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# Spectroscopic Fingerprints of MgCl<sub>2</sub>/TiCl<sub>4</sub> Nanoclusters Determined by Machine Learning and DFT

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## Abstract

Understanding the structure and properties of MgCl<sub>2</sub>/TiCl<sub>4</sub> nanoclusters is a key to uncover the origin of Ziegler-Natta catalysis. In particular, vibrational spectroscopy can sensitively probe the morphology and active species of MgCl<sub>2</sub>/TiCl<sub>4</sub>. Here, we determined vibrational spectroscopic fingerprints of 50MgCl<sub>2</sub> and 50MgCl<sub>2</sub>/3TiCl<sub>4</sub> which were obtained by non-empirical structure determination based on an evolutionary algorithm and DFT. The adsorption of CO, TiCl<sub>4</sub> and Ti<sub>2</sub>Cl<sub>8</sub> dimers was also modelled on each of coordinatively unsaturated Mg<sup>2+</sup> sites available for binding including so-called defect sites, which are likely present at the surface of activated MgCl<sub>2</sub> nano-crystals and plausible sites for strong TiCl<sub>4</sub> species adsorption. The outcomes of thermodynamical and vibrational analysis were compared to results on ideal surfaces of MgCl<sub>2</sub>. Vibrational analysis (IR and Raman) on plausible models of TiCl<sub>4</sub>/MgCl<sub>2</sub> nanoclusters revealed that IR response is useful to distinguish between the different ways of binding of TiCl<sub>4</sub> on different sites of adsorption, whereas Raman response provides a clear fingerprint of supported TiCl<sub>4</sub> species.

Keywords: polymerization catalysis, machine learning, nanoclusters, DFT, Raman spectrum, IR spectrum

## I. INTRODUCTION

The structural unit of the Ziegler-Natta catalyst (ZNC) is nanostructured and disordered  $\text{MgCl}_2$  whose lateral surfaces are capped by  $\text{TiCl}_4$  and Lewis bases (called internal donors). Such an active structure is obtained by forming or reconstructing  $\text{MgCl}_2$  in the presence of  $\text{TiCl}_4$  and/or internal donors during catalyst preparation. The ball-milling of highly crystalline  $\text{MgCl}_2$  or transformation of a  $\text{MgCl}_2$  precursor such as  $\text{Mg}(\text{OEt})_2$  yields disordered  $\delta$  form of  $\text{MgCl}_2$ . Given experimental difficulties in characterizing this catalyst, computational approaches have provided a great contribution to the overall understanding of  $\delta$ - $\text{MgCl}_2$  (and of  $\text{MgCl}_2$ -based ZN catalysts in general), because of the feasibility of modelling the isolated contribution of single surfaces or catalytic sites.<sup>1</sup> Theoretical chemistry due to advances in quantum chemistry, in particular in the Density Functional Theory (DFT) has been decisive in last decades for this field of research. Shortly, the seminal  $\text{MgCl}_2$  models as obtained from molecular mechanics in the 1980s presented the (110) and (104) lateral surfaces as the putative surfaces for the adsorption of monomeric and stereo-selective dimeric  $\text{Ti}_x\text{Cl}_y$  species, respectively.<sup>2</sup> However, more recent DFT studies have claimed the crisis of those models, warning about the critical thermodynamic stability of  $\text{Ti}_x\text{Cl}_y$  species on flat and regular  $\text{MgCl}_2$  surfaces, and moving towards a much more complex morphology of the  $\delta$ - $\text{MgCl}_2$  particles.<sup>3-11</sup> Recent theoretical calculations on  $\text{MgCl}_2$  bulk and surface structure by means of periodic Density Functional Theory methods including dispersion (DFT-D\*) predicted that well-formed  $\text{MgCl}_2$  crystals in the absence of adsorbates predominantly feature the (104) surfaces, however, the situation drastically changes in the presence of adsorbates (including electron donors). DFT-D simulations<sup>12,13</sup> demonstrated that  $\text{MgCl}_2$  crystals mainly expose the (110) surfaces when they are formed in the presence of Lewis bases (especially small molecules such as methanol, ethanol, and dimethyl ether) or in presence of alkoxy silanes adopted as external donors. The application of Bravais' law allowed the identification by some of us of thermodynamically most stable surfaces and the construction of a comprehensive set of slabs as model surfaces of increasing stability in terms of surface Gibbs Free Energy namely (107), (012), (101), (015) and (110) ones.<sup>14</sup> Nano-size and crystallite shapes are key features of many catalysts and, among others, the morphology of the primary particles and details of exposed surfaces of  $\text{MgCl}_2$ -based Ziegler-Natta catalysts for olefin polymerization still remain experimentally inaccessible. Together with detailed structural

analysis of the supporting  $\delta$ -MgCl<sub>2</sub> nanoparticles by synchrotron X-ray total scattering<sup>15</sup>, the construction of the Wulff's plot of the whole MgCl<sub>2</sub> particles revealed that ball-milling of naked MgCl<sub>2</sub> not only promotes an increase in the total surface area, but also changes the relative extension of the surfaces, favoring the formation of the lateral surfaces exposing strongly acidic Mg<sup>2+</sup> sites (i.e., the (110), (012) and (015) ones) at the expenses of the basal (001) one. Moreover, theoretical calculation predicted the existence of several possible edges involving the (110) surface.<sup>16</sup> Such inter-surfaces edges are remarkably relevant because in some recent theoretical models they were advocated as the favorable place for stereo-selective active sites.<sup>17</sup> The morphology and surface properties of  $\delta$ -MgCl<sub>2</sub> nanoparticles (i.e. the relative extension of the exposed surfaces) have been elucidated by vibrational spectroscopies for a series of mechanically and chemically activated MgCl<sub>2</sub> samples, and by building up a comprehensive set of model structures (both ordered and disordered) in order to highlight nanosizing effects. Far-IR spectroscopy coupled with quantum-mechanical simulations and complemented by mid-IR spectroscopy of CO adsorbed at 100 K gave a comprehensive picture of the morphology of MgCl<sub>2</sub> nano-particles and of their surface properties. More recently, different nanostructures were obtained in terms of disorder and morphology, which in turn influence the overall catalytic performance. The investigation was further extended by looking at the lattice dynamics of MgCl<sub>2</sub> systems by means of Inelastic Neutron Scattering (INS) spectroscopy,<sup>18</sup> which is a valuable method to probe the motion of atoms within a material and hence understand the structural disorder of nano-sized systems. In recent years, some of the authors have sharpened the use of FT-IR spectroscopy of adsorbed carbon monoxide as a technique to get information on the MgCl<sub>2</sub> exposed surfaces and their relative extent.<sup>14,19</sup> The method, which was attempted for the very first time by Zakharov and co-workers<sup>20</sup>, was demonstrated to be particularly powerful, especially when the MgCl<sub>2</sub> surfaces are not fully occupied by the other components and/or by side residues of the synthesis. This technique efficiently reveals the type and amount of exposed Mg<sup>2+</sup> sites, which in turn are correlated with the extension of specific lateral surface.<sup>14</sup>

In this work, model nanoplates (50MgCl<sub>2</sub> and 50MgCl<sub>2</sub>/3TiCl<sub>4</sub>) were obtained by non-empirical structure determination based on the genetic algorithm and DFT, which was developed by some of us.<sup>21,22</sup> The exposed surfaces and the defective sites contained in these 'realistic' models were probed by CO adsorption to identify weakly acidic Mg<sup>2+</sup> cations and strongly acidic Mg<sup>2+</sup> cations. The obtained vibrational behavior was compared with that

emerged in the 2D periodic treatment for surfaces and ‘classical’ clusters built by Wulffs’ polar plots. So far, various computational methodologies have been adopted to explore stable docking sites for  $\text{TiCl}_4$  and its dimeric species but the calculations were mostly based on the assumption of ideal or simplified clusters of  $\text{MgCl}_2$ . Going beyond the too simplified surface models present in literature, here we adopted well assessed DFT methodology previously employed for surfaces, while stepped forward to a more realistic model of  $\text{MgCl}_2$  nanoclusters by means of the non-empirical structure determination. On these nanostructures we carried out vibrational Far-IR and Raman analysis to discuss to which extent exposed tetra and penta Mg sites are distinguishable and, even more interestingly, the possibility to recognize: i) the effect of adsorption of different precatalytic complex  $\text{Ti}_x\text{Cl}_y$  on IR and/or Raman bands, ii) to what extent it is possible to distinguish between  $\text{Ti}_x\text{Cl}_y$  species on the basis of features occurring in IR and/or Raman spectra; that with the aim to discuss whether or not it is possible to obtain a vibrational evidence of the presence of a precatalytic species on a specific site. With this target in mind, we identified spectroscopic IR features and more evidently Raman bands specific of each adduct as possible fingerprints of Ziegler-Natta catalysts.

