

In-situ catalytic upgrading of bio-oil derived from fast pyrolysis of sunflower stalk to aromatic hydrocarbons over bifunctional Cu-loaded HZSM-5

Nichaboon Chaihad^a, Aisikaer Anniwaer^a, Surachai Karnjanakom^c, Yutaka Kasai^d, Suwadee Kongparakul^e, Chantip Samart^e, Prasert Reubroycharoen^f, Abuliti Abudula^a, Guoqing Guan^{a,b,*}

^a Graduate School of Science and Technology, Hirosaki University, 1-Bunkyocho, Hirosaki, 036-8560, Japan

^b Energy Conversion Engineering Laboratory, Institute of Regional Innovation, Hirosaki University, 2-1-3, Matsubara, Aomori, 030-0813, Japan

^c Department of Chemistry, Faculty of Science, Rangsit University, Pathumthani, 12000, Thailand

^d Industrial Research Institute, Aomori Prefectural Industrial Technology Research Center, 4-11-6, Daini-Tonyamachi, Aomori, 030-0113, Japan

^e Department of Chemistry, Faculty of Science and Technology, Thammasat University, Pathumtani, 12120, Thailand

^f Department of Chemical Technology, Faculty of Science and Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Bangkok, 10330, Thailand

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ABSTRACT

Commercial HZSM-5 zeolite (Si/Al = 24) was modified with Cu species using the wet impregnation method, and applied in the *in-situ* upgrading of bio-oil from the fast sunflower stalk pyrolysis with a catalyst to biomass ratio of 1:1 at 500 °C. The main objective was to study the Cu doping effect on the HZSM-5 catalytic performance in terms of the selectivity to aromatic hydrocarbons (especially the specific aromatic hydrocarbons including benzene, toluene and xylene) yield. It was found that Cu/HZSM-5 with low Cu loading amounts preserved HZSM-5 crystalline structure as well as its acid sites. The HZSM-5 with 0.5 wt.% Cu loading amount exhibited the best catalytic performance with a high relative amount of aromatic hydrocarbons of 73.2 % and a yield of specific aromatic hydrocarbons as high as 56.5 mg/g-biomass (d.a.f), which were much higher than those based on the parent HZSM-5 (55.0 % and 26.0 mg/g-biomass (d.a.f)). It should be mainly attributed to its suitable acidity and best textural properties for the deoxygenation of the bio-oil thanks to the optimum Cu loading amount. In addition, the 0.5 wt.% Cu loaded HZSM-5 catalyst also showed excellent catalytic reusability and regeneration property, and the spent catalyst was easily recovered by a simple calcination in air for a short time.

1. Introduction

As fossil fuel resources continue to decline and the high production of carbon dioxide and other pollutants are always generated from them, it becomes more and more important to find alternative energy to replace the traditional ones. Biomass energy is one of the attractive and promising options for countries with abundant agriculture and forest resources [1]. Biomass can be converted into various gaseous, liquid and solid fuels and considered to be a zero-net-CO₂ emission energy with high sustainability [2,3]. Combustion, pyrolysis, gasification and liquefaction are the general methods for converting biomass into

convenient energy. Among them, fast pyrolysis could maximize the bio-oil yield from biomass resources (even more than 60 %) under the absence of oxygen using a high heating rate with a short residence time of volatile [4,5]. Although the fast pyrolysis process is capable of producing a high amount of bio-oil with other products such as fuel gases and char, the obtained bio-oil usually includes abundant oxygenated compounds, resulting in the fast pyrolysis oil unstable and corrosive in storage with a low heating value [6]. In addition, the high H₂O concentration hinders the spontaneous blending of the bio-oil with the petroleum. Thus, it cannot be directly applied as a liquid transportation fuel and various catalysts have been developed for the bio-oil upgrading

* Corresponding author at: Energy Conversion Engineering Laboratory, Institute of Regional Innovation, Hirosaki University, 2-1-3, Matsubara, Aomori, 030-0813, Japan.

E-mail address: guan@hirosaki-u.ac.jp (G. Guan).

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[7–10]. In particular, high aromatic components in the upgrading bio-oil have been achieved by applying zeolites to crack heavy oxygenated compounds to light aromatic hydrocarbons (AHs) like benzene, toluene, ethylbenzene, xylene and naphthalene (BTEXN).

Zeolites are extensively used in refinery plants. Among them, ZSM-5 with shape selection activity, ion-exchange ability and large surface area is an active catalyst for various reactions such as cracking, alkylation, aromatization and isomerization of hydrocarbons [11–14]. Especially, HZSM-5 exhibits good performance in effective converting of oxygenated compounds to aromatics during catalytic fast pyrolysis of biomass residues [15–17] since it has suitable acid sites and appropriate pore diameter for the shape selectivity toward aromatics production [18]. In our previous study [19], it was found that the HZSM-5 with Si/Al = 24 catalytically upgraded the bio-oil from the fast biomass pyrolysis to produce more aromatic hydrocarbons when compared with other zeolites. Meanwhile, sunflower stalk was proven to be a potential biomass as the feedstock for bio-oil production with high aromatic hydrocarbons production. However, the performance of such a kind of catalyst could be further improved by adjusting the acidity and texture properties for the catalytic bio-oil upgrading. Various metals (e.g., Ni, Ga, Zn, Fe, Co and Pd) have been applied for the modification of zeolite catalysts to adjust the acidic and textural characteristics for the bio-oil upgrading [20–28]. Particularly, non-noble transition metals are receiving much more attention due to their low cost in large-scale industrial applications. Li et al. investigated the Cu-modified ZSM-5 catalysts for the upgrading of oil and found that it increased the hydrocarbon yield in the upgrading bio-oils and also showed the acceptable reusability. However, they mainly focused on the use of high metal doping amounts (>5 wt.%) and did not report the H₂O concentration in the upgrading bio-oil and the actual aromatic hydrocarbons yield [29]. Widayatno et al. found that the introduction of Cu with a low loading amount (0.25–3 wt.%) on the β zeolite promoted the selectivity towards hydrocarbons in the bio-oil significantly owing to the moderate acidity property [30]. Although this Cu doped β zeolite exhibited excellent performance, a catalyst to biomass weight ratio as high as 3.3 to 1 was also needed. It still remains a challenge for the pyrolysis bio-oil upgrading with less amount of the catalyst. On the other hand, fast pyrolysis in a short period of time (several seconds) is a general way for the high-yield bio-oil production. Herein, the in-situ fast pyrolysis bio-oil upgrading is also full of challenges since only a short residence time (0.5–10 s) is for the bio-oil vapor passing through the catalyst layer [31]. Thus, high-performance catalysts are required in the in-situ fast pyrolysis bio-oil upgrading. The key factors of the catalyst that cause the oxygen-containing compounds to be converted into aromatic compounds include the acidity, pore size and pore shape of catalysts. For the ZSM-5 based catalysts, as summarized in Table S1, metal loading on the ZSM-5 could improve the catalytic upgrading performance. The upgraded oil yield and the selectivity to the aromatic hydrocarbons are two important parameters for evaluating the upgrading performance of the prepared catalysts. From Table S1, one can see that most of metal loaded ZSM-5 catalysts had upgraded oil yields lower than 30 % and/or the selectivities to the aromatic hydrocarbons lower than 60 %.

