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Optimizing anti-coking abilities of zeolites by ethylene diamine tetraacetie acid modification on catalytic fast pyrolysis of corn stalk

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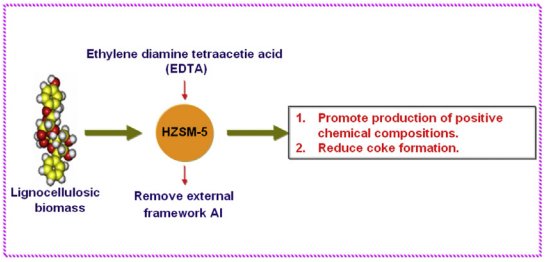
HIGHLIGHTS

- We use EDTA modification methods to dealuminate external surface of HZSM-5.
- Treatment time of 2 h is optimal for acid removal and hydrocarbon formation.
- Modified HZSM-5 can promote the production of positive chemical compositions.
- Modified HZSM-5 can minimize coke yield.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to minimize coke yield during biomass catalytic fast pyrolysis (CFP) process, ethylene diamine tetraacetie acid (EDTA) chemical modification method is carried out to selectively remove the external framework aluminum of HZSM-5 catalyst. X-ray diffraction (XRD), nitrogen (N_2)-adsorption and ammonia-temperature programmed desorption (NH_3-TPD) techniques are employed to investigate the porosity and acidity characteristics of original and modified HZSM-5 samples. Py-GC/MS and thermogravimetric analyzer (TGA) experiments are further conducted to explore the catalytic effect of modified HZSM-5 samples on biomass CFP and to verify the positive effect on coke reduction. Results show that EDTA treatment does not damage the crystal structure of HZSM-5 zeolites, but leads to a slight increase of pore volume and pore size. Meanwhile, the elimination of the strong acid peak indicates the dealumination of outer surface of HZSM-5 zeolites. Treatment time of 2 h (labeled EDTA-2H) is optimal for acid removal and hydrocarbon formation. Among all modified catalysts, EDTA-2H performs the best for deacidification and can obviously increase the yields of positive chemical compositions in pyrolysis products. Besides, EDTA modification can improve the anti-coking properties of HZSM-5 zeolites, and EDTA-2H gives rise to the lowest coke yield.

1. Introduction

Catalytic fast pyrolysis (CFP) is a good method for the direct conversion of solid biomass into high-quality liquid fuels or chemicals [1–5], and it will be widely applied in the future for the low cost, simple reactors and time-saving operations [6,7]. During CFP process, a series of oligomerization, decarboxylation and dehydration reactions can remove the pyrolytic oxygenated compounds (oxygen will be removed as CO, H_2O and CO_2) [6–8] and

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produce hydrocarbons. Among all the studied catalysts, HZSM-5 zeolites have attracted wide attentions for its excellent deoxygenation effect and good shape-selectivity to aromatics and olefins [9–13]. Huber et al. [14] studied the CFP of glucose over different types of catalysts, and they found that the micropore openings of HZSM-5 had a size near to the molecular diameter of benzene, toluene, and xylene, thus resulting in a high yield of aromatics.

Coking is the main reason for catalyst deactivation in CFP [6,15–17]. For HZSM-5 zeolite, coke is hard to be formed inside the internal intracrystalline pores [18], because its unique microporous structure coupled with two-dimensional channel-like pore system limits the formation of the coke precursors (long chain chemicals or PAHs). However, the external acid sites of HZSM-5 zeolite can prompt the generation of coke on its outer surface. As a result, the generated coke will block the channels. Although most of the internal acid sites have not been inactivated, the blocked channels restrict the pyrolysis intermediates diffusing into the internal space and hamper the subsequent upgrading reactions. Usually, acid sites of HZSM-5 zeolite are closely related to the framework aluminums, and there exists a positive correlation between acidity and framework aluminum. EDTA, a compound that acts as a strong chelating agent, has obvious effect on the removal of framework aluminums. Kerr and his co-workers [19] used EDTA to deprive the framework aluminums of NaY zeolite and achieved a removal efficiency of 70%, and the treated NaY zeolite maintained a high crystallinity level. Szostalk et al. [20] found that EDTA treatment could lead to the surface dealuminization of Y zeolite.

To improve the anti-coking properties of HZSM-5 zeolite, EDTA chemical modification was carried out to remove the framework aluminums in this paper. Actually, EDTA can keep the internal acid sites as the bulky molecular structure of EDTA cannot enter into the internal channels of HZSM-5 zeolites. In our study, XRD, NH_3-TPD and N_2 adsorption techniques were used to investigate the effect of EDTA treatment time on the porosity and acidity characteristics of original and modified HZSM-5 samples. The original and modified HZSM-5 samples were employed as the catalysts for CFP of corn stalk using Py-GC/MS, and the catalytic effect was investigated and the anti-coking property of modified HZSM-5 was discussed.

