



Controlled regeneration of ZSM-5 catalysts in the combined oxygen and steam atmosphere used for catalytic pyrolysis of biomass-derivates



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ARTICLE INFO

Keywords:

Biomass
Catalytic pyrolysis
Coke
Controlled regeneration
Oxygen concentration
Steam

ABSTRACT

Catalyst deactivation by coke deposition was the main barrier in the catalytic pyrolysis of biomass for hydrocarbons, thus deactivated catalysts should be regenerated timely. In this study, several measures were applied in the regeneration process to obtain higher yield of hydrocarbons in the catalytic conversion of biomass-derivates. The effect of oxygen concentration in the regeneration atmosphere on catalytic performance was firstly investigated, and then steam was introduced on the basis of the optimal oxygen concentration to further decrease the internal temperature of catalyst particle. Finally the deactivated catalysts were partially regenerated by retaining some coke. The results showed that 15% was the optimal oxygen concentration, at which the catalysts still showed steady production of olefins and aromatics after 30 cycles of catalysis-regeneration. When 15% oxygen and 5% steam was combined in the regeneration atmosphere, the temperature of catalyst bed was reduced efficiently. The stable yield of hydrocarbons by combined regeneration method was boosted by 31.3% compared with pure 15% oxygen. At retaining coke amount of 2.18%, yield of hydrocarbons was promoted by 27.4% compared with completely regenerated. With the combined oxygen/steam atmosphere and controlled regeneration, the temperature of catalyst particles was well regulated and stable catalysis-regeneration process to produce hydrocarbons via thermochemical utilization of biomass can be realized.

1. Introduction

Catalytic fast pyrolysis (CFP) of biomass can convert solid biomass into high-valued chemicals like olefins and aromatics, namely, biomass was firstly pyrolyzed into oxygen-containing molecules, and then working on the catalysts to undergo a series of reaction steps like dehydration, decarbonylation, decarboxylation, cyclization, oligomerization, etc. [1–3]. Compared with biomass fast pyrolysis and following bio-oil upgrading technology, CFP of biomass is simplified a lot, avoiding the energy loss during pyrolysis condensation [4,5]. The addition of catalysts brings a series of issues, like catalyst deactivation due to coking and difficult regeneration of deactivated catalysts [6,7]. Some pyrolysis vapor of large molecules (like levoglucosan) cannot enter catalyst pores and polymerize to form coke, and the catalyst pores are blocked [8]. On the other hand, some active molecules (like furan) enter the catalyst pores and a series of reaction steps like dehydration, dehydrogenation, hydrogen transfer happened [9]. Thus, catalyst coking is the central obstacle which hinders the production of high-valued chemicals (hydrocarbons) from CFP of biomass.

The catalysts should be regenerated timely when their activity

decreased significantly [10–12]. Usually used regeneration methods are oxidization, sweeping, washing, etc. [13,14]. Oxidization, coke reacting with oxygen and carbon deleted as CO and CO₂, can realize on-line regeneration, is an often used regeneration technology [15,16]. Abundant heat is generated during coke combustion. If the heat are too much or concentrated, it can be not be taken out timely. Some hot spots may occur in the catalysts, which leads to the change of catalyst property [17,18]. The combustion of coke results in regional overheating [19]. The removal of framework Al generates voids in the internal space of catalysts, thus the skeleton structure is easily changed. Therefore, the internal temperature of catalyst particle should be strictly controlled during the regeneration of deactivated catalysts due to coking [20].

Catalyst temperature is very important in the regeneration process for coke combustion [21]. If it is too low, coke cannot be removed clearly and the regeneration unit may be extinguished. If it is too high, coke may be graphitized, and catalyst bed is easily to be overheating. To well control the oxygen concentration to avoid overheating and catalyst damage, nitrogen and steam are often used as dilute gas [22,23]. In the process of coke combustion after CFP of biomass, air is usually applied as regeneration atmosphere, since it is the oxidization

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gas which is the easiest to obtain [24]. A fixed oxygen concentration of 21% has been studied adequately, however, whether a higher or lower oxygen concentration for regeneration can keep well the catalytic activity for CFP of biomass is still unknown. A new regeneration technology by multi steps at low oxygen concentrations and setting temperatures has been proposed [16]. It is actually a long process (> 4 h), which determines that it is not a preferential choice. Therefore, the single step regeneration with appropriate oxygen concentration is urgent in CFP of biomass for hydrocarbons. Another technology to lower the temperature of catalyst particle is to add steam into the oxidation, since it can easily enter catalyst pores due to its small volume and strong polarity. O₂ was surrounded by large amounts of steam, which was beneficial to reduce combustion rate [25]. Steam with large heat capacity can take the combustion heat out timely and then overheating can be controlled efficiently. However, if high partial pressure of steam is used in the regeneration atmosphere, activity loss will happen due to the damage of catalyst framework, i.e. partial four-coordinated Al is converted irreversibly into non-framework Al of octahedron. Thus, if the concentration of steam (V_{stm}) is well controlled, steam can be undoubtedly introduced into regeneration atmosphere to lower the catalysts temperature in the stage of severe combustion, ensuring the catalyst property as well.

It is well known that the pore structure and acid property of catalyst have a significant effect on its catalytic performance. Deactivated catalysts are usually regenerated completely, i.e. the total coke is removed, to recover their activity as much as possible. In methanol to olefins (MTO) reaction, when certain amount of coke was retained in catalyst, an optimal selectivity of olefins can be obtained [26]. The retaining coke can modify the acid property and pore dimension of catalyst, and the selectivity of targeted products is improved [27]. The controlled regeneration of deactivated catalysts should also be considered in CFP of biomass, though the reactant is of larger molecule and the catalysts are of smaller size, to understand the influence of retained coke on the production of hydrocarbons.

