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The effect of mild hydrogenation on the catalytic cracking of bio-oil for aromatic hydrocarbon production

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ABSTRACT

In order to reduce the coke formation and improve catalyst activation in the catalytic cracking of bio-oil, ethanol addition and mild hydrogenation pretreatment were introduced to improve the cracking stability. According to the analysis on the bio-oil molecular distillation, several typical compounds were selected as the representative of bio-oil distillation. Based on the two-stage fixed-bed reactor, the effect of mild hydrogenation on the cracking behavior of bio-oil model compound mixture was studied in detail. In a single-stage cracking process, the selectivity of oil phase was only 28–23 wt%, with the formation of abundant oxygenated byproducts. When mild hydrogenation was introduced before the cracking, the selectivity of oil phase increased up to 40wt% at 8 h, with an aromatic hydrocarbon content of over 90%.

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Introduction

The concern for the exhaustion of fossil fuel has made biomass energy draw extensive attentions in the world [1,2]. Bio-oil via biomass fast pyrolysis is supposed to be a substitute for conventional transport fuels. However, the inferior properties of crude bio-oil, including high oxygen and water contents, low heating value and strong corrosiveness [3,4], limit its direct utilization. Therefore, upgrading technology is essential for the bio-oil high-grade utilization.

Various upgrading techniques have been studied in recent decades, such as catalytic cracking, catalytic hydrogenation, esterification, steam reforming, emulsification, etc [5,6]. Catalytic cracking is an effective bio-oil upgrading technology, which can transform bio-oil into the liquid fuel abundant in aromatic hydrocarbons by removing oxygen in the form of CO, CO₂ and H₂O [7]. Various catalysts, such as HZSM-5, H-Y, H-mordenite, silicalite and silica-alumina, were investigated in catalytic cracking process, in which HZSM-5 was favorable for aromatic hydrocarbon production [8]. However, the composition of crude bio-oil is quite complicated, which consists of

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ketones, acids, aldehydes, phenols, sugars, etc. Therefore, even the cracking of bio-oil over HZSM-5 could not achieve satisfactory results. Previous studies on the cracking of bio-oil model compounds over HZSM-5 showed that, ketones and acids could be converted into hydrocarbons, whereas large-molecular-weight phenolic oligomers and sugars resulted in the coke formation, which caused rapid catalyst deactivation [9–11]. Consequently, the removal of phenolic oligomers and sugars in bio-oil is of great significance. Molecular distillation is an effective separation technology, which can separate bio-oil into a distilled fraction with high reactivity and a residual fraction with low reactivity. The distilled fraction mainly enriches ketones and acids, while the phenolic oligomers and sugars are reserved in the residual fraction [12]. Therefore, the study on bio-oil catalytic cracking based on molecular distillation is more feasible and efficient. Due to the high oxygen content and unsaturation degree, the bio-oil components in the distilled fraction still have the propensity for coke formation. The concept of the effective hydrogen to carbon ratio $((H/C)_{\text{eff}})$ [13] was introduced to evaluate the cracking performance of different compounds. As shown in Eq. (1), H, O and C represent the mole percentages of hydrogen, oxygen and carbon in the corresponding compounds, respectively.

$$(H/C)_{\text{eff}} = (H-2O)/C \quad (1)$$

It was reported by Mentzel and Holm that a higher $(H/C)_{\text{eff}}$ had a positive impact on the catalyst stability in the cracking of bio-oil model compound mixture [13]. In view of the difference between bio-oil $((H/C)_{\text{eff}} < 1)$ and targeted aromatic hydrocarbons $(1 < (H/C)_{\text{eff}} < 2)$, it is necessary to deal with the feedstock to increase the integral $(H/C)_{\text{eff}}$. The introduction of aliphatic alcohols as co-cracking reactants is an effective way to increase the overall $(H/C)_{\text{eff}}$ of reactants. In a study on the co-cracking of bio-oil and methanol [14], the initial conversion of bio-oil and the selectivity of aromatic hydrocarbons reached 90% and 40%, respectively. It was also reported by Mentzel and Holm that the addition of methanol into bio-oil model compounds could significantly prolong the lifetime of catalysts during cracking process [13]. In our previous study, the co-cracking of bio-oil model compounds (acids and ketones) with ethanol was investigated, and an oil phase selectivity of 31.5wt% was achieved. The oil products entirely consisted of hydrocarbons, 91.5% of which were aromatic hydrocarbons [15]. Subsequently, we carried out the co-cracking of bio-oil distilled fraction and ethanol in the ratio of 2:3. The oil phase selectivity achieved 25.9wt%, and a hydrocarbon content of 98.3% was obtained within 3 h [16]. However, the blend ratio of ethanol is still relatively high. Furthermore, phenolic oligomers remaining in the distilled fraction have low reactivity and easily lead to the coke formation and poor stability via condensation reactions. Consequently, the cracking process still requires further improvement.

