder and 136 mL of toluene. 20 mL of TiCl₄ was dropwise introduced by
137 keeping the temperature 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 TiCl₄ 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 TiCl₄ 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 N₂ for characterization. The timing of the
148 extraction and the corresponding sample codes are as follows: (A) after the first TiCl₄ 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/H₂SO₄, and then H₂O₂ 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.⁴⁴ Organic contents
183 were analyzed by ¹H NMR on a Bruker AVANCE III 400 MHz spectrometer according to our
184 previous study.³⁹ 10–30 mg of a sample was dissolved in 0.7 mL of DMSO-*d*₆ 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⁻¹). The cooled sample was
194 then heated up to 230 °C at a heating rate of 20 °C min⁻¹ 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 \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.⁴⁷ 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.⁴⁸

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 N₂-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 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 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 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 N₂ 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)₂ is chlorinated by TiCl₄ to produce
248 MgCl₂ and TiCl_x(OEt)_{4-x}. The OEt group remains in the catalyst to a greater or lower extent
249 due to both/either incomplete chlorination of Mg(OEt)₂ and/or persistence of surface
250 TiCl_x(OEt)_{4-x} species, which greatly reduces the activity and stereospecificity of the catalyst.

251 Here, the OEt group was quantified by the methylene peak in ^1H 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 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 TiCl_4 treatment has
 258 almost no impact on the Ti content (**E,F**), but the OEt further decreases to below 0.2 mmol g^{-1} ,
 259 suggesting that $\text{TiCl}_x(\text{OEt})_{4-x}$ species are replaced by TiCl_4 . Concerning DBP, its content at the
 260 end of ZN catalyst synthesis (**F**) converges to about 0.6 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 TiCl_4 at an elevated temperature. In
 264 our analysis, POC were not observed during the first TiCl_4 treatment (**C,D**), but was slightly
 265 observed (column Cl in Table 1) after the second TiCl_4 treatment (**E,F**), which suggests that
 266 the fresh TiCl_4 is more reactive towards the surface adsorbates.

267

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

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

E	0.63	0.18	0.73	0.48	0.03	0.63
F	0.56	0.18	0.68	0.46	0.04	0.61

269 ^a Determined by titration.

270 ^b Determined by ¹H NMR.

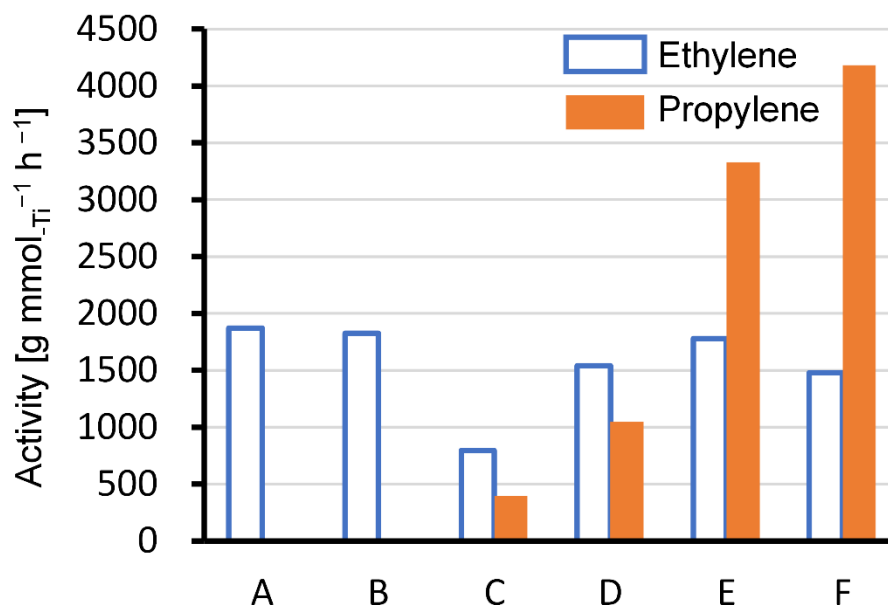
271 ^c The *n*-Butoxy groups of DBP is known to be substituted by ethoxy groups as well as
272 chlorine atoms during catalyst preparation. The total phthalate amount was calculated as half
273 of the total amount of possible substitutional groups: (*n*-Bu + Et + Cl)/2.

274 ^d 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. ^a	
	[g-PE g-cat ⁻¹ h ⁻¹]	[g-PE mmol-Ti ⁻¹ h ⁻¹]	[g-PP g-cat ⁻¹ h ⁻¹]	[g-PP mmol-Ti ⁻¹ h ⁻¹]
A	4300	1900	n.d.	n.d.
B	4800	1800	n.d.	n.d.
C	840	800	420	400
D	880	1500	600	1000
E	1100	1800	2100	3300
F	820	1500	2300	4200

294 ^a No polymer was obtained when **A** or **B** was used as the catalyst.

