# Preparation of various hierarchical HZSM-5 based catalysts for *in-situ* fast upgrading of bio-oil

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## ARTICLE INFO

## ABSTRACT

Hierarchical HZSM-5 zeolites were prepared by desilication of commercial HZSM-5 in aqueous NaOH solutions with the assistance of tetrapropylammonium hydroxides (TPAOH), and applied for the catalytic upgrading of bio-oil derived from the fast pyrolysis of sunflower stalk. The hierarchical HZSM-5 by using 0.2 M NaOH with 0.25 M TPAOH for the desilication exhibited the best catalytic performance and the relative total peak area related to the aromatic hydrocarbons reached 65.8% with a yield of the detected aromatic hydrocarbons up to 45.2 mg/g-bio-oil. With the assistance of 0.25 M TPAOH for the desilication, the formation of mesopores became highly controllable, resulting in the increase in the surface area and maintenance of enough acid amounts, however, the coking on the surface of catalyst was not hindered. To solve the coking problem and increase the aromatic hydrocarbons production, the hierarchical HZSM-5 with the best performance was modified by various metals. It is found that 0.25 wt% Cu loaded hierarchical HZSM-5 increased the yield of the detected aromatic hydrocarbons up to 54.5 mg/g-bio-oil with a decrease in the coke formation.

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## 1. Introduction

Various aromatic compounds such as benzene, toluene, and xylene (BTX), naphthalene and ethylbenzene are in great demand in the world market [1]. More than 85% of aromatics production traditionally depends on the catalytic reforming of petroleum resources. With a shortage of fossil resources and a continuously growing demand of aromatics, production of aromatics from alternative and environmentally friendly resources has received widespread attention [2]. Biomass is a renewable and abundantly available resource that is considered an attractive feedstock for producing liquid biofuels as well as valuable chemicals such as

aromatics [3–5]. Fast pyrolysis is widely used for the production of liquid product (bio-oil) from biomass under the oxygen-free condition, atmospheric pressure and moderate temperatures (450–600 °C) [6,7]. As the crude oil, the bio-oil can be used as an important intermediate feedstock for the chemical and biofuel production. However, different from the crude oil, a high amount of oxygenated compounds are contained in the bio-oil so that it has low calorific value with high viscosity, high density, corrosive nature, thermal instability, extreme ignition delay, and incomplete volatility [8–10]. To improve the quality of bio-oil, catalytic cracking is an effective way since it can deoxygenate to produce valuable compounds suited for fuel through the removal of oxygen [11–13]. Zeolites such as beta, zeolite Y, and ZSM-5 have been used extensively for the catalytic upgrading of bio-oils since their pore structure and acidity can control the composition and distribution of upgraded bio-oil [9,14]. Especially, ZSM-5 has a well-defined microporous structure, high hydrothermal stability, and strong

acidity, which exhibited high activity and high selectivity towards aromatic hydrocarbons [15–17]. However, the micropores of ZSM-5 zeolite usually lead to slow diffusion of molecules with different sizes including reactants, intermediates and products, which seriously restrict its catalytic application for the upgrading of bio-oil [18]. In particular, the mass transfer limitations would reduce the access of the pyrolysis vapor to the acid sites, resulting in a low catalyst utilization with less desirable products. In order to overcome the steric limitations in the micropores of ZSM-5, mesopores can be generated in the ZSM-5 to reduce the diffusion path lengths and meanwhile increase the external surface area [18–20]. Recently, hierarchically structured zeolites with the generated mesopores have been widely investigated [21,22]. The occurrence of mesoporosity facilitates molecular diffusion in the zeolites and allows the reagents to have better accessibility towards the active sites in the zeolite structure, removing steric limitations and shortening the intracrystalline diffusion pathways [21]. Desilication is an effective way to obtain mesopores in the ZSM-5 zeolite, and maintain suitable Brønsted acidity, which can increase the yield of aromatic hydrocarbons when used for the upgrading of bio-oil [23]. To date, alkaline agents such as NaOH, $Na_2CO_3$, tetrapropylammonium hydroxide (TPAOH) and tetrabutylammonium hydroxide (TBAOH) are widely used for the fabrication of hierarchical zeolites [24–26]. By using NaOH as an alkaline medium, the silicon in the framework can be extracted to create mesopores [27]. However, in this case, the extraction of silicon is too fast and strong, resulting in the uncontrollable formation of mesopores and the loss of a certain amount of micropores and acid sites in the zeolite structure. Meanwhile, some organic quaternary ammonium hydroxides such as TPAOH and TBAOH were also used for the desilication, however, they are less reactive towards silicon dissolution than inorganic hydroxide. Thus, to tailor the degree of mesoporosity, NaOH was combined with the organic base such as the TPAOH and TBAOH for the desilication [18,19]. Herein, the addition of the organic base can maintain more acid sites and increase the surface area in the final hierarchical zeolites than that using NaOH alone. It should be noted that the acidity and surface area have great influences on the catalytic upgrading process [28]. To date, the hierarchical zeolites with highly mesoporous structure prepared by using NaOH combined with an organic base have been applied for the conversion of methanol to hydrocarbons and $N_2O$ decomposition [19,29], however, the in-situ catalytic upgrading of bio-oil derived from fast pyrolysis of biomass over such zeolite catalysts has not yet been reported. In this case, the generated bio-oil from the real biomass always passes through the catalyst layer rapidly. It should be important to achieve fast catalytic upgrading of the bio-oil over the hierarchical zeolites. Moreover, the hierarchical zeolites prepared based on different parent zeolites could lead to different properties. Thus, it should be important to achieve fast catalytic upgrading of the bio-oil over various hierarchical zeolites. In addition, it is reported that the hierarchical zeolites modified by metals such as Cu and Mg can enhance the deoxygenation process and lead to an increase in the aromatic hydrocarbon yield and a decrease in the coke formation on the catalysts [30,31].

In this study, the desilication of HZSM-5 to fabricate hierarchical HZSM-5 was performed by using the fixed concentration of NaOH with the addition of different concentrations of TPAOH, and the obtained hierarchical HZSM-5 catalysts were applied for the catalytic upgrading of bio-oils derived from the fast pyrolysis of sunflower stalk. Physicochemical properties of the obtained catalysts were characterized, and the catalytic upgrading performance related to the yield of aromatic hydrocarbons was investigated. To solve the coking problem and increase the aromatic hydrocarbons production, the hierarchical HZSM-5 was also modified by various metals including Cu, Mg and Ag. It is expected to enhance the basic

knowledge of hierarchical zeolite for in-situ catalytic upgrading of bio-oil from the fast pyrolysis of biomass.