Based on the previous study [19], this research focused on the use of HZSM-5 modified with low Cu species doping amounts (0–5 wt.%) and the appropriate Cu doping amount was expected to further improve catalytic upgrading performance for the bio-oil from the fast sunflower stalk pyrolysis with a low catalyst to biomass weight ratio of 1:1. The chemical composition in the upgraded bio-oil, the actual aromatics yield and the total mass balance (char, gas, bio-oil, water, coke) were analyzed. Furthermore, the deoxygenation routes were discussed based on the lignin, cellulose and hemicellulose components in the sunflower stalk. Furthermore, the reusability and regeneration property of the catalysts were investigated for the catalysts with the best performance.

2. Experimental

2.1. Biomass feedstock

Sunflower stalk was the agricultural residue in Aomori city, Japan, which was dried overnight at 110 °C at first, and then ground and sieved to a 0.5–1 mm particle size. Proximate analyses of moisture and ash were carried out following the ASTM D7582 standard, and ultimate analysis was conducted with a Vario EL cube elemental analyzer and the results were reported in our previous study [19].

2.2. Preparation of catalysts

The commercial HZSM-5 zeolite (Si/Al = 24) was purchased from TOSOH Corp. and calcined for 2 h at 650 °C in the air to remove impurities. The calcined zeolite was pressed into pellet shapes and ground through a sieve to obtain particle sizes in the range of 0.5–1.0 mm. The zeolite samples were modified with Cu species by the wet impregnation method, where the zeolite powders were immersed in 25 mL of Cu (NO₃)₂·3H₂O solutions with different concentrations for the loading of 0.25, 0.5, 1, 3 and 5 wt.% of Cu respectively on the zeolites, and stirred at room temperature for 8 h. After that, the solution was evaporated overnight at 100 °C and finally, the sample was calcined at 650 °C for 4 h. The as-prepared samples were called as the parent zeolite and x wt.% Cu/HZSM-5 (x = 0.25, 0.5, 1, 3 and 5), respectively.

2.3. In-situ catalytic upgrading

In-situ catalytic bio-oil upgrading was carried out in a quartz fixed-bed reactor, where biomass (0.5 g) and catalyst (0.5 g) were separated by a quartz wool layer in the center of the reactor, and the carrier gas was passed in the reactor from the biomass to catalyst bed. The quartz fixed-bed reactor was then put in an infrared furnace. The underside of the reactor was connected to a bottle containing cold acetone, which was used for the condensation of upgraded bio-oil. The collected bio-oil was further evaluated offline by a GC–MS. In order to start the reaction under oxygen-free environment, a nitrogen flow (100 cm³/min) was used to purge the inside of reactor for 10 min. Then, the reaction was performed by heating to 500 °C rapidly from room temperature with a 100 °C/s heating rate and maintaining at 500 °C for 5 min. The gas product was also collected using the gasbag. Each run was carried out repeatedly for 3 times at the same condition to ensure reproducibility, and the average value was used for the discussion in the following.

The bio-oil was measured by a GC/MS instrument (GCMS-QP2020, Shimadzu, Japan). As soon as the automatic injection of the sample into the column, the oven was heated to 300 °C from 50 °C (heating rate: 10 °C/min) and held at 300 °C for 10 min. Chromatographic peaks were confirmed by using the data of the NIST mass spectrum library. The quantitative analysis of specific aromatic hydrocarbons including benzene, toluene, o-xylenes, p-xylenes, ethylbenzenes, naphthalenes (e.g., 2,6-dimethyl-naphthalene, 6-methyl-1,2-dihydronaphthalene, 2-ethyl-naphthalene, 2-methyl-naphthalene and so on) and other aromatics (mainly included indene and other alkylbenzenes (e.g., mesitylene, styrene, Benzene, 1-ethyl-2-methyl-benzene, 1-ethenyl-3-methyl-benzene, 1,3,5-trimethyl-benzene) were carried out using an external standard method. The detected bio-oil main components in this study were the light bio-oil compounds only since the quantitative analysis using the present GC/MS was performed at an oven temperature of 300 °C.