295

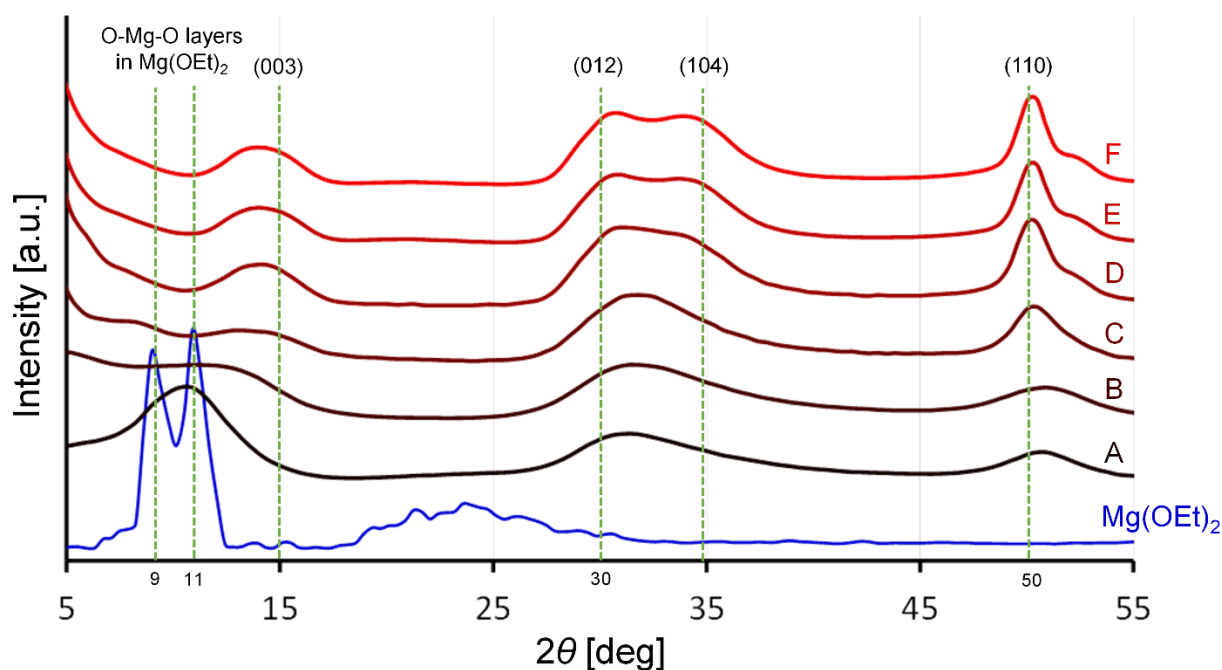
296 3.3. Formation of Nanostructure Along the Synthetic Steps

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° . 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.^{27, 49, 50} 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° are
305 most likely originated from the stacking of the O-Mg-O layers. A broad peak centered at $2\theta =$
306 10° is also observed in the pattern of **A** (right after the first 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° , which correspond to
309 the (012)/(104) and (110) reflections of MgCl_2 , and indicate that the 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°C (**B**), and eventually disappears after the addition of
312 DBP and heating up to 110°C (**C**). Instead, the peak corresponding to the Cl-Mg-Cl stacking
313 along the c -axis emerges at 15° . 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 MgCl_2
315 crystallites both in the lateral and vertical directions. The patterns of **C**–**F** are typical for δ -
316 MgCl_2 : three broad peaks are observed at around 15° , $27\text{--}40^\circ$, and 50° , which correspond to
317 (003), (012)/(104), and (110) reflections. The broadness of the peaks indicates the nano size of
318 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.⁸ Hence, PXRD measurements clearly indicate that the MgCl_2 crystallites or their

321 seeds are formed just after the first 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 Mg(OEt)_2 starting material. The X-axis was scaled with the
328 wavelength of 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 Mg(OEt)_2 is
332 an aggregate of plate-like particles with a length of several micrometers.⁵¹ The surface of A,
333 just after contact with 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.^{44, 52}