## II. COMPUTATIONAL MODELS AND DETAILS

### A. Machine Learning construction of nanoplate

Non-empirical structure determination was performed for  $50\text{MgCl}_2$  and  $50\text{MgCl}_2/3\text{TiCl}_4$  on the basis of a program that combines global structure search using a genetic algorithm and local geometry optimization using DFT.<sup>21,22</sup> The size of  $50\text{MgCl}_2$  is about 3 nm in diameter, consistent with the experimentally observed size of the primary particles (ca. 2.4-4.0 nm).<sup>15</sup> Three  $\text{TiCl}_4$  molecules with respect to 50  $\text{MgCl}_2$  units correspond to 2.69 wt%, similar to a typical Ti content of industrial Ziegler-Natta catalysts.<sup>23</sup> The structure determination program assumes a convex  $\text{MgCl}_2$  monolayer with its lateral surfaces capped by  $\text{TiCl}_4$ . A  $\text{MgCl}_2$  skeleton consists of  $N$   $\text{Mg}^{2+}$  cations and  $2N$   $\text{Cl}^-$  anions respectively placed at atomic positions in the ionic crystal, where the  $\text{Cl}^-$  anions are placed in the descending order of the coordination number. Adsorption sites were defined on the lateral periphery of the  $\text{MgCl}_2$  skeleton. The  $\text{TiCl}_4$  adsorption occurs in a way that a  $\text{Ti}^{4+}$  cation

becomes hexacoordinated or pentacoordinated, e.g., mononuclear species on  $\{110\}$  surfaces, and mononuclear and dinuclear species on  $\{104\}$  surfaces. The structures are subjected to DFT geometry optimization, and evolved through genetic operators, where the energy of the optimized structures is used to derive the fitness. As in our previous works,<sup>21,22,24</sup> the DFT geometry optimization was performed using DMol3 at a level of GGA PBE as the exchange-correlation functional, and the double-numerical basis set with polarization functions (DNP) and effective core potential (ECP). Further details are given in literature.<sup>21,22</sup>

## B. DFT calculations

The DFT<sup>25,26</sup> calculations reported in this paper were mainly based on the B3LYP global hybrid functional,<sup>27,28</sup> as implemented in the CRYSTAL program.<sup>29,30</sup> Since dispersion plays a key role in the investigated chemical systems the semi-empirical DFT-D2 approach based on Grimme’s empirical correction<sup>31,32</sup> was adopted in combination with the hybrid B3LYP functional; that combined scheme have been found to successfully describe surface interactions.<sup>33,34</sup> PBE0-D3 (including three bodies correction) adsorption energies, together with the outcomes of a non local meta-GGA by Truhlar have been also reported as Supplementary Information for plausible precatalytic  $\text{Ti}_x\text{Cl}_y$  species on the nanocrystal.

Split valence triple-zeta basis sets plus polarization (TZVP) of Gaussian type functions have been adopted for all the elements (Mg, Ti and Cl atoms).<sup>9</sup> For most of the surfaces the adsorption of CO has been modeled adopting the same level of calculation described above and also an Ahlrichs QTZV plus polarization (QTZVP2) quality basis set. The coefficients of the polarization Gaussian functions ( $\alpha_{pol}$ ) were optimized in a previous study on adsorbed CO.<sup>35</sup>

To inspect the molecular vibrational shifts of CO and  $\text{TiCl}_4$  due to the interaction with the support, we performed geometry optimizations followed by harmonic vibrational frequency calculations (and the corresponding IR and Raman intensities) of the molecular adducts. Thermodynamic properties have been computed at standard conditions ( $P = 1$  bar,  $T = 298$  K) and additionally at  $T = 100$  K. Details concerning the computational set up and the calculations of the vibrational frequencies are collected in the Supplementary Information Section.

### III. RESULTS AND DISCUSSION

#### A. Structure, morphology of nanoplates

The structures of  $50\text{MgCl}_2$  and  $50\text{MgCl}_2/3\text{TiCl}_4$  were determined using a non-empirical structure determination program developed and modified by some of us.<sup>21,22</sup>  $50\text{MgCl}_2$  was adopted, considering that the surface extensions and far-IR are size sensitive. Its size (ca. 3 nm) is comparable to the known size of the primary particles (2.4-4.0 nm). Note that  $50\text{MgCl}_2$  is much larger than  $19\text{MgCl}_2$ , the largest structure determined in the previous papers,<sup>21,22</sup> and therefore is computationally quite demanding because of the intrinsic cubic scaling of DFT and an exponential increase of the possible configuration space. Figure 1 shows evolutionary progress plots for the structure determination of  $50\text{MgCl}_2$  and  $50\text{MgCl}_2/3\text{TiCl}_4$ , respectively. The energy of the best-of-generation structure decreased as a result of evolution. The high computational cost impeded multiple runs implemented over a sufficient number of generations, i.e., the global minima were not guaranteed. Nonetheless, (however, as expected from our experiences in smaller clusters), the obtained structures exhibited features similar to those of the most stable structures for smaller  $\text{MgCl}_2/\text{TiCl}_4$  systems.<sup>21</sup> As shown in Figure 2b, bare  $\text{MgCl}_2$  dominantly exposed  $\{104\}$  or analogous surfaces as lateral surfaces exposing the most stable pentacoordinated  $\text{Mg}^{2+}$  to minimize the coordinative vacancy. Besides, two terminal  $\text{Cl}^-$  anions were symmetrically placed at  $\text{Mg}^{2+}$  corners situated in a tetrahedral symmetry. In the presence of  $\text{TiCl}_4$ , the structure of  $\text{MgCl}_2$  was reconstructed in a way to expose  $\{110\}$  surfaces, and the  $\{110\}$  surfaces were necessarily capped by the  $\text{TiCl}_4$  molecules (Figure 2a).

Only monomeric species,  $\text{TiCl}_4$  bound the stronger undercoordinated  $\text{Mg}^{2+}$  was formed since the low concentration of  $\text{TiCl}_4$  (the Mg to Ti molar ratio is 50:3) prevents the formation of  $\text{TiCl}_4$  aggregates. This finding is in line with previous indications from Zerbi et al. (see Ref.<sup>36</sup>) and with the energy estimates reported in Refs. 9 and in Table S1 of Supported Information. Nevertheless, the fractions of the  $\text{Ti}_2\text{Cl}_8$  dimer and penta-coordinated  $\text{TiCl}_4$  at P sites are not completely negligible, but much smaller than that of the hexacoordinated  $\text{TiCl}_4$  at T sites. The fractions decrease of course along with the decrease in the Ti content. Bare  $50\text{MgCl}_2$  (hereafter simply referred to as  $\text{MgCl}_2$ ) and  $50\text{MgCl}_2/3\text{TiCl}_4$  nanoplates as derived from machine learning algorithm are sketched in Figure 1. For sake of clarity and because

of its relevance in the following discussion, the cluster obtained from 50MgCl<sub>2</sub>/3TiCl<sub>4</sub> after removal of the three TiCl<sub>4</sub> (hereafter referred to as MgCl<sub>2</sub>\*) is also reported in the Figure. The size of a nanocluster is about 37Å × 25Å.

The distribution of Mg<sup>2+</sup> ions in their different coordinations is described in Table 1 where pentacoordinated Mg<sup>2+</sup> ions typical of (012), (104), (015) surfaces are denoted as P sites and tetraordinated Mg sites typical of (110) surfaces as T sites. In the bare nanoplate the tetraordinated Mg<sup>2+</sup> ions (T) are about the 8 % of total exposed sites and are all isolated sites; in 50MgCl<sub>2</sub>\* the tetraordinated Mg<sup>2+</sup> ions amount to about 14 % (i.e.36.8% of total exposed sites) and mainly composed by couples of vicinal T sites; the hexacoordinated Mg<sup>2+</sup> ions form the largest part of total Mg<sup>2+</sup> ions amounting to 62%; the last part is formed by pentacoordinated Mg<sup>2+</sup> ions that forms 20% of the total sites; the minority of 4% of tetrahedral sites closes the list, see Table 1. The increase in the fraction of the T sites in MgCl<sub>2</sub>\* occurs mainly at the expense of the P sites and to the extent that this occurs, it is therefore the coordination of TiCl<sub>4</sub> that dictates the final shape of the nanoparticles.

The P sites belonging to different surfaces (listed above) can be easily identified in infinite models, but due to the finite nature of the clusters we cannot distinguish (or not properly can distinguish) different P sites present on nanoplatelet terminations.

The occurrence of tetraordinated Mg sites mainly upon reconstruction in presence of TiCl<sub>4</sub> supports the finding that in microcrystal the presence of the related (110) surface accounts for 1.4 % of the total exposed surface by means of previous Wulff polyhedron simulations.<sup>16</sup> The existence of several edges due to the combination of adjacent faces<sup>37,38</sup>, such as the (110)/(104), (110)/(012) and (110)/(015) were identified as possible interest for catalysis. In particular, the former (110)/(104) edge have been recently considered as a privileged site for strong TiCl<sub>4</sub> adsorption to generate a stereo-selective active site<sup>10,17</sup> bringing tetraordinated sites (T) close to pentacoordinated (P) ones; also in our models of MgCl<sub>2</sub> support the T sites with attached TiCl<sub>4</sub> molecules lie close to P sites.

