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Catalytic upgrading of fast pyrolysis biomass vapors over fresh, spent and regenerated ZSM-5 zeolites

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ABSTRACT

Fresh ZSM-5 zeolite in the proton form was used for the catalytic pyrolysis of biomass to form spent zeolite, which was then combusted to regenerate the zeolite. Catalytic upgrading of vapors of fast pyrolyzed corn stover over fresh, spent, and regenerated zeolites (referred to as FZ, SZ and RZ, respectively) was carried out using quantitative pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Pre-coking was found to minimize coke yield and favor the formation of target products with higher hydrocarbon and lower oxygen contents. Among all the parameters of the specific surface area, pore volume, and total acid sites (both weak acid sites and strong acid sites), FZ has the highest value, and SZ has the lowest value (FZ > RZ > SZ). The SZ and RZ lowered the total product yields compared to FZ (yield of FZ > RZ > SZ). The coke yields of these zeolites followed the order of FZ > RZ > SZ. Besides, RZ slightly promoted the production of phenols, whereas SZ reduced the relative content of phenols dramatically.

1. Introduction

As a promising candidate to substitute traditional petroleum-based fuels, bio-oil derived from renewable biomass resources has stimulated extensive interests [1]. A large number of researches have been focused on producing high quality bio-oil, and one of the most attractive methods is catalytic fast pyrolysis (CFP) technology [2–5]. A range of zeolite catalysts has been researched in the literatures [6–8], and previous experimental results have confirmed that ZSM-5 zeolite performs the best to de-oxygenate pyrolysis vapors and favor hydrocarbon production [9–11].

However, this acid catalyzed transformation process usually results in polymerization of oxygenates and formation of large molecules (known as "coke") which remain trapped and covered on the surface of catalysts [12–14]. Typically, biomass CFP technique causes a significant coke yield with a consequence of pore blockage and fast deactivation of catalysts, thus preventing the subsequent shape-selective reactions. For ZSM-5 zeolite, it has a 3-dimensional intersecting pore system with straight channels of 0.54 × 0.56 nm and Z-shaped channels of 0.51 × 0.54 nm [9]. Indeed, coke cannot enter the internal intracrystalline pores of ZSM-5 zeolite due to its bulky molecule; hence coke precursors only polymerize on the external surface [15–17]. Obviously, it is the internal acid sites of ZSM-5 zeolite having the catalytic effect to form target products, while the external acid sites produce coke [15,18,19]. Therefore, in order to suppress coke formation and promote hydrocarbon production, it is necessary to cover the external acid sites of ZSM-5 zeolite but retain the internal acid sites [20].

In contrast with fresh ZSM-5 zeolite, the spent ZSM-5 zeolite already has some coke deposited on its external surface, thus reducing its external acid site density and weakening the external acidity and activity. Therefore, for ZSM-5, the spent zeolite (SZ) has the potential to reduce coke yield, and its catalytic effect may be better than that of fresh zeolite (FZ). Actually, Bauer and his co-workers had passivated the external acid sites of ZSM-5 zeolite by pre-coking treatment, and their results showed that pre-coked ZSM-5 zeolite showed a better shape-selective effect for the generation of target products and led to a reduced formation of undesirable compounds [18,19]. On the other hand, the regeneration of SZ will inevitably affect the porosity and acidity characteristics, so the in-depth study of regenerated zeolite (RZ) is also needed.

In this work, FZ, SZ and RZ were collected, and quantitative pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) experiments were carried out to investigate the influence of FZ, SZ and RZ on the catalytic upgrading of corn stover fast pyrolysis vapors. The chemical compositions of the products were analyzed, and their relative contents were determined and discussed.

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2. Materials and methods

2.1. Materials

Corn stover (provided by a trading center in the city of Zhumadian in Henan Province, China) used in this study was pulverized mechanically and then sieved through a 40-mesh sieve before pyrolysis. The proximate and ultimate analyses of corn stover are presented in Table 1.

For ZSM-5 zeolite, FZ in the proton form applied in this experiment was supplied by the Catalyst Plant of Nankai University, with Si/Al ratio of 50 and particle diameter of 2–5 μm. FZ was used for a two-step CFP of corn stover in a horizontal tubular reactor (65 mm i.d. and 1000 mm length) to form SZ. The experimental setup of this two-step pyrolysis process was given in previous literature [21]. 3 g corn stover and 2 g ZSM-5 zeolite were used, and the reaction temperature was set at 400 °C. During this experiment, nitrogen was used as the carrier gas at a flow rate of 300 ml/min. A sample holder, consisting of a stainless steel stick and a quartz boat, was used to transport the corn stover to the heated zone in the reactor. Corn stover was placed in the quartz boat of the sample holder, which initially rested in an unheated section of the tube. Once the desired temperature was achieved, the sample holder was pushed to a predetermined location in the reactor and then pyrolyzed for 40 min. At the end of the experiment, the solid residue and catalyst layer were cooled to room temperature. After pyrolysis, SZ was collected, dried at 120 °C for 1 h in a drying oven and used in this paper. Besides, RZ was obtained when the dried SZ was combusted with air in a muffle furnace at 650 °C for 2 h. N_2 porosimetry and ammonia TPD methods were applied to test the porosity and acidity characteristics of FZ, SZ and RZ, and the specific surface areas were calculated using BET equation.

