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Formation of Highly Active Ziegler-Natta Catalysts Clarified by a Multifaceted Characterization Approach / Piovano, A.; Wada, T.; Amodio, A.; Takasao, G.; Ikeda, T.; Zhu, D.; Terano, M.; Chammingkwan, P.; Groppo, E.; Taniike, T.. - In: ACS CATALYSIS. - ISSN 2155-5435. - ELETTRONICO. - 11:22(2021), pp. 13782-13796. [10.1021/acscatal.1c03067]

Availability: This version is available at: 11583/2969762 since: 2022-07-08T09:09:41Z

Publisher: American Chemical Society

Published DOI:10.1021/acscatal.1c03067

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# On the formation of highly active Ziegler-Natta 1 catalysts clarified by a multifaceted 2 characterization approach 3 Alessandro Piovano, \*\*\*\*, \*, ‡ Toru Wada, \*\*, ‡, § Alessia Amodio, † Gentoku Takasao, § 4 Tomohiro Ikeda,<sup>§</sup> Zhu Dongzhi,<sup>§</sup> Minoru Terano,<sup>‡,§</sup> Chammingkwan Patchanee,<sup>‡,§</sup> 5 Elena Groppo,<sup>†, ‡</sup> and Toshiaki Taniike<sup>\*, ‡, §</sup> 6 \* Corresponding authors 7 \*\* These two authors contributed equally to this work, and both are cited as first authors. 8 9 10 <sup>†</sup>Department of Chemistry, INSTM and NIS Centre, University of Torino, Via Giuria 7, 11 10125 Torino, Italy <sup>‡</sup>Dutch Polymer Institute, P.O. Box 902, 5600 AX Eindhoven, the Netherlands 12 <sup>§</sup>Graduate School of Advanced Science and Technology, Japan Advanced Institute of Science 13 14 and Technology, 1-1 Asahidai, Nomi, Ishikawa, 923-1292, Japan 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  $\delta$ -MgCl<sub>2</sub> 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)<sub>2</sub>, and subjected to the analysis. 26 Several interesting results were found. The addition of TiCl<sub>4</sub> almost spontaneously converts 27 Mg(OEt)<sub>2</sub> into MgCl<sub>2</sub> 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 convert them into chemisorbed 6-fold coordinated TiCl<sub>x</sub>(OEt)<sub>4-x</sub>, while the subsequent addition 30 31 of an internal donor (here dibutyl phthalate, DBP) promotes a substantial reconstruction and 32 growth of MgCl<sub>2</sub> 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 MgCl<sub>2</sub> 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 TiCl<sub>4</sub> addition replaces the chemisorbed TiCl<sub>x</sub>(OEt)<sub>4-x</sub> with 6-fold coordinated TiCl<sub>4</sub> species, but it also causes side reactions with DBP, 36 as testified by the formation of phthaloyl chloride (POC). After activation by triethylaluminum 37 38 (TEAl), the activity per Ti for ethylene was almost constant throughout the whole preparation 39 process after the initial TiCl<sub>4</sub> 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.

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#### 48 1. INTRODCUTION

After almost seventy years since Karl Ziegler and Giulio Natta broke the monopoly of Nature on the synthesis of stereoregular polymers, Ziegler-Natta (ZN) catalysts are nowadays responsible for 99% of the world polypropylene (PP) production as well as one fourth of that of high-density polyethylene (HDPE).<sup>1</sup> The economic turnover of this industrial process brushes the verge of 300 billion dollars in 2020 and is forecasted to still grow at a compound 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 cocatalyst), together with other organic Lewis bases (the external donors).<sup>3-6</sup> The internal/external 59 60 donors are considered to be located at the vicinity of the Ti active species and to improve stereospecificity through steric hindrance. Such complex composition allows, by means of 61 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<sub>4</sub>, MgCl<sub>2</sub>, and an electron donor into a single solid material, usually called pre-catalyst.<sup>3</sup> Note that the electron 66 67 donor in the pre-catalyst is termed as internal donor to distinguish it from the external one, which is added directly in the reactor along with the AlR<sub>3</sub> activator. The former route 68 (traditional) is based on the mechanical ball-milling of highly crystalline MgCl<sub>2</sub> ( $\alpha$  form) with 69 the internal donor and/or TiCl<sub>4</sub>.<sup>7-13</sup> The latter route (advanced) employs the chemical 70 transformation of a MgCl<sub>2</sub>-precursor into nanostructured and highly defective MgCl<sub>2</sub> (δ form) 71 by TiCl<sub>4</sub> itself in the presence of the donor,<sup>14-29</sup> and generally leads to more disordered and 72 more active nanostructures.<sup>30-32</sup> In a typical chemical preparation route, all the components are 73 intimately connected to each other. TiCl<sub>4</sub> promotes the chlorination of the precursor into MgCl<sub>2</sub> 74 and exerts a capping effect on the newly formed MgCl<sub>2</sub> nanoparticles.<sup>33</sup> The electron donor not 75 only influences the MgCl<sub>2</sub> morphology by stabilizing specific surfaces,<sup>20, 22</sup> but also interacts 76 with the Ti sites through direct coordination<sup>34-37</sup> or more plausibly through coadsorption.<sup>38</sup> By-77 78 products formed during the chlorination must not be overlooked as these products could adsorb on MgCl<sub>2</sub> surfaces, and work as catalytic poisons unless properly removed.<sup>39</sup> 79

