

A reactive molecular dynamics simulation of catalyst deactivation during biomass thermochemical conversion

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ABSTRACT

The application of heterogeneous catalysis in biomass thermochemical conversion is considered as one of the most promising methods to improve biofuel production by minimizing its undesirable properties and producing renewable fuels and high-value chemicals. However, the catalyst used in practical industrial reforming application undergoes deactivation inevitably, which is a problem of great and continuing concern. In this study, molecular dynamics simulation with reactive force field is performed to gain atomic insights into the thermal stability of Ni nanocrystal and the effect of coke deposition on catalyst deactivation.

Keywords: biomass, catalyst deactivation, molecular dynamics, surface premelting, coke deposition

1. INTRODUCTION

Biomass as the organic material stored in plants is widely considered as a promising energy resource with great potentials. Lignocellulose is the most abundant form of biomass, with an annual production of around 170 billion metric tons [1]. Lignocellulose can be transformed into high-value-added products after thermochemical treatment, and it has long been recognized as a promising alternative for fossil fuels. However, the thermochemical conversion processes involve complex reactions relying on catalysts to speed up, where the mechanisms have not been fully understood.

In the last ten years, a large number of advanced analytical techniques have been developed to understand the structure and reaction mechanism of lignin, e.g. molecular dynamics (MD) simulation with

reactive force field (ReaxFF) at the atomic level [2]. The ReaxFF MD bridges the gap between quantum mechanics and the classical MD. For example, the main products of lignin depolymerization on the Pd-based heterogeneous catalyst in methanol-water solution obtained from ReaxFF MD simulation were in excellent agreement with the experimental results [3]. This shows the capability of ReaxFF MD to study the stability and activity of nanoscale catalyst during biomass conversion.

2. SIMULATION SETUP

2.1 Multiscale conversion of biomass into biofuel chemicals

Lignocellulosic biomass is composed of three major components, i.e., cellulose, hemicellulose and lignin as illustrated in Fig. 1 (a). Compared with cellulose and hemicellulose, lignin is a complex polymer composed of three basic units, phydroxyphenyl alcohol, guaiacyl alcohol and syringyl alcohol through various linkages as shown in Fig. 1 (b). A simplified breakdown of lignin considers it as a mixture of three β -O-4 skeleton-based aromatic dimers, i.e., LigC ($C_{15}H_{14}O_4$, composed of 67.8% C, 5.6% H and 26.6% O), LigH ($C_{18}H_{17}O_5(OCH_3)_4$, composed of 60.4% C, 6.6% H and 33.0% O) and LigO ($C_{16}H_{11}O_6(OCH_3)_4$, composed of 56.7% C, 5.4% H and 33.0% O) as shown in Fig. 1 (c) [4, 5]. Due to the complexity of the lignin molecular structure and various reaction pathways in thermochemical conversion, several hundred types of compounds with distinct properties are produced. By adding appropriate catalyst like metal nanoparticles into the reactors as shown in Fig. 1 (d), the desirable reaction pathways can be selectively enhanced, leading to the optimization of the products distribution and thus achieving the biomass valorization.

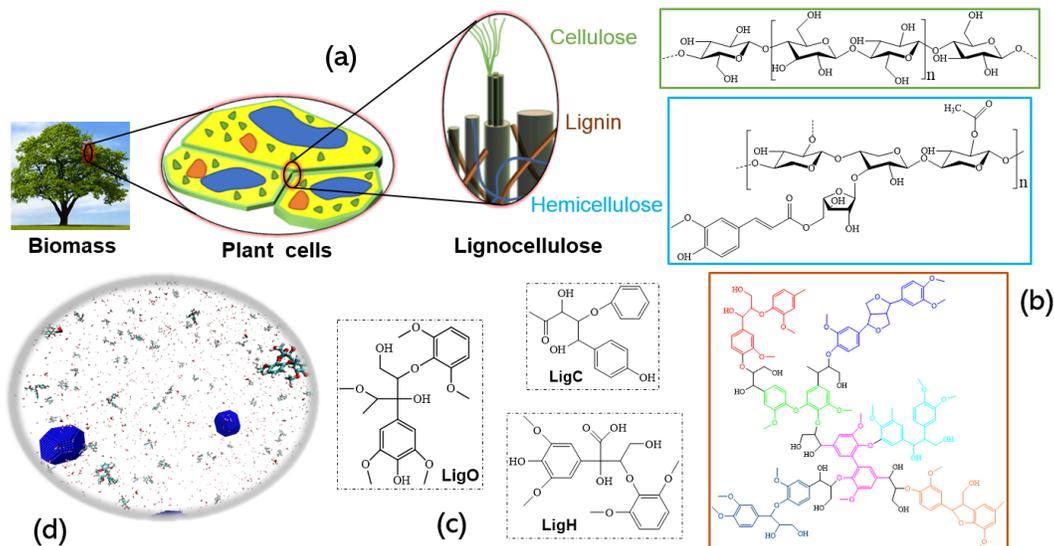


Fig. 1. (a) schematic depiction of the cellulose, hemicellulose and lignin in plant cells of lignocellulosic biomass, (b) representative molecular structures of β -D-glucose cellulose, hemicellulose and softwood lignin fragment highlighting the most common linkages adapted from Beste [6], (c) lignin surrogate models proposed by Faravelli et al. [5] based on the characterization and composition of lignin structures, (d) molecular modelling of lignin decomposition over nanocatalysts.