Relative stabilities of nanoplates is evaluated by considering the cluster formation reaction starting from bulk MgCl<sub>2</sub> and gas phase TiCl<sub>4</sub>; the relative energy,  $E_{cluster}$ , has been computed from the calculated energy of a structure (E) according to the formula

$$E_{cluster} = E - N_{MgCl_2} \cdot E_{MgCl_2} - M_{TiCl_4} \cdot E_{TiCl_4} \quad (1)$$



where  $N_{\text{MgCl}_2}$  indicates the number of formula unit of  $\alpha\text{-MgCl}_2$  bulk and  $E_{\text{MgCl}_2}$  the relative electron energy whereas,  $M_{\text{TiCl}_4}$  is the number of  $\text{TiCl}_4$  molecules adsorbed on cluster with relative energy  $E_{\text{TiCl}_4}$  in gas phase.

Following the GA evolution (see Figures 1),  $50\text{MgCl}_2/3\text{TiCl}_4$  is more stable than the  $50\text{MgCl}_2$  bare nanocluster by about 170 kJ/mol. Thus the energy penalty to reconstruct in order to expose T sites (33 kJ/mol) is largely compensated by the  $\text{TiCl}_4$  adsorption energy (-203 kJ/mol, corresponding to -67.7 kJ/mol for each  $\text{TiCl}_4$ ), PBE results. PBE0-D3 calculations on the same clusters (including three bodies correction) provide a similar picture with a stabilization predicted in about 238 kJ/mol that is perfectly reasonable due to the inclusion of dispersion correction.

### B. Surface Lewis acidity of $\text{MgCl}_2$ nanoplatelet: probing by CO

Nanoplates presented in this work simulates nanostructured  $\text{MgCl}_2$ . Even still at the lower side of dimensional range of typical industrial samples it is large enough to show all possible catalytic sites. To characterize the Lewis acidity of the different exposed lateral sites in the nanoplate (exposed  $\text{Mg}^{2+}$  sites either belong to small terraces or are close to edges connecting different surfaces), the adsorption of CO on  $\text{MgCl}_2^*$  (with many different sites available for adsorption) has been studied. The proposed models of CO bound to different edge sites of the nanoplatelet are reported in Figure 3. The site indicated as A corresponds to a tetracoordinated  $\text{Mg}^{2+}$  ion of the kind exposed by (110) surfaces but close to a tetrahedral  $\text{Mg}^{2+}$  one. In the panel B of the same figure, the tetracoordinated  $\text{Mg}^{2+}$  ion is the one typical of (110) families of surfaces i.e. close to another analogous tetracoordinated  $\text{Mg}^{2+}$  ion but on the other side close to a row of pentacoordinated  $\text{Mg}^{2+}$  ions that is at the edge of the type (110)/(104). Panel C hosts the model for a CO molecule adsorbed on a tetrahedral  $\text{Mg}^{2+}$  ion; the D model represents a CO molecule adsorbed on a pentacoordinated  $\text{Mg}^{2+}$  ion but still at the edge pentacoordinated  $\text{Mg}^{2+}$ /tetracoordinated  $\text{Mg}^{2+}$  whereas the model E reports the adsorption on a pentacoordinated  $\text{Mg}^{2+}$  of the kind of sites of both (104) and (107) families of planes. Finally, to see whether CO frequency can be perturbed by a  $\text{TiCl}_4$  adsorbed in the proximity, CO has been adsorbed at an edge of the type (110)/(104), sharing the T site with  $\text{TiCl}_4$  (model F).

All data are collected in Table 2 including (only for binary CO/MgCl<sub>2</sub> systems) results from regular surfaces exposing Mg atoms with the same coordination number (from periodic 2D calculations). In this latter case isolated CO adsorption (degree of coverage equal to 0.25) has been considered for a one-to-one comparison with the nanoplate sites.

The thermochemical analysis performed at 100 K reveals that, in agreement with the experimental observation, the CO adsorption energy is rather weak on all the sites also at 100 K and, as expected, the interaction is stronger with the tetra-coordinated ones. The Gibbs free energy of adsorption,  $\Delta G_{ads}$  is about -25 kJ/mol on sites A, B and about -20 kJ/mol on sites D and E. The difference between tetra and pentacoordinated site is indeed small (less than 5 kJ/mol) but enough to recognize a significantly different chemical response from the two types of Mg<sup>2+</sup> ions.

The formation of mono-carbonyl species is characterized by a relevant polarization that red shifts the CO stretching frequency.  $\Delta\nu$  is 74 cm<sup>-1</sup> for sites A and B and  $\sim$  62 cm<sup>-1</sup> for sites D and E respectively (they differ only by 2 cm<sup>-1</sup>). Thus, these two groups of sites exhibit different Lewis acidity, and as expected T Mg<sup>2+</sup> are stronger Lewis acid than the P ones. The CO red shift is 72 cm<sup>-1</sup> for site F, in this case we can argue that due to polarizing effect of adsorbed TiCl<sub>4</sub> the pentacoordinated Mg<sup>2+</sup> behaves as the sites A and B instead of P type sites as proved by both the enthalpy ( $\Delta E_{ads} = -42.3$  kJ/mol) and the shift in CO ( $\Delta\nu=71.3$  cm<sup>-1</sup>) absorption frequency. That may justify the fact that, after reaction with TiCl<sub>4</sub>, the IR absorption band falling at high wavenumbers and assigned to CO adsorbed on highly polarizing surfaces (i.e. (110), (015), and/or on the (012) surface) greatly decreases in intensity but it does not disappear completely, maybe due to the presence of local adducts indicated as type F in Fig.3.

On regular surfaces the trend on energies and frequencies is similar to that found for the nanocluster:  $\Delta G_{ads}$  is about -18/-14 kJ/mol on 107 and 104 surfaces (D and F sites) and  $\sim$  -14.5 kJ/mol on 110 planes (A and B sites).  $\Delta\nu$  is  $\sim$  54 cm<sup>-1</sup> on 107 and 104 surfaces and  $\sim$  64 cm<sup>-1</sup> on 110.  $\Delta\nu$  for CO adsorbed at T nanoplate sites is larger than that obtained on a surface homologous (110) by about 15 cm<sup>-1</sup> (both the A and B sites behaves that way), while by about 8-10 cm<sup>-1</sup> for P nanoplate sites as compared to the shift on (107) and (104). On the basis of presented results we can conclude that CO molecules on nanoplates:

i) can successfully probe T sites but cannot distinguish between T sites in different environments (i.e. between isolated or adjacent sites); in addition in the presence of TiCl<sub>4</sub>, the

stretching frequency of a CO molecule adsorbed in its proximity is close to a signal from a T site (they differ by  $2\text{ cm}^{-1}$ ); that justifies the fact that after reaction with  $\text{TiCl}_4$ , the IR absorption band falling at high wavenumbers and assigned to CO adsorbed on highly polarizing surfaces (i.e. (110), (015), and/or on the (012) surface) greatly decreases in intensity but it does not disappear completely, maybe for the presence of local adducts indicated as type F in Figure 3;

ii) the non-negligible increases of adsorption energies and frequencies values on nanoplate sites, reveal the presence of stronger acidic sites on highly nanostructured support of activated catalysts with respect to the homologous surface sites.

For sake of completeness, the adsorption on site C (tetrahedral  $\text{Mg}^{2+}$ ) has been also modeled although tetrahedral terminations did not emerge in surface studies.

### C. IR and Raman response of $\text{TiCl}_4$ on nanoplatelet: naked vs. covered

We considered the naked nanoplatelet and the  $50\text{MgCl}_2/3\text{TiCl}_4$  adduct obtained by GA, the platelet  $\text{MgCl}_2^*$  and its  $\text{TiCl}_4$  on site B and both  $\text{Ti}_2\text{Cl}_8$  and  $\text{TiCl}_4$  on site E. All that aiming at a reexamination of the mononuclear adsorption of  $\text{TiCl}_4$  on (110)  $\text{MgCl}_2$  surfaces, the mononuclear on  $\text{MgCl}_2$  (104), as well as dinuclear adsorption on  $\text{MgCl}_2$  (104); the last three cases correspond to those proposed by Corradini as possible precursors of active species. For all the above-mentioned cases the thermodynamics of adsorption has been carried out by means of B3LYP-D2 method we adopted all along the paper, also M06 and PBE0-D3 results are reported in table S1 in Supplementary Information Section. For most plausible catalytic species (according to traditional literature)  $\text{Ti}_2\text{Cl}_8$  and  $\text{TiCl}_4$  on site E spectroscopic simulations, both IR and Raman have been performed. In the case of dimer even though, at the adopted ratio N/M between  $\text{MgCl}_2$  formula units and  $\text{TiCl}_4$  molecules, GA and previous  $\Delta G_{ads}$  estimates may reasonably exclude the occurrence of that site, we performed spectroscopic studies to identify possible features typical of that way of binding particularly in relation with monomeric  $\text{TiCl}_4$  fingerprint on tetracoordinated site. In the following subsections, we analyze to which extent exposed tetracoordinated and pentacoordinated Mg sites are distinguishable in IR and/or Raman spectra and the effect of adsorption of different precatalytic complex  $\text{Ti}_x\text{Cl}_y$  on those bands, to discuss whether or not it is possible to obtain an indirect vibrational evidence of the presence of precatalytic

species on specific sites.