## 2. Experimental

### 2.1. Material

Sunflower stalk was collected from Aomori, Japan. The collected sample was dried at 110 °C and crushed with a grinder, and then sieved into a particle size of 0.5–1.0 mm. The results on the proximate and ultimate analyses for the samples were shown in our previous work [32]. NaOH, TPAOH, $Mg(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and $AgNO_3$ were purchased from Wako, Japan. HZSM-5 (Si/Al of 40) zeolite powder was provided by TOSOH Corp., Japan.

### 2.2. Hierarchical HZSM-5 zeolite preparation

The catalysts were prepared by desilication of commercial HZSM-5 in aqueous base solutions. The conditions were optimized according to the acidity (Table S1) as well as textural property (Table S2) and the selectivity and yield of aromatic hydrocarbons as shown in Fig. S1. The three typical hierarchical HZSM-5 zeolites in Tables S1 and S2 were prepared by adding 10 g of HZSM-5 zeolite powders into 100 mL of 0.2 M NaOH solution, 100 mL of a mixed solution composed of 50 mL of 0.2 M NaOH and 50 mL of 0.25 M TPAOH, and 100 mL of 0.5 M pure TPAOH, respectively, under stirring at 80 °C for 1 h. After the treatment, the solids were collected by filtration, washed with distilled water until the neutral pH, and then dried at 110 °C overnight. Thereafter, the alkaline-treated zeolites were dispersed in 200 mL of 1 M $NH_4NO_3$ at 80 °C for 4 h, collected by filtration, and finally calcined at 550 °C for 4 h. Herein, the parent zeolite is denoted as HZ5, the zeolites treated by NaOH, the mixture of NaOH and TPAOH, and TPAOH are denoted as HZ5-0.2N, HZ5-(0.2N + 0.25TP) and HZ5-0.5TP, respectively. The metal-modified hierarchical HZSM-5 zeolites were prepared by the wet impregnation method. Firstly, metal nitrates with the calculated metal-loading amounts (i.e., 0.1, 0.25, 0.5 and 1 wt%) were dissolved in deionized water and the HZ5-(0.2N + 0.25TP) powders with the best catalytic performance were impregnated in it for 10 h with stirring, followed by drying at 110 °C for 12 h and calcined at 550 °C for 4 h. Prior to the performance testing, the obtained catalyst powders were pressed, crushed, and sieved to a particle size in the range of 0.5–1.0 mm. The preparation of each sample was repeated at least 3 times.

### 2.3. Characterizations

$N_2$-adsorption/desorption isotherms were measured on an automated surface area and pore size analyzer (NOVA 4200e,Quantachrome Instruments, USA) at the liquid nitrogen temperature (77 K). Prior to analysis, the catalysts were vacuum-degassed at 200 °C for 2 h. The multipoint Brunauer–Emmett–Teller method (BET) in a pressure range of 0.05–0.30 $P/P_0$ was used to determine the total specific surface area. The total pore volume was estimated from the $N_2$ amount adsorbed at $P/P_0 = 0.99$ and converted to liquid $N_2$ volume. The micropore surface area ($S_{micro}$) and volume ($V_{micro}$) of micropores were calculated using t-plot method while the external specific surface area ($S_{external}$) and the mesopore volume ($V_{meso}$) were calculated by difference. The pore size distribution and the average pore size were determined by Barrett-Joyner-Halenda (BJH) method with the desorption branch.

The acidity and acid site distribution of the catalysts were determined by $NH_3$-Temperature Programmed Desorption method ($NH_3$-TPD) (Belcat, Japan), in which the catalyst was heated from

room temperature to 700 °C with a heating rate of 10 °C/min in a 50 cm³/min of helium flow rate and held at that temperature for 1 h. Then the catalyst was cooled down to 120 °C and stabilized for 10 min. Thereafter, NH₃ stream was introduced into the measurement cell for 1 h. To ensure the single layer adsorption of NH₃ on the catalyst surface, the catalyst was then flushed with 50 cm³/min of helium stream for 1 h to remove the physically adsorbed NH₃. After stabilization at 120 °C for 10 min, NH₃ desorption was carried out until 800 °C with a heating rate of 10 °C/min in 30 cm³/min of helium stream and held for 10 min. Herein, the NH₃ desorption peak, which expresses the amount of the desorbed ammonia, was detected using a thermal conductivity detector (TCD), and converted using the calibration data and presented as a function of temperature.

XRD measurement of catalysts was conducted by an X-ray Diffractometer (Smartlab, Rigaku, Japan). The scanning angle ($2\theta$) was ranged from 10° to 90° using filtered Cu-K$\alpha$ radiation ($\lambda = 0.1542$) with a scanning step of 0.02°. The relative crystallinity of parent HZ5 was set to 100% and calculated the relative crystallinity of hierarchical HZSM-5 catalysts by comparing the sum of peak intensities between $2\theta = 0\text{-}80°$ from the XRD pattern with that of the parent HZ5. The existence of metal species on the catalysts was investigated using a scanning electron microscopy (SEM, SU8010, Hitachi, Japan) coupled with an energy dispersive X-ray detector (EDX). The effect of alkaline treatment at different conditions on the porous structure of the hierarchical zeolite was investigated by a transmission electron microscopy (TEM).

### 2.4. In-situ catalytic upgrading of bio-oil

In-situ catalytic upgrading of bio-oil was performed in a quartz fixed-bed reactor placed inside an infrared furnace (VHT series, ULVAC, Japan) with a N₂ flow as the carrier gas from the upper to lower side direction, in which 0.5 g of prepared sunflower stalk (the upper side) and 0.5 g of catalysts (the lower side) were separately placed in the middle of the reactor with quartz wool. Before heating the reactor, the reactor was purged with a N₂ flow for 10 min. Then, the reactor was rapidly heated to 500 °C with a heating rate of 1000 °C/min, and held at that temperature for 5 min. The obtained bio-oil carried by the N₂ flow was condensed with cold acetone and collected for the analysis [32]. The non-condensable gases were collected in a gasbag. The reliability of experimental data was confirmed by repeating the experiments at least three times. The gas chromatography/mass spectrometry (GC-MS) (GC-2010 Plus for GC, QP-2010 Ultra for MS, Shimadzu Japan) equipped with an Ultra ALLOY+ −5 capillary column was used to determine the composition of bio-oil. Compound identification was carried out using the NIST (National Institute of Standards and Technology) mass spectrum library. In this analysis, only the light components with a boiling point below 300 °C were detected. Specific aromatic hydrocarbons were used as the external standards to determine the yields of main aromatic hydrocarbon products. The amount of coke deposited on the spent catalysts was determined from the difference in the weight of the catalyst before and after the calcination at 650 °C in air for 30 min in a muffle furnace. The gas analysis was implemented on a gas chromatography (Agilent 7890A GC system, USA) equipped with a thermal conductivity detector (TCD) and 3 packed columns (1 molecular sieve 5A column +1 HayeSep Q column +1 molecular sieve 5A column). A standard gas mixture with constant concentrations of CO₂, CO, N₂, H₂, and CH₄ was used for the calibration of gaseous products. The water content in the bio-oil was determined by a Karl-Fischer titrator (MKS-500, KEM, Japan).