In this work, we consider such simplified composition of lignin and use MD to simulate their thermal breakdown during a heterogeneous catalytic process that uses Ni as catalyst. We concentrate our investigation on the main mechanisms that affect the catalytic activity of Ni, i.e. thermal stability of the catalyst crystals (softening/melting) and coke deposition on its surface.

2.2 Simulation method

Ni nanoparticles were created on a web-based crystallographic tool [7]. The minimum surface energy of corresponding Miller indices of (111), (100) and (110) was adopted from the work of Jiang et al.[8]. All the simulations were performed in LAMMPS with the CHONi force field parameters of ReaxFF developed by Mueller et al. [9]. Canonical ensemble (NVT) was used for all the simulations with time step of 1fs. The melting of Ni nanoparticles was investigated in the simulated environment at a temperature increase from 300 K to 3000 K in 500 ps. Lignin decomposition over the catalyst was simulated, whereby 1 Ni nanocrystal and 100 lignin surrogate molecules were placed randomly in a cubic box of 100 Å. The constant temperature ranged from 1500 K to 4000 K. In ReaxFF simulations, using a high temperature and pressure to accelerate the reactions and facilitate the pyrolysis process is a common strategy [10]. This allows the mechanisms of catalyst deactivation to be explored.

3. RESULTS AND DISCUSSION

3.1 Deactivation of Ni due to the surface melting

Compared with cellulose and hemicellulose, lignin is more difficult to decompose with temperatures ranging from 160 to 900 °C [11]. Temperatures of hydrogen production from the gasification of lignin with Ni catalysts in supercritical water can also be above 1000 K [12-14]. When nanoparticles are heated up, the atoms on their surfaces are highly mobile. Previous work has shown that a temperature around 900 K is sufficient to modify the surface morphology of the nanocrystals, resulting in the “surface premelting” during reaction which would in turn affect the catalytic activation [15]. The resulting thermal stabilities of Ni nanocrystals of various sizes are shown in Fig. 2 (a).

The bulk melting temperature of nanocrystal can be obtained by the time evolution of the average potential energy. The turning point of the potential energy curve corresponds to the melting temperature. The melting temperature also depends on the size of nanocrystals, increasing with the increase of the crystal size. ReaxFF MD simulation overestimated the bulk melting temperature compared with the theoretical values obtained by Abudukelimu [16]. As shown in Fig. 2 (b), mobility of atoms on the surface is observed after 200 ps at temperature of 1200 K, leading to surface premelting. This is a value below the complete melting point. The melting process is also shown by the radial distribution function (RDF) as depicted in Fig. 2 (c), which represents

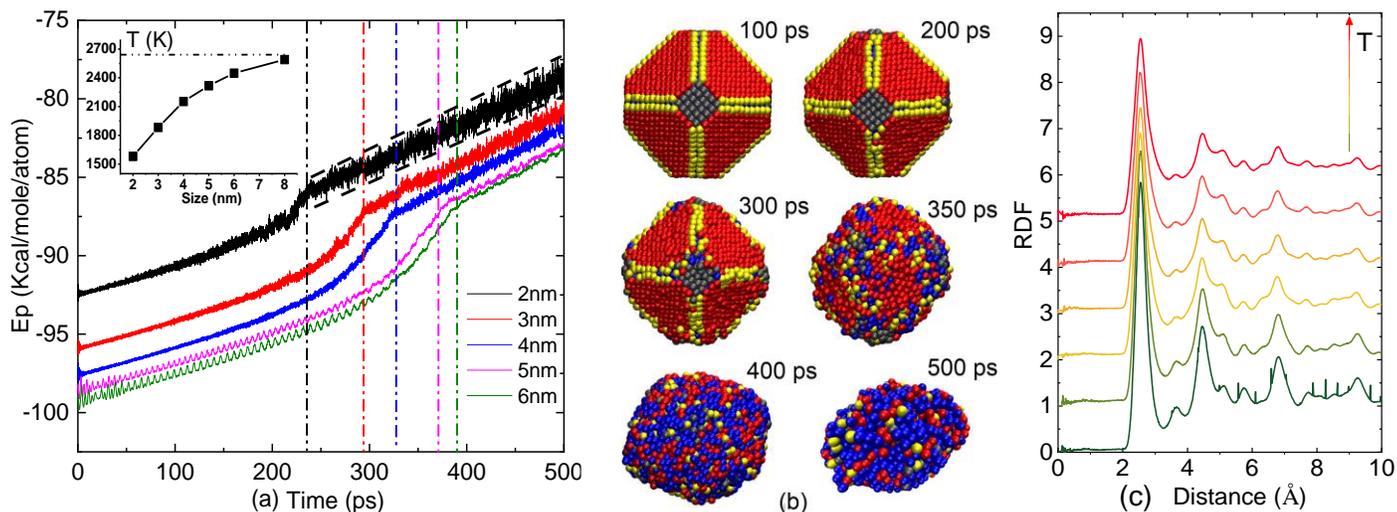


Fig. 2. (a) time evolution of the average potential energy per atom of Ni nanocrystal with dimeters of 2-6 nm during heating and (b) snapshots of the atom rearrangement at different surfaces of the 4nm Ni nanocrystal, red: the outer layer of Ni (111) facet, grey: the outer layer of Ni (100) facet, yellow: the outer layer of Ni (110) facet, blue: the inner bulk Ni atoms, (c) time evolution of the RDF of the 4nm Ni nanocrystal during melting.