Off-line analysis of the non-condensable gases was performed using an Agilent 7890A GC system (USA), where He carrier gas was used for the CO, CH₄ and CO₂ analysis and Ar carrier gas was for H₂ detection. The quantification of those gases was measured by comparing to the calibration curve of each standard gas using an external standard method. The H₂O concentration in the bio-oil was analyzed with an MKS-500 Karl-Fisher instrument (Japan). The solids remaining in the

biomass layer were considered as the char, which was directly measured by weight difference. The amounts of coke on the catalysts during the reaction were determined by analyzing 10 mg of the catalyst after the reaction with a DTG-60H thermogravimetric analyzer (Shimadzu, Japan), where the oven temperature was started from a room temperature and ended at 900 °C (heating rate: 10 °C/min) under airflow. The coke amount was estimated by the weight difference.

2.4. Catalyst characterization

Powder XRD profiles of the parent HZSM-5 and metal loaded HZSM-5 zeolites were measured on a Rigaku Smartlab XRD instrument (Japan) using a $\text{CuK}\alpha$ radiation ($\lambda = 0.1542$ nm) with a step of 0.02° in the 2θ range of $10\text{--}80^\circ$. The surface area and pore size distributions were determined with a NOVA 4200e Quantachrome instrument (USA). Prior to N_2 adsorption (77 K), zeolite powders were treated under vacuum for degassing for 8 h at 473 K. Herein, the Brunauer-Emmett-Teller (BET) method was used to determine the specific surface area. Pore size distribution and average pore size were determined based on the desorption branch. The t-plot method was used to determine the micropore surface area (S_{micro}) and microporous volumes (V_{micro}). The morphologies of the samples were examined by a SU8010 SEM machine (Hitachi, Japan) and the Cu distribution on the catalyst was confirmed by an EDX detector (Horiba). The acidity was measured by using NH_3 -TPD method (BELCAT, Japan). Herein, about 0.1 g of sample was pretreated for 1 h at 700 °C and then NH_3 gas was flowed into the catalyst cell for 1 h at 120 °C. Finally, the desorption of NH_3 was carried out from 120 °C to 800 °C under helium gas flow.

3. Results and discussion

3.1. Zeolite characteristics before the reaction

The diffraction peaks of the parent HZSM-5 and various Cu/HZSM-5 catalysts were examined by XRD analysis. As shown in Fig. 1, the HZSM-5 zeolite crystalline structures were preserved even in the case up to 5% of the metal doping. The peaks at 2θ of 23.1° , 23.8° and 24.4° belonged to HZSM-5 [32,33] whereas the peaks at 2θ of 35.55° and 38.70° corresponded to the Cu species [34]. One can see that Cu modification of HZSM-5 did not alter the zeolite crystalline structure. However, it is mentioned that no obvious peaks relating to Cu species were observed for any percentage doping of Cu, implying that Cu species were

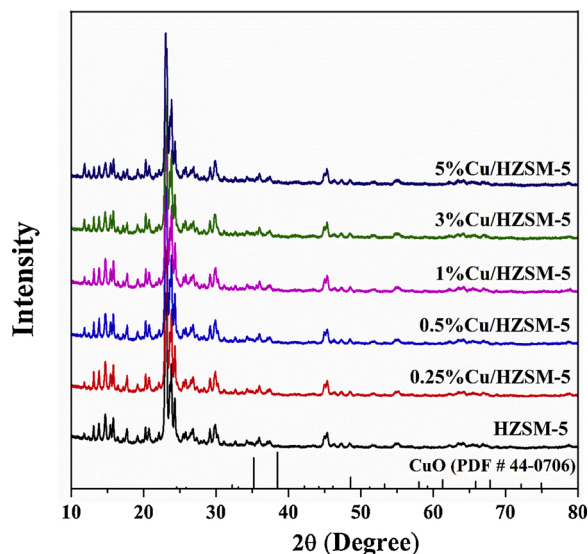


Fig. 1. XRD patterns of the parent HZSM-5 catalysts and the obtained Cu/HZSM-5 catalysts.

dispersed well on the HZSM-5 and the low content of the Cu doping effectively reduced the agglomeration of Cu particles on the surface of HZSM-5, which could occur during the calcination [30].

Fig. 2 shows NH_3 -TPD curves of the HZSM-5 and Cu/HZSM-5 catalysts. The acidity amounts evaluated based on the peak areas are listed in Table 2. Two typical peaks appeared at the two temperature ranges of $115\text{--}325^\circ\text{C}$ and $325\text{--}700^\circ\text{C}$ represented the weak and the strong acid sites, separately. The desorption temperature of ammonia on weak acid sites slightly shifted to low temperature as the Cu doping amount was raised from 0.25 to 0.5 wt.%. Herein, after the Cu was doped on HZSM-5, some of the H^+ cations on the zeolite were replaced by Cu^{2+} cations, and the Cu species could be in the forms of the isolated Cu^{2+} cation or CuO cluster, which caused the shift of the weak acid to lower temperatures with an increased amount of strong acid sites [35]. However, further increasing Cu doping amount from 0.5 wt.% caused a weak acid site peak shift to higher temperature, and as the Cu doping amount was increased to 3 wt.% and more, the weak acid site peak shift to the higher temperature became more obvious, which could promote the coke formation. In general, the increase of acid amount presents that more active sites can be provided for pyrolytic vapor decomposition, promoting the catalytic deoxygenation [3,36]. However, it also leads to the formation of coke on the active sites due to the polymerization and condensation, resulting in the deactivation [37–39]. Thus, an optimum Cu doping amount should exist.

Table 1 shows the specific BET surface area and porous properties of the catalysts and Fig. 3 shows the related isotherms and pore distributions. The parent HZSM-5 had a $332\text{ m}^2/\text{g}$ of surface area with a combined characteristic IUPAC types I and IV isotherms as the nitrogen was adsorbed at low relative pressures ($P/P_0 < 0.1$) with a hysteresis loop as $P/P_0 > 0.4$, indicating the presence of microporous and mesoporous structures [40]. With the introduction of Cu species, the total pore volume and the surface area were remarkably decreased since Cu species could enter into the meso- and micropores of HZSM-5 [41].