## 3. Results and discussion

### 3.1. Desilication mechanism

Since the desilication of HZSM-5 zeolite is the extraction of Si from the structure. In NaOH solution containing both Na⁺ and OH⁻ ions, Si extraction could begin from the outer surface area of HZSM-5 by the attack of OH⁻ ions on the Si species at first, then, the Na⁺ ions are also absorbed to reach a balance with the negative charge. As such, the desilication occurs continuously without any protection, resulting in mesopores with the further attack by OH⁻ ions on the Si species inside the HZSM-5 bulk body so that the mesopores are formed in the interior of HZSM-5 crystals and the pore size becomes larger and larger with the increase in the desilication time. Thus, as illustrated in Scheme S1(a), the desilication is difficult to be controlled in the case using NaOH solution. In comparison, with the addition of suitable TPAOH into the NaOH solution, the total OH⁻ ion content in the solution is from both NaOH and TPAOH, but the alkalinity is decreased to some extent. More importantly, this mixed solution has two different Na⁺ and TPA⁺ cations, and the nature of the organic base is different from that of the inorganic base in the terms of steric hindrance, solvation, and stability [33], which could result in a different desilication pathway. That is, when these two cations are absorbed on the outer surface of the HZSM-5 to balance the negative charge, the extraction of Si from OH⁻ ion attack should more easily occur near the Si sites adsorbed with Na⁺ cations because Na⁺ cation has smaller size and less steric hindrance, which cannot hinder the attack by the OH⁻ ions. In contrast, TPA⁺ cation has a large size, making it better protect the adsorbed Si sites from the attack by the OH⁻ ions. Also, the hydrophobicity of
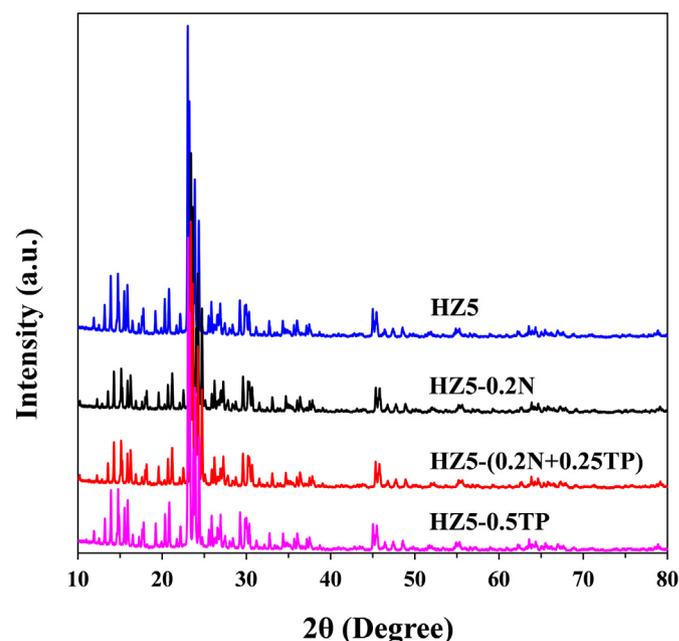


**Fig. 1.** XRD patterns of the prepared hierarchical HZSM-5 catalysts and the parent HZSM-5.

**Table 1**
The relative crystallinity of hierarchical HZSM-5 catalysts to the parent HZSM-5 catalyst.

| | HZ5 | HZ5-0.2N | HZ5-(0.2N + 0.25TP) | HZ5-0.5TP |
|---|---|---|---|---|
| Relative crystallinity (%) | 100 | 87.2 | 88.6 | 97.3 |

the long hydrocarbon chain of TPA$^+$ cation is benefit for the propyl groups to protect the hydrophobic silicate [33]. As such, the parts with the absorbed TPA$^+$ cations should be more stable than those absorbed by Na$^+$ cations [33]. Thus, the Si extraction starts from the absorbed Na$^+$ cation areas, and by adjusting the amount of TPAOH in the solution, the formation of suitable mesopores in the HZSM-5 becomes controllable. As illustrated in Scheme S1(b), when small mesopores are formed on the outer surface by the attack of OH$^-$ ions, some TPA$^+$ cations will enter the inside with the Na$^+$ cations to balance the negative charge but they can prevent the increasing Si extraction by the OH$^-$ ion attacks, resulting in that the desilication of the HZSM-5 becomes more controllable [19]. In the case of using only TPAOH solution, a large amount of TPA$^+$ cations balance the negative charges on almost all surface areas. This causes excessive protection to inhibit the desilication as well as the formation of large mesopores. As illustrated in Scheme S1(c), after HZSM-5 is treated by using TPAOH alone, only some mesopores with small sizes could be formed on the outer surface of zeolite crystals, which could decrease the external surface area and mesopore volume [19].

## 3.2. Characterizations of catalysts

Fig. 1 shows the XRD patterns of the prepared hierarchical HZSM-5 zeolites and the parent HZ5. One can see that all the catalysts retained the typical framework of HZ5 since the characterized diffraction peaks at 2θ of 12−18° and 20−26° remained the same as those of the HZ5. It suggested that the crystalline structure of HZ5 was maintained after the desilication. However, as shown in Table 1, the HZ5-0.2N exhibited lower relative crystallinity of 87.2%. It should be attributed to the severe desilication by the strong alkaline solution since it could result in the collapse of zeolite framework. In contrast, with the assistance of TPAOH, the obtained hierarchical HZSM-5 zeolite of HZ5-(0.2N + 0.25TP) had higher relative crystallinity, indicating that the existence of TPAOH helped

to maintain the framework structure of zeolite [19]. In addition, the HZSM-5 zeolite treated by 0.5 M TPAOH only decreased the crystallinity a little due to the weak alkalinity.