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. Therefore, monitoring the evolution of the catalysts along the synthesis is the only way to 82 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 Mg(OEt)<sub>2</sub> precursor, using dibutyl phthalate (DBP) as an 86 internal donor. The Mg(OEt)<sub>2</sub>-based ZN catalysts are among one of the most employed catalysts in industrial PP production, because of their high activity and stereoselectivity. The 87 difficulties of this investigation rely not only on the chemical lability or air sensitivity of 88 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 the reactor, and characterized for their chemical composition, structure, and activity.<sup>40-42</sup> 93 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 drastically the stereospecificity of the catalyst (enhancing the isotacticity of the produced PP 96 from less than 50 % up to 95 % in *mmm*).<sup>40</sup> More in details, Chumachenko et al. found out 97 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  $m^2/g$ ) 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 MgCl<sub>2</sub> crystallites (the surface area decreases to 211  $m^2/g$ ), and a significant increase of the 101 overall activity and stereospecificity.<sup>42</sup> Finally, Kim et al. mostly focused on the mutual 102 103 reactions between Mg(OEt)<sub>2</sub>, TiCl<sub>4</sub> and the benzoyl chloride (BzCl) used as an electron donor or its precursor, demonstrating the high interchangeability of (OEt)<sup>-</sup> and Cl<sup>-</sup> anionic ligands.<sup>41</sup> 104 Recently, we proposed a combination of cutting-edge characterization techniques to clarify 105

the identity of  $\delta$ -MgCl<sub>2</sub>, which includes X-ray total scattering for defining the nano-sized and

disordered structure,<sup>30</sup> and vibrational spectroscopies for determining the exposed surfaces and

their relative extension.<sup>43</sup> In this study, the same approach has been adopted, but complemented

by chemical analysis, polymerization tests and UV-Vis spectroscopy, in order to elucidate the

chemical reactions and structural evolution taking place during the ZN catalyst preparation.

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#### 112 2. EXPERIMENTAL

#### 113 2.1. Reagents

114 Mg powder was purchased from Merck, KGaA. Ethanol (purity > 99.5%, Kanto Chemical) was dried over 3A molecular sieve with N<sub>2</sub> bubbling. Iodine (I<sub>2</sub>, purity > 99.999%, FUJIFILM 115 Wako Pure Chemical) was used as a halide initiator. *n*-Heptane (purity > 99.5%, ), toluene 116 117 (purity > 99.5%), and di-n-butylphthalate (DBP, purity > 98%) were purchased from FUJIFILM Wako Pure Chemical and dried over 4A molecular sieve with N<sub>2</sub> bubbling. 118 119 Triethylaluminium donated (TEAl) was 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 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 500 127 128 mL jacket-type flask equipped with a mechanical stirrer rotating at 180 rpm. After dissolving 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 129 130 of Mg powder and ethanol were repeatedly added with sufficient intervals between individual additions. The total amount of Mg powder and ethanol were 25.0 g and 125 g. The resultant 131 solid product was recovered by washing with 200 mL of ethanol and dried in vacuo at below 132 133 40 °C.

The procedures for catalyst preparation and sampling are shown in Scheme 1. A three-necked flask (500 mL) equipped with a mechanical stirrer and purged with N<sub>2</sub> was charged with 20 g of Mg(OEt)<sub>2</sub> powder and 136 mL of toluene. 20 mL of TiCl<sub>4</sub> was dropwise introduced by keeping the temperature of the mixture below -5 °C. The mixture was gradually heated, and 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 to 4 hours in this study for the sake of characterization. Finally the mixture was sufficiently 143 144 washed with toluene and *n*-heptane to obtain the catalyst. At several key points in the above preparation, samples were extracted from the flask using a syringe. The amount of each 145 146 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.

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155 Scheme 1. Schematic description of the main steps upon ZN catalyst preparation, with156 indication of sampling points.



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#### 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 polymerization, or with 300 mL of heptane, 3.0 mmol of TEA1, and 0.30 mmol of CMDMS 162 163 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 pressure, and the stirring speed were maintained at 70 °C, 0.4 MPa, and 500 rpm, respectively. 166 167 The obtained polymer powder was recovered by filtration and vacuum drying at 60 °C for 6 168 hours.