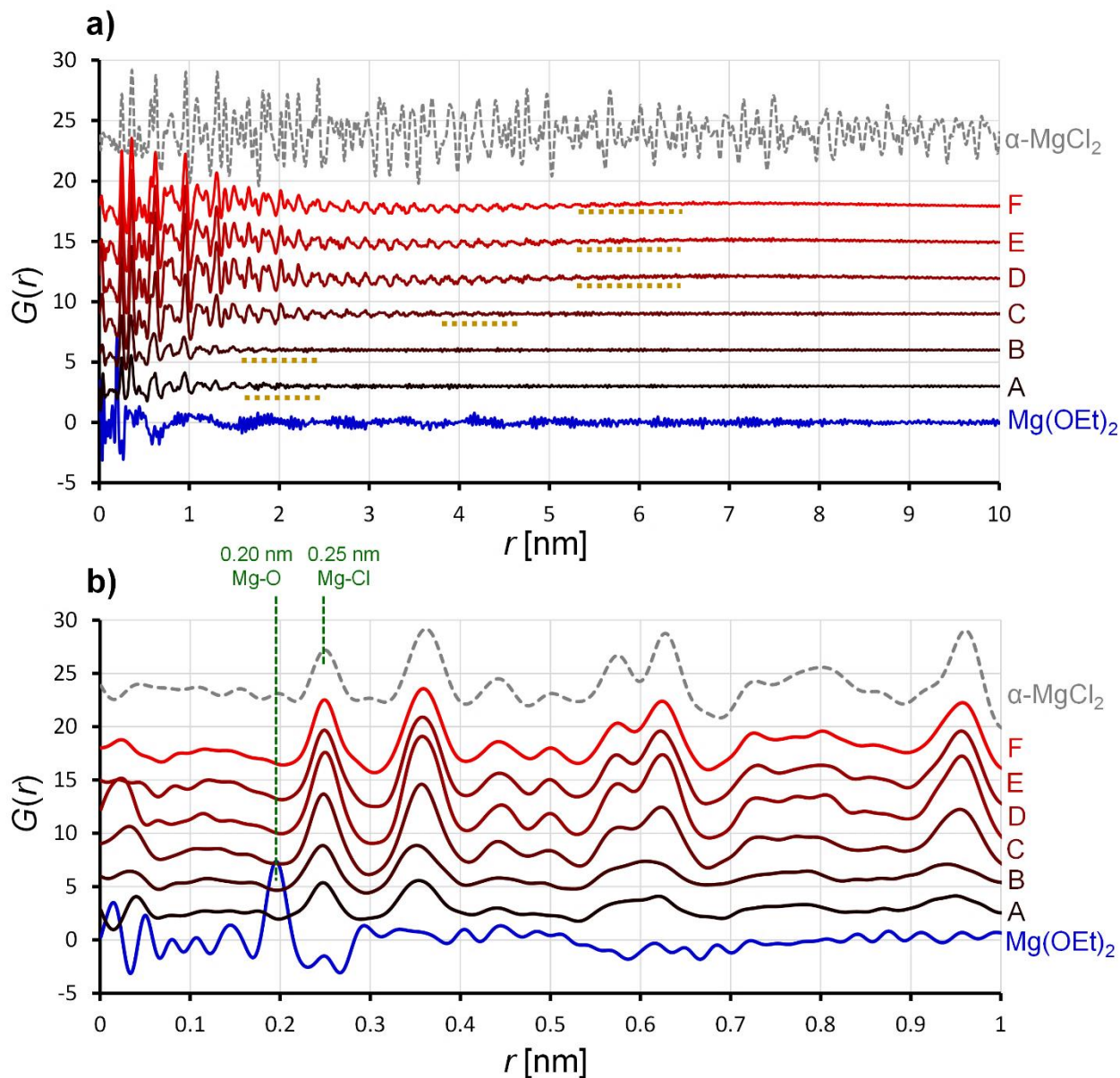
341

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.⁵³ 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.⁵⁴ The fact that limiting the Q_{\min} to 1.0 \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 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 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 MgCl_2 /Lewis base adducts.^{55,56} 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 \AA^{-1} . The
 375 PDFs of Mg(OEt)₂ and highly crystalline α -MgCl₂ (acquired at AichiSR, $Q_{\max}=15 \text{ \AA}^{-1}$. See
 376 ref³⁰) 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 δ -MgCl₂ 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.³⁰ Table 3 summarizes the structural parameters of MgCl₂ 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 α -MgCl₂
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)₂ with TiCl₄, the MgCl₂ 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 MgCl₂ seeds.
390 The addition of donor and heating up to 110 °C (**C**) significantly promotes the growth of the
391 MgCl₂ 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 TiCl₄ 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 MgCl₂ is almost kept
396 constant from **D** to **F** (Table 1). It is likely that the presence of DBP (only in the first TiCl₄
397 treatment) is a primary factor to promote the growth of MgCl₂.