Fig. 4(a) and (b) show morphologies of HZSM-5 and 0.5 %Cu/HZSM-5 samples prepared by the wet impregnation method, and Fig. 4(d) shows EDX mapping of 0.5 %Cu/HZSM-5 catalyst. Multi-particle agglomerations were observed for the HZSM-5 powder due to the interconnection of small particles with a fractured cubic-like shape [27]. The morphology of Cu/HZSM-5 was similar to that of the parent HZSM-5 catalyst, but it was difficult to observe the particles related to Cu species on the surface of HZSM-5. However, based on the Cu EDX mapping (Fig. 4(d)), it was found that the Cu elements were evenly distributed on the HZSM-5 surface.

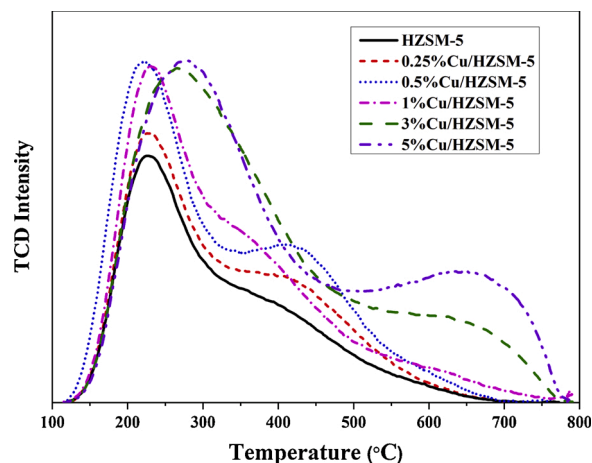


Fig. 2. NH_3 -TPD profiles of the parent HZSM-5 catalysts and the obtained Cu/HZSM-5 catalysts.

Table 1

Textural properties of the parent HZSM-5 and the obtained Cu/HZSM-5 catalysts.

Catalyst	S_{BET} (m^2/g)	S_{micro} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	Average pore size (nm)
HZSM-5	332.1	365.1	0.28	0.134	3.15
0.25%Cu/HZSM-5	322.7	258.5	0.27	0.130	3.56
0.5 %Cu/HZSM-5	316.8	254.9	0.27	0.128	3.53
1%Cu/HZSM-5	310.5	236.5	0.27	0.130	3.50
3%Cu/HZSM-5	306.6	249.0	0.25	0.126	3.25
5%Cu/HZSM-5	280.6	212.8	0.26	0.107	3.35

Table 2

Acidity of the parent HZSM-5 catalysts and the obtained Cu/HZSM-5 catalysts.

Catalyst	Acidity (mmol/g, low temp)	Acidity (mmol/g, high temp)	Total acidity (mmol/g)
HZSM-5	0.47	0.40	0.87
0.25%Cu/HZSM-5	0.41	0.32	0.73
0.5 %Cu/HZSM-5	0.60	0.52	1.12
1%Cu/HZSM-5	0.55	0.49	1.04
3%Cu/HZSM-5	1.02	0.37	1.39
5%Cu/HZSM-5	1.01	0.53	1.54

3.2. Catalytic bio-oil upgrading

Fig. 5(a) displays the percentages of various chemical compositions in the all chemicals (hereafter, it was called as “relative amount”) determined by the peak areas in the GC–MS spectrum, which are considered as the key indicator to evaluate the upgraded bio-oil quality and catalyst performance. The relative amounts on the GC–MS spectra related to the upgraded bio-oil compositions from the *in-situ* upgrading of fast pyrolysis oils over the parent HZSM-5 and the various Cu modified HZSM-5 catalysts, which were categorized into 7 groups: (1) aromatic hydrocarbons; (2) aliphatic hydrocarbons; (3) phenols, (4) ketones, (5) acids, (6) aldehydes, and (7) other oxygenated compounds consisted of alcohol, esters and amines. For the parent HZSM-5, deoxygenation could take place on the Brønsted acid sites on either the

external surface or internal surface and as a result, the main compounds were aromatic hydrocarbons (55.0 %) followed by acids (13.5 %) mainly including acetic acid, and other oxygenated compounds (7.9 %). After the Cu doping, the relative aromatic hydrocarbon amount was raised to 59.8 % for 0.25 wt.% Cu and reached a maximum of 73.2 % for 0.5 wt.% Cu while the acids, phenols and ketones were mainly reduced. However, with the further increasing Cu doping amounts to 1, 3 and 5 wt.%, the relative amounts of the aromatic hydrocarbons were decreased to 67.7 %, 59.6 % and 53.7 %, respectively. Thus, the low content of Cu doping could enhance the efficiency of deoxygenation (dehydration, decarboxylation, decarbonylation), thereby increasing the selectivity towards aromatic hydrocarbons. Herein, it should be noted that 0.5 %Cu/HZSM-5 exhibited the best selectivity towards aromatic hydrocarbons. Fig. 5(b) displays the specific aromatic hydrocarbons yields in the upgrading bio-oils based on dried ash-free (d.a.f) biomass. Herein, those aromatic hydrocarbons with large molecules were not determined, and only the yields of specific aromatic hydrocarbons which can be determined by calibration using the standard chemicals were obtained. It is obvious that the specific aromatic hydrocarbons in the upgrading bio-oil based on all Cu loaded HZSM-5 catalysts showed higher aromatics yield than that from the parent HZSM-5. Especially, the use of 0.5 %Cu/HZSM-5 also gave a maximum specific aromatic hydrocarbons yield of 56.5 mg/g-biomass (d.a.f). This amount is much more than that from the parent HZSM-5 (26.0 mg/g-biomass (d.a.f)). These results indicated that 0.5 wt.% should be the optimum Cu doping amount. Herein, the doping of Cu on HZSM-5 changed the acid properties including acid amount and acid strength, which could effectively influence the catalytic deoxygenation activity and product selectivity. However, the excessive Cu loading could result in excessive acidity and simultaneously the covering of the active sites on the zeolite and the blockage of zeolite channels with the decrease in surface area, thereby reducing the catalyst activity [42].

