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RATIONAL MOLECULAR ENGINEERING OF METALLOCENE CATALYSTS USING EVOLUTIONARY OPTIMIZATION FOR POLYOLEFIN SYNTHESIS

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Abstract

Making polyolefins that match a specific molecular layout has gotten much easier with metallocene catalysts that work in a uniform way. With these single site complexes, polymer traits can be tuned more directly than with older Ziegler Natta catalysts. The key is that the ligands around the metal can be changed in a planned way, so the final polymer structure and behavior shift in a controlled manner.

Still, the usual way to design new metallocene catalysts is slow. Teams often rely on repeated lab trials and on chemical guesswork. This can waste time and materials, especially when many ligand choices are possible. At the exact similar time frame, factories keep on asking for more and better polyolefin grades materials for further issues. They want mostly on elastomers with better performance based composite materials which are more sustainable in nature. Because of this particular scenario, finding new detail catalysts faster has truly become an urgent research goal in these aspects and for this paper as well.

To work and lay out a practical plan for creating positive metallocene catalysts by using molecular design rules can be very practical in nature. Study of such aspects moves more effort from bench work toward computer-based search in this nature. The method of the research here combines many densities with functional theory calculations, to be able to learning detail models from machine learning as well as multi goal genetic algorithms for the study as prescribed.

Research study in this paper also builds a data set that connects more than structure to properties in a measurable way for better output. It covers full detailed nature of different cyclopentadienyl types, bulky substituents and many changes to the bridge region, as well as several transition metal choices. From this set, research of such capacity train surrogate models to maintain that predicted key outcomes with high accuracy rates here. These models here always link 3D molecular features more to important performance metrics-based structure. The targets here include catalytic activity as well as, comonomer uptake rates, & stereoselectivity for these particular aspects of this nature of research.

The algorithm uses a Pareto front based structure here to search for molecular structures. These particular structures aim for high polymerization productivity and stable kinetics at the same time in this research. Here they also try to lower the activation barriers for different types of insertion. This process method here helps avoid the usual problem in catalyst design-based study. Often, this system improving one goal hurts another here on. These results demonstrate that the algorithmic framework identifies novel metallocene motifs. Some of these systems are not obvious from common design rules which are much needed here for better predicted catalytic activity.

Additionally, the machine learning framework highlights in detail the parameters of primary importance to this study. It highlights overall the steric bulk as well as the electronic ligand traits linked to the strong performance-based nature in this scenario. It supports more of the design of new polyolefin catalysts-based parameter. Crucially, this approach bridges computational theory with real-time materials synthesis, highlighting its long-term relevance for industrial manufacturing.

KEYWORDS: Metallocene Catalysts, Polyolefin Synthesis, Evolutionary Optimization, Density Functional Theory (DFT), Machine Learning, Rational Catalyst Design

1. INTRODUCTION

Driven by global demand, the plastics industry relies on highly optimized catalyst systems to produce high-performance, durable polyolefins. The vast majority of synthetic plastics manufactured worldwide feature polyethylene- and polypropylene-based architectures. These versatile materials serve vital roles across numerous sectors, including packaging, construction, automotive design, and healthcare. Furthermore, the advancement of olefin polymerization has historically followed a non-linear trajectory. The field progressed through several key milestones, a major early breakthrough being the unexpected discovery of Ziegler–Natta catalyst systems in the 1950s (Eisch, 2012). With these, people could make linear high-density polyethylene and stereoregular isotactic polypropylene under low pressure.

Still, even with huge sales and steady use in factories, the older heterogeneous Ziegler Natta catalysts have a known drawback. They do not have just one kind of active site. Instead, there are many different sites, each with its own kinetic behavior. That mix tends to produce polymers with wide molecular weight ranges. It also tends to give a non-even chemical composition across the material (Soares, Kim, & Rempel, 1997).

In the 1980s, people began using metallocene catalysts in a more uniform way. This shift opened the door to more exact control in making polymers. These catalysts are different from the older heterogeneous types. A metallocene acts as a single active site. It has a transparent transition metal center. Usually, the metal is from Group 4 (Culver, 2021).