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#### 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 intensity of the band at 410 nm was recorded on a UV-vis spectrometer (V-670 JASCO), which 181 was used to calculate the titanium content based on external calibration.<sup>44</sup> Organic contents 182 were analyzed by <sup>1</sup>H NMR on a Bruker AVANCE III 400 MHz spectrometer according to our 183 previous study.<sup>39</sup> 10–30 mg of a sample was dissolved in 0.7 mL of DMSO- $d_6$  with 40 µg of 184 185 1,1,2,2-tetrachloroethane as an internal standard. The morphology of the catalyst particles was observed by scanning electron microscopy (SEM, Hitachi Ltd., S-4500). In order to minimize 186 187 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.

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#### 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.

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#### 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 Å). 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 (O) was 25.7 Å<sup>-1</sup>. The measured X-ray scattering data were corrected for polarization, absorption, and background. The contribution of Compton scattering was 207 subtracted using standard analysis procedures.<sup>47</sup> The calculated total structure factor S(Q) was 208 converted into reduced pair distribution function (PDF) G(r) via Fourier transformation with a 209 Lorch modification function.<sup>48</sup> 210

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#### 212 2.5.4. IR Spectroscopy

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

For the Far-IR measurements, the samples were prepared directly inside a  $N_2$ -filled glovebox as thin layers deposited on a highly pure Si wafer (from a suspension in hexane), and placed inside a quartz cell with PE windows, allowing to measure the spectra without exposing the samples to air. Far-IR spectra were acquired at a resolution of 4 cm<sup>-1</sup>, and are shown after subtracting the weak contributions of both the Si wafer and the PE windows.

For the IR measurements, the samples were diluted in anhydrous KBr, compressed in the form of thin self-supporting pellets (with a resulting density of 10 mg of sample per cm<sup>2</sup>) inside the glove-box, and placed inside a quartz cell with KBr windows. The IR spectra were acquired at a resolution of 2 cm<sup>-1</sup>. The curve fitting of the spectra in the v(C=O) region was carried out by OPUS software (Bruker), imposing the Gaussian shape to the contributions.

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

228 UV-Vis spectra were collected in diffuse reflectance mode (DR), with a Varian Cary5000 spectrophotometer, equipped with a reflectance sphere. The powder samples were directly 229 230 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.

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#### **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 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 248 due to both/either incomplete chlorination of Mg(OEt)2 and/or persistence of surface 249 250  $TiCl_x(OEt)_{4-x}$  species, which greatly reduces the activity and stereospecificity of the catalyst.

251 Here, the OEt group was quantified by the methylene peak in <sup>1</sup>H NMR, so the OEt residual can 252 be associated to either  $Mg(OEt)_2$  or  $TiCl_x(OEt)_{4-x}$ . Initially (A,B), the Ti content is pretty high (about 2.5 mmol  $g^{-1}$ ) and the Ti:OEt molar ratio is about 1:1. By introducing DBP and heating 253 254 up to 110 °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 TiCl<sub>3</sub>(OEt). Heating 257 with DBP causes a reduction in the amount of TiCl<sub>3</sub>(OEt). The second TiCl<sub>4</sub> treatment has almost no impact on the Ti content (E,F), but the OEt further decreases to below 0.2 mmol  $g^{-1}$ , 258 259 suggesting that  $TiCl_x(OEt)_{4-x}$  species are replaced by  $TiCl_4$ . Concerning DBP, its content at the end of ZN catalyst synthesis (F) converges to about 0.6 mmol  $g^{-1}$ , which corresponds to a 260 261 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<sub>4</sub> at an elevated temperature. In 264 our analysis, POC were not observed during the first TiCl<sub>4</sub> treatment (C,D), but was slightly 265 observed (column Cl in Table 1) after the second TiCl<sub>4</sub> treatment (E,F), which suggests that 266 the fresh TiCl<sub>4</sub> is more reactive towards the surface adsorbates.

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

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

Ε	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 <sup>*b*</sup> Determined by <sup>1</sup>H NMR.

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

274 d Not detected.

275

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

Samples A–F have been used as catalysts for ethylene and propylene homopolymerization 277 278 after activation by TEA1. 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 110 °C (A,B), but then the activity increased significantly along with the synthesis. The 285 286 characterization of all the produced polymers is summarized in Table S1 and Figure S1.



Figure 1. Ethylene and propylene polymerization activity of the samples extracted at different stages in the course of catalyst preparation. Reaction conditions: monomer pressure = 0.4 MPa, catalyst = 10-50 mg, *n*-heptane = 300 mL, TEA1 = 3.0 mmol, 70 °C, 30 min, CMDMS (for propylene polymerization) = 0.30 mmol.

