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

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ABSTRACT

In order to minimize coke yield during biomass catalytic fast pyrolysis (CFP) process, ethylene diamine tetraacetic acid (EDTA) chemical modification method is carried out to selectively remove the external framework aluminum of HZSM-5 catalyst. X-ray diffraction (XRD), nitrogen (N₂)-adsorption and ammonia-temperature programmed desorption (NH₃-TPD) techniques are employed to investigate the porosity and acidity characteristics of original and modified HZSM-5 samples. Py-GC/MS and thermo-gravimetric 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 2h (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.

Keywords: Zeolites; Ethylene diamine tetraacetic acid; Chemical modification; External framework aluminum; Coke

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, H₂O and CO₂) [6-8] and produce hydrocarbons. Among all the studied catalysts, HZSM-5 zeolites have attracted wide attentions for its excellent deoxygenation effect

45 and good shape-selectivity to aromatics and olefins [9-13]. Huber et al. [14] studied
46 the CFP of glucose over different types of catalysts, and they found that the micropore
47 openings of HZSM-5 had a size near to the molecular diameter of benzene, toluene,
48 and xylene, thus resulting in a high yield of aromatics.

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

65 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, NH₃-TPD and N₂ 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 (SiO₂/Al₂O₃=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, 0.33mol/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 1h, 2h and 4h, 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 2h and calcined on muffle at 500 °C for 4h 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 CuK α radiation. XRD patterns were accumulated in the range of 5 - 50° 2 θ every 0.02° (2 θ). Textural characterization of the catalysts was conducted with a Belsorp-Max adsorption instrument (Bel Japan, Inc.) using N₂ gas at 77 K. The specific surface area was determined using BET and Langmiur 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 NH₃-TPD using a FineSorb 3010 automatic temperature programmed chemical adsorption instrument. 100mg samples were put in the U-shaped quartz cell and kept at 600 °C in a He steam for 1h. Then, samples were cooled to 150 °C and NH₃ was injected. NH₃-TPD was performed after NH₃ 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 24h. The catalysts were collected after reactions and coke yield was determined by TGA methods using Pyris 1 Thermogravimetric Analyzer (Perkin-Elmer). 2-3mg 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 relative crystallinity is calculated according to Zhang et al. [22] and Fan et al [23], and the results are summarized in Table 1.

EDTA treatment can slightly increase the relative crystalline of HZSM-5 zeolites. The reason is that proton ions (H^+) inside HZSM-5 are exchanged with sodium ions and then the free H^+ dissolves extra-framework aluminum. The results are also in good agreement with previous literature [23].

3.1.2 Analysis of N_2 -adsorption

Adsorption-desorption isotherms of original and modified HZSM-5 samples are shown in Fig. 2(a) and the results are listed in Table 2. According to IUPAC classification of adsorption isotherms, Type I (micropore) adsorption equilibrium curves are observed. The results are also in accordance to the most probable aperture (Table 2, Column $d_{p,peak}$) 0.49-0.62 nm. From Fig. 2(a) and Table 2, we can see that the total pore volume tends to increase while the specific surface area (especially the specific surface area of micropore) decreases with the increase of EDTA treatment time. As we know, EDTA can remove the external framework aluminums, thus forming many hydroxy holes and increasing the pore size. As a result, the generation of hydroxy holes and increase in pore size will lead to the increase in total pore volume. On the other hand, the generation of hydroxy holes and increase in pore size will result in the loss of original micropores, and the disappearance of micropores will decrease the overall specific surface area.

Besides, it can be seen that the porosity characteristics of EDTA-2H are similar to the original catalyst. On one hand, as aforementioned, EDTA can remove the external framework aluminums and lead to the loss of original micropores, thus decreasing the overall specific surface area. On the other hand, it should be pointed out that there are some non-framework aluminums (unbonded extra-framework amorphous Al_2O_3) in the crystal structures of HZSM-5 zeolite, and some non-framework aluminums can deposit on the surface of HZSM-5 and give rise to the blockage of pore mouth. It is reported that suitable EDTA treatment time can remove these non-framework aluminums [23], thus avoiding the blockage of pore mouth and increasing the specific surface area. The overall characteristics of modified HZSM-5 catalyst are controlled by these two factors together. In our study, EDTA treatment time of 2h may be optimal for the removal of these non-framework aluminums, and the overall specific surface area of EDTA-2H is almost not affected due to these two factors. Therefore, the overall characteristics of EDTA-2H are similar to the original catalyst.