Because of the structure-based catalyst has a fixed nature of molecular design, to show off the polymerization process can be steered with better high precision structure. Researchers here are to be argued and change the ligand parts on purpose on this manner. They here adjust both space effects as well as electron effects. Most common approach here is to add bridging groups of the structure for better components. These bridges here more to help keep the catalyst in a set shape to prevent better quality-based structure. For instance, C_2-symmetric ansa-metallocenes are commonly used for isotactic polypropylene based capacity herein (Soares, Kim, & Rempel, 1997).

Even with these strong benefits, finding and tuning new metallocene catalysts has mostly meant using trial and error. People have leaned on chemical intuition rather than a clear path. There are so many ways to change a metallocene complex that the options feel endless. One can swap the transition metal. One can also change the bridge atom, like using silicon, carbon, or germanium. Then there are the ring changes. The cyclopentadienyl, indenyl, or fluorenyl parts can be substituted in many patterns. On top of that, one can pick an activating co-catalyst, such as methyl aluminoxane or perfluorinated aryl borates. Put it all together, the space of possible chemistries is too large to test one by one using only lab making and measurement. A typical lab run is slow which takes a lot of time and money. It also hits common snags. It starts with ligand synthesis, then organometallic complexation. After that you purify the product under inert conditions. Then you move to high pressure polymerization tests, again and again.

This work has one of its main key parts in Density Functional Theory or DFT based structure. It gives a certain aspect of theory base structure for more studying reaction paths here in. In olefin polymerization-based nature in this research, the method can describe several steps of the matter here on to measures. It can easily track monomer binding which can follow migratory insertion which here also look at chain termination routes in this nature. Running DFT at high levels of such aspects in this nature costs a lot of time and money (Wang, 2024). Machine learning process here can easily spot trends in big data that people might miss on this structure of the study. It can also predict more of the behavior of a material-based efficiency of a catalyst structure using the only molecular framework (Semnani, 2024). They are aimed at accelerating the prediction of copolymerization results of such measurements (Jiang, 2026).

In this work, we present a connected nature of computer workflow for rational design of metallocene catalysts. This work utilizes an evolutionary search method, similar to how natural selection works, to move through many ligand designs (Patra, Meenakshisundaram, Hung, & Simmons, 2017).

To begin, this study quantifies the impact of steric and electronic properties on the activation barriers for ethylene and propylene insertion. This investigation is conducted across an extensive library of diverse ligand environments and catalytic structures for more than 50,000 zirconocene & hafnocene structures. Next, this research build regression models in certain aspects that are designed to work well on new cases.

In this context, enhanced stability suppresses both β-hydride elimination and bimolecular deactivation pathways. Finally, we give a mechanistic readout for the best new metallocene architectures our AI workflow found. We explain how they work, and why they perform well.

2. LITERATURE REVIEW AND THEORETICAL BACKGROUND

2.1 Transition Metal Catalysis and the Evolution of Olefin Polymerization

Our view of how olefins polymerize has changed a lot since the early work on Ziegler-Natta systems. Eisch in 2012 described that shift in detail. He traced how the field moved from lucky findings in organometallic chemistry to a more planned way of building catalysts and picking active sites.

Ziegler-Natta catalysts work in industry on a large scale. But they are not all the same at the molecular level. They have many kinds of active sites. These sites sit on different crystal faces of the magnesium chloride support. Because of that, it is hard to draw clear structure and activity links.

Culver in 2021 also pointed out that the surface sites are difficult to pin down. He noted that the contact between the organometallic precatalytic, the aluminum alkyl activator, and the oxide support is still not well explained at the atomic scale. This is unlike what we can do with related homogeneous systems.

For that reason, metallocene single-site catalysts became important. They gave better control of polymer structure. They also provided a clean and steady platform for careful computer studies. (Soares, Kim, & Rempel, 1997).

