Title	Machine learning-aided structure determination of the heterogeneous Ziegler-Natta catalyst: insight into donor adsorption
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Machine learning-aided structure determination of the heterogeneous Ziegler-Natta catalyst: insight into donor adsorption

Abstract

INTRODUCTION

There are still many unknowns about how the supported Ziegler-Natta catalyst (ZNC), responsible for almost all the production of polypropylene (PP) worldwide, is improved by the addition of organic Lewis bases called donors. Nonetheless, their addition is essential for the production of highly isotactic PP, and the ZNC's evolution in the last 50 years is defined by the family of internal donor (ID) used during the catalyst's synthesis.[1] The lack of knowledge about the mechanism of said improvement, however, has resulted in a trial-and-error approach towards the search for new donors in the field. Considering that 20 years have already passed since the last groundbreaking finding, the discovery of succinates as IDs, a deeper understanding of the system is clearly required for the rational development of new donors.

Several difficulties have thwarted research on the ZNC. Its high reactivity to water limits the range of experimental techniques available for characterization, which is aggravated by the high complexity inherent to the system, due to the interaction among multiple components: $MgCl_2$ support, $TiCl_4$ active site, internal and external electron donors, and cocatalyst.[2] These experimental hindrances have fostered the use of computational chemistry in the field. However, the effect of ID on the formation of the support and surface exposure, in specific, has been hardly investigated in ab initio studies. Previously, in our group, structure determination of $MgCl_2$ nanoplates capped with $TiCl_4$ was performed, successfully replicating the reconstruction of the support in the presence of $TiCl_4$.[3–5] In this thesis, the ID-driven reconstruction of the support was investigated by applying the same combination of density functional theory (DFT) and genetic algorithm (GA). DFT was used to optimize and evaluate the energy of the structures generated by the GA, which performed the search for the global minimum by generating nanoplates composed of $MgCl_2$ capped with $TiCl_4$ and ID. This combination allowed a one-of-a-kind non-empirical study on the impact that IDs can have on the $MgCl_2$ support and, consequently, on the active site precursor, $TiCl_4$.

NUMERICAL METHODS

The composition of the nanoplates was set as $19MgCl_2/4TiCl_4/5ID$, where ID was either diethyl phthalate (DEP) or 9,9-bis(methoxymethyl)fluorene (DE), to compare how these two very different IDs would reconstruct the support. Their difference is believed to originate from their adsorption capabilities, with DE exhibiting a strong preference for chelation which is not observed in phthalates. Structure determination on a supplementary composition of $19MgCl_2/9TiCl_4$ was also performed. The number of $MgCl_2$ units was defined as 19 to balance size and computational cost, considering that the experimental size of the primary particles is between 2 and 10 nm, and the amount of adsorbates and their ratio were also decided referring to experimental data. The GA utilized in this thesis was based on the one previously developed in Taniike laboratory by Takasao et al.[4] and its functioning can be summarized as: GA randomly generates the first generation, and