As shown in Table 2, the BET surface area ($S_{BET}$) of hierarchical HZSM-5 zeolite of HZ5-(0.2N + 0.25TP) increased to some extent (359.9 m$^2$/g) with a little decrease of micropore surface area ($S_{micro}$ = 317.4 m$^2$/g) but an increase of total pore volume ($V_{total}$ = 0.22 cm$^3$/g) and an enlargement of average pore size (D = 3.78 nm) in the case using NaOH with the assistance of TPAOH for the desilication when compared with the parent HZ5 ($S_{BET}$ = 325.9 m$^2$/g, $S_{micro}$ = 307.7 m$^2$/g, $V_{total}$ = 0.18 cm$^3$/g, D = 2.97 nm). In contrast, the desilications with either strong NaOH solution or weak TPAOH solution resulted in the decrease of the
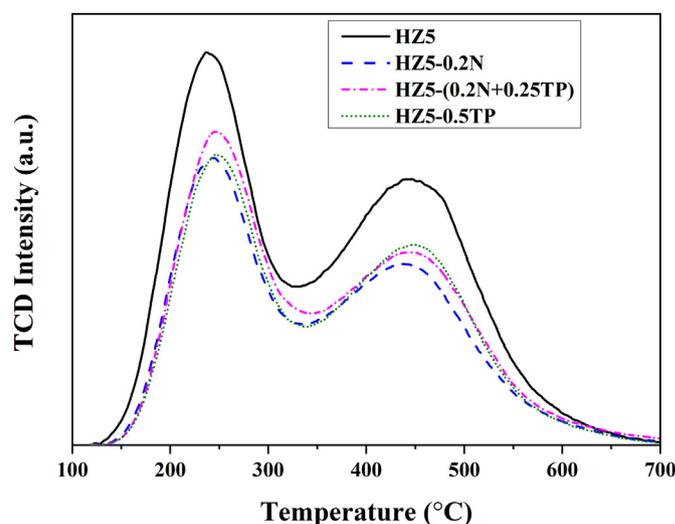


**Fig. 3.** NH$_3$-TPD profiles of the hierarchical HZSM-5 catalysts.

**Table 2**
Textural properties of the prepared hierarchical HZSM-5 catalysts and the parent HZSM-5 catalyst.

| Catalyst | Si/Al molar ratio on Surface[a] | $S_{BET}$ (m$^2$/g) | $S_{micro}$ (m$^2$/g) | $V_{total}$ (cm$^3$/g) | $V_{micro}$ (cm$^3$/g) | Average pore size (nm) |
|---|---|---|---|---|---|---|
| HZ5 | 22.0 | 325.9 | 307.7 | 0.18 | 0.15 | 2.97 |
| HZ5-0.2N | 16.6 | 319.1 | 281.5 | 0.20 | 0.13 | 3.95 |
| HZ5-(0.2N + 0.25TP) | 21.6 | 359.9 | 317.4 | 0.22 | 0.15 | 3.78 |
| HZ5-0.5TP | 18.3 | 292.6 | 271.7 | 0.17 | 0.14 | 3.14 |

[a] Si/Al ratios were obtained using EDS-SEM.
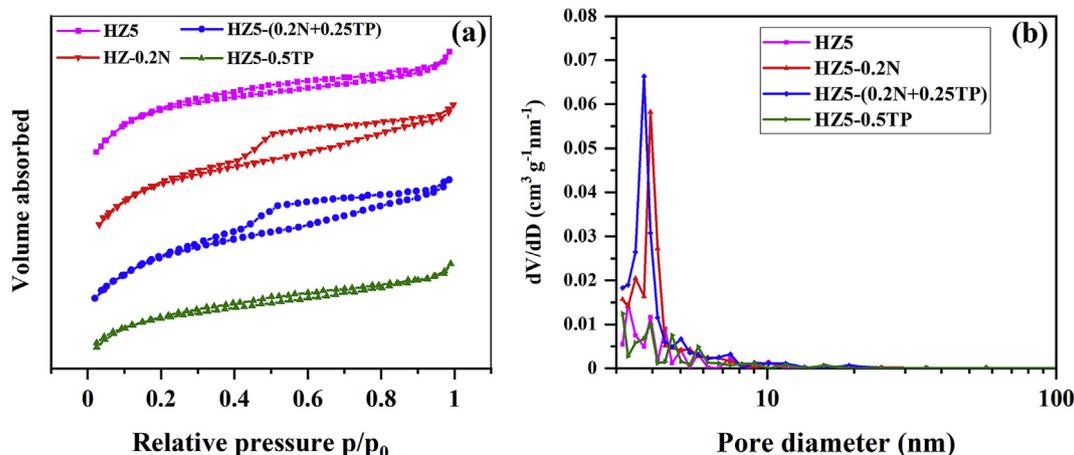


**Fig. 2.** N$_2$ adsorption/desorption isotherms (a) and DFT pore size distributions (b) for the hierarchical HZSM-5 catalysts.

**Table 3**
Acidity of hierarchical HZSM-5 catalysts and the parent HZSM-5 catalyst.

| Catalyst | Acidity (mmol/g, low temp) | Acidity (mmol/g, high temp) | Total acidity (mmol/g) |
| --- | --- | --- | --- |
| HZ5 | 0.58 | 0.67 | 1.25 |
| HZ5-0.2N | 0.48 | 0.39 | 0.87 |
| HZ5-(0.2N + 0.25 TP) | 0.52 | 0.43 | 0.95 |
| HZ5-0.5 TP | 0.48 | 0.43 | 0.91 |
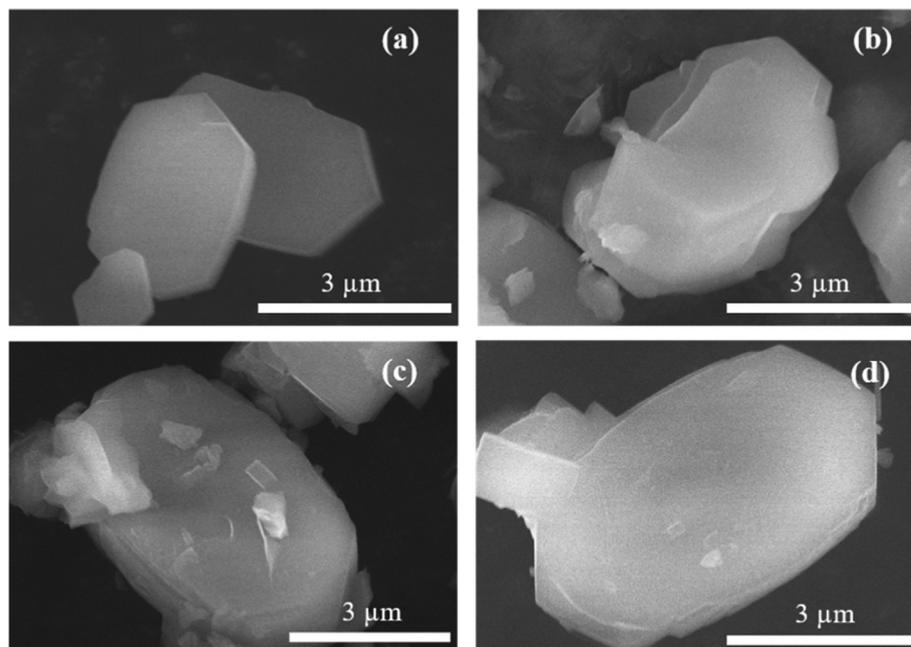