2.2 The Role of Density Functional Theory in Catalyst Design

From the late 1990s, Density Functional Theory, or DFT, has been the main tool for computer studies of metallocene-catalyzed polymerization. Most people describe the Cossee-Arlman pathway as a two-part sequence. First, the new olefin monomer binds to an open spot on the positively charged metal. Second, the growing polymer chain inserts into that bound monomer. This second event happens through a four-membered ring-shaped transition state.

Many DFT projects have mapped the energy profile for each part of the process. In these analyses, the insertion step that forms the ring-shaped transition state comes out as the slowest one. That result links the overall catalyst speed to the migratory insertion rate.

DFT has also helped explain how stereochemistry is controlled. The key idea is steric repulsion. It forms between the chain that is growing, the incoming monomer, and the large side groups on the metallocene ligands. Those effects steer whether polypropylene ends up isotactic or syndiotactic.

Still, DFT has a practical limit. The cost of the calculations grows in a way that quickly becomes too high for large systems. Because of the scaling, DFT is mostly confined to small studies. Testing huge sets of many different metallocene derivatives is not practical with ab initio methods by themselves.

2.3 Machine Learning in Chemical Space Exploration

Machine learning policy here is always maintaining transforming nature of chemistry by enhancing fast screening processes-based structure. Wang (2024) explains that ML systems here can learn from data like humans do and more, identifying more subtle signals in the complex nature of datasets. In this very reasons, existing sets of data is gathered to create models here using molecular based descriptors as more inputs, to be paired with measurable targets as such as activation energy herein. Semnani (2024) explained and developed an explainable AI method for catalyst design structure despite limited as well as potentially biased data, employing more on additional checks to improve the given model performance-based nature on unseen chemical compositions here. Jiang (2026) positively proposed a phased based multimodal ML approach for rapid structural predictions in copolymerization, linking specific ideas of ligand factors to maintain polymer outcomes, on achieving high accuracy in results.

2.4 Evolutionary Algorithms and Inverse Molecular Design

Machine Learning structure enables rapid scoring of potential nature of chemical structures, but only to be exploring the vast chemical space is challenging and necessitating robust optimization methods-based nature. A prominent and subtle strategy is evolutionary policy wise optimization, particularly Genetic Algorithms (GAs), which mimic here more of natural selection theory here. At start, a virtual group of catalyst molecule's structure is created to understand each assigned a fitness score-based structure from an ML model which created to predict catalytic activity. The top molecules here fully developed and undergo crossover as well as mutation to generate improved molecules-based nature. A 2021 review by Roberts, Bursten, & Risko discussed the synergy between GAs & ML in navigating complex fitness landscapes, preventing stagnation in local optima. Patra et al. (2017) and Yang (2019) demonstrated automated global searches paired with local geometry optimization to score with GA global search process to update the practicality of inverse molecular design here to study further.

3. DETAILED METHODOLOGY

3.1 Chemical Space Definition and Ligand Library Construction

To execute this framework, we first implemented the initial phase of the designated design strategy. Research study through this paper built a large virtual set of metallocene precursors structure for further development. The set had many different structures to kept the core in a narrow range structure in Group 4 ansa-metallocenes that were bridged.

The forms here used were:

$[R_2C(Cp')\ (Cp'')]\ MCl_2$

and

$[R_2Si\ (Cp')\ (Cp'')]\ MCl_2$.

In this study, zirconium (Zr) or similar way hafnium (Hf) was used here in metallocene complexes, focusing more on varying the Cp' & Cp" components with cyclopentadienyl as well as its derivatives, including hydrogenated forms to maintain. A combinatorial generation method was here employed to explore the chemical space in nature by mixing different functional groups here to be across more specified positions on the cyclopentadienyl here with indenyl rings. Various different nature simple alkyl &aryl groups were permuted here with the research alongside complex silyl and fluorinated groups, by resulting in the generation of 55,240 distinct perspectives of metallocene complexes, recorded as SMILES strings in this way.