creates the following generations by applying the operations of mutation, crossover and elitism to the current population. For the structure determination of ID containing systems, the algorithm was enhanced to add ID molecules as capping agents. The DFT calculations were performed utilizing the DMol^3 module of Materials Studio, with the PBE functional, DNP basis set and effective core potentials.
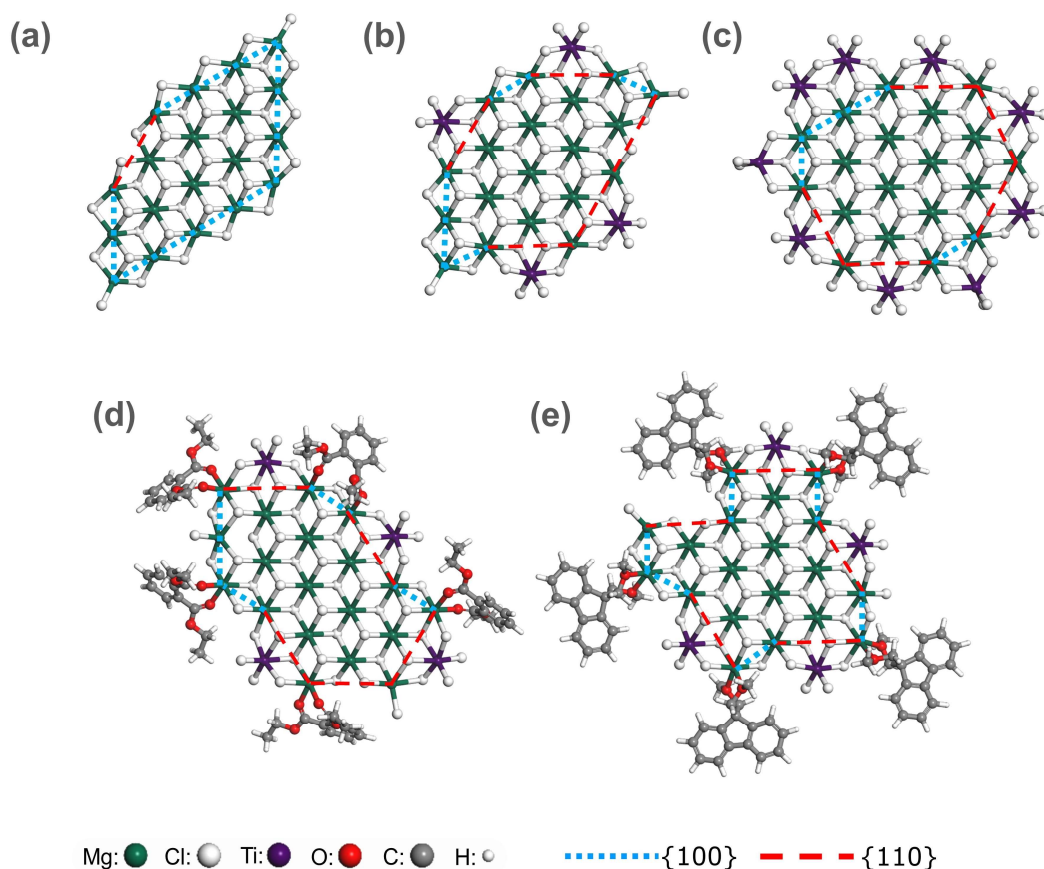
RESULTS AND DISCUSSION

Figure 1: Most stable structure per composition: (a) $19MgCl_2$, (b) $19MgCl_2/4TiCl_4$, (c) $19MgCl_2/9TiCl_4$, (d) $19MgCl_2/4TiCl_4/5DEP$ and (e) $19MgCl_2/4TiCl_4/5DE$.

Figure 1 shows the most stable structures for each composition determined in this thesis, as well as the previously published $19MgCl_2$ and $19MgCl_2/4TiCl_4$. ID caused significant changes to the morphology of the nanoplates, making the overall shape more angular. This is due to more frequent and sharper transitions between surfaces (edges). These sharp edges, in turn, necessarily increased the appearance of concavities to balance the overall shape of the nanoplates. In the absence of ID, the nanoplates increasingly exposed the {110} surface with the increase of $TiCl_4$, due to the preference of $TiCl_4$ for the {110} adsorption. However, because exposure of fourfold Mg^{2+} atoms is not favorable, the exposure of the {110} surface was generally limited to small terraces that were capped with $TiCl_4$. Considering that {110} $TiCl_4$ with stereo-controlling ligands at the neighboring adsorption sites is considered the origin of the stereospecific active site in

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the ZNC, stabilization of the Mg^{2+} terminating these terraces, either by chelation at an edge or by forming a concavity, might be an important source of the ID-induced improvement to the catalyst's stereospecificity.

Beyond individual nanoplates, the existence of a database allowed the study of a population that can represent ZNCs with similar composition. The distribution of many species within the whole population was determined by utilizing a Boltzmann factor to account for the contribution of every nanoplate to the population, depending on the relative energy to the most stable structure. First, ID population by the absorption mode was determined. DE, as expected from its adsorption energies, exclusively chelated, but DEP also was dominated by chelation (78%), with only 22% bridging on {100}. {110} bridge did not appear in DEP, probably due to the higher energy of {110} exposure, limited surface and competition with $TiCl_4$.