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

Sample	Activity in e	thylene polym.	Activity in propylene polym. <sup>a</sup>		
Sample –	$[g_{-PE} g_{-cat}^{-1} h^{-1}]$	$[g_{PE} \text{ mmol}_{-Ti}^{-1} \text{ h}^{-1}]$	$[g_{-PP} g_{-cat}^{-1} h^{-1}]$	$[g_{-PP} \operatorname{mmol}_{-Ti}^{-1} h^{-1}]$	
А	4300	1900	n.d.	n.d.	
В	4800	1800	n.d.	n.d.	
С	840	800	420	400	
D	880	1500	600	1000	
Ε	1100	1800	2100	3300	
F	820	1500	2300	4200	

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

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

#### 297 **3.3.1. PXRD**

The solid samples extracted in the course of catalyst preparation (A to F), as well as the 298 299 Mg(OEt)<sub>2</sub> starting material, were subjected to X-ray total scattering measurements. The X-ray 300 diffraction patterns are shown in Figure 2. The pattern of Mg(OEt)<sub>2</sub> exhibits two strong peaks 301 at  $2\theta = 9$  and 11°. The structure of Mg(OEt)<sub>2</sub> has not been clearly identified yet, but it is 302 believed that it resembles that of Mg(OH)<sub>2</sub> (Brucite,  $P\overline{3}m1$ ), where the H atoms are substituted with ethyl groups, and the split peaks correspond to (001) reflection.<sup>27, 49, 50</sup> That is, the O-Mg-303 304 O layers are stacked across a layer of  $-C_2H_5$  groups, and hence the peaks at  $2\theta = 9$  and  $11^\circ$  are most likely originated from the stacking of the O-Mg-O layers. A broad peak centered at  $2\theta =$ 305 306 10° is also observed in the pattern of A (right after the first TiCl<sub>4</sub> addition), which suggests that 307 the structure of A memorizes the layered structure of Mg(OEt)<sub>2</sub> to some extent. The same pattern, however, also contains weak reflections at  $2\theta = 27-40^{\circ}$  and  $50^{\circ}$ , which correspond to 308 309 the (012)/(104) and (110) reflections of MgCl<sub>2</sub>, and indicate that the MgCl<sub>2</sub> seeds are already 310 formed at the very initial stage of the synthesis. The peak at  $2\theta = 10^{\circ}$  becomes weaker when the temperature is increased up to 60 °C (B), and eventually disappears after the addition of 311 312 DBP and heating up to 110 °C (C). Instead, the peak corresponding to the Cl-Mg-Cl stacking along the *c*-axis emerges at 15°. In the following steps of the preparation (from **D** to **F**), the 313 broad peak in the 27-40° range becomes stronger, reflecting the growth of the MgCl<sub>2</sub> 314 315 crystallites both in the lateral and vertical directions. The patterns of C-F are typical for  $\delta$ -MgCl<sub>2</sub>: three broad peaks are observed at around 15°, 27–40°, and 50°, which correspond to 316 317 (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-Cl layers.<sup>8</sup> Hence, PXRD measurements clearly indicate that the MgCl<sub>2</sub> crystallites or their 320

321 seeds are formed just after the first TiCl<sub>4</sub> addition, and they gradually grew through the 322 subsequent steps of preparation, maintaining a disordered structure along the Cl-Mg-Cl 323 stacking direction.

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#### 325

Figure 2. Powder X-ray diffraction (PXRD) patterns of the samples extracted at different steps of the synthesis and of the Mg(OEt)<sub>2</sub> starting material. The X-axis was scaled with the wavelength of Cu Kα ( $\lambda$ =1.5418 Å) for comparison with the literature. The typical diffraction peaks of α-MgCl<sub>2</sub> are denoted by dotted lines. The patterns are vertically shifted for clarity.

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The SEM images of the catalyst samples are shown in Figure S2. The spherical  $Mg(OEt)_2$  is an aggregate of plate-like particles with a length of several micrometers.<sup>51</sup> The surface of **A**, just after contact with TiCl<sub>4</sub>, is notably rough since the plate-like particles partially retain their shape. In **B**, the macroparticles became smoother and more spherical due to the fusion of platelike particles. After adding the donor (**C**), the surface became even smoother, and the platelike particles were completely fused. From **C** to **F**, no significant changes were observed. In addition, the macroparticles seem to grow slightly from **A** to **C**, which is probably due to the fusion of small Mg(OEt)<sub>2</sub> macroparticles or the growth of the catalyst primary particles. Such ripening phenomenon has been reported previously, where the resultant catalyst particles were about 10% bigger in diameter than the original Mg(OEt)<sub>2</sub> 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 Mg(OEt)<sub>2</sub> and  $\alpha$ -MgCl<sub>2</sub> 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 positions correspond to atomic distances; ii) the broadness represents their distribution, 346 347 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 completely negligible corresponds to the crystalline dimensions.<sup>53</sup> For Mg(OEt)<sub>2</sub>, a weak 349 350 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 caused by O-Mg-O layers.<sup>54</sup> The fact that limiting the  $Q_{\min}$  to 1.0 Å<sup>-1</sup> completely diminishes 352 353 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 = 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<sub>2</sub> crystallites 356 slowly grow during the synthesis.