Fig. 6(a) and (b) show product percentage distributions and the yield of gases during the upgrading of fast pyrolysis oils on the parent HZSM-5 and the various Cu modified HZSM-5 catalysts at 500 °C. Herein, the results were also based on the biomass (d.a.f). Obviously, the highest upgraded bio-oil yield of 37.3 % with a gas yield of 14.1 % and a coke yield of 5.6 % was obtained when using the parent HZSM-5, and the bio-oil yield decreased when the Cu/HZSM-5 zeolites with the different Cu doping contents were used, where the upgraded bio-oil yields decreased to 33.4 %, 29.8 %, 32.2 %, 32.9 % and 28.5 % for 0.25, 0.5, 1, 3 and 5 wt.% Cu doping amounts, respectively, and meanwhile, the yields of gas, water and coke were greater than those using the parent HZSM-5. These differences should be attributed to the changes of the acidity and the physical properties of the Cu modified catalyst as observed by NH_3 -TPD and BET results. Herein, the increase in the yields of gases, water, and coke was related to the deoxygenation of those oxygenated compounds.

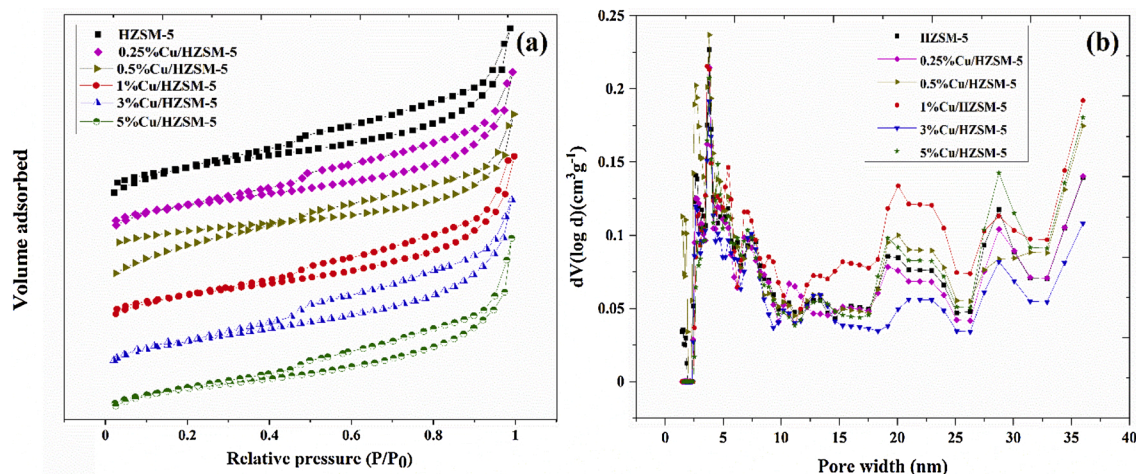


Fig. 3. N_2 adsorption/desorption isotherms and pore size distributions of the parent HZSM-5 catalysts and the obtained Cu/HZSM-5 catalysts.

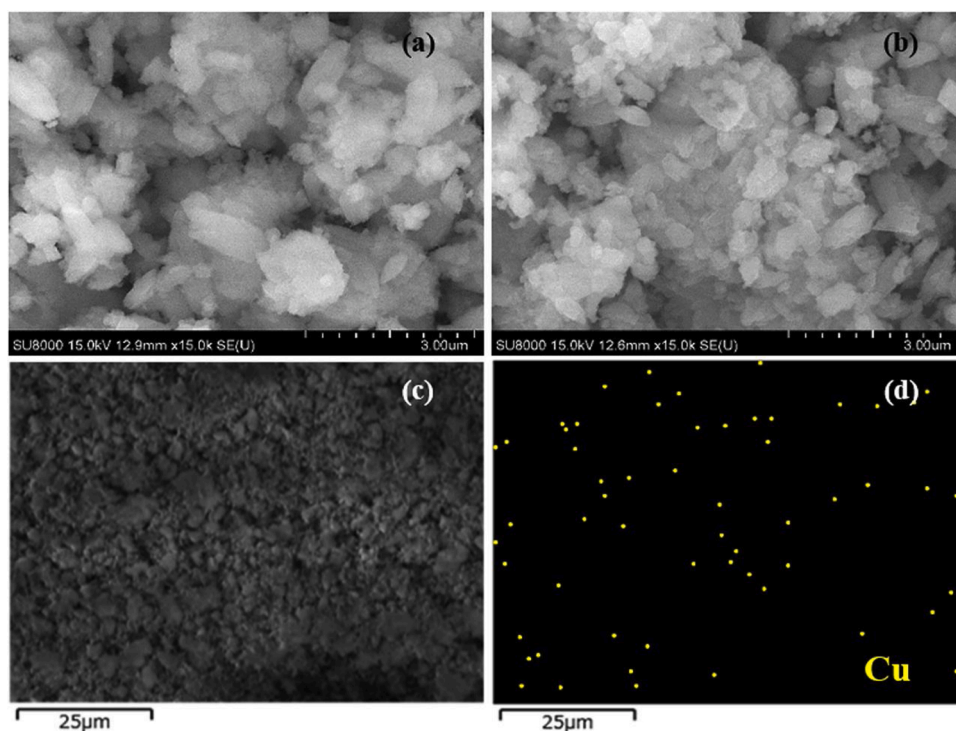


Fig. 4. SEM images of (a) parent HZSM-5 and (b-c) 0.5 wt.%Cu/HZSM-5, and EDX mapping image (d) of 0.5 wt.%Cu/HZSM-5.