3.1.3 NH_3 -TPD

Fig. 2(b) shows the results of NH_3 -TPD. HZSM-5 zeolite has two ammonia desorption peaks at 260-270 °C (weak acid sites) and 470-480 °C (strong acid sites), respectively. After EDTA treatment, the weak acid desorption peak shifts to the high temperature direction (300-320 °C), and the corresponding peak intensity decreases with a longer EDTA treatment time. Besides, the complete elimination of strong acid peak is observed from Fig. 2(b), and this may be caused by the following two factors:

firstly, H^+ ions on the surface of HZSM-5 zeolites are exchanged with large quantities of Na^+ through reaction (1); secondly, the external framework aluminums, confirmed the correlation with mediate and strong acidity, are removed due to the significant chelating effect of EDTA through reactions (1)-(5) [24]. In addition, the increase of weak peak intensities after EDTA treatment indicates that the deprived framework aluminums are converted into unbonded extra-framework aluminums.

To verify the two factors above, H^+ ions exchange method is further used to treat EDTA-1H. Procedures are as followed [25]: 1 mol/L HCl and the sample were mixed with the mass ratio of 10:1 and treated at 90 °C for 3 h, followed by vacuum filtration combing with deionized water washing. Finally, the sample was dried and analyzed

by NH_3 -TPD. Results are shown as curve EDTA+HCl in Fig. 2(b). After HCl treatment, the re-emerging strong acid peak reveals that Na^+ ions of EDTA-1H are exchanged again with H^+ , but the strong acid peak does not restore to the level of original HZSM-5 zeolite, which proves the occurrence of framework dealumination.

3.2 Effect of EDTA modified HZSM-5 on CFP of corn stalk

3.2.1 Pyrolysis product distribution

NIST MS library and related literature data [2, 26-27] are used for the identification of pyrolysis products. To simplify the analysis and discussion, products are divided into acids, esters, furans, alcohols, ketones, phenols, hydrocarbons (HCs), sugars, aromatic oxygenated derivatives (AODs) and N-containing compounds (NCCs) based on their functional groups and chemical structures. Yield of each product is calculated based on the ratio of the corresponding peak area to total peak area [28-31].

Fig. 3 shows the product distribution with or without HZSM-5 zeolite. Non-catalytic fast pyrolysis mainly leads to the generation of oxygenated compounds. On this condition (see Fig. 3), acids took the largest proportion. In addition, phenols, sugars and AODs also shared a relatively large part. The addition of original or modified HZSM-5 zeolite dramatically affected the product distribution, such as the decrease of acids, sugars and AODs, as well as a significant increase of HCs and esters, but NCCs (3-3.5%), furans (1-3%) and alcohols (1-2%) remained modest. The phenomenon that the decrease of acids and the increase of HCs by modified catalysts,

especially EDTA-2H, verified that modification methods did not damage the crystal structure of HZSM-5 zeolites, which was consistent with the results of XRD. However, in view of a low mass ratio of catalyst to feed, the yield of HCs was less than 20% and lower than that of acids, which was contrary to data reported in the literature [7, 32].

As we know, products can not be collected during the Py-GC/MS experiments, so it seems the yields of total product output can not be analysed quantitatively. However, the changes of product yields can be revealed by the comparison of the total chromatographic peak areas, as the mass of corn stalk and HZSM-5 catalyst, and the operating parameters of the Py-GC/MS equipment are kept exactly the same during each experiment. For each experiment, approximate 50 chemical compounds are discriminated and analysed. Total peak area results are summarized in Table 3. Here, the total peak area is defined as the sum of the peak areas of all the chemical compounds. Compared with non-catalytic fast pyrolysis, the addition of original HZSM-5 zeolites increased the total peak area, but the modified catalysts showed the opposite tendency. For HZSM-5 zeolites, they function as follows: 1) Polymerization of cellulose (an important component of lignocellulosic biomass) is heterogeneous and reacts in the occurrence of positively charged intermediate ions [33]. This reaction can be promoted in the presence of strong acid sites of HZSM-5 zeolites. However, the fast pyrolysis intermediate: activated cellulose, has a comparatively high relative molecular mass (1000 to 2000), and is difficult to diffuse into the internal pores of HZSM-5 zeolites. Therefore, only the external acid sites really work.