**Fig. 4.** SEM images of (a) HZ5, (b) HZ5-0.2N, (c) HZ5-(0.2N + 0.25TP) and (d) HZ5-0.5TP catalysts.
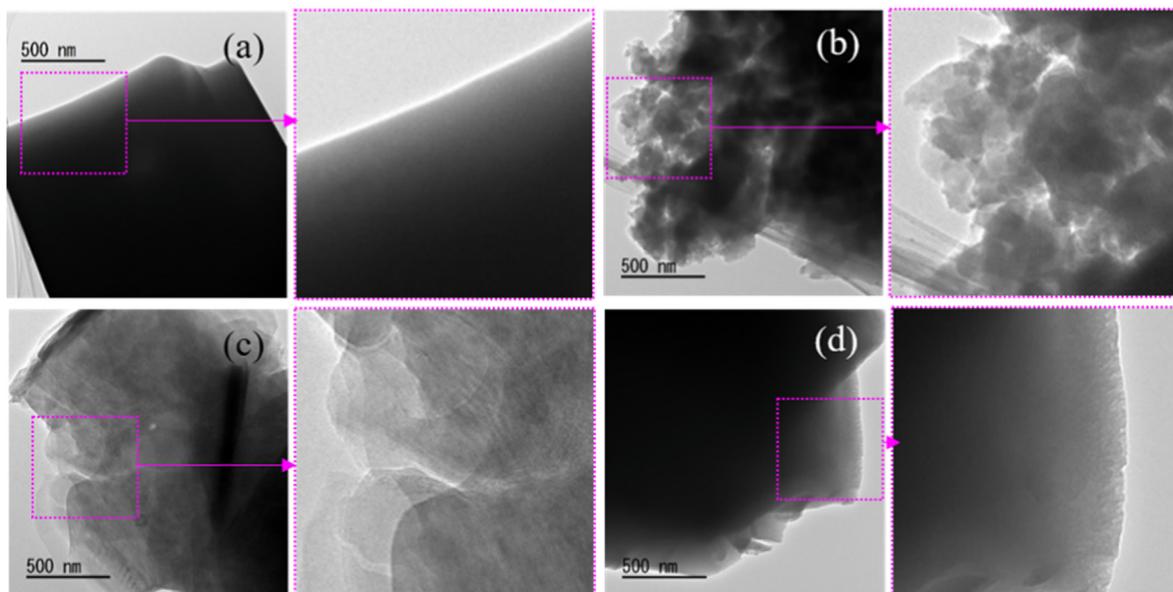


**Fig. 5.** TEM images of (a) HZ5, (b) HZ5-0.2N, (c) HZ5-(0.2N + 0.25TP) and (d) HZ5-0.5TP catalysts.

surface area as well as micropore surface area and volume. Thus, the desilication with a suitable alkaline solution like the solution with 0.2 M NaOH and 0.25 M TPAOH could increase the meso-porosity of the obtained hierarchical HZSM-5 zeolites and simultaneously preserve the microporous structure. Herein, the TPA$^+$ ions tend to interact with hydrophobic silicate generated by the deprotonation of Si–OH groups in the alkaline medium [33], and the preferentially attached TPA$^+$ ions would prevent HZSM-5

crystals from further severe desilication, which is beneficial for the formation of good hierarchical structure. In addition, as shown in Fig. 2(a), the hysteresis loop of HZ-0.2N and HZ5-(0.2N + 0.25TP) exhibited type IV isotherms with H4 hysteresis loop at P/P$_0$ above 0.4, also indicating the existence of mesoporous structures [34—36]. In contrast, the HZ5-0.5TP had a typical type I isotherm, verifying that it had a similar microporous structure as the parent HZ5, but no mesopores were formed under such a pure-TPAOH-solution treatment with relatively weak alkalinity.

Fig. 3 shows NH$_3$-TPD profiles of the hierarchical HZSM-5 zeolites and the parent HZ5 zeolite. The peaks at the lower and higher temperatures were assigned to the desorptions of NH$_3$ on the weak Lewis acid sites and the strong Brønsted acid sites, respectively. One can see that the peaks shifted to the higher temperature direction after the desilication and more NH$_3$ could be adsorbed on the Lewis acid sites for the hierarchical HZ5-(0.2N + 0.25TP) zeolite. The acidities of these catalysts were calculated from the related peak areas and summarized in Table 3. One can see that the acidity of all hierarchical zeolites decreased to great extent at either weak or strong acid sites, which is consistent with the reported results [37]. In addition, the treatment of parent HZ5 in 0.5 M TPAOH alone also decreased the surface Si/Al molar ratio, but the acidities at both weak and strong acid sites were not greatly changed, which is also consistent with the reported results [33].

Fig. 4 shows SEM images of parent HZ5 and the hierarchical HZSM-5 zeolites derived from HZ5, in which the obvious differences were not observed. However, from the TEM images (Fig. 5), the edges of hierarchical HZSM-5 zeolites (Fig. 5 (b-d)) were completely different from that of the parent HZ5 (Fig. 5(a)). It is obvious that the HZ5 crystal had a highly dense edge. In comparison, for the hierarchical HZ-0.2N, a large amount of mesopores were generated with some macropores in the edge part of the crystal (Fig. 5(b)), which is similar as the reported one [19]. Meanwhile, for the hierarchical HZ-(0.2N + 0.25TP) zeolite, abundant uniform mesopores appeared in the edge part of the crystal (Fig. 5(c)) due to the mild desilication with the assistance of a small amount of TPAOH. In addition, no obvious changes on the edge of crystal were observed under the pure-TPAOH-solution treatment even at relatively high concentration. These results are also consistent with the N$_2$ adsorption-desorption isotherms.