In the shorter region (Figure 3b), the pattern of  $Mg(OEt)_2$  shows a prominent peak at 0.20 nm, which is attributed to the Mg-O atomic pair. For comparison, the distance between Mg and O in Mg(OH)<sub>2</sub> is estimated at a very close value, ca. 0.21 nm. The PDF pattern of **A** does not exhibit such peak, providing evidence that the Mg-O bond is immediately converted to Mg-Cl by contacting Mg(OEt)<sub>2</sub> with TiCl<sub>4</sub>. Although there is no traceable Mg-O in the PDF, there is 362 a remnant of the periodic structure formed by Mg(OEt)<sub>2</sub> in the PXRD. Such a memory of the precursor structure on PXRD has also been reported in the formation of  $\delta$ -MgCl<sub>2</sub> from 363 MgCl<sub>2</sub>/Lewis base adducts.<sup>55, 56</sup> The positions of the most relevant peaks in the patterns of the 364 extracted samples are similar to those of  $\alpha$ -MgCl<sub>2</sub>, for example, the peaks at 0.25, 0.35, 0.58, 365 0.63, and 0.97 nm. This fact indicates that the local structures of the extracted samples were 366 almost identical to that of the  $\alpha$ -MgCl<sub>2</sub> even at the stage of seeds formation (A). The relatively 367 weak peak intensity of **A** and **B** over r = 0.5-1.0 nm is due to its finite crystal dimension (<2) 368 369 nm).

370



372

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

#### 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 previous work.<sup>30</sup> Table 3 summarizes the structural parameters of MgCl<sub>2</sub> nanoparticle models as determined by PXRD fitting, where  $L_a=L_b$  correspond to the lateral size in the *ab* plane,  $L_c$ is the crystallite dimension in the basal direction, and  $P_c$  is the probability of finding  $\alpha$ -MgCl<sub>2</sub> sequences as an indicator of the amount of stacking disorders ranging from 25 to 100%; the accuracy of the fit is also provided in terms of  $R_w$ , defined as the residual between the 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 dimension of 1.8 nm and a vertical dimension of 0.3 nm, corresponding to a single Cl-Mg-Cl 388 layer. Heating up to 60 °C (**B**) brings no significant change in the structure of MgCl<sub>2</sub> seeds. 389 390 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 second TiCl<sub>4</sub> addition and further aging (E,F) do not cause a significant structural change, 394 395 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>.

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

Sample Name	$L_a = L_b$ [nm]	<i>L<sub>c</sub></i> [nm]	<i>P</i> <sub>c</sub> [%]	$R_{w,PXRD}$	$R_{w,PDF}$
А	1.8	0.3	n.a. <sup><i>a</i></sup>	0.162	0.374
В	1.8	0.3	n.a. <sup><i>a</i></sup>	0.106	0.377
С	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

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

410

# 408 ${}^{a}P_{c}$ was not specified as the particle model is composed of a single Cl-Mg-Cl layer.

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

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

Figure 4. Far-IR spectra of the extracted samples and of the Mg(OEt)<sub>2</sub> precursor. The spectra
are vertically stacked for clarity.

The Far-IR spectrum of Mg(OEt)<sub>2</sub> is characterized by two main absorptions centered at 330 424 and 450 cm<sup>-1</sup>, very broad and overlapping to each other. Similar bands have been already 425 426 observed in the past for different MgCl<sub>2</sub> adducts with alcoholates and alkoxides, and assigned to the vibrations of Mg-O bonds.<sup>60-62</sup> As observed in the PDF analysis for the same sample, 427 428 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<sub>2</sub>. The spectrum of A shows a main absorption band centered at 235 cm<sup>-1</sup>, together with two weaker bands at 525 and 360 cm<sup>-1</sup>. 430 The sharp band at 235 cm<sup>-1</sup> is assigned to the basal (001) surface,<sup>43</sup> in well agreement with the 431 432 PXRD analysis according to which the first MgCl<sub>2</sub> seeds are mostly formed as monolayers. The band at 525 cm<sup>-1</sup>, instead, is attributed to the v(Ti-O) vibrations of 4-fold coordinated 433 Ti(OEt)<sub>x</sub>Cl<sub>4-x</sub> species (vide infra).<sup>63</sup> The relatively high intensity of this band is in well 434

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

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

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

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

The evolution of the surface species during ZN catalyst synthesis was investigated by IR 462 463 spectroscopy in the Mid-IR region, as reported in Figure 5a. The spectrum of Mg(OEt)<sub>2</sub> is analogous to the spectra of Mg alkoxides already reported and described in literature.<sup>68, 69</sup> 464 465 Briefly, most of the bands are due to the vibrational modes of the OEt moieties: the  $v(CH_x)$ bands at 2800-3000 cm<sup>-1</sup>, the  $\delta$ (CH<sub>2</sub>) and  $\delta$ (CH<sub>3</sub>) bands at 1450 and 1380 cm<sup>-1</sup>, v(C-O) at 1120 466 cm<sup>-1</sup>, v(C-C) at 1050 cm<sup>-1</sup> and some rocking modes at 890 cm<sup>-1</sup>. Below 600 cm<sup>-1</sup> the tail of the 467 468 absorption band due to the v(Mg-O) vibrations, contributing in the Far-IR region, is also 469 observed.