222 2) HZSM-5 zeolites can convert oligosaccharides into smaller molecules, which can
223 be separated and recognized by GC/MS. 3) HZSM-5 zeolites are possessed with
224 strong acid sites, where oxygenates produced by direct pyrolysis of biomass will
225 undergo a series of oligomerization, decarbonylation and dehydration reactions to
226 generate HCs, CO, CO₂ and H₂O. Function 1 and 2 can increase the output, but
227 Function 3 does on the contrary, so change tendency of the total peak area are affected
228 synthetically by all these three factors above. For the original HZSM-5 zeolites,
229 Function 1 and 2 are greater than Function 3, so the total peak increases. As for the
230 modified catalysts, Function 1 and 2 are deprived and weakened respectively due to
231 removal of external acid sites, which results in the decrease of total peak area. CO₂
232 peak area can reveal the oxygen removal efficiency. As shown in [Table 3](#), the results
233 that CO₂ peak areas of original and modified catalysts are higher than that of no
234 catalyst affirm the effects of Function 3. It can also be found that CO₂ peak area of the
235 original catalyst is not as many as the modified one's indicates Function 1 is more
236 important than Function 3 for original HZSM-5 zeolites.

237 Positive composition yields are shown in [Table 4](#). Positive compositions (including
238 HCs, esters, alcohols, furans and ketones) are those products which contribute to
239 combustion performance, bio-oil stability, pollutant emission control and so on in the
240 process of pyrolysis oil used as fuels. Conversely, acids, phenols, AODs, sugars and
241 NCCs are considered as negative compositions for their bad performances. Positive
242 composition yield of non-catalytic pyrolysis was 21.01%, and was enhanced with the
243 addition of catalysts including both the original and modified. Thereinto, EDTA-2H

obtained the best result of 45.79%.

Acids are the most abundant product (in Fig. 3), which mainly compose of acetic acids and long-chain unbranched aliphatic acids (C16-18). Usually, acetic acids can be generated from parallel competitive reaction I and III of cellulose (see Fig. 4) and cracking of acetyl groups of hemicellulose [33-35], but the formation mechanism of aliphatic acids is reported rarely. We assume that aliphatic acids are produced through reaction II as shown in Fig. 4 based on detailed selectivity of both acids (Fig. 5) and acetic peak areas (Table 5). For non-catalytic fast pyrolysis process, it is very complex for reaction 1 and 3 to produce acetic acid due to a series of reactions involved, but aliphatic acids are easier to be formed through reaction 2, so it has high selectivity to aliphatic acid. As for original HZSM-5 zeolites, the selectivity to aliphatic acid is higher, because the original catalyst can promote reaction 1, 2 and 3, nevertheless, the generated acetic acids can be further converted by the catalyst. However, modified catalysts have better selectivity to acetic acid, totally different from aforementioned two cases. Although modified catalysts have deacidification effects, they can promote reaction 1 and 3, and the rate of formation exceeds that of conversion, which consequently results in higher selectivity to acetic acid.

HZSM-5 zeolites have a better conversion efficiency of HCs in the biomass CFP process. Therefore, studies on the selectivity to HCs over original and modified catalysts can be guidance for adopting appropriate modified methods to obtain desired chemicals. HCs mainly include toluene, xylene, D-limonene, and naphthalene. As

shown in Fig. 6, only a small amount of HCs were produced when no catalyst was used. But the addition of HZSM-5 zeolites led to a rapid increase in the yield of aromatic HCs. Pyrolysis products over original and modified HZSM-5 zeolites exhibit a different distribution tendency. HCs over original catalyst are mainly toluene and xylene and a small amount of naphthalene. For the modified catalysts, HCs mainly comprise of D-limonene and toluene with the naphthalene undetected. Among the modified catalysts, EDTA-2H gave rise to the biggest amount of HCs and a near and even higher yield to that of HZSM-5 zeolites, but there still exists a relatively large difference of absolute output between EDTA and HZSM-5 zeolites.