2. Experimental

2.1. EDTA modification

Powdered HZSM-5 zeolite (SiO_2/Al_2O_3 = 50), which was obtained from the Catalyst Plant of Nankai University, was used as the catalyst in this study. EDTA-2Na (AR), which was purchased from Nanjing Chemical Reagent Co. Ltd., was applied as the chemical modification reagent. During the EDTA chemical modification experiments, 0.33 mol/L EDTA solution was prepared with deionized water, and then HZSM-5 catalyst and EDTA solution were fully mixed (with the solid to liquid mass ratio of 1:10 [21]) using a magnetic stirrer at 80 °C water bath for 1 h, 2 h and 4 h, respectively. Next, the mixture went through vacuum filtration steps by Buchner funnel and deionized water washing until the pH of the filtrate was neutral. Finally, the modified catalysts were dried in an air-circulating oven at 120 °C for 2 h and calcined on muffle at 500 °C for 4 h to eliminate the residues of EDTA. The modified catalysts were labeled EDTA-1H, EDTA-2H and EDTA-4H based on the treatment time.

2.2. Catalyst characterization

XRD patterns were obtained using a Rigaku SmartLabTM 9-KW Automatic Diffractometer operated at 40 kV and 40 mA with CuKα radiation. XRD patterns were accumulated in the range of 5–50° 2θ every 0.02° (2θ). Textural characterization of the catalysts was conducted with a Belsorp-Max adsorption instrument (Bel Japan, Inc.) using N_2 gas at 77 K. The specific surface area was determined using BET and Langmuir methods, and the volume and specific surface area of microporous were calculated using t-plot methods. The size distribution was calculated with SF methods.

Acidity characteristics of original and modified samples were studied by NH_3-TPD using a FineSorb 3010 automatic temperature programmed chemical adsorption instrument. 100 mg samples were put in the U-shaped quartz cell and kept at 600 °C in a He steam for 1 h. Then, samples were cooled to 150 °C and NH_3 was injected. NH_3-TPD was performed after NH_3 chemisorption in a He stream from 150 °C to 600 °C with a 15 °C/min heating rate [21].

2.3. CFP and TGA experiments

Biomass CFP experiments were carried out using Py-GC/MS. The pyrolysis unit was a CDS5200 pyrolyzer equipped with an Agilent 7890A/5975C gas chromatograph-mass spectrometer (GC–MS). Pyrolysis experiments were performed at 650 °C with the heating rate of 20 °C/ms and the pyrolysis time of 10 s and catalyst to feed mass ratio 2:1. The probe was a computer-controlled resistively heated element, which held an open-ended quartz tube. Catalyst and feed were placed in the tube separately with loose quartz wool packing so as to separate and analyze the coke on the catalyst. Corn stalk was used as the biomass feedstock. Prior to the experiments, corn stalk was smashed and sieved through a 40 mesh sieve, and then dried at 105 °C for 24 h. The catalysts were collected after reactions and coke yield was determined by TGA methods using Pyris 1 Thermogravimetric Analyzer (Perkin–Elmer). 2–3 mg samples were heated to 800 °C at a rate of 10 °C/min under natural ambient conditions.

3. Results and discussion

3.1. Effect of EDTA modification on physicochemical properties of HZSM-5 zeolite

3.1.1. XRD

Fig. 1 shows the XRD patterns of original and modified HZSM-5 samples. As can be seen, all of these samples present typical peaks and retain MFI topological structure. Obviously, EDTA treatment does not damage the crystalline structure of HZSM-5 zeolite. The

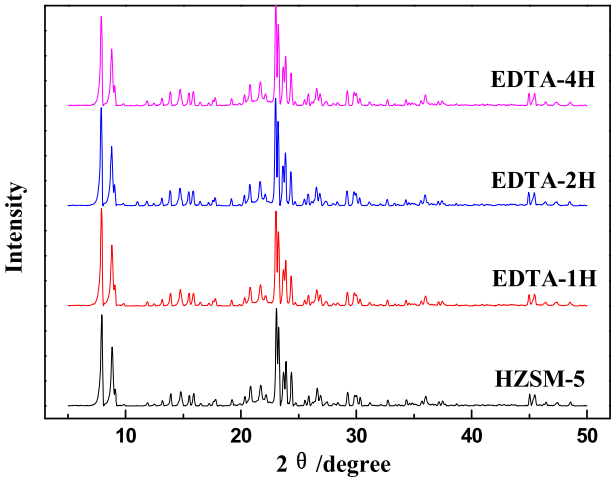

Fig. 1. XRD patterns of original and modified HZSM-5 samples.