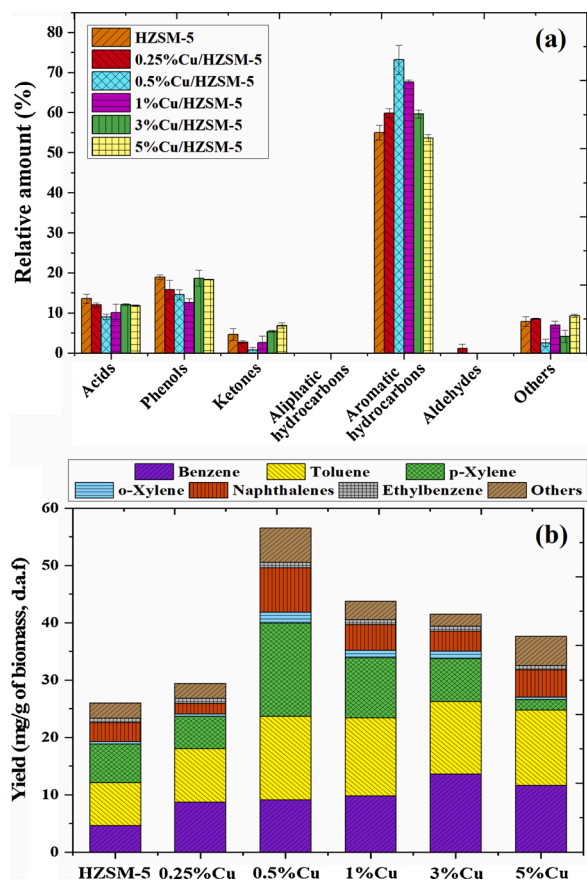


Fig. 5. Chemical compositions in the upgraded bio-oils with various Cu/HZSM-5 catalysts (a) and the yields of specific aromatic hydrocarbons based biomass (d.a.f) (b).

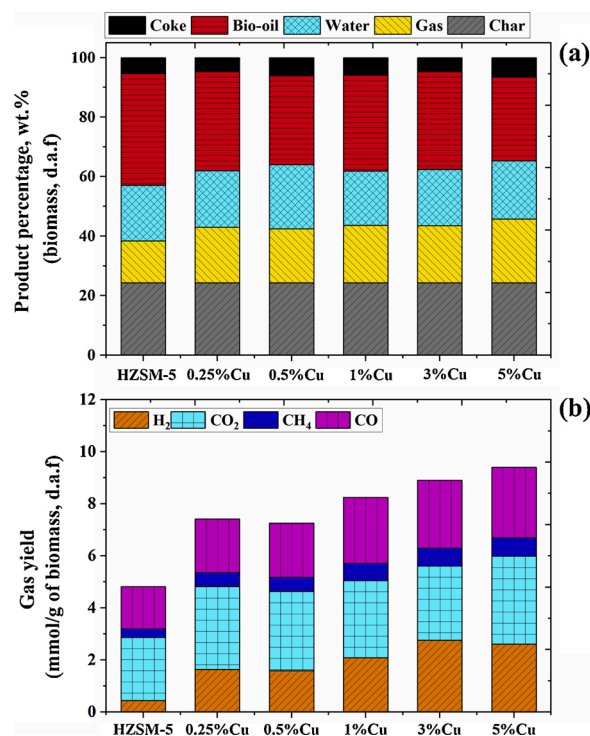


Fig. 6. The product percentage distributions (a) and gas yields (b) obtained from the *in-situ* catalytic upgrading of bio-oil derived from fast pyrolysis of sunflower stalk over the parent HZSM-5 and various Cu/HZSM-5 catalysts.

In the case of using 5%Cu/HZSM-5, which had the strongest acidity as detected by NH₃-TPD, the upgraded bio-oil yield decreased to a higher extent while the gas and coke yields increased to 21.5 % and 6.3 % respectively as shown in Table 3. Herein, the excessive acid amount could promote not only the deoxygenation but also some secondary

Table 3
Coke amounts on the spent catalyst.

Catalyst	Coke deposition (wt.%)
HZSM-5	5.6±0.2
0.25%Cu/HZSM-5	4.6±0.0
0.5 %Cu/HZSM-5	6.3±0.2
1%Cu/HZSM-5	5.9±0.1
3%Cu/HZSM-5	4.7±0.0
5%Cu/HZSM-5	6.3±0.2
1 st Reuse	8.4±0.1
2 nd Reuse	9.3±0.0
3 rd Reuse	9.7±0.1
4 th Regen	5.6±0.1

reactions (e.g., polycondensation, condensation, cyclization) of primary products like aromatics, phenols and ketones to form coke on the catalyst, resulting in the lower aromatics selectivity and yield. In addition, the blockage of micropores of HZSM-5 by the excessive Cu species resulted in the decrease in the surface area, thereby limiting the diffusions of the reagent as well as the products. It should be noted that the char yields of all experiments were the same since the biomass layer and the catalysts layer were separately located in the reactor. For the gas yields, as can be seen from Fig. 6(b), the use of HZSM-5 resulted in lower gas yield than those cases using Cu/HZSM-5 catalysts. The increase in the gas products including CO, CO₂ and H₂ in the cases using the Cu/HZSM-5 was related to dehydrogenation, dehydration, oligomerization, decarbonylation, and decarboxylation accompanying the increase in the aromatic hydrocarbon yields and the reduction of the oxygen content in the upgrading bio-oils [3,43]. In addition, it should be noted that the yield of gas increased with the increasing of Cu loading amount, which should be resulted from the gradual enhancement of the secondary cracking reactions of pyrolysis vapor as well as the further pyrolysis of the coke intermediates on the catalyst [9]. Moreover, the increase of acid amount by the modifying by Cu may be more conducive to the improvement of catalytic activity toward gas production as observed in the case using 5%Cu/HZSM-5, which led to the highest gas yield.