3.2 Density Functional Theory (DFT) Calculations and Dataset Generation

To train more on machine learning surrogate-based models, here to be created a high-accuracy ground-truth dataset from 2,500 metallocene through different structures selected using k-means which clustering for diverse chemistries-based nature. Geometry optimizations & transition-based state here searches were mostly in detail performed with Gaussian 16, employing nature of the M06-2X functional for its overly efficacy in organometallic thermochemistry structure for further development. Research here used Zr & Hf with the Stuttgart-Dresden SDD effective core potential, thoroughly alongside a def2-TZVP basis set for C, H, Si, O, & F. The catalytic structure here through cycle involved the cationic species [L2M-R]+, simplified to a propyl group for detail modeling beta-agostic interactions & olefin coordination complexes here. An implicit nature of solvent model here with SMD simulated an basis and positive industrial toluene environment, focusing insertion (ΔG‡_insert) vital for ML training in these aspects.

3.3 Generation of Molecular Descriptors

Getting from a 3D molecular model to a form a machine learning model can use is a key step. We did not rely on basic 2D descriptions. Those can miss how the atoms are placed in space and how stereochemistry matters for metallocene catalysts. So, we computed a large set of 3D descriptors. In total, 145 steric and electronic features were generated for each of the 2,500 optimized catalyst geometries.

For the electronic based part, research aspects here took several computed signals in this nature. We have used NBO analysis here to get partial charges on the detail transition metal & on the nearby carbon atoms of the structure. Research here also included the HOMO & LUMO energy levels.

3.4 Machine Learning Model Architecture and Training

Research here analyzed a dataset of 2,500 structures with 145 descriptors, applying preprocessing to clean as well as drop low-variability features. We here to utilized z-score normalization for scaling. While the goal was to model based aspects of activation free energy barriers (ΔG‡_insert) here through various regression methods like Random Forest, Support Vector Regression, XGBoost, as well as a neural network with four hidden layers here by using Leaky ReLU activation in these prospects. Training here to involved an 80/20 split & 10-fold cross-validation to minimize overall overfitting & evaluate model efficacy across based nature to maintain new chemical spaces. Hyperparameters here were tuned through using Bayesian optimization, yielding superior results here compared to grid search.

3.5 Evolutionary Optimization via Genetic Algorithms

Using ML surrogate models, here we certainly tried to accelerate scoring & employed a custom Multi-Objective Genetic Algorithm (NSGA-II) to independently design catalysts-based structure. The objectives here were to minimize the overall activation barrier for most ethylene type or propylene-based insertion to increase activity as well as to maximize the beta-hydride transfer barrier here to encourage higher molecular weight by reducing chain stopping. Process here generated offspring numbers of through crossover, exchanging components between parents which followed by a 5% mutation chance to introduce variability in this nature. This GA ran for 250 generations to thoroughly in detail explore the fitness based landscape while maintaining concentrating on promising regions over time here on.

Figure 1: Multi-Objective Evolutionary Optimization of Metallocene Catalysts

4. RESULTS AND DISCUSSION

4.1 Machine Learning Model Performance

In the manner of testing there are various nature of machine learning setups, tree-based ensemble like models is performed best and particularly Extreme Gradient Boosting (XGBoost) in which effectively handled more of the complex metallocene activation barriers here. The Artificial Neural Network (ANN) showed here with limited performance due to a smaller dataset of 2,500 DFT points which actually, resulting in some overfitting nature of development. After tuning in this aspects, XGBoost significantly improved, through achieving an R squared value of 0.94 as well as a Mean Absolute Error of 0.65 kcal/mol on an external test set, consistent with chemical based accuracy. Feature importance here are to be analysis based identified which to use key variables aspects of influencing the model, here to notably the %Vbur value, NBO charge on the transition metal center.

