A Multiscale Machine Learning Approach for Elucidating Polymer Pyrolysis Mechanisms

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1. Introduction

Polymer chemistry is a relatively young subject, and polymeric materials—particularly plastics—have become ubiquitous in everyday life due to their combination of low weight, widespread availability, and durability. However, the widespread use of plastics has led to severe environmental pollution, making the efficient recycling of waste polymers a critical research focus [1]. There is an urgent need for degradation methods that are both efficient and environmentally friendly. Common strategies for managing plastic waste include landfilling (which is environmentally hazardous), incineration (which is high carbon emissions), mechanical recycling, and chemical recycling. Among chemical recycling approaches, catalytic pyrolysis has emerged as a preferred method because of its low emissions, high selectivity, and ability to generate high-value products [1, 2].

In catalytic pyrolysis, catalysts play a crucial role, and their presence can significantly influence not only reaction conditions but mechanisms. Among various catalysts, single-atom catalysts have emerged as a preferred choice due to their high atomic utilization and enhanced selectivity [3, 4]. Unlike small-molecule reactions, polymer degradation demands consideration of both chemical reactions at the microscopic scale and the motion of polymer chains at the mesoscopic scale. Incorporating a mesoscopic perspective—describing the dynamics of long polymer chains and their behavior after adsorption—provides a more comprehensive understanding of the catalytic system [5]. Furthermore, recent studies have shown that designing catalyst structures with constrained entropy at the mesoscopic scale can further enhance catalytic efficiency [6].

Machine learning has emerged as a powerful tool for tackling complex problems. Addressing such challenge requires using machine learning from a multiscale perspective. At the microscopic scale, machine learning can assist in catalyst design and elucidate reaction mechanisms, whereas at the mesoscopic scale it can model reaction kinetics and provide predictive insights for complex systems.

Recent efforts in polymer pyrolysis research have focused primarily on experimental catalyst optimization, with limited integration of machine learning. Notably, in the development of single-atom catalysts for small-molecule reactions, data-driven approaches have already yielded significant improvements. However, extending such approaches to polymer degradation is challenging due to the scarcity of comprehensive degradation databases and the lack of key descriptors of degradation mechanisms [7, 8]. Overcoming these hurdles will require data-efficient learning strategies (e.g., transfer learning, few-shot learning) that remain effective even with limited datasets [9]. Additionally, given the uncertainty in reaction mechanisms, physics-informed neural networks (PINNs) provide a way to embed prior physical knowledge into model training, enhancing model reliability [10]. In parallel, reaction kinetics at the mesoscale can benefit from integrating diffusion generative models with molecular dynamics simulations; this combination captures the complex motion and interaction of polymer chains and thus improves reaction prediction accuracy.

For example, Cao et al applied diffusion generative models to develop a novel framework for ligand docking, demonstrating the capability of these models to generate high-fidelity predictions under uncertain reaction conditions. This work provides a valuable blueprint for extending such techniques to polymer catalytic degradation, where multiscale dynamics and complex catalyst–polymer interactions must be accurately captured [11].

This confluence of methodologies—from microscale catalyst design informed by PINNs and data-efficient learning to mesoscale kinetic modeling via diffusion generative networks—represents a promising direction for overcoming current limitations in polymer degradation research and advancing the predictive accuracy of complex catalytic systems.

2. Research

2.1 Methodology

Our research employs machine learning to elucidate polymer reaction mechanisms and to guide catalyst design. Considering limited experimental data, we adopt data-efficient learning strategies to characterize polymer reactions at both the microscale and mesoscale, capturing intrinsic reaction mechanisms as well as reaction accessibility.

In describing polymer pyrolysis reactions across microscopic and mesoscopic scales, our approach can be summarized as from "points" to "lines," where the "points" means the reactive active sites, and the "lines" represent the motion and diffusion of polymer chains. Because the rate of polymer pyrolysis is several orders of magnitude slower than the thermal motion of these chains, we consider this multi-scale model to be feasible.

At the microscopic scale, the primary focus is on the docking between the active sites and polymer chains, with particular attention paid to the adsorption energies among those sites. Under thermal catalytic conditions, the ester oxygen in PET chains—given its high reactivity—docks with the active sites to form a bound structure. We adopt a reaction model to characterize and describe this process.

At the mesoscopic scale, we further examine the polymer chain's motion following microscopic docking. Specifically, we use a diffusion-generative-network–based molecular dynamics approach to simulate the diffusion and collision behavior of the polymer chains. The polymer treats the catalyst's active site on the surface as an "endpoint" and, driven

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by thermal motion, continuously collides and bonds with the catalyst surface, thereby achieving chain diffusion onto the catalyst. Once the chain has fully diffused and adsorbed onto the catalyst surface, it proceeds to the subsequent catalytic reaction stage. By employing this multi-scale model, we couple the microscopic docking at active sites with mesoscopic chain diffusion to provide a comprehensive description of the polymer pyrolysis mechanism.

In this work, we integrate machine learning with multiscale modeling and experimental validation to design PET (polyethylene terephthalate) pyrolysis catalysts that achieve selective ester bond cleavage and maximize high-value product yields.