1. *Vibrational characterization of tetrahedral  $TiCl_4$*

Gas phase molecule ( $T_d$  point group) shows nine vibrational modes; we discuss the relevant frequencies: a triple degenerate  $F_2$  mode at  $516\text{ cm}^{-1}$  (experimental  $500\text{ cm}^{-1}$  for liquid  $TiCl_4$ ) active in Raman (weak) and Far-IR (strong), the totally symmetric  $A_1$  mode at  $405\text{ cm}^{-1}$  (exp.  $396\text{ cm}^{-1}$ ), Raman active and very strong as generally expected for  $A_1$  modes in Raman, the  $F_2$  mode at  $146\text{ cm}^{-1}$  (exp.  $143\text{ cm}^{-1}$ ), very weak in IR and medium in Raman, the doubly degenerate  $E$  mode at  $121\text{ cm}^{-1}$  (experimental  $119\text{ cm}^{-1}$ ) active only in Raman (medium).

2. *IR characterization of  $MgCl_2$  and  $MgCl_2/TiCl_4$*

The vibrational spectrum of naked nanoplatelets  $50MgCl_2$  and  $50MgCl_2^*$  are reported in Figure 4 (top panels). The spectrum extends from  $200$  to  $550\text{ cm}^{-1}$ . In the spectrum we can clearly identify a low wave-number region in the range  $235$ - $360\text{ cm}^{-1}$  that comes from bulk modes. Although this spectral region appears strongly dependent on the shape of the nanoplate, on the number and type of edge ions (compare spectra of  $MgCl_2$  and  $MgCl_2^*$  reported in Figure 4), some common features can be recognized:

- i) a region between  $250$ - $270\text{ cm}^{-1}$  (a tail in the spectra of Figures 4) mainly due to vibrations involving hexacoordinate ions;
- ii) a strong peak at  $275$ - $280\text{ cm}^{-1}$  and a couple of weak signals at  $328$  and  $340\text{ cm}^{-1}$  due to bulk-like modes coupled with vibrations of T and P sites.

The spectral region between  $360$  and  $500\text{ cm}^{-1}$  is instead not shape dependent. The vibrational analysis of this region permits to attribute distinctive features to P and T  $Mg^{2+}$  ions:

- iii) the modes in the range  $382$  - $398\text{ cm}^{-1}$  with a maximum at  $393\text{ cm}^{-1}$  are due to the movement that brings closer the two Mg of a four-membered Mg-Cl-Mg-Cl cycles, this mode can be easily compared to vibration falling at  $393\text{ cm}^{-1}$  typical of (104) surfaces;
- iv) the modes falling at  $429\text{ cm}^{-1}$  and at  $436$ - $459\text{ cm}^{-1}$  with a maximum at  $445\text{ cm}^{-1}$  typical of tetraordinated  $Mg^{2+}$  ions (absorption at  $435\text{ cm}^{-1}$  is present in the case of

(110) surfaces). Notice the larger intensity of the  $445\text{ cm}^{-1}$  band for  $50\text{MgCl}_2^*$ , consistent with the larger fraction of the T site as compared to  $50\text{MgCl}_2$ .

To complete the picture we find that the Mg-Cl stretching of a tetrahedral termination falls at  $493\text{ cm}^{-1}$ .

Simulated IR spectrum of  $\text{TiCl}_4$  adsorption on T site of  $50\text{MgCl}_2$  and  $50\text{MgCl}_2^*$ , are reported in the bottom panels of Figure 4. In both cases we analyze only the spectral regions of interest for Ti species and omit to explain about the bands associated to bulk movements. The presence of  $\text{TiCl}_4$  produces:

- v) a reduction of the intensity of the band at  $448\text{ cm}^{-1}$  related to tetracoordinated  $\text{Mg}^{2+}$  and concomitantly the appearance of two new bands at  $465$  and  $485\text{ cm}^{-1}$ , associated to the symmetric and antisymmetric stretching of the Ti-Cl bonds derived from the F2 mode at  $500\text{ cm}^{-1}$  that splits into more components due to the symmetry reduction;
- vi) the band at  $429\text{ cm}^{-1}$  associated to isolated T sites remains unperturbed;
- vii) an increase of the intensity of the signals in the region between  $311\text{ cm}^{-1}$  and  $322\text{ cm}^{-1}$  due to both symmetric and antisymmetric stretching of the bonds formed between the Cl atoms of  $\text{TiCl}_4$  and the anchoring Mg atoms of the support;
- viii) the appearance of an extra weak band at  $278\text{ cm}^{-1}$  can be due to a frustrated rocking of  $\text{TiCl}_4$  moiety on support.

The findings are in agreement with infrared transmission spectra of  $\text{MgCl}_2/\text{TiCl}_4$  precatalyst reported by Ystenes<sup>39</sup> where distinct bands near  $450\text{ cm}^{-1}$  appear.

### 3. Raman characterization of $\text{MgCl}_2$ and $\text{MgCl}_2/\text{TiCl}_4$

Unlike IR spectra, Raman spectra appear much less sensitive to the nanoplate shape. By comparing spectra of  $50\text{MgCl}_2$  and  $50\text{MgCl}_2^*$  (see panels a and c of Figure 5) we see that they are characterized by similar signals:

- i) a very weak mode at  $161\text{ cm}^{-1}$  together with other weak and unidentified lines in the  $100\text{-}200\text{ cm}^{-1}$  range all due to bulk movements;
- ii) a very intense peak at  $263\text{-}267\text{ cm}^{-1}$  and a slightly less intense one at  $\sim 300\text{ cm}^{-1}$  due to bulk and terminations models coupled together (a very strong band at  $243\text{ cm}^{-1}$  and a weak band at  $157\text{ cm}^{-1}$ , were also identified by Zerbi et al.<sup>36</sup> for naked ball-milled  $\text{MgCl}_2$

particles);

iii) a weak mode at  $384\text{ cm}^{-1}$  (termination modes);

iv) signals at  $429$  and  $445\text{ cm}^{-1}$  (assigned to T mode in the IR spectra) are here hardly detectable because of their very low intensity.

Upon  $\text{TiCl}_4$  adsorption the Raman spectra undergo a spectacular change (bottom panels in Figure 5): the bulk modes at  $161\text{ cm}^{-1}$ ,  $263\text{-}267\text{ cm}^{-1}$  (bulk and terminations) and  $384\text{ cm}^{-1}$  (termination modes) drastically reduce their intensities and two new intense lines appear at  $465$  and  $484\text{ cm}^{-1}$ . Zerbi<sup>36</sup> et al. identified similar bands for a ball-milled  $\text{TiCl}_4/\text{MgCl}_2$  precatalyst. In particular they reported two weak signals at  $157$  and  $243\text{ cm}^{-1}$  and two neat lines at  $449$  and  $464\text{ cm}^{-1}$ ; the latter lines were assigned to the  $\text{TiCl}_4$  F2 mode also Raman active. Thus, the  $\text{TiCl}_4$  symmetric and antisymmetric stretchings, very weak in IR spectra, appear as the dominant bands in the Raman spectra providing indeed an unambiguous fingerprint of the presence of the adduct.

The effect of  $\text{TiCl}_4$  coverage (compare  $50\text{MgCl}_2/3\text{TiCl}_4$  and  $50\text{MgCl}_2^*/\text{TiCl}_4$  spectra, panels b and d in Figure 5) can be easily traced by comparing the relative intensities of the bulk like bands (in the  $260\text{-}300\text{ cm}^{-1}$  spectral region) and the intensities of the  $\text{TiCl}_4$  signals; note in addition the almost complete annihilation of the  $384\text{ cm}^{-1}$ , irrespective of the  $\text{TiCl}_4$  coverage.

#### 4. IR and Raman characterization of $\text{Ti}_2\text{Cl}_8$ dimer

We modeled  $\text{Ti}_2\text{Cl}_8$  on site E; the simulated IR and Raman spectra are reported in Figure 6. We focus on the  $450\text{-}495\text{ cm}^{-1}$  spectral region where the signals from the monomeric species were observed (a detailed analysis of the spectra is reported in the Supplementary Information). In IR spectrum,  $\text{Ti}_2\text{Cl}_8$  produces a triplet of bands at  $458$ ,  $476$ ,  $495\text{ cm}^{-1}$  that, although of low intensity, can eventually overlap those of the monomer. A set of three intense bands is also observed in Raman, at  $458$ ,  $476$  and  $495\text{ cm}^{-1}$  but redshifted by  $\sim 10\text{ cm}^{-1}$  with respect to  $\text{TiCl}_4$  vibrations; thus, the Raman features of the two adducts appear distinguishable from each other as they differ in shape and frequency values.