### 3.3. In-situ catalytic upgrading of bio-oil over hierarchical HZSM-5

In-situ catalytic upgrading of bio-oil derived from the fast pyrolysis of sunflower stalk over hierarchical HZSM-5 catalysts was performed at a reaction temperature of 500 °C based on the preliminary experiments. As shown in Fig. 6(a), based on the GC-MS analysis results, the chemicals in the upgraded bio-oil can be classified into seven groups, i.e., acids, phenols, ketones, aliphatic hydrocarbons, aromatic hydrocarbons, aldehydes, and others including alcohol, ether, ester, sugar, amide and amine. Herein, the total relative peak area of all detected aromatic hydrocarbons in the upgraded bio-oil was considered as the indicator to determine the upgrading effectivity of the catalysts, which was defined as the ratio of the total peak area related to the aromatic hydrocarbons and the total peak area of all detected chemicals. As a result, the relative peak area of aromatic hydrocarbons from the upgrading over the hierarchical HZ-(0.2N + 0.25TP) zeolite increased to 65.8% from 49.8% over the parent HZ5, which was also higher than that over HZ5-0.2N (60.0%) catalyst. Especially, those undesirable compounds such as ethers, amides, and amines, ketones, phenols, and esters were greatly reduced in the upgraded oil by using this hierarchical HZSM-5 catalyst. This result should be attributed to the higher S$_{BET}$ with the preservation of the microporous volume as well as the higher acidity of HZ5-(0.2N + 0.25TP). Generally, high

acidity could enhance the cracking, dehydrogenation and aromatization of oxygenated compounds to aromatic hydrocarbons [23,31]. Therefore, it is important to generate suitable acidity on the hierarchical HZSM-5 catalyst for the increasing of aromatization.

The specific aromatic hydrocarbons produced during the in-situ catalytic upgrading process can be categorized into seven typical chemicals, i.e., benzene, toluene, o-xylene, p-xylene, ethylbenzene, naphthalenes, and others. Herein, the naphthalenes included naphthalene and alkyl naphthalenes such as 2,6-dimethyl-naphthalene, 1,6-dimethyl-naphthalene, 2,3-dimethyl-naphthalene, 2-methyl-naphthalene, 2-ethyl-naphthalene, 1,7-dimethyl-naphthalene and others included indene, 2-methylidene, other substituted benzenes such as 1-ethyl-2-methyl-benzene, 1-ethyl-3-methyl-benzene, 1,3,5-trimethyl-benzene, and 1,3-dimethyl-benzene. Fig. 6(b) shows the yields of these specific aromatic hydrocarbons in the upgraded bio-oil obtained by using the parent HZ5 and the hierarchical HZSM-5 catalysts. In this study, those large polycyclic aromatic hydrocarbons such as anthracene, phenanthrene, and fluorene were not detected in all samples. As shown in Fig. 6(b), the
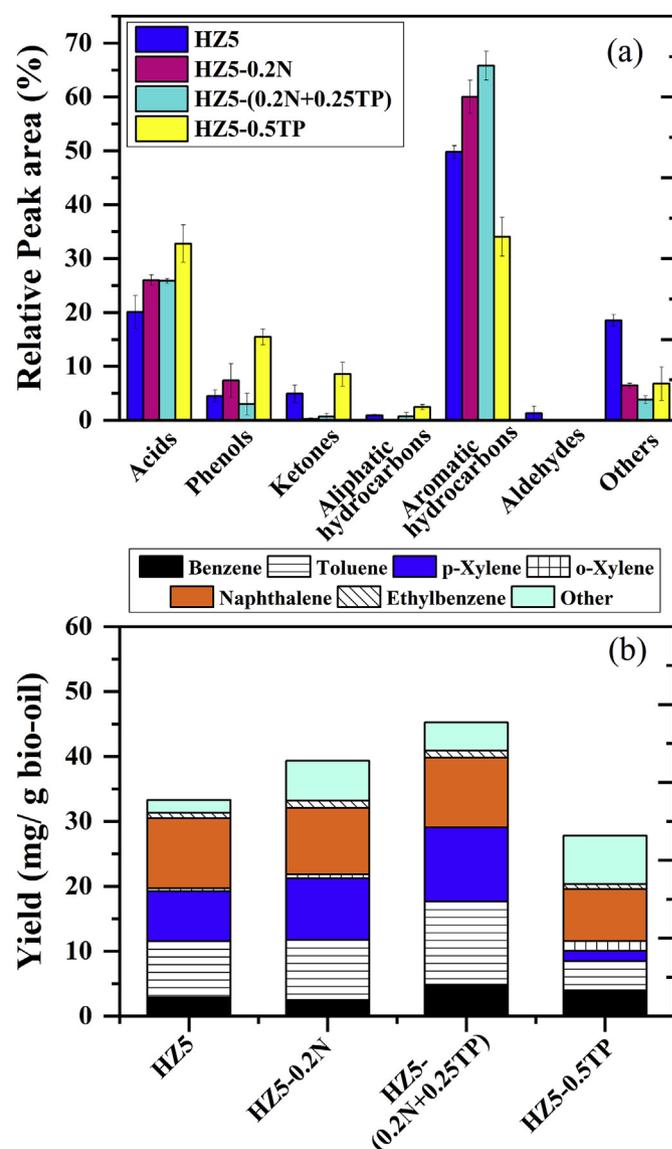


**Fig. 6.** Chemical compositions in the upgraded bio-oils with hierarchical HZSM-5 catalysts (a) and the selectivity towards specific aromatic hydrocarbons in the upgraded bio-oils (b).

yield of specific aromatic hydrocarbons in the upgraded bio-oil derived from the upgrading over the HZ5-(0.2N + 0.25TP) reached to 45.2 mg/g bio-oil, which was much higher than that from the parent HZ5 (33.1 mg/g bio-oil), also higher than that from the HZ5-0.2N (38.8 mg/g bio-oil), indicating that the hierarchical HZ5-(0.2N + 0.25TP) catalyst had higher selectivity and activity than other prepared catalysts. Herein, the enlarged channel and pore sizes should be suitable for the large molecules in the bio-oil easily entering the inside of the HZ5-(0.2N + 0.25TP) zeolite, whereas the increased surface area provided more active sites for the upgrading reaction, leading to the generation of more

monoaromatic hydrocarbons and small polyaromatic hydrocarbons [38].

