

# Development of a Hydrocarbon Pyrolysis Model Considering Catalyst Deactivation Behavior

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Fuel pre-treatment-based carbon recovery using hydrocarbon pyrolysis is a promising approach for achieving carbon neutrality, particularly in applications where internal combustion engines remain relevant due to regional energy infrastructure and usage constraints. In this approach, hydrocarbons are decomposed into hydrogen and solid carbon prior to combustion, enabling efficient carbon separation and recovery while avoiding CO<sub>2</sub> formation during the combustion process. Moreover, the recovered solid carbon can potentially be utilized as a valuable carbon material, further enhancing resource efficiency. However, during hydrocarbon pyrolysis, carbon is deposited on the catalyst surface as a reaction intermediate, leading to catalyst deactivation that limits reaction sustainability and directly affects overall system feasibility. As the catalytic activity decreases over time, both hydrogen yield and process stability are degraded, making it difficult to evaluate long-term performance without explicitly accounting for deactivation behavior. Despite its importance, catalyst deactivation has not been sufficiently considered in existing pyrolysis models, which mainly focus on reaction rates and carbon yields under steady or idealized conditions. To address this issue, the present study aims to develop a hydrocarbon pyrolysis model that describes catalyst deactivation at a level of detail suitable for system-level evaluation, while retaining computational practicality.

In order to simultaneously describe hydrocarbon decomposition and catalyst deactivation, a pyrolysis model was constructed by coupling three component models. First, a kinetic Monte Carlo-based sintering model was developed to represent the diffusion and aggregation behavior of Ni-based catalyst particles under high-temperature conditions, allowing the time evolution of the particle size distribution to be calculated as the reaction proceeds. Based on this framework, a kinetic model integrating surface decomposition, carbon diffusion within the catalyst particle, and carbon emission in the form of CNTs/CNFs was then formulated to describe carbon accumulation dynamics inside the particles. This approach enables the influence of particle size on carbon storage capacity and deactivation behavior to be systematically evaluated. Furthermore, catalyst deactivation was defined based on carbon saturation for each particle size, and the resulting effective Ni active site density was incorporated into a one-dimensional reaction rate model, thereby enabling prediction of the time-dependent production of H<sub>2</sub> and CH<sub>4</sub> while accounting for activity decay.

Using the particle size distribution obtained from TEM observations of fresh catalysts as an initial condition, the sintering model successfully reproduced particle growth behavior consistent with the size distribution of carbon nanomaterials formed after the reaction (Fig. 1). Based on the calculated particle size distribution, the temporal evolution of the effective Ni active site density was evaluated, showing a stepwise decrease in catalyst activity as the reaction proceeded. When this activity decay was incorporated into the reaction rate model, the experimentally observed reduction in H<sub>2</sub> and CH<sub>4</sub> production rates over time was qualitatively reproduced (Fig. 2). Although discrepancies were observed in the decay rates and the onset timing of deactivation, these differences highlight the sensitivity of product evolution to carbon accumulation and surface reaction kinetics. Importantly, the modular structure of the present model allows the contributing phenomena to be systematically identified and independently refined.

Through these results, a hydrocarbon pyrolysis model integrating catalyst sintering behavior with carbon accumulation and deactivation processes was established. By introducing a particle-size-based deactivation criterion, the model enables simultaneous prediction of product gas behavior and catalyst activity decay without explicitly resolving detailed microscopic phenomena. Consequently, the proposed framework provides a practical basis not only for reaction performance evaluation but also for system feasibility studies and future optimization of carbon recovery processes under realistic operating conditions.

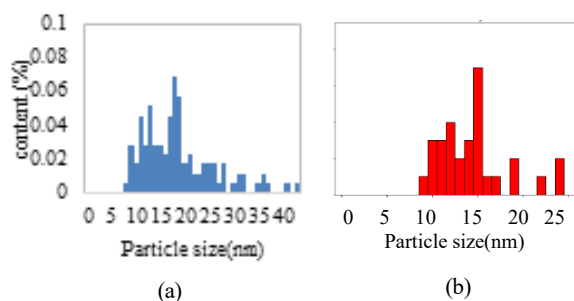


Fig.1 (a)CN Size Distribution (b) Predicted Particle Size Distribution (After Sintering)

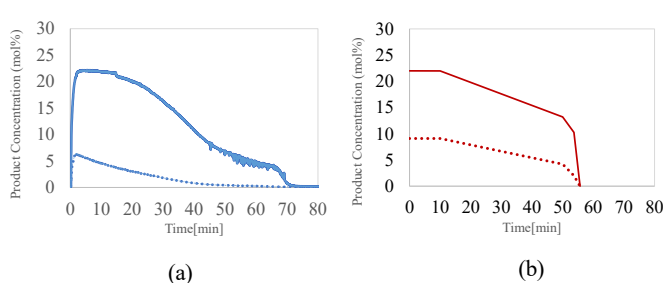


Fig.2 Time Profiles of H<sub>2</sub> and CH<sub>4</sub> Production (a)Experiment (b)Calculation (Solid:H<sub>2</sub>, Dashed:CH<sub>4</sub>)