## IV. CONCLUSIONS

Model nanoclusters of naked  $\text{MgCl}_2$  and  $\text{MgCl}_2/\text{TiCl}_4$  support have been obtained by means of a non-empirical structure determination method exploiting an evolutionary algorithm. The bare 50  $\text{MgCl}_2$  predominantly exposes pentacoordinated sites (P) of the kind of  $\text{Mg}^{2+}$  sites typically exposed by (104), (107) (012) surfaces and isolated tetraordinated sites (T). In the presence of  $\text{TiCl}_4$ , a significant increase in the fraction of T sites is found in 50 $\text{MgCl}_2/3\text{TiCl}_4$  system, T sites are present as isolate site but mostly as couples and close to rows of P sites. The couple of adjacent T sites allows the binding of  $\text{TiCl}_4$  molecules in octahedral geometry locally repropounding the edges between adjacent faces exposing pentacoordinated and tetraordinated  $\text{Mg}^{2+}$  ions, respectively. Those features represent the topological preconditions to generate favourite sites for strong  $\text{TiCl}_4$  adsorption (such as the (110)/(104), (110)/(012) and (110)/(015) as reported in previous literature).

The proposed model sites, probed by CO, satisfy the requirement of the well-assessed existence of multiple sites (i.e. P and T sites) in the catalytic mixtures and, at the same time, the superposition of vibrational responses of multiple sites differing by only few  $\text{cm}^{-1}$ , is perfectly in line with the presence of two bands differing about 20  $\text{cm}^{-1}$  in FT-IR spectra in the  $\nu(\text{CO})$  region on ball-milled  $\text{MgCl}_2$  samples. CO molecules on nanoplates can successfully probe T sites but cannot distinguish between T sites in different environment (that is between isolated or adjacent sites); the non-negligible increases of adsorption enthalpies and frequencies shifts on nanoplate sites (by 15-20  $\text{cm}^{-1}$ ), reveal the presence of stronger acidic sites on highly nanostructured support with respect to the homologous ideal surfaces.

The outcomes of IR and even more of Raman simulations on  $\text{MgCl}_2/\text{TiCl}_4$  molecular clusters appear to be of pivotal importance. In IR spectra, the presence of  $\text{TiCl}_4$  mainly causes the reduction of the intensity of the band at 448  $\text{cm}^{-1}$  related to couples of tetraordinated  $\text{Mg}^{2+}$  and concomitantly the appearance of two new bands at 465 and 485  $\text{cm}^{-1}$ , associated to the symmetric and antisymmetric stretching of the Ti-Cl bonds. The bands are well separated from those of both isolated  $\text{TiCl}_4$  and bare  $\text{MgCl}_2$  but unfortunately, they are very weak in Far-IR spectra in comparison with the vibrations of the support. On the contrary in Raman spectra, the two very intense lines of  $\text{TiCl}_4$  at 465 and 485  $\text{cm}^{-1}$ , appear as the dominant bands providing indeed an unambiguous fingerprint of the presence of the adduct. Indeed, the aforementioned bands at 465  $\text{cm}^{-1}$  and 485  $\text{cm}^{-1}$  due to the symmetric and

antisymmetric stretching of the two "terminal Chlorines" bound to Titanium undoubtedly allow us to identify the presence of  $\text{TiCl}_4$  with an octahedral coordination on a tetracoordinated  $\text{Mg}^{2+}$  in really nanostructured samples of ZN catalysts, in fact they fall in a spectral region that is far from both bulk modes and organic functional groups like the ones adopted as internal and external donors. When we pass to dimer  $\text{Ti}_2\text{Cl}_8$  on P sites again the Raman spectrum is highly informative, that can be particularly ascribed to the Ti-Cl-Ti bridges. The features of monomeric and dimeric adducts are different in shapes and are also well separated by about  $10\text{ cm}^{-1}$ .

The present manuscript provides strong evidence that structural and vibrational simulation of catalysts, by means of truly nanosized models together with machine learning methodology is a powerful tool to establish, at the atomic level, the occurrence of catalytic sites mainly when they reside at defective positions i.e. terminations and edges between "perfect surfaces", to better establish the acidity of multiple sites and to discriminate different catalytic adducts.

The accuracy of the simulated data, the reliability and the easily affordable cost of the calculation by machine learning algorithms support this new combined methodology.



## Supporting Information

Details of the adopted DFT methodology. Adsorption energies through other density functionals and complementary material for spectroscopic characterization of  $\text{Ti}_2\text{Cl}_8$  dimer.

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## Figures

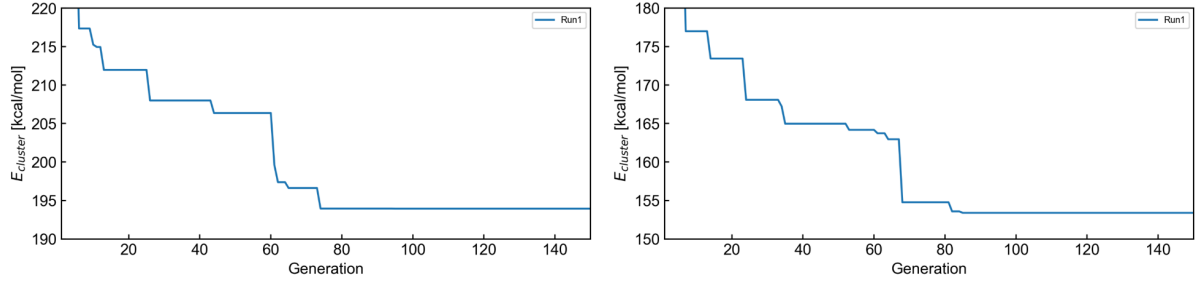


FIG. 1: Evolutionary progress plot for the structure determination of naked  $50\text{MgCl}_2$  (left panel) and  $50\text{MgCl}_2/3\text{TiCl}_4$  (right panel). The energy of the best-of-generation individual (i.e., the most stable structure in a generation) is plotted against the generation.

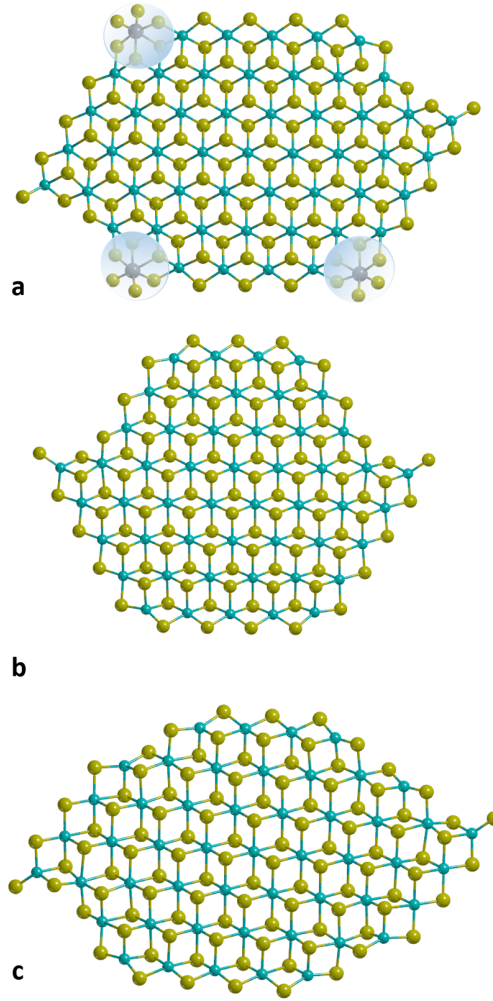


FIG. 2: Nanoplatelet with three adsorbed  $\text{TiCl}_4$  moieties ( $50\text{MgCl}_2/\text{TiCl}_4$ ) as obtained by machine learning methodology described in the text (panel a); model of naked  $\text{MgCl}_2$  nanoplatelet obtained by the same methodology without  $\text{TiCl}_4$  ( $50\text{MgCl}_2$ ) (panel b); nanoplatelet obtained by the first one after removal of the three adsorbed  $\text{TiCl}_4$  moieties ( $50\text{MgCl}_2^*$ ) (panel c). Structures have been optimized at B3LYP-D2/TZVP level. Chlorine, Magnesium and Titanium atoms are shown in green, yellow and dark grey, respectively. In panel a terminations exposing 4-coordinated  $\text{Mg}^{2+}$  sites as the ones belonging to (110) covered by  $\text{TiCl}_4$  in octahedral coordination are enclosed in shaded spheres.