398 The obtained MgCl₂ 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.** MgCl₂ nanoparticle models derived via PXRD fitting and cross-validated by PDF
405 fitting with the aid of software, DISCUS,⁵⁷ PDFgui,⁵⁸ and DShaper.⁵⁹ $L_a = L_b$: 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. ^a	0.162	0.374
B	1.8	0.3	n.a. ^a	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

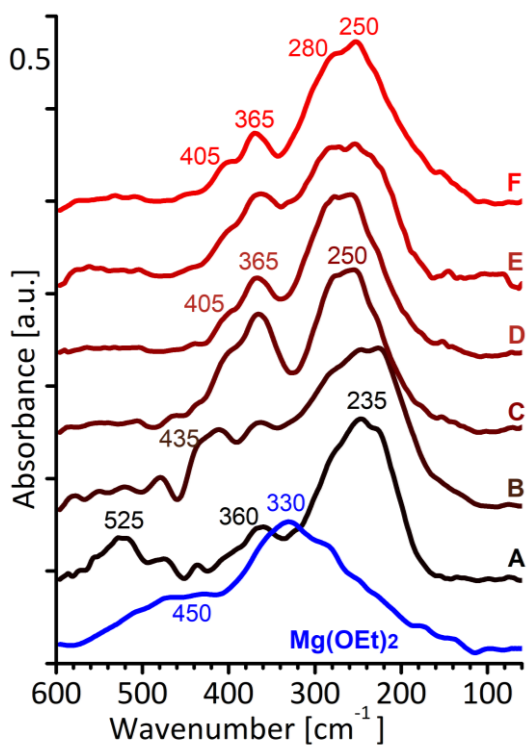
408 ^a P_c was not specified as the particle model is composed of a single Cl-Mg-Cl layer.

409

410 3.4. Morphology of MgCl₂ 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 MgCl₂ nanoparticles. As a matter of fact, we have previously
413 demonstrated that the vibrations in the region of 600 – 100 cm⁻¹, 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 MgCl₂ surfaces.⁴³ 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 MgCl₂ 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)₂ 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 cm^{-1} , very broad and overlapping to each other. Similar bands have been already
 426 observed in the past for different MgCl_2 adducts with alcoholates and alkoxides, and assigned
 427 to the vibrations of Mg-O bonds.⁶⁰⁻⁶² 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 MgCl_2 . The spectrum of **A** shows a main
 430 absorption band centered at 235 cm^{-1} , together with two weaker bands at 525 and 360 cm^{-1} .
 431 The sharp band at 235 cm^{-1} is assigned to the basal (001) surface,⁴³ in well agreement with the
 432 PXRD analysis according to which the first MgCl_2 seeds are mostly formed as monolayers.
 433 The band at 525 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).⁶³ 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⁻¹, respectively). Finally, the band at 360 cm⁻¹ is attributed to a few ethoxide residues
437 on the MgCl₂ seeds.

438 In the spectrum of **B**, the main absorption band is still located at 235 cm⁻¹, indicating that
439 even after heating at 60 °C MgCl₂ particles mainly expose the basal surface (001). The band at
440 525 cm⁻¹ is no more observed, while a new band with similar intensity is present at 435 cm⁻¹.
441 This band is assigned to $\nu(\text{Ti-Cl})$ of 6-fold coordinated Ti species,¹¹ and indicates that a fraction
442 of the Ti ethoxy chloride complexes are chemisorbed on the MgCl₂ 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⁻¹ in **F**), which makes the band too weak in intensity.