Fig. S2(a) shows the mass balance in the upgrading of bio-oil over the parent HZ5 and the hierarchical HZSM-5 catalysts. One can see that the water content in the upgraded bio-oil derived from the upgrading over the HZ5-(0.2N + 0.25TP) catalyst increased to 25.1 wt% from 22.4 wt% for the parent HZ5, and simultaneously, the gas yield (Fig. S2(b)) was also increased from 15.8 wt% to 20.8 wt%. Whereas, the bio-oil yield was reduced from 35.1 wt% for the HZ5 to 26.4 wt% for the HZ5-(0.2N + 0.25TP). It indicated that the deoxygenation by using these catalysts resulted in the formation of $H_2O$,
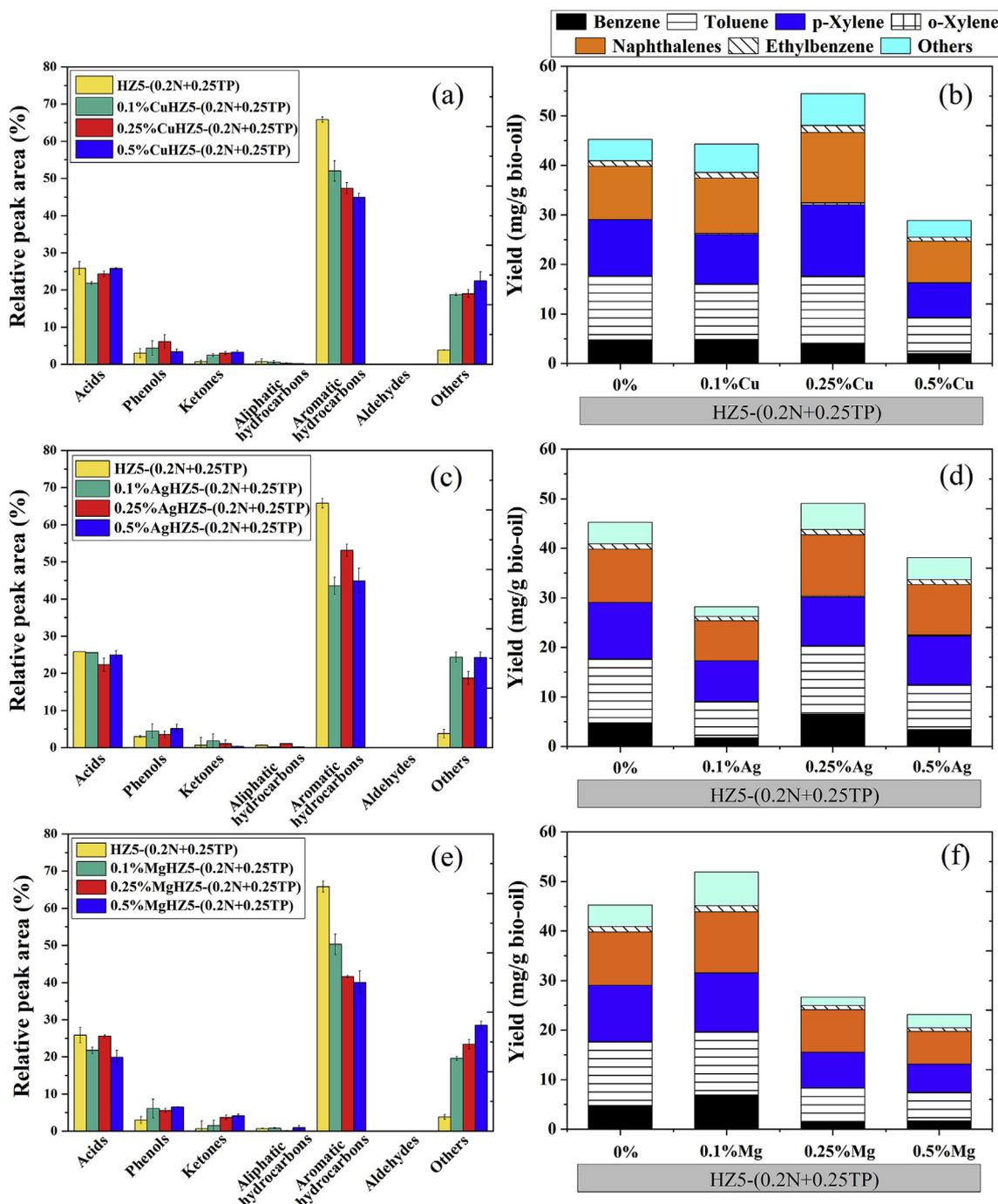


**Fig. 7.** Chemical compositions of the bio-oils upgraded with the metal doped hierarchical HZSM-5 catalysts, Cu (a), Ag (c) and Mg (e) doped ones and the selectivity towards specific aromatic hydrocarbons in the upgraded bio-oils in the cases of Cu (b), Ag (d) and Mg (f) dopings.

$CO_2$ and CO via various reactions such as dehydration, decarboxylation, and decarbonylation [39,40]. Meanwhile, it is found that the obtained hierarchical zeolites did not inhibit the coke formation on their surface, and the coke yield was even increased to some extent along with the obvious increase in the yield of aromatic hydrocarbons by using the HZ5-(0.2N + 0.25TP). Herein, the increase of the acidity of HZ5-(0.2N + 0.25TP) on the Lewis acid sites should be the main reason for the more coke formation since the cracking reactions also easily occur on such sites. Thus, to modify the acid sites for reducing the coking, metal doping on the HZ5-(0.2N + 0.25TP) was also performed in the following study.

### 3.4. Influence of metal-doping on the performance of hierarchical HZSM-5

In this study, to investigate the influence of metal-doping on the performance of hierarchical HZSM-5 catalyst, Cu, Ag and Mg were separately doped on the hierarchical HZ5 (0.2N + 0.25TP) zeolites. Fig. 7(a), (c) and (e) show the relative peak areas of various chemicals in the upgraded bio-oils obtained by using the Cu, Ag and Mg doped catalysts with different doping amounts, respectively. Meanwhile, the related specific aromatic hydrocarbon yields were also determined and shown in Fig. 7(b), (d) and (f), respectively. One can see that the chemical compositions in the upgraded bio-oil were greatly affected the aromatic hydrocarbon production, and

the optimum doping amounts of Cu, Ag and Mg were found to be 0.25 wt%, 0.25 wt% and 0.1 wt%, respectively. In particular, although the relative peak areas related to the aromatic hydrocarbons in the upgraded bio-oil were reduced (Fig. 7(a), (c) and (e)) with the 0.25 wt% Cu, 0.25 wt% Ag and 0.1 wt% Mg doping amounts, the specific aromatic hydrocarbon yields obviously increased to 54.5, 49.1 and 51.9 mg/g-bio-oil from 45.2 mg/g-bio-oil for the undoped hierarchical HZ5 (0.2N + 0.25TP) zeolite, respectively (Fig. 7(b), (d) and (f)), indicating that the doping with the optimum amount of metal could increase the selectivity of the hierarchical zeolite. Herein, all the metal doped HZ5-(0.2N + 0.25TP) zeolites showed high selectivity towards naphthalenes, toluene, p-xylene and a few other types of aromatic hydrocarbons, therefore increasing the overall aromatic hydrocarbons production.