Figure 5. Part a) IR spectra of the extracted samples, normalized to the optical thickness of the pellets. Part b) Magnification of the C-F spectra in the v(C=O) region. Part c) Curve fitting in the v(C=O) region for F (the black curve is the sum of all the calculated contributions). Part d)

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

477

The original bands due to the Mg-ethoxide groups are no more observable in the spectrum 478 of A. Nevertheless, the spectrum still contains intense bands in the  $v(CH_x)$ ,  $\delta(CH_x)$ , v(C-O) and 479 v(C-C) regions, which correspond well to those observed in the spectra of tetrahedral 480 Ti(OEt)<sub>2</sub>Cl<sub>2</sub> and Ti(OEt)<sub>3</sub>Cl complexes.<sup>63</sup> Hence, at this stage most of the ethoxide groups look 481 associated into TiCl<sub>x</sub>(OEt)<sub>4-x</sub> species rather than incompletely chlorinated Mg(OEt)<sub>x</sub>Cl<sub>2-x</sub>. 482 483 Beside the ethoxide bands, the spectrum of A displays a weak and broad band in the v(OH)484 region (around 3400 cm<sup>-1</sup>), which is due to a small amount of moisture contamination. The 485 spectrum of **B**, obtained after heating **A** up to 60 °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.

The IR spectra radically change after the addition of DBP in the reaction mixture ( $\mathbf{C}$ ).<sup>70</sup> Most 489 490 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 the vibrational features of DBP, with the characteristic v(C=O) band around 1700 cm<sup>-1</sup> (as 493 494 magnified in Figure 5b). The analysis of the v(C=O) region allows to obtain information on the 495 coordination modes of DBP at the MgCl<sub>2</sub> surfaces and hence, indirectly, on the types of 496 exposed sites. A curve fitting of the v(C=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 v(C=O) contributions: for liquid-like DBP at 1728 cm<sup>-1</sup>,<sup>71, 72</sup> DBP in interaction with different Mg<sup>2+</sup> sites at 1657, 1680 and 1707 500 cm<sup>-1</sup>,<sup>71-74</sup> DBP in interaction with TiCl<sub>4</sub> at 1634 cm<sup>-1</sup>,<sup>75, 76</sup> and the POC produced by a side 501 reaction between DBP and TiCl<sub>4</sub> at 110 °C<sup>42</sup> at 1758, 1836 and 1862 cm<sup>-1</sup> (identical bands were 502 observed by directly co-milling MgCl<sub>2</sub> and POC).<sup>76, 77</sup> The fit is completed by including the 503 two ring vibrations of the ortho-disubstituted phenyl ring at 1581 and 1595 cm<sup>-1</sup>,<sup>78</sup> and an 504 additional band at 1615 cm<sup>-1</sup> ascribable to  $\delta$ (OH) of water traces. Focusing on the three bands 505 due to DBP in interaction with different  $Mg^{2+}$  sites, the band at 1707 cm<sup>-1</sup> can be assigned to 506 DBP both in a chelate configuration on 4-fold coordinated Mg<sup>2+</sup> sites (the most 507 508 thermodynamically favored configuration for DBP on the (110) surface) and monodentate on 5-fold coordinated Mg<sup>2+</sup> sites,<sup>79, 80</sup> the band at 1680 cm<sup>-1</sup> is ascribed to monodentate DBP at 4-509 fold coordinated Mg<sup>2+</sup> sites,<sup>79,80</sup> whereas the band at 1657 cm<sup>-1</sup> is due to DBP on defect sites.<sup>71,</sup> 510 <sup>73, 74</sup> It is important to notice that, at a difference than what happens with ethylbenzoate, it is 511 not possible to quantify the DBP coordinated at 4-fold and 5-fold Mg<sup>2+</sup> sites, but only to 512 513 discriminate between DBP adsorbed at MgCl<sub>2</sub> surfaces and defects.