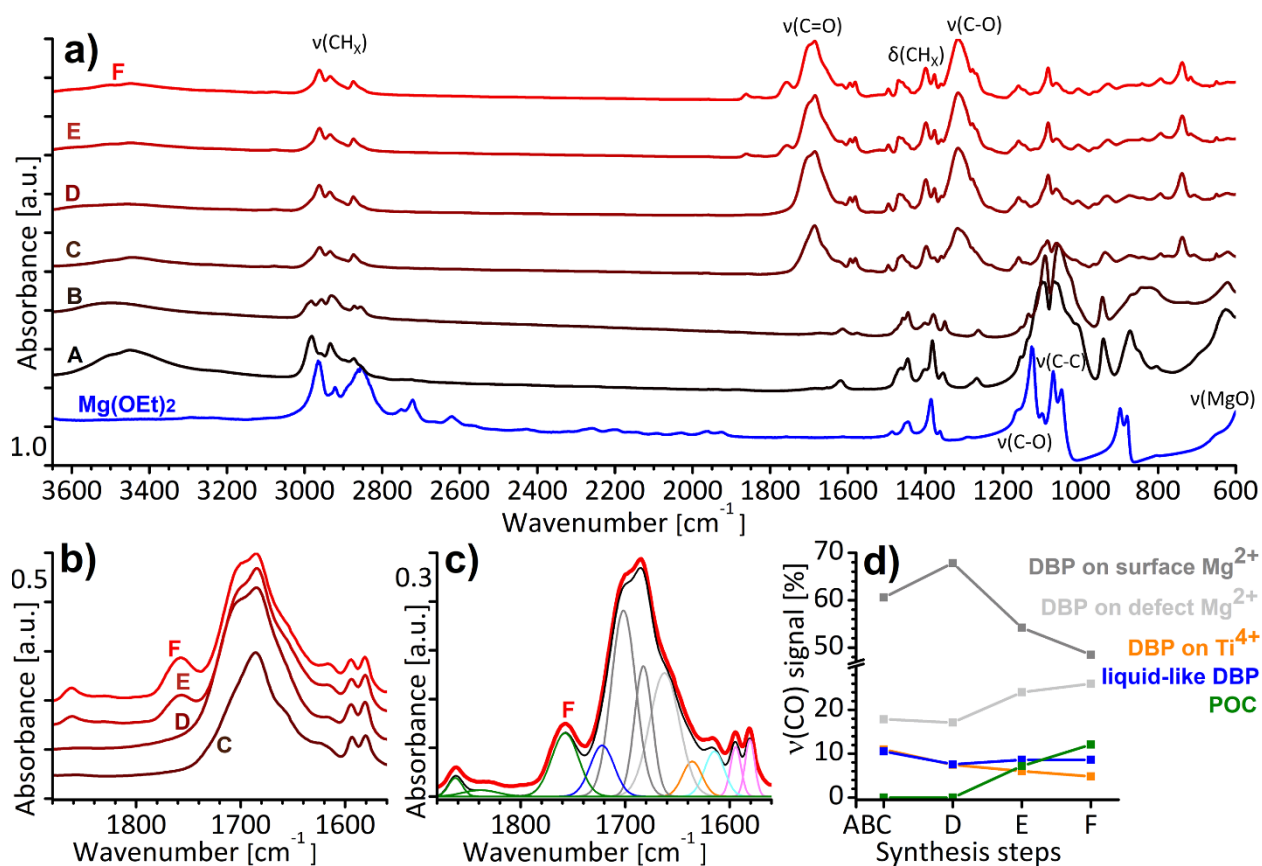
446 The addition of DBP (**C**) causes a significant change in the Far-IR spectrum: the main
447 absorption band upward shifts to 250 cm⁻¹ (with a shoulder at 280 cm⁻¹) and a sharp and intense
448 band appears at 365 cm⁻¹ (with a pronounced hump at 405 cm⁻¹). According to previous
449 calculations, both manifestations can be associated to a morphological reconstruction of the
450 MgCl₂ 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⁻¹
452 ¹, while both the (012) and (015) surfaces significantly contribute at 280 and 405 cm⁻¹.⁴³

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.⁴³ Briefly, with respect to the spectrum of **C**, the main absorption band at 250 cm⁻¹
456 undergoes a slight enlargement and the band at 365 cm⁻¹ slightly decreases in intensity. Overall,
457 the spectrum indicates that MgCl₂ 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.⁶⁴⁻⁶⁷

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.^{68, 69}
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 cm^{-1} , $\nu(\text{C-O})$ at 1120
467 cm^{-1} , $\nu(\text{C-C})$ at 1050 cm^{-1} and some rocking modes at 890 cm^{-1} . Below 600 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 MgCl_2 surfaces, DBP on defective Mg^{2+} sites, DBP on
476 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.⁶³ 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 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**).⁷⁰ 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 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 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 cm^{-1} ,^{71, 72} DBP in interaction with different Mg^{2+} sites at 1657, 1680 and 1707
501 cm^{-1} ,⁷¹⁻⁷⁴ DBP in interaction with TiCl_4 at 1634 cm^{-1} ,^{75, 76} and the POC produced by a side
502 reaction between DBP and TiCl_4 at $110\text{ }^\circ\text{C}$ ⁴² at 1758, 1836 and 1862 cm^{-1} (identical bands were
503 observed by directly co-milling MgCl_2 and POC).^{76, 77} The fit is completed by including the
504 two ring vibrations of the ortho-disubstituted phenyl ring at 1581 and 1595 cm^{-1} ,⁷⁸ and an
505 additional band at 1615 cm^{-1} ascribable to $\delta(\text{OH})$ of water traces. Focusing on the three bands
506 due to DBP in interaction with different Mg^{2+} sites, the band at 1707 cm^{-1} can be assigned to
507 DBP both in a chelate configuration on 4-fold coordinated Mg^{2+} sites (the most
508 thermodynamically favored configuration for DBP on the (110) surface) and monodentate on
509 5-fold coordinated Mg^{2+} sites,^{79, 80} the band at 1680 cm^{-1} is ascribed to monodentate DBP at 4-
510 fold coordinated Mg^{2+} sites,^{79, 80} whereas the band at 1657 cm^{-1} is due to DBP on defect sites.^{71,}
511 ^{73, 74} 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 Mg^{2+} sites, but only to
513 discriminate between DBP adsorbed at 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.⁸¹ 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.⁴² 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 TiCl_4 (orange line) is formed at MgCl_2 surfaces. The