the probability to find an atom in a shell dr at the distance r of another atom chosen as a reference point. During heating the sharp peaks of the RDF of the crystal structure become diffused, but long-range order is well visible as long as the particle remains crystalline. In complete melting liquid phase, long-range order vanishes, and the oscillations of the radial function decay quickly with increasing distance.

3.2 Deactivation of Ni due to the coke deposition

Catalyst is shown to undergo rapid and severe deactivation by means of a series of physicochemical phenomena, including melting, metallic phase oxidation and more notoriously, coke deposition [13]. The effect of

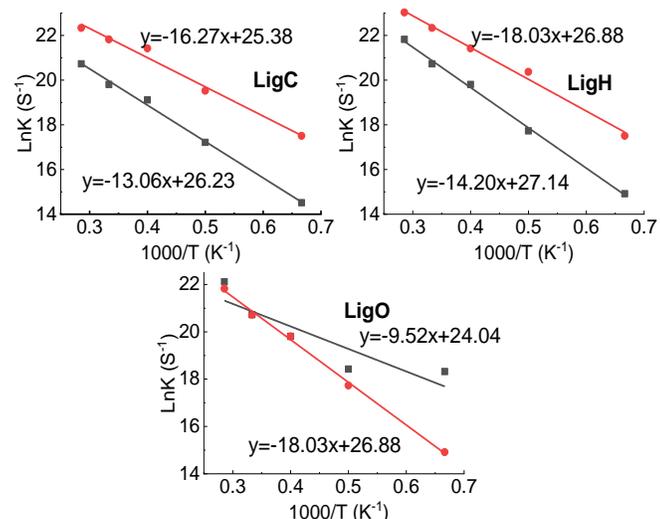


Fig. 3. Comparison of the chemical kinetics of lignin surrogate models in the conditions with and without the Ni nanocrystal of 4nm.

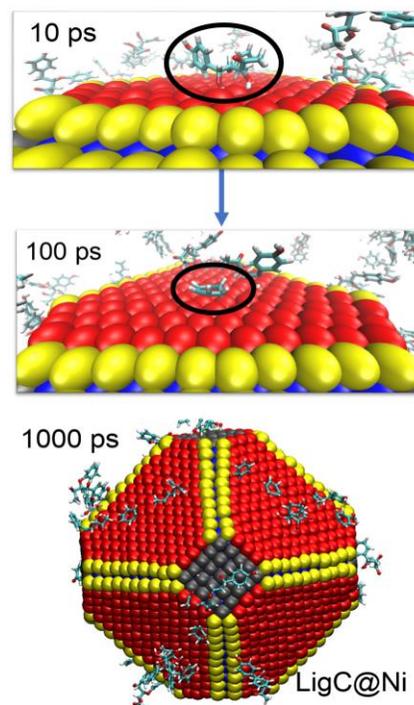


Fig. 4. Snapshots of the adsorption and cleavage process of the lignin on Ni surface and the deposition of soot precursors.

Ni nanocrystals on decomposition of lignin is evaluated as shown in Fig. 3. Results show that Ni nanocrystal increases the reaction rate for LigC and LigH. However, opposite effect is observed for LigO particularly at high temperature. The adsorption and decomposition processes of lignin on catalyst surfaces are captured by

MD simulation as shown in Fig. 4. Soot precursor chemisorption and physisorption are observed. This would coat the active sites of catalysts, impeding contacts with the reactants. The effect of deactivation due to coke deposition can be quantified by evaluating the Arrhenius parameters and site-loss rate.

4. CONCLUSIONS

The deactivation of Ni nanocrystal as catalyst on lignin thermochemical conversion into biofuels was investigated in this study. There are a number of findings from the simulation results. Firstly, atom rearrangement on surfaces was observed at the temperature of supercritical gasification from the ReaxFF MD simulation, which results in the surface premelting and the irreversible catalyst deactivation. This also shows the feasibility and potential of MD simulation to study the thermal stability and to evaluate the crystalline heterogeneous metal nanocatalysts. Secondly, deposition of the unwanted carbonaceous contaminant onto the catalyst surface, resulting in the activity loss due to the blockage of active sites, was also evaluated in the ReaxFF MD simulation. This can be used to quantify the loss of catalytic activity and selectivity over time. The atomic insights obtained from the MD simulations can be used to understand the mechanisms of catalyst deactivation and guide the design of effective catalytic reactions that enhance the thermochemical conversion of biomass. Further studies will be focused on more quantitative analyses of the deactivation process.

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