Hydrocracking of Biomass Tar Model Compounds into BTX: Unraveling Mechanisms, Reaction Micro-Kinetics, and Modeling with H-ZSM-5 Catalyst

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- Tetralin, naphthalene and 1-methylnaphthalene conversion over HZSM-5 was modelled.
- Hydrogenation, isomerization, dehydrogenation, and cracking reactions were included.
- Kinetic rate parameters were optimized using experimental data with good agreement.
- Sensitivity analysis was performed for a better insight into the surface mechanisms.

1. Introduction

Gasification of biomass presents an appealing technological approach to generating syngas (also known as combustible gas, comprising CO, CO_2, H_2, CH_4, H_2O, etc.) and heat [1]. However, a significant hurdle in biomass gasification lies in the presence of tar in the resulting syngas. Tar can pose a threat to the commercial viability of this technology by causing blockages in filters and pipes, damaging turbines and engines, and poisoning downstream catalysts. Biomass tar, characterized as a high molecular weight hydrocarbon, typically exceeding benzene, can be represented by various model compounds such as naphthalene (NP), 1-methylnaphthalene (1-MN), toluene, phenol, tetralin, anthracene, and more [2]. Numerous methods exist to mitigate biomass tar, including physical treatment, thermal cracking, plasma-assisted cracking, and thermal catalytic cracking. Among these, thermal catalytic cracking stands out as the most promising due to its high efficiency and economic advantages. This study focuses on tetralin, NP, and 1-MN as model compounds for biomass tar [3-7]. Experimental and microkinetic modeling techniques were employed to investigate these compounds. A pioneering surface reaction model for tetralin dehydrogenation on zeolites was developed, and its reaction rate constants were determined through experimental data [1]. The model's accuracy was confirmed through validation against experiments, demonstrating excellent agreement. It successfully simulated coke deposition, various feedstocks, and different reaction directions.

2. Methods

The diagram of the reactor employed for converting biomass tar model compounds, specifically pure tetralin or a mixture of 5 wt% NP dissolved in 95 wt% 1-MN, has been depicted in our previous publications [3,6]. In essence, the reaction took place in a packed-bed microactivity reactor. Typically, 0.5 g of powdered catalyst was loaded into a tubular reactor with a packed bed. The catalytic packed-bed reactor underwent pretreatment in N_2 (50 mL/min) flow before reaching the programmed temperature. Subsequently, the reactor was exposed to H_2 (150 mL/min) flow for 2 h at 370 °C before initiating the reaction. Figure 1 illustrates the proposed surface tetralin hydrocracking reaction network. The depicted gas species are those detected in our reaction runs, showing concentrations significant enough to be relevant to the mechanism. Computational analyses were carried out using the CERRES (Chemical Reaction and Reactor Engineering Simulations) software. In the program's backend, the reactor equation is reformulated into a finite number of discretized volumes along the reactor length, resulting in a set of ordinary differential equations (ODEs).

3. Results and discussion

Biomass tar model compounds, including tetralin, NP, and 1-MN, have been extensively explored over a range of zeolite materials and zeolite catalysts modified with metal(s) in previous studies [3-7]. This mechanistic investigation represents a pioneering effort in quantifying the relationship between cascade molecular structures, intermediates, and reactivity through detailed micro-kinetic modeling [1]. The current work presents a systematic analysis of kinetics based on measurements, encompassing 17 gas-phase species, 23 bonded adsorbed molecules, and sites, involving 41 reactions between them. The experimental data for tetralin, aromatics, and isomer hydrocracking, hydrogenation, and isomerization processes were used to test the system. The derived representation demonstrated consistent agreement with only statistical numerical variations, covering hydrogen-activated hydrocarbon conversion, BTX (benzene, toluene, and xylenes) selectivity, and coking. Experiments were conducted in a packed bed reactor over H-beta, H-mordenite, H-USY, H-Y, and H-ZSM-5, or (Ga, Nb, Ni, NiMo, Sn, W, Zr, or $H_3[P(W_3O_{10})_4]$)/ZSM-5, without sulfide standard procedures in the functional temperature range of 370–500 °C under atmospheric pressure. The most promising results were achieved over H-ZSM-5 (Figure 1). Various reactor configurations, including plug flow reactor (PFR), ideal continuous stirred tank (CSTR) vessel, and coupling the PFR with diffusion, were considered, with the first one found to be the most fitting to the results. The impact of feedstock on catalytic activity performance was also investigated. Deactivation was observed due to stable coke formation, leading to decreased stability but demonstrated predictability. A technique sensitivity analysis was performed for BTX products. Simulations indicated that heat or mass transfer resistances, either intra- or inter-particle, were negligible.