524 thermodynamics driving this process was evaluated in the past by experimental
525 calorimetric measurements⁸² and by theoretical calculations.⁸³ An analogous behavior
526 has been already observed upon dosing ethyl benzoate (EB) on MgCl₂/TiCl₄ from the
527 vapor phase.⁸⁴ 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.

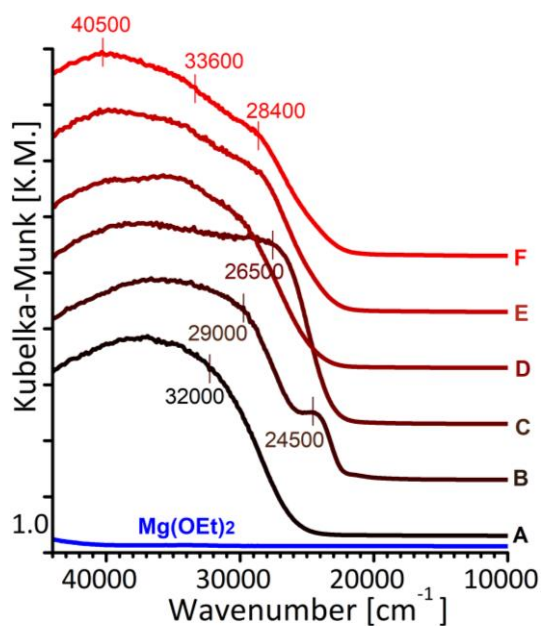
529 iii. DBP on MgCl₂ surfaces (grey line) are the most abundant species in all the samples,
530 although their amounts slightly decrease along the series in favor of DBP on defective
531 sites (light grey line), likely because their formation and stabilization is promoted by
532 DBP itself.⁸⁵

533 iv. Finally, after the second addition of TiCl₄ (E), some DBP molecules are converted into
534 phthaloyl chloride,⁴² which was not present at all upon the first addition of TiCl₄. 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 Mg(OEt)₂ precursor. The
 545 spectra are vertically stacked for clarity.

546 Whereas the spectrum of Mg(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 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 Cl(π) \rightarrow Ti(d) CT transition.^{86, 87} Moreover, on
 552 this band the Jorgensen semi-empirical rule on the optical electronegativity of transition metals
 553 and their ligands can be applied.⁸⁸

554 The spectrum of **A** shows the maximum of the first absorption at ca. 32000 cm⁻¹, which is
 555 compatible with a charge transfer transition from Cl⁻ ligands to a 4-fold coordinated Ti⁴⁺
 556 (expected around 34500 cm⁻¹ according to the Jorgensen rule).⁸⁸ This indicates that most of the
 557 Ti in **A** is present as physisorbed 4-fold coordinated TiCl_x(EtO)_{4-x} species,⁶³ in fair agreement
 558 with both Far-IR and Mid-IR data, and compatibly with the sequence proposed by Brambilla
 559 et al. for TiCl₄ chemisorption on MgCl₂.¹² Then, after heating at 60 °C (**B**), the main absorption

560 downward shifts to ca. 29000 cm⁻¹ and a new sharp band appears at 24500 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 Cl⁻ ligands to octahedral Ti⁴⁺ is 28200
563 cm⁻¹),⁸⁸ indicating that 4-fold coordinated TiCl_x(EtO)_{4-x} species at 60 °C have adjusted in the
564 more stable 6-fold coordinated octahedral configuration on the nascent MgCl₂ 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 TiCl₄ chemisorption from the vapor phase onto bare MgCl₂.⁸⁹ The
567 two bands, which differ of ca. 4500 cm⁻¹, might arise from the same Cl(π)→Ti(d) CT transition
568 localized on slightly different Ti species (for example with a different number of ethoxide
569 ligands) and/or from two Cl(π)→Ti(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).⁹⁰