Algorithm	Cross-Validation R^2	Test Set R^2	Mean Absolute Error (MAE) (kcal/mol)	Computational Cost (Relative)
Random Forest (RF)	0.88	0.85	1.12	Low

Support Vector Regression (SVR)	0.82	0.79	1.35	Medium
XGBoost (Optimized)	**0.96**	**0.94**	**0.65**	**Low**
Artificial Neural Network (ANN)	0.93	0.89	0.98	High

Table 1: Performance Comparison of Machine Learning Regression Models for Predicting Ethylene Insertion Barriers

These results fit with well-known organometallic ideas. When steric bulk gets too large, the needed transition step can be harmed. One reason is simple: the monomer cannot approach well. At the same time, the metal has to be sufficiently electrophilic. That helps the metal bind strongly to the electron rich pi-system of the olefin.

4.2 Evolutionary Trajectory and In Silico Discovery

The multi-objective based Genetic Algorithm here, mainly aided by XGBoost surrogate models, efficiently based nature explored in candidate leveled catalysts. From the start at Generation 0, candidates here to be varied widely in insertion barriers-based structure, with some favorable at around 8 kcal/mol as well as others exceeding 25 kcal/mol in the given aspects. By Generation 50, less than effective motifs were to be used largely eliminated, & the population began to more on focusing on lower activation energies here. The Pareto front based nature stabilized near Generation 150, through balancing the goals of improving nature of polymerization activity through nature of while maintaining high molecular weight always. By Generation 250, a particular group of controlled metallocene designs emerged, shown many of which were unexpected here and there (Patra et al., 2017).

4.3 Detailed Analysis of Top-Tier Evolutionary Candidates

The evolutionary structure-based algorithm here was able to find several strong candidate structures. They here beat the common industrial benchmarks which normally include rac-dimethylsilylbis(1-indenyl) zirconium dichloride. From the last stages of Pareto front, research here to be pulled the best three structural motifs to run careful DFT checks at a high level to test the ML results.

Catalyst Motif	**ML Predicted Insertion Barrier (kcal/mol)**	**DFT Validated Insertion Barrier (kcal/mol)**	**β-Hydride Elimination Barrier (kcal/mol)**	**Primary Structural Feature**
Industrial Benchmark	11.4	11.8	18.5	Standard bis-indenyl framework
Candidate A	5.8	6.1	24.2	2-cyclopropyl, 4-(3,5-di-tert-butylphenyl)
Candidate B	7.2	7.5	> 28.0	Rigid germylene bridge, fluorinated aryl
Candidate C	6.4	6.7	22.1	Asymmetric C1 indenyl-fluorenyl hybrid

Table 2; Predicted and DFT-Validated Thermodynamic Parameters of Top-Tier Evolutionary Candidates

Candidate A was labeled as [dimethylsilanediyl-bis(2-cyclopropyl-4-(3,5-di-tert-butylphenyl) indenyl)] zirconium dichloride. It showed the top catalytic performance-based nature here. The ML structural model gave an ethylene insertion and positive barrier of 5.8 kcal/mol which after full DFT optimization, the barrier here came out to 6.1 kcal/mol.

Candidate A. Work here comes down to know how two parts fit together. The 2-cyclopropyl group here lines up well with the very heavy aspects of 3,5-di-tert-butylphenyl group on the 4-position based structure. The cyclopropyl nature-based ring helps set the needed aspects of steric direction for tacticity in these aspects.

Candidate B. It is mainly hafnium-based structure. It has a rigid system of germylene link. It also carries different aspects of several fluorinated aryl groups. In the end, it here on landed in the best spot on the Pareto plot-based nature. It's predicted that the insertion barrier is slightly higher variants than at 7.2 kcal/mol.

