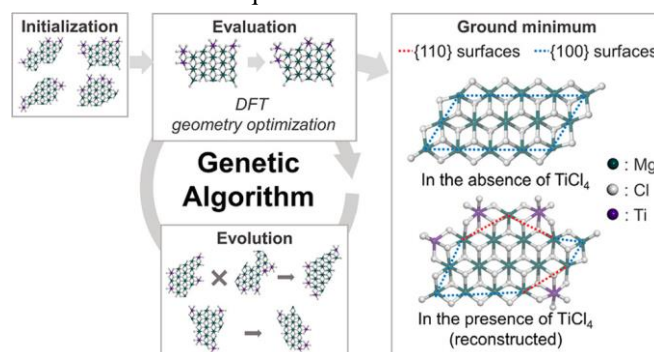


Title	機械学習によるチーグラ・ナツタ触媒一次粒子の非経験的構造決定と構造性能相関解明
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Citation	
Issue Date	2022-03
Type	Thesis or Dissertation
Text version	ETD
URL	<a href="http://hdl.handle.net/10119/17768">http://hdl.handle.net/10119/17768</a>
Rights	
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Heterogeneous Ziegler-Natta catalysts are the main catalysts for the industrial production of polyolefins. Their building unit, called primary particles, are composed of  $\text{MgCl}_2$  nanoplates whose lateral surfaces are capped by  $\text{TiCl}_4$  as the active site precursor and donors as the modifier. The detailed morphology and surface exposure of the primary particles are still unclear despite its importance for understanding the adsorption of catalytic components and catalytic performance. It is experimentally known that the structure of primary particles is not only nano-sized, but also defective. Such structural aspects are believed to cause the active-site distribution, namely the multisite nature, which is an essential feature of the Ziegler-Natta catalysts. However, these aspects have been hardly considered in previous computational studies. In this thesis, I developed a machine-learning aided structure determination program for a modeling of primary particles of heterogeneous Ziegler-Natta catalysts, and used these models to elucidate the origin of the multisite nature.

In Chapter 2, a non-empirical structure determination program for  $\text{TiCl}_4$ -capped  $\text{MgCl}_2$  nanoplates of Ziegler-Natta catalysts was developed by a combination of a genetic algorithm for global search and DFT geometry optimization for local optimization. The program was demonstrated for  $7\text{MgCl}_2$ ,  $15\text{MgCl}_2$  and  $15\text{MgCl}_2/4\text{TiCl}_4$  and their most stable structures were successfully obtained without pre-knowledge. The stable structure of bare  $\text{MgCl}_2$  was terminated by the  $\{100\}$  surface with the lowest coordinative unsaturation. In contrast, in  $\text{TiCl}_4$ -capped  $\text{MgCl}_2$ , the preferential adsorption of  $\text{TiCl}_4$  on the  $\{110\}$  surface reconstructed  $\text{MgCl}_2$  to expose small  $\{110\}$  terraces. Furthermore, the adsorption of  $\text{TiCl}_4$  greatly increased the variety of energetically accessible structures. Thus,  $\text{TiCl}_4$  reconstructs the  $\text{MgCl}_2$  skeletons and  $\text{TiCl}_4$  is intrinsically distributed as a combined consequence of non-ideal surfaces and structural diversity.



**Figure 1.** Program flow of a non-empirical structure determination program developed in this thesis.

In Chapter 3, I attempted to determine the structure of  $\text{TiCl}_4$ -terminated  $\text{MgCl}_2$  nanoplates of various sizes and compositions. The structure and charge distributions were analyzed for a million structures obtained in the process of structure determination. These systematic investigations revealed that  $\text{TiCl}_4$  prefer the monomeric adsorption on the  $\{110\}$  surface, but adsorption on the  $\{100\}$  surface cannot be ignored, and that there is a distribution of the steric environment and charge state of  $\text{TiCl}_4$  among the same adsorption mode. Such distribution of  $\text{TiCl}_4$  could cause the performance distribution, i.e., the primary structure distribution of the synthesized polymer. This chapter proposes a hypothesis for the origin of the multi-site nature of the Ziegler-Natta catalysts.

In Chapter 4, propylene polymerization simulations were performed based on  $\text{MgCl}_2/\text{TiCl}_4$  nanoplates derived in Chapter 3. The relationship between the structure of Ti active sites and their performance were investigated. The distribution of the active site structure led to a distribution of catalyst performance in propylene polymerization. Ti species having two stereocontrolling ligands, such as mononuclear species of Type 3 on  $\{110\}$  surfaces and dinuclear species on  $\{100\}$  surfaces showed isospecificity. Defective surfaces and a high coverage tend to produce such species.

In Chapter 5, I improved the search efficiency of the structure determination program by implementing an asynchronous distributed genetic algorithm with a migration operator from a structure database. The structure database holds all the structures and calculation results generated in different GA runs, and each GA adds structures from the database to the population. This implementation solved the premature convergence problem by preserving genetic diversity in the population of GAs and significantly improved convergence to the global solution. This resulted in structure determination for  $30\text{MgCl}_2$ ,  $50\text{MgCl}_2$ , and  $50\text{MgCl}_2/3\text{TiCl}_4$ , systems with sizes comparable to those of real catalysts.

Thus, this thesis has firstly achieved the modeling of the structural distribution of heterogeneous Ziegler-Natta catalysts by means of machine learning-aided structure determination. Simulations on the derived structure models clarified the origin of the active-site-performance distribution.

**Keywords:** Ziegler-Natta catalyst, genetic algorithm, structure determination, DFT, active site distribution