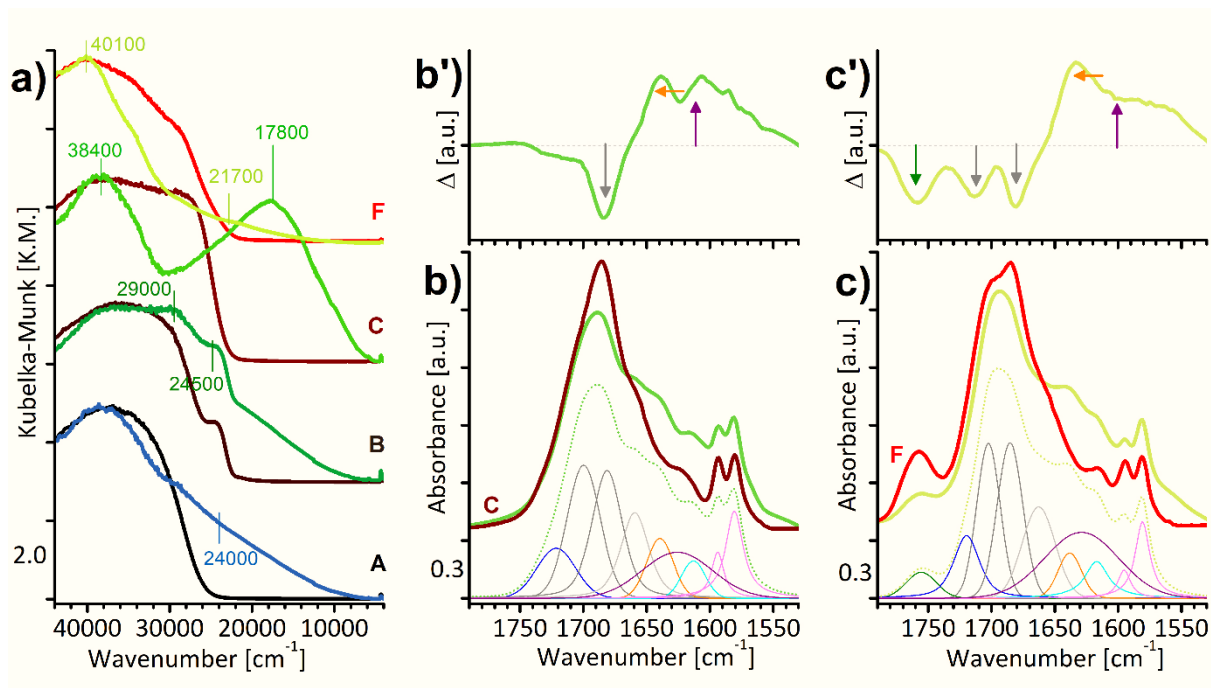
571 The successive synthetic step (C) is dominated by the introduction of DBP, which not only
572 coordinates to the MgCl₂ surfaces and defects, but also directly to the Ti centers, as revealed
573 by the IR spectra in Figure 5c. The corresponding UV-Vis spectrum shows an intense band
574 peaked at 26500 cm⁻¹, which is always ascribed to a Cl(π)→Ti(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 TiCl₄-DBP complexes are formed. Most of the TiCl₄-DBP complexes are then removed from
578 MgCl₂ 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 Cl(π)→Ti(d) CT transitions for Ti⁴⁺ in a 6-fold coordination, with small differences due to
582 slight distortions in the geometry and minor changes in the effective charge distribution.⁸⁶

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 cm^{-1} , which is compatible with the
 598 reduction of the Ti sites from +4 to +3 oxidation state.⁸⁸ At the same time, a broad absorption
 599 grows up centered at about 24000 cm^{-1} , whose position corresponds to a 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,⁹¹ 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).⁹⁰ 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).⁹² 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),⁹³ 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 Mg^{2+} sites drops down (especially for surface 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 cm^{-1} , which can be reasonably assigned to DBP in interaction with the 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 cm^{-1}), likely
640 because of the reduction from Ti^{4+} to Ti^{3+} . This suggests that the 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 TiCl_4 , all Mg-O bonds are converted into Mg-Cl ones, forming the first seeds
653 of 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.