2.2 Results

We leverage diverse data sources—including curated databases (e.g., PoLyInfo and Catalysis-Hub), published experimental datasets, and data generated from molecular dynamics (MD) simulations and low-accuracy DFT calculations—to pretrain a reaction model on extensive datasets. This model is subsequently fine-tuned with physical insights specific to PET degradation. Additionally, we incorporate diffusion generative models into molecular dynamics simulations (tailored for polymer systems) to simulate the dynamic adsorption–reaction–desorption processes in PET pyrolysis. The obtained catalyst exhibits good performance under the thermocatalytic degradation conditions of the PET polymers. The resulting catalyst structure and composition are characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM), while product distributions are analyzed via high-performance liquid chromatography (HPLC) and gas chromatography–mass spectrometry (GC–MS). The obtained results further confirm the successful synthesis of the catalyst and its catalytic effectiveness. This comprehensive, data-efficient approach not only optimizes PET degradation but also provides a robust framework for the rational design of advanced pyrolysis catalysts.

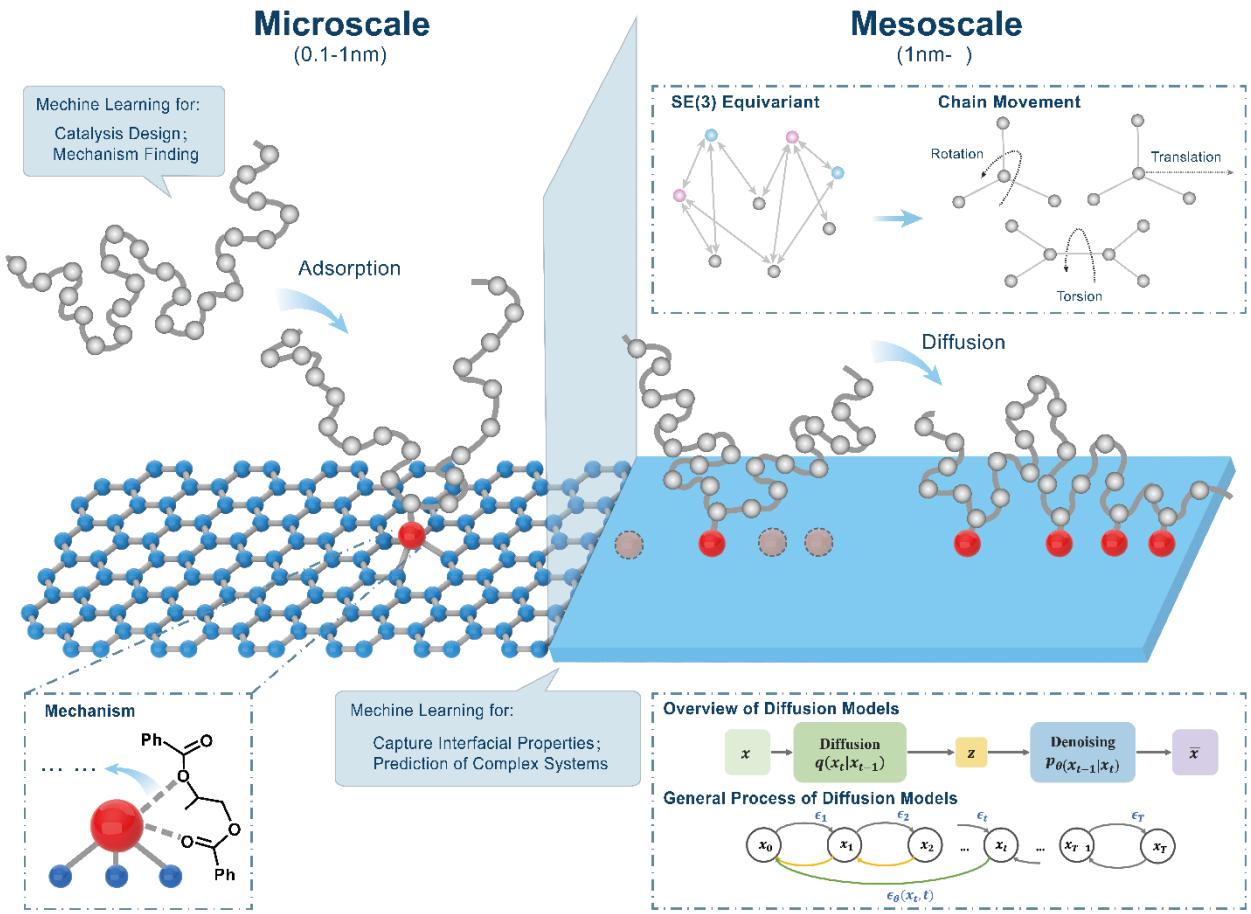

Fig. 1: Overall Work Introduction:
Microscopic scale, catalyst active sites dock with polymer chains; Mesoscopic scale, the polymer chains diffuse—with docking sites as endpoints—as described by a diffusion generative network, further facilitating additional docking events between the chains and active sites.

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