As for the Ti species distribution, it was classified by the adsorption mode and presence of stereo-controlling ligands next to {110} mononuclear $TiCl_4$ — according to the three-site model (Figure 2). Though coverage was a factor in the occupation around $TiCl_4$, given that {110} mono_3 was practically non-existent in $19MgCl_2/4TiCl_4$ and became 32% in $19MgCl_2/9TiCl_4$, the presence of ID certainly had a more drastic effect, evidenced by this species almost tripling in ID-containing systems, composing more than 95% of the $TiCl_4$. This is not only a result of IDs becoming a stereo-controlling ligand, but also of the appearance of concavities, which allow Cl^- atoms from the bulk to become a stereo-controlling ligand. Cl^- from the bulk was a stereo-controlling ligand in more than 70% and 40% of $TiCl_4$, for DE and DEP respectively, but in less than 1% for $19MgCl_2/9TiCl_4$. This suggests that ID's role in the creation of stereospecific sites in the Ziegler-Natta catalyst is not only of adsorption next to the active site, but also of shaping the $MgCl_2$ support in order to create a stereospecific environment.
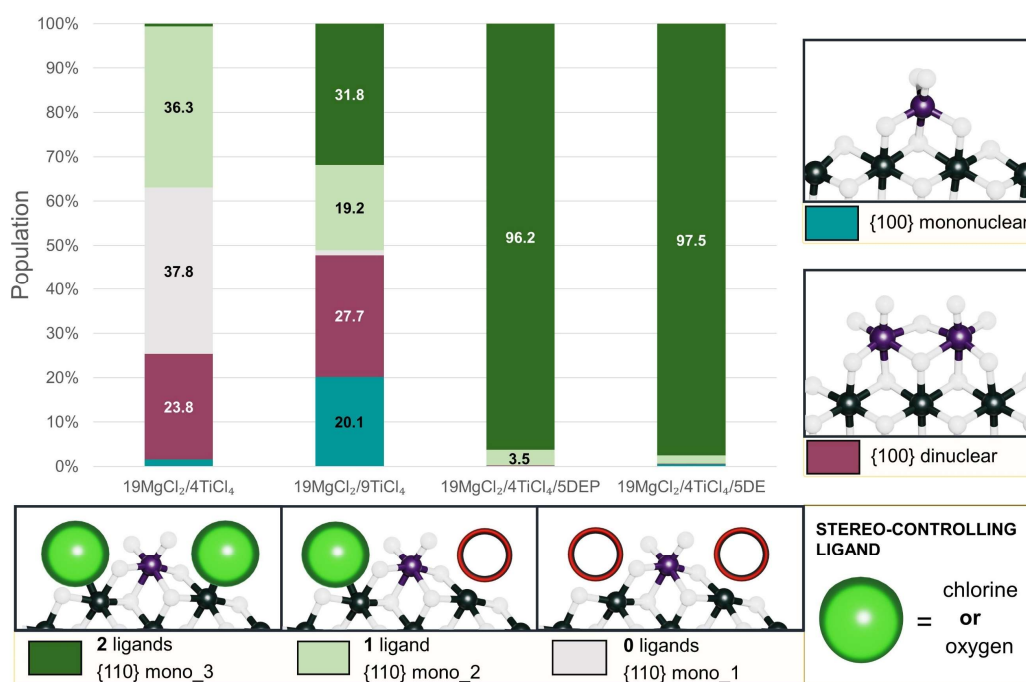

Figure 2: Population of $TiCl_4$ species, classified according to the adsorption mode and, in the case of {110} mononuclear, presence of stereo-controlling ligands.

CONCLUSION

A novel ab initio study of the internal donor-driven enhancement of the heterogeneous Ziegler-Natta catalyst was performed, based on structure determination utilizing a combination of density functional theory and genetic algorithm. Internal donor (ID) adsorption preferences increased the appearance of sharp angled edges, which could only be easily stabilized by chelating donors. The stabilization of these edges was so favorable that chelation was the only adsorption mode observed in 1,3-diether, while 78% of phthalate chelated. In addition, these edges tended to terminate small {110} terraces, which were exposed by the adsorption of $TiCl_4$, thus not only allowing ID to become stereo-controlling ligands, but also promoting $TiCl_4$ adsorption on this surface. Therefore, edge-stabilization by chelation, in conjunction with the appearance of concavities to balance the sharp edges, was identified as the main reason for the drastic increase in the stereospecific {110} $TiCl_4$ mononuclear species, with two stereo-controlling ligands, in the presence of IDs. In addition, the stereo-controlling ligands in ID-containing compositions were more strongly bound to the surface, e.g. oxygen or bulk Cl^-, and thus more capable of enforcing stereospecificity in comparison with the labile stereo-controlling ligands in their absence: Cl^- from {100} mononuclear $TiCl_4$ and terminal Cl^-. This thesis presents a first attempt at non-empirical structure determination of structures with the same composition as the heterogeneous Ziegler-Natta catalyst, and sheds light into the ID-driven support reconstruction, and its effects on the $TiCl_4$ active site, by explaining differences found in polypropylene produced by catalysts with and without ID.

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