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

i. As soon as DBP is added (C), some DBP molecules are trapped as liquid-like in the
 interparticle pores of the material (blue line). This is compatible with the porosity data
 reported by Chumachenko et al.<sup>42</sup> The amount of liquid DBP slightly decreases in the
 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<sub>2</sub> surfaces. The 524thermodynamics driving this process was evaluated in the past by experimental525calorimetric measurements<sup>82</sup> and by theoretical calculations.<sup>83</sup> An analogous behavior526has been already observed upon dosing ethyl benzoate (EB) on MgCl<sub>2</sub>/TiCl<sub>4</sub> from the527vapor phase.<sup>84</sup> According to the trend in Figure 5d, some of these complexes are washed528away 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 phtaloyl 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 Mg(OEt)<sub>2</sub> precursor. The
545 spectra are vertically stacked for clarity.

Whereas the spectrum of Mg(OEt)<sub>2</sub> displays no absorption in the whole UV-Vis region, the 546 spectra of the extracted samples are dominated by intense absorptions above 30000 cm<sup>-1</sup>, due 547 548 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 identifiable and straightforwardly assigned to a  $Cl(\pi) \rightarrow Ti(d)$  CT transition.<sup>86, 87</sup> Moreover, on 551 552 this band the Jorgensen semi-empirical rule on the optical electronegativity of transition metals 553 and their ligands can be applied.<sup>88</sup>

The spectrum of **A** shows the maximum of the first absorption at ca. 32000 cm<sup>-1</sup>, which is compatible with a charge transfer transition from Cl<sup>-</sup> ligands to a 4-fold coordinated Ti<sup>4+</sup> (expected around 34500 cm<sup>-1</sup> according to the Jorgensen rule).<sup>88</sup> This indicates that most of the Ti in **A** is present as physisorbed 4-fold coordinated TiCl<sub>x</sub>(EtO)<sub>4-x</sub> species,<sup>63</sup> in fair agreement with both Far-IR and Mid-IR data, and compatibly with the sequence proposed by Brambilla et al. for TiCl<sub>4</sub> chemisorption on MgCl<sub>2</sub>.<sup>12</sup> Then, after heating at 60 °C (**B**), the main absorption

downward shifts to ca. 29000 cm<sup>-1</sup> and a new sharp band appears at 24500 cm<sup>-1</sup>. The downward 560 561 shift of these bands is associated to a change in the coordination of the Ti ions from 4-fold to 6-fold (the theoretical value for the CT transition from Cl<sup>-</sup> ligands to octahedral Ti<sup>4+</sup> is 28200 562 cm<sup>-1</sup>),<sup>88</sup> indicating that 4-fold coordinated TiCl<sub>x</sub>(EtO)<sub>4-x</sub> species at 60 °C have adjusted in the 563 564 more stable 6-fold coordinated octahedral configuration on the nascent MgCl<sub>2</sub> surfaces. This 565 is again in agreement with the analysis of the Far-IR and Mid-IR spectra. Notably, an analogous trend was observed during TiCl<sub>4</sub> chemisorption from the vapor phase onto bare MgCl<sub>2</sub>.<sup>89</sup> The 566 two bands, which differ of ca. 4500 cm<sup>-1</sup>, might arise from the same Cl( $\pi$ ) $\rightarrow$ Ti(d) CT transition 567 568 localized on slightly different Ti species (for example with a different number of ethoxide 569 ligands) and/or from two Cl( $\pi$ ) $\rightarrow$ Ti(d) CT transitions on the same Ti cation from two different Cl species (e.g. axial and equatorial Cl atoms with respect to the ethoxide ligands).<sup>90</sup> 570

The successive synthetic step (C) is dominated by the introduction of DBP, which not only 571 coordinates to the MgCl<sub>2</sub> surfaces and defects, but also directly to the Ti centers, as revealed 572 573 by the IR spectra in Figure 5c. The corresponding UV-Vis spectrum shows an intense band peaked at 26500 cm<sup>-1</sup>, which is always ascribed to a  $Cl(\pi) \rightarrow Ti(d)$  CT transition for 6-fold 574 575 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 TiCl<sub>4</sub>-DBP complexes are formed. Most of the TiCl<sub>4</sub>-DBP complexes are then removed from 578 MgCl<sub>2</sub> 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  $Cl(\pi) \rightarrow Ti(d)$  CT transitions for  $Ti^{4+}$  in a 6-fold coordination, with small differences due to 581 slight distortions in the geometry and minor changes in the effective charge distribution.<sup>86</sup> 582

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





Figure 7. Part a) DR UV-Vis spectra of samples A, B, C and F, before and after TEAl activation. Part b) Magnification in the v(C=O) of the IR spectra of C before and after TEAl activation. Curve fitting is also shown for activated C. Part b') Difference spectrum calculated by subtracting to the spectrum of activated C the spectrum before TEAl activation. Parts c and c') same as in parts b and b' for F.

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

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

An analogous trend is observed also in **B**, although in this case the two bands at 29000 and 24500 cm<sup>-1</sup> remain unaltered, revealing that the fraction of 6-fold coordinated  $TiCl_x(EtO)_{4-x}$ species responsible for those bands are evidently less reactive towards TEA1.