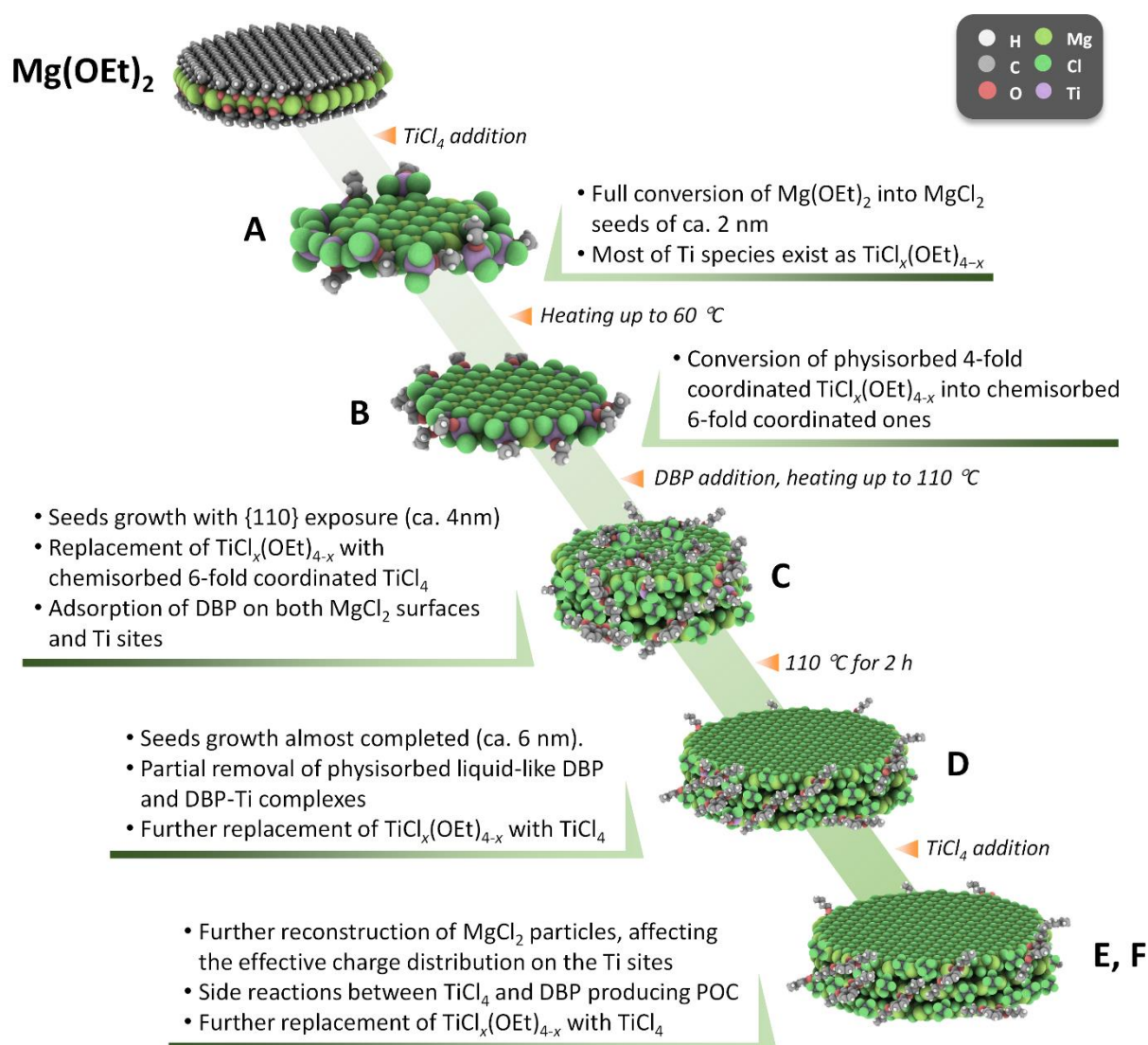
657 The addition of the DBP electron donor significantly promotes the growth of MgCl_2 seeds
658 with the preferential exposure of lateral surfaces, including those relevant for the catalysis; as
659 a matter of fact, only after the DBP addition the catalyst becomes active in propylene
660 polymerization. Most of DBP is coordinated to 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 TiCl_4 is mostly chemisorbed as 6-fold coordinated on MgCl_2
667 surface largely replacing the $\text{TiCl}_x(\text{OEt})_{4-x}$ species, although a fraction of 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 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 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 Mg(OEt)_2 . The MgCl_2

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

685 Vesta.⁹⁴

686

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691

692 **Author Contributions**

693 A.P.[†] and T.W.[†] wrote the manuscript. A.P.[†] and A.A. acquired and analyzed the vibrational
694 and electronic spectroscopies. T.W.[†] 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.

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701

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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 \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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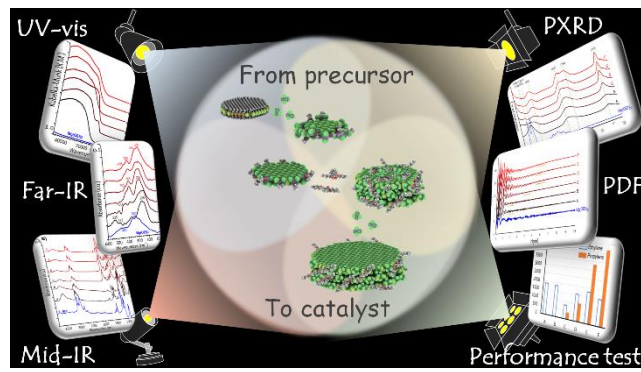
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