Fig. 7 shows the similar distribution tendency of phenols: the highest yield of 4-Hydroxy-3-methoxystyrene and a close output of guaiacol, 2,6-Dimethoxyphenol and 2,6-tert-butyl-4-methoxyphenol. The total yield of phenols followed this order: without catalyst > original HZSM-5 > modified HZSM-5. Phenols are usually produced from the decomposition of lignin. Macromolecular substances are firstly formed by the primary pyrolysis of lignin and then go through further pyrolysis into micromolecular phenols. The external active sites of HZSM-5 zeolites play an important role in converting the generated phenols into aromatic HCs. Therefore, the original HZSM-5 zeolites get the lowest yield of phenols. It can be also concluded that HZSM-5 zeolites have poor selectivity to the phenols for the small change of phenols distribution and production after using the catalysts.

3.2.2 Anti-coking properties

Coke yields over original and modified HZSM-5 samples are shown in [Table 5](#). Coke yield was calculated by mass difference before and after experiment. As can be seen, EDTA treatment results in a decrease in coke yield, and the coke yield tends to decrease with increasing treatment time. Obviously, EDTA-2H gives rise to the lowest coke yield. The anti-coking properties of modified HZSM-5 are improved and this modification method reaches the target.

Among all the studied catalysts (such as HZSM-5, FCC, LOSA-1, MCM-41, SBA-15, CNT and so forth), HZSM-5 aluminosilicate zeolite performs the best for bio-oil deoxygenation and hydrocarbon production in biomass CFP process. The reaction mechanism for biomass CFP process over HZSM-5 zeolite is shown in [Fig. 8](#). During the fast pyrolysis of corn stalk, thermal decomposition of cellulose will lead to the formation of anhydrosugars. Then these anhydrosugars will be converted into oxygenates through rearrangement and dehydration reactions. Once passing through the HZSM-5 catalyst layer, some oxygenates will undergo deoxygenation reactions to form hydrocarbons (especially olefins and aromatics) through a common intermediate (called “hydrocarbon pool”) in the HZSM-5 framework. However, it should be pointed out that some oxygenated pyrolysis vapors can polymerize on the surface of HZSM-5 catalyst, leading to the formation of coke (see [Fig. 8](#)). For HZSM-5 zeolite, as aforementioned in introduction, coke can only be generated on the outer surface, as coke is a kind of large-molecule aromatic compound and cannot enter into the narrow inner micropores. Coke usually leads to the blockage of pore openings and the deactivation of HZSM-5 catalyst, so it is necessary to reduce coke formation during

biomass CFP process.

A feasible way to reduce coke formation is to remove the external acid sites (external framework aluminums) of HZSM-5 zeolite but meanwhile keep the internal acid sites (internal framework aluminums). In this paper, selective removal of external framework aluminums of HZSM-5 zeolite is carried out by means of EDTA modification. As a bulky organosilicon compound, EDTA molecule cannot enter the intracrystalline void space. As a result, only framework aluminums on the external surface of HZSM-5 are removed by EDTA, whereas the internal framework aluminums are not altered. In our study, the external framework aluminums are removed due to the significant chelating effect of EDTA through aforementioned reactions (1)-(5).

Our experimental results show that EDTA modified HZSM-5 can inhibit coke formation and fine-tune catalytic performance. Shao et al. used H_3PO_4 to selectively remove the external framework aluminums of HZSM-5 catalyst, and their results showed that the modified HZSM-5 could improve hydrocarbon production and minimize coke yield compared to original HZSM-5 [37]. Bauer and his co-workers also passivated the external framework aluminums of HZSM-5 catalyst with pre-coking treatment, and they found that pre-coked HZSM-5 had a better shape-selective effect for the formation of target products and gave rise to a reduced formation of undesirable compounds [38,39]. In our previous study, we also selectively inactivated the external framework aluminums of HZSM-5 with chemical

vapor deposition of inert silica ($\text{SiO}_2\text{-CVD}$), and achieved a good result as well [40].