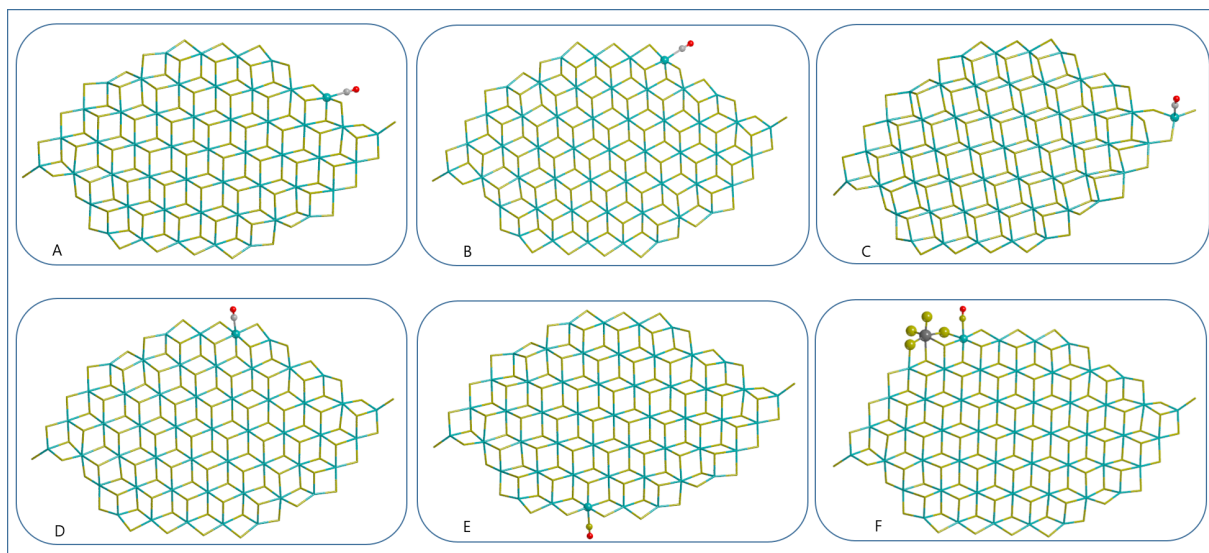


FIG. 3: Optimized CO probed  $\text{MgCl}_2$  nanoplates ( $50\text{MgCl}_2^*$  cluster with CO adsorbed on different sites), minima are reported for each unsaturated site of  $\text{Mg}^{2+}$ . Chlorine and Magnesium atoms are shown in green and yellow colors, respectively. C, O atoms of adsorbed CO are shown in black and red respectively, they are represented as balls along with the adsorbing  $\text{Mg}^{2+}$  site. All the rest of atoms belonging to nanoplatelet and not involved in the adsorption process are represented as sticks. (A) CO adsorption on tetra-coordinated 110-like  $\text{Mg}^{2+}$  and next to a tetrahedral site. CO adsorbed on 110-like  $\text{Mg}^{2+}$  model is reported in (B) and on tetrahedral site in (C). Model of CO adsorption on penta-coordinated  $\text{Mg}^{2+}$  close to tetra-coordinated 110-like  $\text{Mg}^{2+}$  (D) and penta-coordinated  $\text{Mg}^{2+}$  (E). Panel (F) sketches the adsorption of CO close to an adsorbed  $\text{TiCl}_4$  in its octahedral configuration. All calculations were done by employing B3LYP functional including D2 type correction and TZVP basis set and QZVP type basis set on CO moiety.

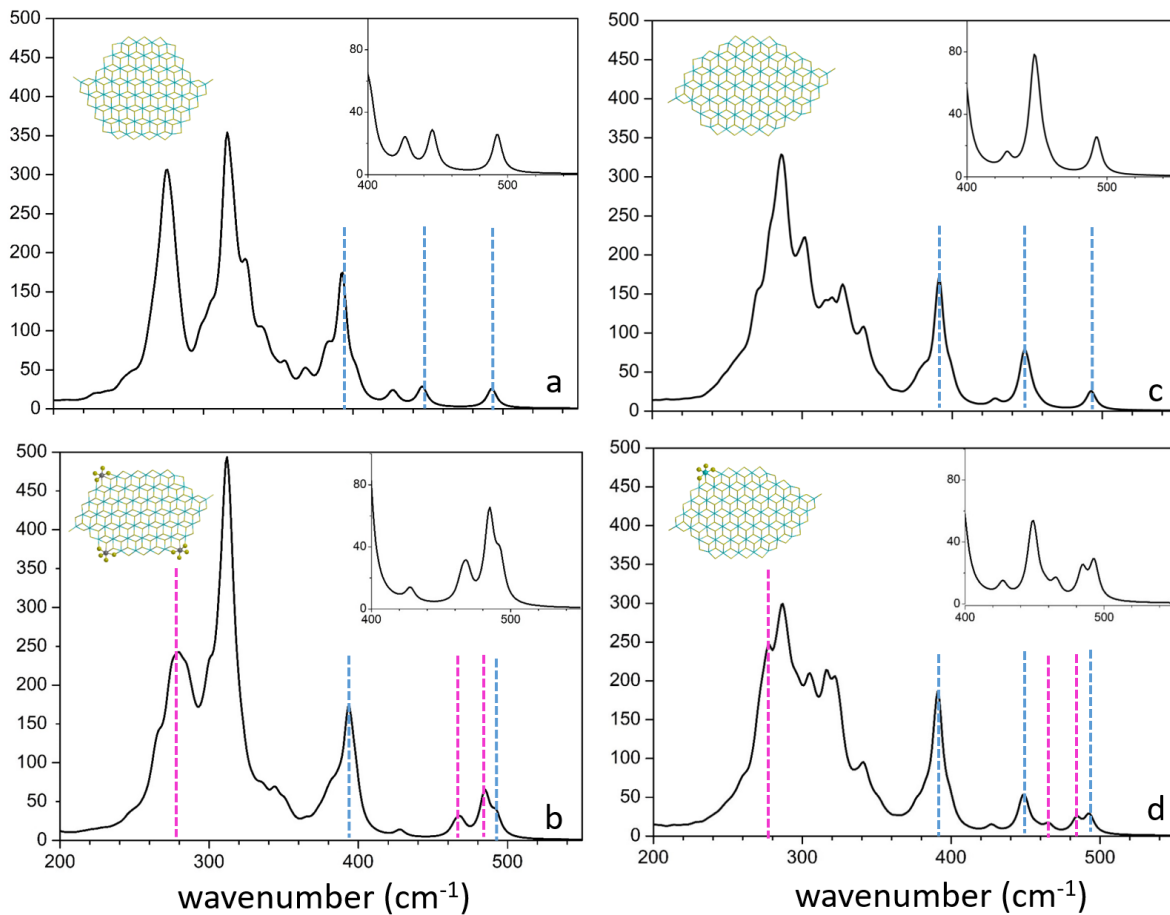


FIG. 4: Simulated IR spectra at B3LYP-D2/TZVP level of calculation of: both naked nanoplatelet and  $50\text{MgCl}_2/\text{TiCl}_4$  system as obtained by genetic algorithm (a and b panels respectively); naked cluster reoptimized after removal of the three  $\text{TiCl}_4$  molecules ( $50\text{MgCl}_2^*$ ) and with one  $\text{TiCl}_4$  molecule adsorbed on site B of the same cluster (c and d panels respectively). Peaks of interest discussed in the text are indicated by dashed lines: in blue color for support modes, pink for typical  $\text{TiCl}_4$  modes, respectively. The insets in each graph clearly report data in the range of frequency  $400 - 550 \text{ cm}^{-1}$ . Simple models of adducts are also reported: atoms belonging to the nanoplatelet and not involved in the adsorption process are represented as sticks whereas atoms of  $\text{TiCl}_4$  molecules as balls; Chlorine and Titanium atoms are shown in green and dark grey, respectively.