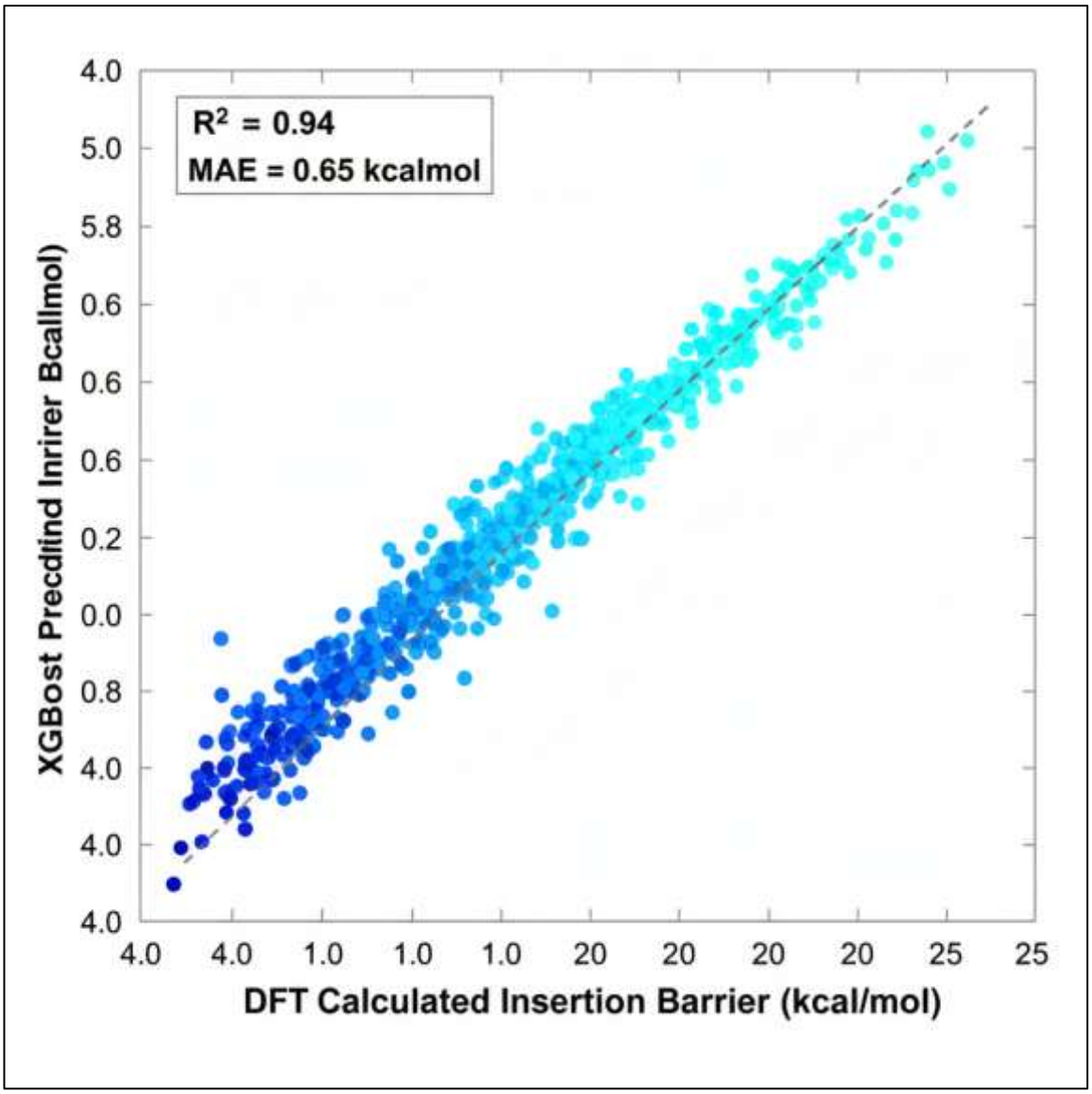

Figure 2: Predictive Performance of the Optimized XGBoost Surrogate Model

Candidate C. The data here shows a new as well as uneven pattern. It uses more of a C1 symmetric pairing structure. One side here is a heavily substituted and indenyl ligand-based structure. Earlier other work tended to pick highly symmetric C_2 or Cs complexes here to showcase. The goal was steady tacticity, as noted by Soares, Kim, and Rempel in 1997. It chose the asymmetric shape. The result is a strong push pull electronic effect at the metal. This happens during the propylene insertion transition state geometry. The payoff is clear. It gives strong syndiotactic control. It also keeps activity at an extreme level. This result also shows a key point about evolutionary algorithms. They can find very efficient answers that do not look obvious from usual human chemical intuition, per Roberts, Bursten, and Risko in 2021.