To the best of our knowledge, it is the first time in the world to employ EDTA modified HZSM-5 catalyst to reduce coke formation in biomass CFP process.

4. Conclusion

EDTA modification method can effectively remove the external framework aluminums of HZSM-5 zeolite without damaging the crystal structure. Modified HZSM-5 samples will maintain the typical microcellular structure of HZSM-5, but meanwhile its average pore size and total pore volume will increase and its specific surface area will decrease compared to original HZSM-5. The overall porosity characteristics of EDTA-2H are similar to the original catalyst. Py-GC/MS experimental results show that the addition of HZSM-5 catalyst can significantly increase the yield of HCs and reduce the yields of acids and saccharides. On the other hand, it should be pointed out that the phenol production is not affected. Besides, EDTA-2H obviously enhances the yield of positive chemical compositions from 21.01% to 45.79%, which is higher than 39.53% over original HZSM-5 zeolite. TGA results show that EDTA treatment can significantly improve the anti-coking properties of HZSM-5, and EDTA-2H leads to the lowest coke yield.

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427 **Table captions**

428 **Table 1.** Relative crystallinity of original and modified HZSM-5 samples.

429 **Table 2.** Porosity characteristics of original and modified HZSM-5 samples.

430 **Table 3.** Peak areas.

431 **Table 4.** Yields of positive chemical compositions.

432 **Table 5.** Anti-coking properties of original and modified HZSM-5 samples.

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Table 1

Relative crystallinity of original and modified HZSM-5 samples.

Catalyst	HZSM-5	EDTA-1H	EDTA-2H	EDTA-4H
Relative crystallinity (%)	100	102.4	105.3	103.5

Table 2

Porosity characteristics of original and modified HZSM-5 samples.

Catalyst	Surface area ($\text{m}^2 \text{g}^{-1}$)			Volume ($\text{cm}^3 \text{g}^{-1}$)		$d_{p,\text{peak}}$ (nm)
	BET	Langmuir	Micropore	Total	Micropore	
HZSM-5	342.27	371.88	194.83	0.1717	0.1294	0.49
EDTA-1H	309.66	339.92	125.53	0.1838	0.1245	0.62
EDTA-2H	320.91	359.59	162.46	0.1685	0.1239	0.52
EDTA-4H	309.74	356.64	102.36	0.2058	0.1466	0.59

Table 3

Peak areas.

Catalyst	No catalyst	HZSM-5	EDTA-1H	EDTA-2H	EDTA-4H
Total peak area ($\times 10^9$)	4.70	5.51	4.05	4.56	4.13
CO ₂ peak area ($\times 10^8$)	4.38	6.17	7.21	6.69	7.49
Acetic acid peak area ($\times 10^8$)	5.09	3.40	6.15	5.64	6.09

Table 4

Yields of positive chemical compositions.

Catalyst	No catalyst	HZSM-5	EDTA-1H	EDTA-2H	EDTA-4H
Yields of positive chemical compositions (%)	21.01	36.53	36.55	45.79	41.79

550 **Table 5**

551 Anti-coking properties of original and modified HZSM-5 samples.

Catalyst	HZSM-5	EDTA-1H	EDTA-2H	EDTA-4H
Coke yield (wt. %)	3.86	3.13	2.44	2.45

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

(a)

(b)

Fig. 2. Porosity and acidity characteristics of original and modified HZSM-5 samples. (a) N₂ adsorption-desorption isotherms. (b) NH₃-TPD.

Fig. 3. Pyrolysis product distribution.

Fig. 4. Three competing pathways during fast pyrolysis of cellulose.

Fig. 5. Selectivities of acetic acid and aliphatic acid.

Fig. 6. Peak area and total yield of HCs.

Fig. 7. Peak area and total yield of phenols.

Fig. 8. Reaction mechanism for biomass CFP process over HZSM-5 zeolite [36].

Figure captions

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Graphical abstract