Catalytic hydrogenation is another conventional bio-oil upgrading technology. The hydrogen for this technology can be supplied by the steam reforming of partial bio-oil fraction using catalysts such as Ni/Al₂O₃, Co–Fe and Ni/Ash [17–19]. Catalytic hydrogenation mainly including two types: (1) hydrodeoxygenation and (2) mild hydrogenation. For the

purpose of effective deoxygenation, the former removes oxygen in bio-oil to form aliphatic hydrocarbons and H₂O at a high pressure (10–20 MPa) in general [20–22], which leads to high consumption of H₂ and harsh requirement of equipment. The latter is utilized to saturate double bonds and aromatic rings at a relatively low pressure, in order to improve the bio-oil stability [23–28]. The typical catalysts for hydrogenation can be divided into several groups: noble metals [23,25–27], Mo-based sulfides [29], metal phosphides [30] and other metal catalysts [28], among which Pd showed its high reactivity in hydrogenation [23,26]. Considering the frequent catalyst deactivation in the cracking process, the mild hydrogenation can be applied prior to catalytic cracking. Vispute et al. carried out the catalytic hydrogenation of bio-oil aqueous phase at 10 MPa in the fixed-bed reactor, followed by the catalytic cracking of condensation products in another reactor, and achieved the aromatic hydrocarbons and olefins selectivity of 18.3% and 43.0%, respectively [31]. Different from the separated hydrogenation and cracking reactions, a bio-oil upgrading technology based on a two-stage continuous hydrogenation-cracking was proposed in this study. Namely, the gaseous products from hydrogenation reaction are directly fed into the cracking reactor. This technology exhibits better continuousness and feasibility, thus in favor of industrialization. In the first stage, 3%Pd/nano-SiO₂ is adopted for the mild hydrogenation process to increase the integral $(H/C)_{\text{eff}}$ of feedstock. In the second stage, HZSM-5 is used for the cracking process to convert the reactants rich in hydrogen into hydrocarbons. Meanwhile, the coke formation was successfully inhibited by combining the molecular distillation and co-cracking with ethanol [16]. The typical model compounds in distilled fraction, namely, hydroxypropanone, cyclopentanone, acetic acid, guaiacol, phenol and furfural, were mixed with ethanol as reactants.

Experimental section

Nano-SiO₂ and PdCl₂ were purchased from Aladdin Industrial Corporation, and HZSM-5 was obtained from the Catalyst Plant of Nankai University. Similar with that preparation procedure for Pd based catalysts [32], Pd/nano-SiO₂ used for hydrogenation was prepared by incipient wetness impregnation and the loading amount of Pd was 3wt%. A requisite amount of PdCl₂ was dissolved in the deionized water in the presence of hydrochloric acid at ambient temperature to obtain the aqueous solution (PH = 3), and then pretreated nano-SiO₂ was added in the PdCl₂ solution. After stabilization of 12 h, the mixture was dried in an oven at 110 °C overnight. The final sample was calcined at 550 °C for 6 h. As for the catalyst used for catalytic cracking process, the HZSM-5 (Si/Ai = 25) was calcined at 550 °C for 6 h before the experiment. Pd/nano-SiO₂ and HZSM-5 were both sieved to 40–60 mesh.

The bio-oil model compounds consisted of hydroxypropanone, cyclopentanone, acetic acid, guaiacol, phenol and furfural. Hydroxypropanone, guaiacol and cyclopentanone were purchased from Alfa Aesar and Aladdin Industrial Corporation, respectively, while acetic acid, phenol and furfural were purchased from the Sinopharm Chemical Reagent Corporation. The ratio of model compounds was set

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