2.2. Methods

This experiment was carried out using an analytical CDS Pyroprobe 5200 pyrolyser interfaced with an Agilent 7890A/5975C gas chromatograph/mass spectrometer.

An open-ended quartz tube was successively filled with some quartz wool, 0.50 mg ZSM-5 zeolite, some quartz wool, 0.50 mg corn stover, some quartz wool, 0.50 mg ZSM-5 zeolite and some quartz wool. The schematic cross-section of the quartz tube was shown in Fig. 1. The ZSM-5 zeolite was placed at both sides of the feedstock and acted as fixed beds. Thus, the non-catalytic fast pyrolysis took place first and then the primary product vapors were upgraded when they passed through the catalyst layer. During the experiments, the tube was put into a platinum coil for fast pyrolysis. Feedstocks were heated at a high heating rate of 20 °C/ms–550 °C and then maintained isothermally for 20 s for the complete pyrolysis of corn stover feedstocks.

Upon pyrolysis, the pyrolysis vapors flowed from the quartz tube into the GC-MS via the helium sweeper gas stream (99.999%, 1.0 ml/min, Nanjing Maikesi Nanfen Special Gas Co., Ltd.). The GC/MS injector temperature of 275 °C and interface temperature of 300 °C were held. A column (HP-5MS, 30 m × 0.25 mm × 0.25 μm) was applied for the separation of GC, and the split ratio was kept at 1:80. The MS was used with ionization energy of 70 eV, and scan rate of 35–550 amu/s. The experiments were repeated at least three times, and the chromatographic peaks were discriminated and analyzed by means of the NIST MS library.

Table 1
Proximate and ultimate analyses (wt.%) of corn stover.

Proximate analysis (ad)			Ultimate analysis (daf)			
M	A	VM	C	H	N	O*
9.27	6.06	71.73	46.73	6.11	0.59	46.57

ad: air dry base; daf: dry and ash-free base; *: by difference.

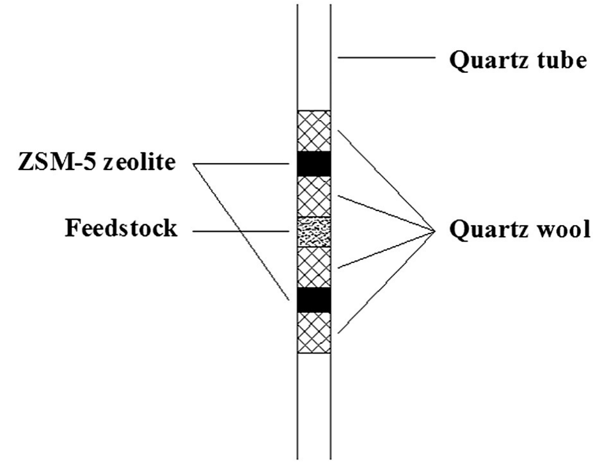

Fig. 1. Schematic cross-section of the quartz tube.

2.3. Data processing

There were various oxygenates (e.g., acetic acid; furfural; phenol; levoglucosan; 1,4:3,6-dianhydro-πd-glucopyranose) in the organic pyrolysis vapors. In order to compare the catalytic behaviors and deoxygenation capacities of different catalysts, it was necessary to determine the oxygen content in organic pyrolysis vapors [9,22,23]. Oxygen content in organic pyrolysis vapors was discussed in this paper, and it was calculated based on the chemical compositions identified in the GC/MS analysis and defined as

$$C_{ox} = \sum (C_i \times C_{i,ox}) \tag{1}$$

where C_{ox} is the oxygen content in organic pyrolysis vapors; C_i is the relative contents of oxygenates, such as acetic acid or phenol; $C_{i,ox}$ is the oxygen contents of corresponding oxygenates.

3. Results and discussion

3.1. Porosity and acidity characteristics of FZ, SZ, and RZ

As listed in Table 2, it could be found that among all the parameters of the specific surface area, pore volume and total acid sites (both weak acid sites (<300 °C) and strong acid sites (>300 °C)), FZ had the highest value, and SZ had the lowest value (FZ > RZ > SZ). For SZ, the pre-formed coke would cover on the external surface and clog some pore channels, thus resulting in a loss of surface area and pore volume. For RZ, most of the deposited coke could be combusted during the regeneration process, so the surface area and pore volume could be restored to a certain extent. Due to the same reason, the total acid sites (both weak acid sites and strong acid sites) showed the same tendency (FZ > RZ > SZ). However, in-depth researches have not been conducted to study the catalytic effect of SZ and RZ, and this paper investigated and compared their positive and negative impacts.

Table 2
Porosity and acidity characteristics of catalyst samples.

Sample	Porosity characteristic			Acidity (mmol NH_3/g)		
	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)	Total acid site	Weak acid site	Strong acid site
FZ	308.08	0.2114	2.7447	1.435	0.578	0.857
SZ	269.99	0.1892	2.8031	1.059	0.395	0.664
RZ	305.81	0.2097	2.7429	1.318	0.522	0.796

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