The reaction routes of the *in-situ* upgrading of fast pyrolysis oils over the parent HZSM-5 and the various Cu modified HZSM-5 catalysts is illustrated in Fig. 7. Generally, lignocellulose biomass with a polymeric structure mainly consists of 3 main constituents, i.e., lignin, cellulose and hemicellulose. The biomass pyrolysis can be classified based on the lignin, cellulose and hemicellulose components. In the cellulose pyrolysis process, anhydro-monosaccharides (e.g., D-glucose and levoglucosan) and anhydro-oligosaccharides will be generated through depolymerization and thermal cracking at first and then, anhydro-monosaccharides are further converted to monoaromatics via diels-alder polymerization on the Brønsted acid sites on either the outer surface or internal surface of zeolite and could continuously convert to polyaromatics such as naphthalene and 2-methylnaphthalene via Diels-alder polymerization [3,44–46]. While, some polyaromatics could be condensed and polymerized to larger polyaromatics and even coke on those Brønsted acid sites. Herein, the acidity of zeolite will play the key role for the coking since the coking often occurs at high acidity condition. Similarly, the anhydro-oligosaccharides can be also converted to the monoaromatics via dehydration, decarboxylation and decarbonylation on the Brønsted acid sites and some could change to coke via further condensation and polymerization. In this study, no anhydro-monosaccharides, as well as anhydro-oligosaccharides, were detected in the final product, suggesting that the components from the thermal pyrolysis of cellulose were effectively converted to aromatic compounds with some acetic acid and ketone compounds. Hemicellulose is more easily decomposed at lower temperatures when compared to cellulose and lignin. It is significantly decomposed into the furfural and acetic acid at first, and then the generated products could be deoxygenated via dehydration, decarboxylation, decarbonylation and dehydrogenation on those Brønsted acid sites. The detected acetic acid in the final upgraded oil should be also mainly driven from the hemicellulose in the sunflower stalk [47]. Lignin consists of numerous branched aromatic rings, which can be divided into three basic units: sinapyl alcohol, coniferyl alcohol, and p-coumaryl alcohol. During the pyrolysis process, lignin could be converted to the compounds based on these three basic units and other heavy compounds at first [48], and

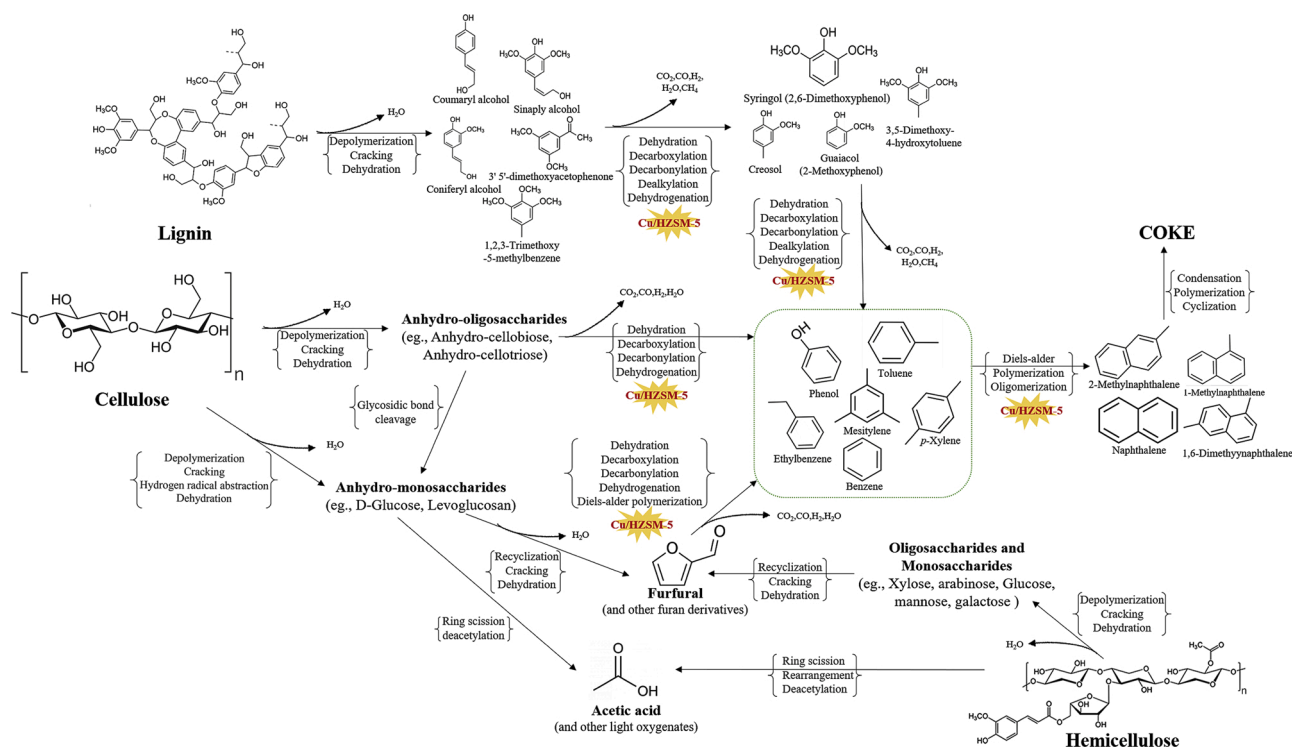


Fig. 7. Reaction pathways for the aromatic productions from catalytic upgrading of bio-oil derived from fast pyrolysis of sunflower stalk over Cu/H-ZSM-5 catalysts.

subsequently, the secondary products like 3,5-dimethoxy-4-hydroxytoluene, guaiacol (2-Methoxyphenol), and creosol and syringol (2,6-Dimethoxyphenol) are further generated, which were also observed in the final upgraded bio-oil (Figs. S2–11). Thereafter, various reactions like dehydrogenation, dehydration, decarbonylation, dealkylation and decarboxylation could take place on the Brønsted acid sites of catalysts, resulting in the formation of phenol and various monoaromatics as those from the cellulose and hemicellulose [1,43]. Meanwhile, some of them can be converted into large polyaromatics and coke via further condensation and polymerization in the same way as those species derived from cellulose and hemicellulose.

