Abstract

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Ziegler-Natta (ZN) catalysts are heterogeneous catalysts, essential for industrial olefin polymerization. Their functional units, called primary particles, consist of $MgCl_2$ nanoplates with chemisorbed $TiCl_4$, active site precursor, and internal donors (IDs), used to improve stereoregularity of resulting polymers. Insights of the primary particles are essential to understanding the functional origin of ZN catalysts. However, surface reconstruction due to chemisorption introduces structural heterogeneity, posing significant challenges for modeling the nano-scaled structure of ZN catalysts. The non-empirical structural determination of primary particles with such surface reconstructions explicitly considered was achieved using a combination of density functional theory (DFT)-based local geometry optimization and global exploration based on a genetic algorithm (GA). However, the computational cost of DFT limits the structure determination to scales smaller than realistic ones.

Accelerating the DFT geometry optimization is crucial to investigate catalyst structures at real catalyst sizes and compositions. In recent years, methods have been proposed to replace computationally expensive DFT calculations by constructing machine learning potentials (MLPs) that accurately reproduce DFT results. Here, the high-dimensional neural network potential (HDNNP) approach2 was introduced to accelerate structure determination of ZN catalyst primary particles. The HDNNP expresses the total energy as the sum of environmentally dependent atomic energies, where the environment of each atom is described based on the atom-centered symmetry functions (ACSFs).

In **Chapter 3**, HDNNPs were developed for the $MgCl_2/TiCl_4$ binary system, enabling rapid non-empirical structural determination. The reference datasets used for training HDNNPs were sampled from a DFT database, which was accumulated through past DFT-based GA calculations. The accuracy of the constructed HDNNPs was evaluated by comparing geometry optimization results with those obtained from DFT. Constructed HDNNP applied for $50MgCl_2/9TiCl_4$ with experimental size and $TiCl_4$ coverage.

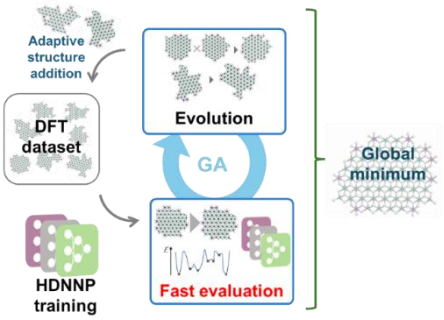

Figure 1. Scheme of constructing HDNNP and its application to structure determination.

Chapter 4 a HDNNP which applies across multiple systems was successfully established, where a reference dataset comprised multiple systems with different numbers of $MgCl_2$ units and $TiCl_4$ molecules. The established HDNNP was used to investigate the impact of the $TiCl_4$ coverage on the stability and active-site distribution. Analysis of metastable structures demonstrated a clear trend of increasing stereospecificity with higher TiCl4 coverage.

Chapter 5 details the development of a HDNNP for a $MgCl_2/TiCl_4$/ID system. While IDs are known to enhance polymer stereoselectivity, their precise impact on catalytic performance remains unclear. Previous studies using DFT and GA by da Silveira et al. identified key structural features for the $19MgCl_2/4TiCl_4$/5diethyl phthalate (DEP) system,[3] but their scope was limited by computational cost. he construction of the HDNNP for this system overcame this limitation, enabling a more comprehensive exploration of the parametric space. This expanded search identified many previously unreported stable and metastable structures, providing deeper insights. Analysis showed that DEP's diverse adsorption patterns significantly contribute to the geometric and electronic diversity of active sites.

In summary, the acceleration of structural determination using HDNNPs enabled the modeling of complex solid catalysts, providing new morphological insights into ZN catalysts that are critical for understanding catalytic systems. This approach demonstrates the importance for large-scale modeling of complex material systems, offering a deeper understanding of their properties.

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(3) Da Silveira, J. M., et al. *ACS Catal.* **2024**, *14* (4), 2300–2312.

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