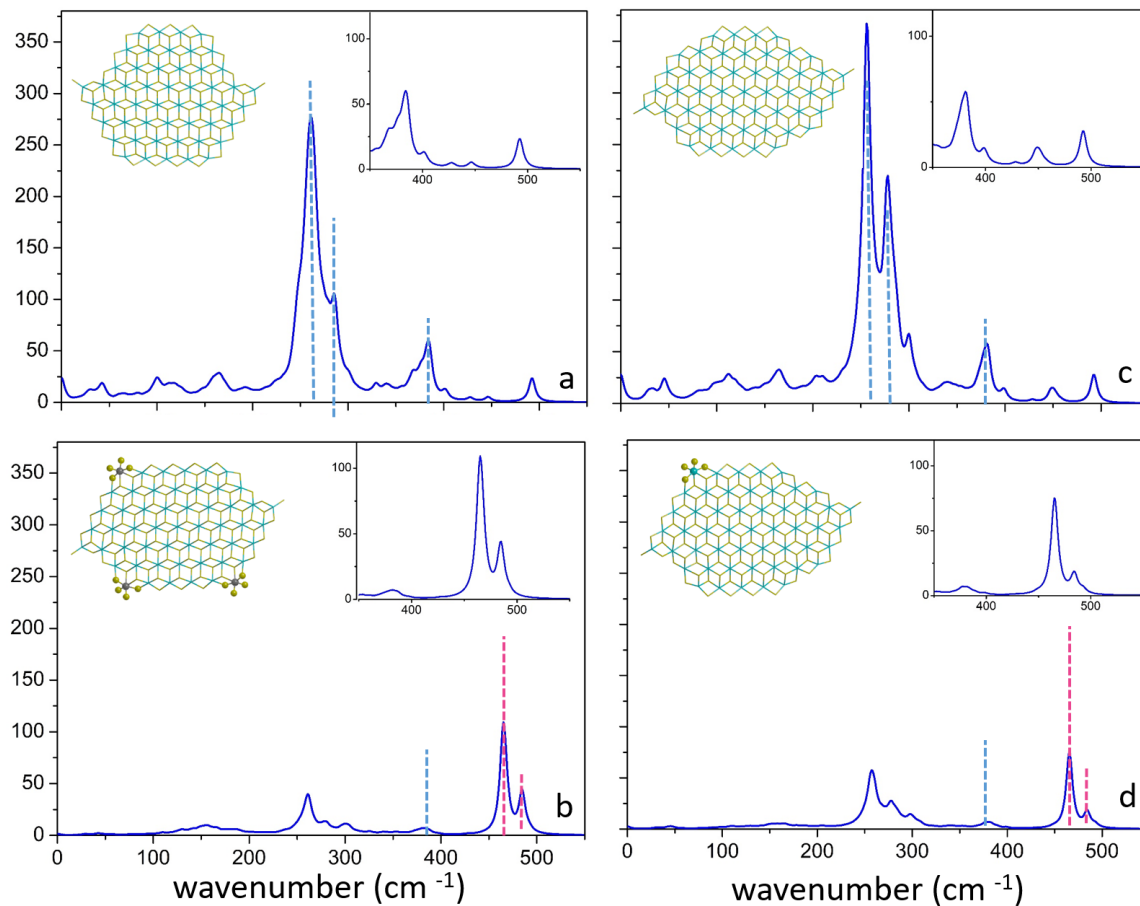


FIG. 5: Simulated Raman spectra at B3LYP-D2/TZVP level of calculation of: naked 50  $\text{MgCl}_2$  cluster (panel a) and  $50\text{MgCl}_2/3\text{TiCl}_4$  (i.e. 3  $\text{TiCl}_4$  molecules chemisorbed on type-B sites of the cluster) (panel b) as obtained by genetic algorithm;  $50\text{MgCl}_2^*$  (panel c) and  $50\text{MgCl}_2^*/1\text{TiCl}_4$  (i.e. one  $\text{TiCl}_4$  molecule chemisorbed on type-B sites of the cluster) (panel d). Simple models of adducts are also reported: atoms belonging to the nanoplatelet and not involved in the adsorption process are represented as sticks whereas atoms of  $\text{TiCl}_4$  molecules as balls; Chlorine and Titanium atoms are shown in green and dark grey, respectively.

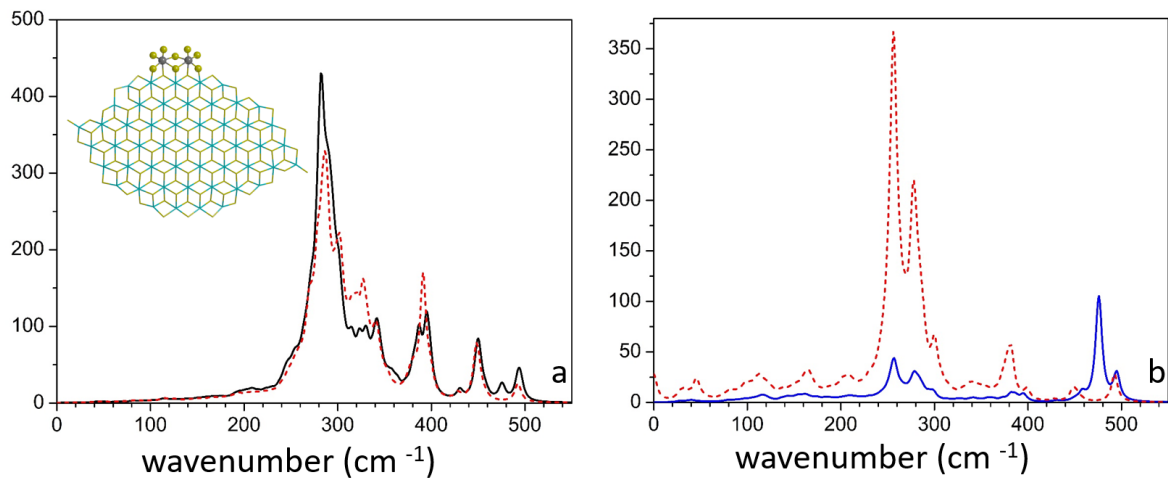


FIG. 6: Simulated IR (panel a) and Raman (panel b) spectra at B3LYP-D2/TZVP level of calculation of the dimer  $\text{Ti}_2\text{Cl}_8$  epitactically bound to site E of  $50\text{MgCl}_2^*$  cluster. In each panel the response relative to naked nanocluster is also reported in dashed red line.



## Tables

TABLE I: Distribution of  $\text{Mg}^{2+}$  cations with different coordination numbers or symmetry, after removing  $\text{TiCl}_4$  in structures reported in Fig.1. The system indicated as  $50\text{MgCl}_2^*$  corresponds to the  $50\text{MgCl}_2/\text{TiCl}_4$  after removing the 3  $\text{TiCl}_4$  molecules in the cluster reported in Fig.1, panel a.

System	distribution of $\text{Mg}^{2+}$ cations (%)			
	$T_d$	4-fold	5-fold	6-fold
$50\text{MgCl}_2$	4	8	30	58
$50\text{MgCl}_2/\text{TiCl}_4$ ( $50\text{MgCl}_2^*$ )	4	14	20	62
Difference	0	6	-10	4

TABLE II: Energetics of CO adsorption on each cluster site as reported in Fig.1 (energies in kJ/mol) ( $G$  at 100 K). Predicted shift  $\Delta\nu(\text{CO})$  in  $\text{cm}^{-1}$  with respect to  $\nu(\text{CO})$  in gas phase and computed intensity (Km/mol) for CO molecule adsorbed on different  $50\text{MgCl}_2^*$  cluster. At the employed level of computation, we predicted for the A mode  $\nu(\text{CO})=2201.3 \text{ cm}^{-1}$  in gas phase and Intensity= 78.45 Km/mol. In the case F the reference structure is the nanoplatelet with one  $\text{TiCl}_4$  molecule adsorbed on site B. The results are compared with those obtained on regular surfaces. All calculations were done by employing B3LYP functional including D2 type correction and TZVP basis set and QZVP type basis set on CO moiety.

Site	$\Delta E_{ads}$	$\Delta G_{ads}$	$\Delta\nu$	Intensity	surfaces	$\Delta E_{ads_{surf}}$	$\Delta G_{ads_{surf}}$	$\Delta\nu$
A	-41.7	<b>-25.5</b>	73.9	87.7	(110)	-40.2	-14.5	63.8
B	-41.3	<b>-25.1</b>	73.6	86.1				
C	-31.8	<b>-16.7</b>	61.5	93.7	-	-	-	-
D	-36.5	<b>-20.8</b>	63.6	104.5	(104),(107)	-41.0,-47.2	-13.9,-18.1	53.6,54.2
E	-36.2	<b>-20.3</b>	61.8	105.8	(104),(107)	-41.0,-47.2	-13.9,-18.1	53.6,54.2
F	-42.3	<b>-25.6</b>	71.3	81.9	-	-	-	-

## References

- <sup>1</sup> Correa, A.; Bahri-Laleh, N.; Cavallo, L. How Well Can DFT Reproduce Key Interactions in Ziegler–Natta Systems? *Macromol. Chem. Phys.* **2013**, *214*, 1980–1989.
- <sup>2</sup> Corradini, P.; Barone, V.; Fusco, R.; Guerra, G. Analysis of models for the Ziegler-Natta stereospecific polymerization on the basis of non-bonded interactions at the catalytic site—I. The Cossee model. *Eur. Polym. J.* **1979**, *15*, 1133–1141.
- <sup>3</sup> Boero, M.; Parrinello, M.; Terakura, K. First Principles Molecular Dynamics Study of Ziegler-Natta Heterogeneous Catalysis. *J. Am. Chem. Soc.* **1998**, *120*, 2746–2752.
- <sup>4</sup> Boero, M.; Parrinello, M.; S. Hüffer, S.; Weiss, H. First Principles Study of Propene Polymerization in Ziegler-Natta Heterogeneous Catalysis. *J. Am. Chem. Soc.* **2000**, *122*, 501–509.
- <sup>5</sup> Monaco, G.; Toto, M.; Guerra, G.; Cavallo, L. Geometry and stability of titanium chloride species adsorbed on the (100) and (110) cuts of the MgCl<sub>2</sub> support of the heterogeneous Ziegler-Natta catalysts. *Macromolecules* **2000**, *33*, 8953–8962.
- <sup>6</sup> Boero, M.; Parrinello, M.; Weiss, H.; Hüffer, S. A First Principles Exploration of a Variety of Active Surfaces and Catalytic Sites in Ziegler-Natta Heterogeneous Catalysis. *J. Phys. Chem. A* **2001**, *105*, 5096–5105.
- <sup>7</sup> Seth, M.; Margl, P. M.; Ziegler, T. A Density Functional Embedded Cluster Study of Proposed Active Sites in Heterogeneous Ziegler-Natta Catalysts. *Macromolecules* **2002**, *35*, 7815–7829.
- <sup>8</sup> Taniike, T.; Terano, M. Reductive Formation of Isospecific Ti Dinuclear Species on a MgCl<sub>2</sub> (110) Surface in Heterogeneous Ziegler-Natta Catalysts. *Macromolecular rapid communications* **2008**, *29*, 1472–1476.
- <sup>9</sup> D’Amore, M.; Credendino, R.; Budzelaar, P. H. M.; Causá, M.; Busico, V. A Periodic Hybrid DFT Approach (Including Dispersion) to MgCl<sub>2</sub>-supported Ziegler-Natta catalysts 1:TiCl<sub>4</sub> Adsorption on MgCl<sub>2</sub> Crystal Surfaces. *J. Catal.* **2012**, *286*, 103–110.
- <sup>10</sup> Breuza, E.; Antinucci, G.; Budzelaar, P. H. M.; Busico, V.; Correa, A.; Ehm, C. MgCl<sub>2</sub>-supported Ziegler-Natta catalysts: A DFT-D ‘flexible-cluster’ approach. TiCl<sub>4</sub> and probe donor adducts. *Int. J. Quantum Chem.* **2018**, *118*, e25721.
- <sup>11</sup> Breuza, E.; Antinucci, G.; Budzelaar, P. H. M.; Busico, V.; Correa, A.; Ehm, C. MgCl<sub>2</sub>-Supported Ziegler–Natta Catalysts: a DFT-D “Flexible-Cluster” Approach to Internal Donor Adducts. *J. Phys. Chem. C* **2018**, *122*, 9046–9053.