3.3. Reusability and regeneration of spent zeolites

Fig. 8(a) and (b) show the reusability and regeneration property of 0.5 %Cu/HZSM-5 with the best catalytic performance, which was tested for 4 cycles in the same condition after the testing for the fresh catalyst. The spent catalyst was reused from the first to the third reuse cycle without the regeneration while the catalyst was recovered by a facile calcining at 650 °C for 30 min in the air before testing in the fourth cycle. Obviously, after the fresh catalyst was used for the catalytic upgrading reaction without regeneration, a significant decrease in the relative amount of aromatic hydrocarbons from 73.2 % (Fresh) to 57.1 % (first reuse cycle) was observed and continuously decreased with the increasing number of cycles until 35.3 % in the third cycle. Herein, since the coke amount was accumulated in each cycle in the case without the regeneration (Table 3). It can be seen that the coke increasing extent decreased with the increase on the reuse cycle since some active sites should be covered by the deposited carbon species on the catalyst surface, which decreased the cracking of bio-oil components. The increased accumulation of coke on the catalyst in the reuse cycles decreased should cause the deactivation of the catalyst, thereby decreasing the aromatic selectivity and yield. Besides, compared to the parent HZSM-5, more coke was formed on the 0.5 %Cu/HZSM-5 with the increased acidity. However, when the spent catalysts after the third reusing cycle was calcined and tested, the activity was almost recovered to the level of the fresh catalyst with a relative amount for the aromatic hydrocarbons of 73.4 % and the high yield of 48.9 mg/g-biomass (d.a.f) for specific aromatic hydrocarbons (Fig. 8(a)). This indicated that the activity of spent 0.5 %Cu/HZSM-5 can be simply recovered by the facile calcination in the air for a short time.

4. Conclusions

Cu modified HZSM-5 catalysts with the appropriate Cu loading amount were successfully prepared using the wet impregnation method and applied for the *in-situ* bio-oil upgrading. 0.5 wt.% of Cu loading on the HZSM-5 resulted in the highest conversion of pyrolytic vapors to the aromatic hydrocarbons with a relative amount of 73.2 % and a yield of specific aromatic hydrocarbons (mainly including BTX) as high as 56.5 mg/g-biomass (d.a.f), which were much higher than those based on the parent HZSM-5 (55.0 % and 26.0 mg/g-biomass (d.a.f)). It should be attributed to the most suitable acidity and best textural structure. In addition, although Cu doping resulted in an increased amount of coke during the deoxygenation process due to the promoting of a series of condensation and polymerization reactions accompanying the deoxygenation, cracking, and aromatization, the deactivated Cu/HZSM-5 catalysts was easily recovered by the simple calcination in the air for a short time.

CRedit authorship contribution statement

Nichaboon Chaihad: Data curation, Formal analysis, Investigation, Writing - original draft. **Aisikaer Anniwaer:** Investigation. **Surachai Karnjanakom:** Investigation. **Yutaka Kasai:** Investigation. **Suwadee Kongparakul:** Investigation. **Chanatip Samart:** Investigation. **Prasert**

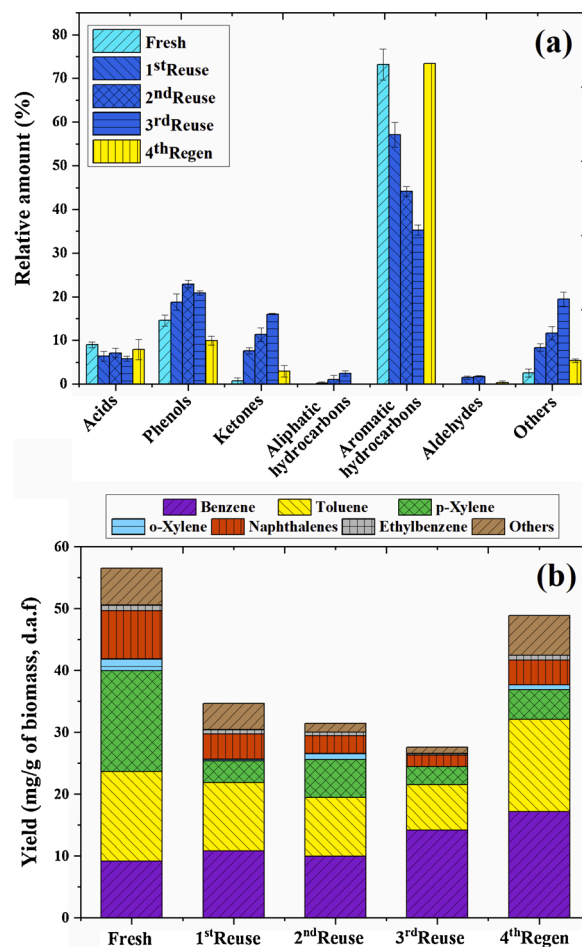


Fig. 8. Reusability and regeneration performance of 0.5 wt.%Cu/HZSM-5 catalyst.

Reubroycharoen: Investigation. **Abuliti Abudula:** Investigation. **Guoqing Guan:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Validation, Writing - review & editing.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jaap.2021.105079>.

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