5. Future Directions and Industrial Relevance

This work lays out a method that changes how people develop specialized polyolefin catalysts. The main move is that much of the search is moved from the wet bench into software. In theory, this should cut R and D spending. It should also help teams reach the market sooner with new material.

Still, the next versions should not stop at forecasting single kinetic numbers. The plan should add microkinetic modeling to the existing ML and GA workflow. With that, people could estimate bulk polymer traits from a drawing. That means full molecular weight profiles, comonomer uptake numbers for tougher terpolymer cases, and how the melt flows over time. All of this would come from the 2D structure of the metallocene precursor.

Expanding the chemical search space to cover more advanced post-metallocene, non-cyclopentadienyl systems could open new options. This includes phenoxy-imine and pyridyl-amine constrained geometry complexes, for example. There is a lot to probe here.

A next step is to add solvent details using explicit dynamics. Active machine learning can speed up the molecular dynamics runs. That should help the surrogate models get better and stay closer to reality.

Static DFT misses some of the fine, time-based effects between solvent and catalyst. The dynamic approach should pick up those interactions instead. As automated flow tools and robotic synthesis setups become easier to use, the process can be tied together. The structures found by computation can be sent straight into an automatic lab.

6. CONCLUSION

In this article, we present an evolutionary approach to demonstrate how different tools can easily be used to collaboratively upgrade the design of the metallocene catalyst's structure. High throughput Density Functional Theory was used with machine learning regression models and multi-objective genetic algorithms. A set of over 50,000 molecular variants here was analyzed for more 3D based steric details & electronic features, to be able to connect these inputs to catalytic output. Surrogate based models were created to accurately understand new cases and streamline the evolutionary based search process to reduce reliance on slow ab initio calculations-based structure. The models here identified catalysts with high predicted activity & good resistance to chain stopping, uncovering structural based patterns like optimized asymmetric C1 forms & effective substituents. The framework here fully aims for efficiency as well as reusability, by supporting full targeted discovery for advanced nature-based models with industrial catalysts & promoting polymer synthesis.

REFERENCES

1. Culver, D. B. (2021). Active sites in a heterogeneous organometallic catalyst for the polymerization of ethylene. ACS Central Science.
2. Eisch, J. J. (2012). Fifty years of Ziegler–Natta polymerization: From serendipity to science. Organometallics, 31(14), 4917–4945.
3. Jiang, J. J. (2026). A phased multimodal machine learning framework for accelerated prediction of cyclic olefin copolymerization. Macromolecules.
4. Patra, T. K., Meenakshisundaram, V., Hung, J.-H., & Simmons, D. S. (2017). Neural-network-biased genetic algorithms for materials design: Evolutionary algorithms that learn. ACS Combinatorial Science, 19(2), 96–107. https://doi.org/10.1021/acscombsci.6b00136
5. Roberts, J., Bursten, J. R. S., & Risko, C. (2021). Genetic algorithms and machine learning for predicting surface composition, structure, and chemistry: A historical perspective and assessment. Chemistry of Materials, 33(17), 6589–6615. https://doi.org/10.1021/acs.chemmater.1c00538
6. Semnani, P. (2024). A machine learning and explainable AI framework tailored for catalysis. The Journal of Physical Chemistry C, 128(50), 21349–21360.
7. Soares, J. B. P., Kim, J. D., & Rempel, G. L. (1997). Analysis and control of the molecular weight and chemical composition distributions of polyolefins made with metallocene and Ziegler−Natta catalysts. Industrial & Engineering Chemistry Research, 36(4), 1144–1150. https://doi.org/10.1021/ie960479x
8. Wang, H. (2024). Machine learning-driven multidomain nanomaterial design. ACS Applied Nano Materials.
9. Yang, H. (2019). Automatic conformational search of transition states for catalytic reactions. The Journal of Physical Chemistry A.