- <sup>12</sup> Capone, F.; Rongo, L.; D'Amore, M.; Budzelaar, P. H. M.; Busico, V. A Periodic Hybrid DFT Approach (Including Dispersion) to MgCl<sub>2</sub>-supported Ziegler-Natta catalysts 2: Model Electron Donor Adsorption on MgCl<sub>2</sub> Crystal Surfaces. *J. Phys. Chem. C* **2013**, *117*, 24345–24353.
- <sup>13</sup> Credendino, R.; Pater, J. T. M.; Correa, A.; Morini, G.; Cavallo, L. Thermodynamics of Formation of Uncovered and Dimethyl Ether Covered MgCl<sub>2</sub> Crystallites. Consequences in the Structure of Ziegler-Natta Heterogeneous Catalysts. *J. Phys. Chem. C* **2011**, *115*, 13322–13328.
- <sup>14</sup> D'Amore, M.; Thushara, K.; Piovano, A.; Causá, M.; Bordiga, S.; Groppo, E. Surface Investigation and Morphological Analysis of Structurally Disordered MgCl<sub>2</sub> and MgCl<sub>2</sub>/TiCl<sub>4</sub> Ziegler-Natta Catalysts. *ACS Catal.* **2016**, *6*, 5786–5796.
- <sup>15</sup> Wada, T.; Takasao, G.; Piovano, A.; D'Amore, M.; Thakur, A.; Chammingkwan, P.; Bruzzese, P. C.; Terano, M.; Civalleri, B.; Bordiga, S.; et al. Revisiting the Identity of  $\delta$ -MgCl<sub>2</sub>: Part I. Structural Disorder Studied by Synchrotron X-Ray Total Scattering. *J. Catal.* **2020**, *385*, 76–86.
- <sup>16</sup> Piovano, A.; D'Amore, M.; Wada, T.; Bruzzese, P. C.; Takasao, G.; Thakur, A.; Chammingkwan, P.; Terano, M.; Civalleri, B.; Bordiga, S.; et al. Revisiting the Identity of  $\delta$ -MgCl<sub>2</sub>: Part II. Morphology and Exposed Surfaces Studied by Vibrational Spectroscopies and DFT Calculation. *J. Catal.* **2020**, *387*, 1–11.
- <sup>17</sup> Credendino, R.; Liguori, D.; Fan, Z.; Morini, G.; Cavallo, L. A Unified Model Explaining Heterogeneous Ziegler-Natta Catalysis. *ACS Catal.* **2015**, *5*, 5431–5435.
- <sup>18</sup> D'Amore, M.; Piovano, A.; Vottero, E.; Rudic, S.; Groppo, E.; Bordiga, S.; Civalleri, B. Insights on inelastic neutron scattering data of MgCl<sub>2</sub> ZN-catalyst support from *ab initio* modelling of nano-sized and disordered models. *ACS Appl. Nano Mater.* **2020**, *3*, 11118–11128.
- <sup>19</sup> Thushara, K.; D'Amore, M.; Piovano, A.; Bordiga, S.; Groppo, E. The Influence of Alcohols in Driving the Morphology of Magnesium Chloride Nanocrystals. *ChemCatChem* **2017**, *9*, 1782–1787.
- <sup>20</sup> Zakharov, V.; Paukshtis, E. A.; Mikenas, T. B.; Volodin, A. M.; Vitus, E. N.; Potapov, A. Surface acidic sites of highly disperse magnesium chloride: IR and ESR spectroscopy studies. *Macromol. Symp.* **1995**, *89*, 55–61.
- <sup>21</sup> Takasao, G.; Wada, T.; Thakur, A.; Chammingkwan, P.; Terano, M.; Taniike, T. Machine Learning-Aided Structure Determination for TiCl<sub>4</sub>-Capped MgCl<sub>2</sub> Nanoplate of Heterogeneous Ziegler-Natta Catalyst. *ACS Catal.* **2019**, *9*, 2599–2609.

- <sup>22</sup> Takasao, G.; Wada, T.; Thakur, A.; Chammingkwan, P.; Terano, M.; Taniike, T. Insight into Structural Distribution of Heterogeneous Ziegler–Natta Catalyst from Non-empirical Structure Determination. *J. Catal.* **2021**, *394*, 299–306.
- <sup>23</sup> Wada, T.; Funako, T.; Thakur, A.; Matta, A.; Terano, M.; Taniike, T. Structure-performance relationship of Mg(OEt)<sub>2</sub>-based Ziegler-Natta catalysts. *J. Catal.* **2021**, *389*, 525–532.
- <sup>24</sup> Taniike, T.; Terano, M. Coadsorption Model for First-Principle Description of Roles of Donors in Heterogeneous Ziegler-Natta Propylene Polymerization. *J. Catal.* **2012**, *293*, 39–50.
- <sup>25</sup> Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, *136*, B864.
- <sup>26</sup> Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133.
- <sup>27</sup> Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- <sup>28</sup> Lee, C.; Yang, W.; Parr, R. Development of the Colle-Salvetti Correlation-Energy Formula Into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785–789.
- <sup>29</sup> Dovesi, R.; Erba, A.; Orlando, R.; Zicovich-Wilson, C. M.; Civalleri, B.; Maschio, L.; Rérat, M.; Casassa, S.; Baima, J.; Salustro, S.; et al. Quantum-Mechanical Condensed Matter Simulations with CRYSTAL. *WIREs Computational Molecular Science* **2018**, *8*, e1360.
- <sup>30</sup> Dovesi, R.; Pascale, F.; Civalleri, B.; Doll, K.; Harrison, N. M.; Bush, I.; D’Arco, P.; Noël, Y.; Rérat, M.; Carbonnière, P.; et al. The CRYSTAL code, 1976–2020 and beyond, a long story. *The Journal of Chemical Physics* **2020**, *152*, 204111.
- <sup>31</sup> Grimme, S. S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *J. Comput. Chem.* **2006**, *27*, 1787–1799.
- <sup>32</sup> Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H–Pu. *J. Chem. Phys.* **2010**, *132*, 5648–5652.
- <sup>33</sup> Fornaro, T.; Brucato, J. R.; Feuillie, C.; Sverjensky, D. A.; Hazen, R. M.; Brunetto, R.; D’Amore, M.; Barone, V. Binding of Nucleic Acid Components to the Serpentinite-Hosted Hydrothermal Mineral Brucite. *Astrobiology* **2018**, *18*, 989–1007.
- <sup>34</sup> Signorile, M.; Vitillo, J. G.; D’Amore, M.; Crocellà, V.; Ricchiardi, G.; Bordiga, S. Characterization and Modeling of Reversible CO<sub>2</sub> Capture from Wet Streams by a MgO/Zeolite Y Nanocomposite. *J. Phys. Chem. C* **2019**, *123*, 17214–17224.

- <sup>35</sup> Civalleri, B.; Maschio, L.; Ugliengo, P.; Zicovich-Wilson, C. M. Role of dispersive interactions in the CO adsorption on MgO(001): periodic B3LYP calculations augmented with an empirical dispersion term. *Phys. Chem. Chem. Phys.* **2010**, *12*, 6382–6386.
- <sup>36</sup> Brambilla, L.; Zerbi, G.; Nascetti, F., S. and Piemontesi; Morini, G. Experimental and calculated Vibrational spectra and structure of Ziegler-Natta catalyst precursor: 50/1 comilled MgCl<sub>2</sub>-TiCl<sub>4</sub>. *Macromol. Symp.* **2004**, *213*, 287–301.
- <sup>37</sup> Correa, A.; Credendino, R.; Pater, J.; Morini, G.; Cavallo, L. Theoretical investigation of active sites at the corners of MgCl<sub>2</sub> crystallites in supported ziegler-natta catalysts. *Macromolecules* **2015**, *45*, 3695–3701.
- <sup>38</sup> Bazhenov, A.; Linnolahti, M.; Pakkanen, T. A.; Denifl, P.; Leinonen, T. Modeling the Stabilization of Surface Defects by Donors in Ziegler–Natta Catalyst Support. *J. Phys. Chem. C* **2014**, *118*, 4791–4796.
- <sup>39</sup> Bache, Ø.; Ystenes, M. Double-Chamber Flow Cell for in Situ Infrared Spectroscopy Studies of Chemical Reactions in Ziegler-Natta Catalyst Systems. *Appl. Spectrosc.* **1994**, *48*, 985–993.