The spectrum of activated **C** is characterized by two very intense and well-defined absorption bands at 38400 and 17800 cm<sup>-1</sup>. The former is assigned to a Cl( $\pi$ ) $\rightarrow$ Ti(d) CT transition for a Ti in the +3 oxidation state (as already discussed for **A**), while the latter is very peculiar, quite different from the fingerprint of the TiCl<sub>3</sub> clusters typically observed in TEAl-activated ZN catalysts. Instead, that band recalls the UV-Vis spectrum reported in the literature for a [TiCl<sub>4</sub>(thf)<sub>2</sub>]<sub>1</sub>[MgCl<sub>2</sub>(thf)<sub>1.5</sub>]<sub>2</sub> adduct after reaction with an Al-alkyl (trioctyl-aluminum, in that case).<sup>90</sup> Therefore we can imagine the formation of DBP-bonded TiCl<sub>3</sub>.

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

623 On the contrary, IR spectroscopy provides new insights on the fate of the donor after TEA1 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 TEA1 (a minimal fraction at room temperature, almost the totality at about 100 °C),<sup>93</sup> but the state of the molecules remaining on the catalyst surfaces is still unclear. Figure 7b and **Figure 7**c display the magnification of the v(C=O) region for **C** and **F** before and after TEA1 activation at room temperature, revealing an analogous trend for the samples corresponding to the initial DBP addition and to the sample at the end of the synthesis (the quantification of the integrated areas for all the individual v(C=O) components are reported in Table S3).

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

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

The multi-technique investigation presented in this work sheds light on the chemical reactions and structural evolution taking place during the formation of an industrial-like Ziegler-Natta pre-catalyst, starting from the  $Mg(OEt)_2$  precursor and in the presence of DBP as an internal donor. Five intermediate samples have been extracted from the glass reactor at different stages, plus the final catalyst, and analyzed in terms of structure, morphology, and surface species. All the techniques converge in demonstrating that as soon as  $Mg(OEt)_2$  is contacted with TiCl<sub>4</sub>, all Mg-O bonds are converted into Mg-Cl ones, forming the first seeds of MgCl<sub>2</sub>, which appear as Cl-Mg-Cl monolayers with a lateral dimension of below 2 nm, and releasing TiCl<sub>x</sub>(OEt)<sub>4-x</sub> as by-products (first physisorbed as 4-fold coordinated, and then chemisorbed as 6-fold coordinated). Those species efficiently polymerize ethylene but not propylene.

657 The addition of the DBP electron donor significantly promotes the growth of MgCl<sub>2</sub> 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<sub>2</sub> surfaces, corroborating the hypothesis 661 that the influence of the electron donors on the stereoselectivity of ZN catalysts is mostly due to a steric modulation of the Ti surroundings. However, a non-negligible fraction of DBP is 662 663 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<sub>4</sub> is mostly chemisorbed as 6-fold coordinated on MgCl<sub>2</sub> 667 surface largely replacing the  $TiCl_x(OEt)_{4-x}$  species, although a fraction of  $TiCl_4$  is also consumed in a side reaction with DBP, as testified by the formation of phthaloyl chlorides. The 668 669 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<sub>2</sub> 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<sup>3+</sup> species. This demonstrates the positive effect of the final thermal treatment to afford truly performant ZN catalysts. All these findings areschematically summarized in Figure 8.

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





Figure 8. Schematic representation of catalyst formation from Mg(OEt)<sub>2</sub>. The MgCl<sub>2</sub>
 nanoparticle models were drawn by atomistic system rendering software Speck with the aid of
 Vesta.<sup>94</sup>

#### 687 AUTHOR INFORMATION

#### 688 **Corresponding Author**

689 Alessandro Piavano \*E-mail: alessandro.piovano@unito.it

- 690 Toshiaki Taniike \*E-mail: taniike@jaist.ac.jp
- 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

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

- and supervised the entire research.
- <sup>†</sup>These authors contributed equally.

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- 702 Funding Sources
- 703 DPI project #802
- 704 JSPS KAKENHI Grant Number JP20J15042

- 706 Notes
- 707 The authors declare no competing financial interest.

#### 709 Supporting Information

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

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#### 716 ACKNOWLEDGMENT

The authors appreciate Japan Polychem Corp. and Tosoh Finechem Corp. for the reagent donation. The authors also appreciate Toho Titanium Co. Ltd. for GPC measurement. The synchrotron X-ray total scattering experiments were performed at BL04B2 in SPring-8 with the approval of RIKEN (Proposal No. 2019A1143 and 2020A1231). The work of A.P., T.W., C.P., E.G., and T.T. forms part of the research programme of DPI, project #802. The work of G.T. was supported by JSPS KAKENHI Grant Number JP20J15042.

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