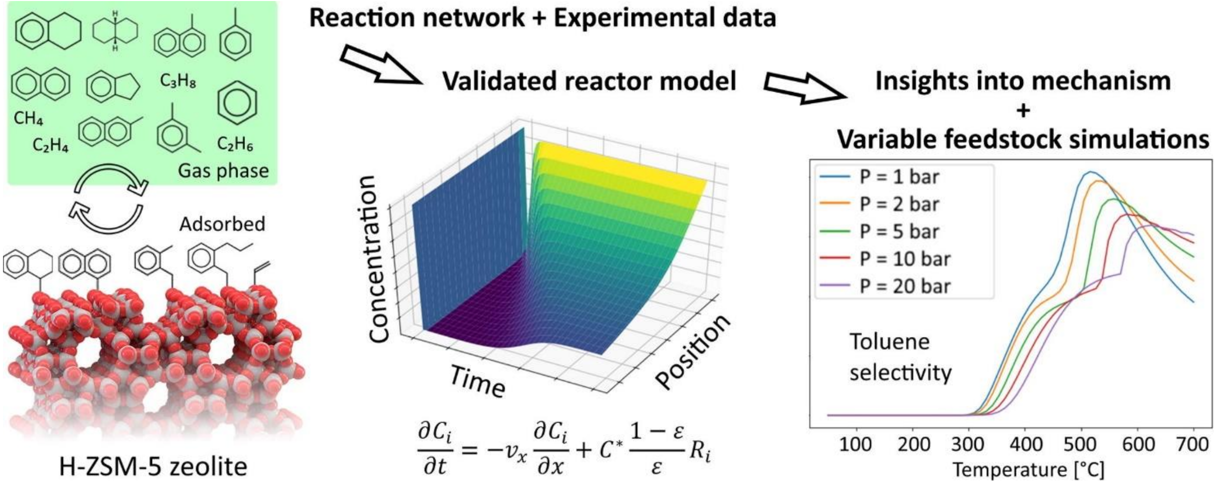

Figure 1. The proposed surface reaction mechanism for tetralin hydrogenation, dehydrogenation, and hydrocracking reactions over H-ZSM-5 zeolite catalyst; tetralin concentration evolution in the PFR model, dependence on time and reactor position. C-based selectivity of toluene - dependence on temperature and pressure (PFR model, 42 mL/min flow rate) [1].

4. Conclusions

A surface microkinetic model was established for the conversion of tetralin, including NP and 1-NP, over H-ZSM-5. This model encompassed hydrogenation, isomerization, dehydrogenation, and cracking reactions. The reaction rate parameters of the model were determined through optimization based on experimental data, resulting in good agreement and accurate prediction. Furthermore, through transient deactivation experiments, the model was enhanced to account for deactivation due to coking, demonstrating good alignment with experimental observations. The optimized model was then employed for simulations to explore a broader range of operating conditions, particularly varying temperatures and pressures. The impact of these parameters on conversion and selectivity was examined, and onset temperatures for cracking, as well as maximal BTX yields, were identified. These findings could be utilized for planning experiments with high-yield operating windows. Sensitivity analysis of the reaction network was conducted to identify rate-limiting steps and assess the significance of different reaction pathways.

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Keywords

Chemical reaction micro-kinetics; Tetralin, naphthalene and 1-methylnaphthalene; H-ZSM-5 zeolite catalyst material; Benzene, toluene and xylenes (BTX).