In this study, the relationship between oxygen concentration in regeneration atmosphere and catalytic performance in CFP of biomass-derivates was firstly explored. On the basis of optimal oxygen concentration, appropriate amount of steam was introduced to further lower the internal temperature of catalyst particle at the violent combustion stage. The cycle tests of catalysis-regeneration were performed with combined oxygen/steam regeneration atmosphere. Finally, controlled regeneration was investigated, in which catalyst were decorated and the distribution of acid sites were changed. Carbon yield of hydrocarbons and product distribution were analyzed as a function of coke retaining amount, and the optimal coke retaining amount was obtained. The optimization of hydrocarbon yield and stable CFP of biomass-regeneration processes can finally be realized.

2. Experimental section

2.1. Materials

Furan as a typical derivate from biomass pyrolysis was used as raw material. HZSM-5 catalysts were purchased from catalyst plant of Nankai University, whose physicochemical property were listed in Table 1. HZSM-5 catalysts (120–200 mesh) were dried at 600 °C in air for 1 h before each experiment.

Table 1
Physicochemical property of ZSM-5 catalysts.

| Parameter | S _{BET} (m ² /g) | V _{micro} (cm ³ /g) | V _{total} (cm ³ /g) | Si/Al |
|-----------|--------------------------------------|---|---|-------|
| Value | 239 | 0.11 | 0.14 | 22.28 |

2.2. Experimental set-up and procedure

The schematic diagram for catalytic conversion of biomass derivates and the process of catalytic pyrolysis of biomass-derivates have been provided in supplementary information [28,29]. The operation parameters for catalytic conversion were set as follows, catalytic temperature, 600 °C; weight hourly space velocity, 11.2 h⁻¹; partial pressure, 12.30 Torr. Correspondingly, the feeding rate was 29.72 μL/min, the catalysts amount was 150 mg, and the flow rate of carrier gas was 560 mL/min. The total catalysis time was 20 min, and sampling gas was collected in the time range of 0–1 min, 1–2 min, 2–3 min, 4–5 min, 6–7 min, 8–9 min, 12–13 min, 17–18 min.

The catalysis-regeneration tests were performed in a fixed-bed reactor. After catalytic process, the micro-injection pump was closed and the catalysts bed was purged for another 10 min to remove unreacted furan and physically absorbed species on the surface of catalysts. Then the carrier gas was switched to oxygen/nitrogen or oxygen/nitrogen/steam, and the regeneration time can be set as required. First, oxygen/nitrogen mixture gas was introduced with volume concentration of oxygen (Voxy) of 10%, 15%, 20%, 25%, 30%, 50%, 70% and 100% after the above catalytic process. The total regeneration time was 30 min and the regeneration temperature was 600 °C. Then steam was introduced into the regeneration gas, and the volume concentration of steam (V_{stm}) was 5% and 20%, in which Voxy was set as optimal value from the first step. Finally, the regeneration time was adjusted as 0 min, 5 min, 10 min, 15 min, 25 min and 30 min at the optimal oxygen concentration. The above regeneration time was corresponded to different retaining coke amount which was determined by thermogravimetric analyzer. The standard of complete regeneration was the catalysts recovering absolutely to white. It has been indicated in the initial trial experiment that 30 min was enough to realize complete regeneration at Voxy of 10%. Shorter time was required at higher Voxy, thus regeneration time of 30 min was reasonable. When cycle tests were performed, the mass flowmeters for oxygen and steam were then closed and that for nitrogen was set as required. The reactor was purged for 10 min, and then the catalytic process was repeated.

2.3. Characterization

The structures of the ZSM-5 samples were determined through X-ray powder diffraction (XRD) by a Bruker instrument using Cu Kα radiation at 40 kV and 40 mA with a scanning speed of 0.02 min⁻¹ in the range of 5° ≤ θ ≤ 80°. Nuclear Magnetic Resonance from Bruker instrument (AVANCE III 400WB) was applied to investigate the influence of regeneration conditions on the bonding condition of Al. The acidity of the regenerated catalysts with different Voxy was estimated by the NH₃ temperature programmed desorption (NH₃-TPD) technique. The sample was pre-treated at 600 °C in flowing He for 0.5 h. After pre-treatment, the sample was cooled to 100 °C and saturated with NH₃ gas. The physical absorbed NH₃ was then blown out. Finally, NH₃-TPD was carried out under a constant flow of He (20 mL/min). The temperature was raised from 100 to 600 °C at a heating rate of 15 °C/min. The magnetic field was 9.4 T with Larmor frequency of 15 kHz. Scanning electron microscopy (SEM) experiments were performed to obtain the morphology of the fresh and catalysts after several catalysis-regeneration cycles. The measurements were performed with a FEI Inspect F50 system at 10 kV. Prior to each measurement, the samples were prepared on a carbon pad and sputtered with gold to obtain the necessary conductivity. The experimental chemical composition of the supports and metallic phases were obtained via X-ray fluorescence (XRF) (ARL, Switzerland) with Rh Xray based tube. Deactivated catalysts were regenerated in a flowing air atmosphere of 50 mL/min in a thermogravimetric analyzer to determine the coke content by weight loss during oxidation. Typically, 15 mg of the sample was placed in the alumina crucible and heated from ambient temperature to 800 °C at a rate of 15 °C/min.

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