Fig. 8(a) shows the mass balance in the upgrading of bio-oil over the metal doped hierarchical HZ5-(0.2N + 0.25TP) zeolites. One can see that the water contents in the upgraded bio-oil derived from the upgrading over the 0.25% Cu and 0.1% Mg doped HZ5-(0.2N + 0.25TP) catalysts increased to 26.2 wt% and 25.3 wt%, respectively, but decreased to some extent for the 0.25% Ag doping. Meanwhile, Gas yields (Fig. 8(b)) slightly decreased to 20.4% and 19.7% for 0.25 wt% Cu and 0.25 wt% Ag dopings, respectively, whereas increased to 21.1% for the 0.1 wt% Mg doping when compared with that for the non-doped HZ5-(0.2N + 0.25TP) catalyst (20.8%). It is reported that Mg doping could promote the
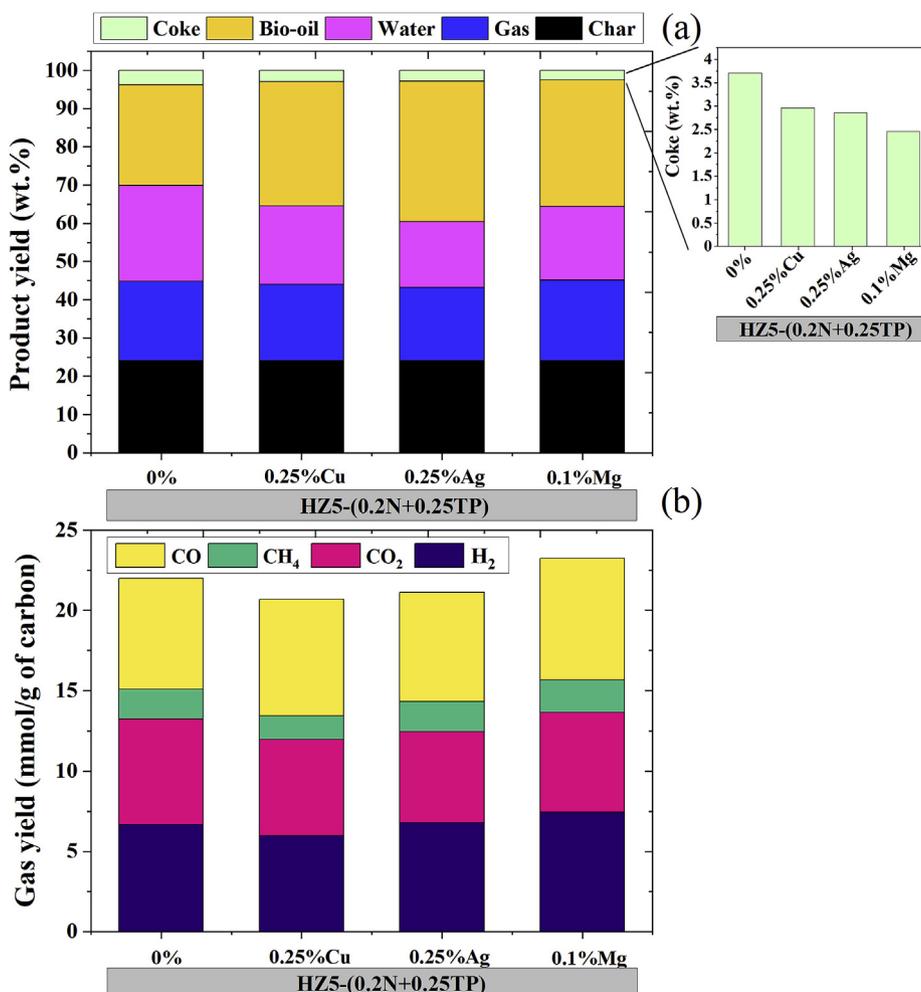


**Fig. 8.** The product distribution (a) and gas yield (b) obtained from the *in-situ* catalytic upgrading of bio-oil derived from fast pyrolysis of sunflower stalk over metal doped hierarchical HZ5-(0.2N + 0.25TP) catalysts.

formation of gaseous products by cracking, reforming, and other reactions [41]. Furthermore, as shown in **Fig. 8(b)**, the coke yields decreased after the metal doping when compared with that in the case using the undoped HZ5-(0.2N + 0.25TP) zeolite catalyst. Herein, the replacement of H$^+$ on the surface of hierarchical HZ5-(0.2N + 0.25TP) zeolite by the metal species, resulting in the decrease of acidity (Fig. S3 and Table S3). which could reduce the coke formation on the acid sites [31]. In addition, as shown in Fig. S4, due to the very low doping amount and/or well dispersion of the doping species on the surface of the catalysts, after Cu, Mg and Ag were doped on the surface of hierarchical HZ5-(0.2N + 0.25TP) catalysts, the catalyst framework had no any changes and meanwhile no characteristic peaks corresponding to the doped metal species were observed [8,30,42]. However, the S$_{BET}$ and total pore volume (Table S4) decreased to some extent after the metal doping on the HZ5-(0.2N + 0.25TP), which should be related to the blocking of some micropores by the metal species and/or the presence of metal oxide aggregates on the external surface [43,44].

## 4. Conclusions

Hierarchical HZSM-5 zeolites were prepared by desilication of commercial HZSM-5 with aqueous NaOH-TPAOH mixture, and successfully applied for the *in-situ* catalytic upgrading of bio-oil derived from the fast pyrolysis of sunflower stalk. The obtained hierarchical HZSM-5 by using a mixture of 0.2 M NaOH with 0.25 M TPAOH for the desilication showed the best catalytic performance. It is found that the relative total peak area related to the detected aromatic hydrocarbons reached 65.8% with a yield of aromatic hydrocarbons up to 45.2 mg/g-bio-oil. However, the coking on the surface of catalyst was not hindered. To solve the coking problem and increase the aromatic hydrocarbons production, the hierarchical HZSM-5 zeolites were modified by Cu, Ag, and Mg. It is found that the doping amount had a great effect on the catalytic performance, and with the optimum doping amounts, i.e., 0.25 wt% Cu, 0.25 wt% Ag and 0.1 wt% Mg doping amounts, the specific aromatic hydrocarbon yields were obviously increased to 54.5, 49.1 and 51.9 mg/g-bio-oil from 45.2 mg/g-bio-oil for the undoped hierarchical HZSM-5 zeolite, respectively. Also, the coking formation was hindered by the metal doping.

## CRediT authorship contribution statement

**Nichaboon Chaihad:** Investigation, Data curation, Formal analysis, Writing - original draft. **Yohanes Andre Situmorang:** Investigation. **Aisikaer Anniwaer:** Investigation. **Irwan Kurnia:** Investigation. **Surachai Karnjanakom:** Investigation. **Yutaka Kasai:** Investigation. **Abuliti Abudula:** Investigation. **Prasert Reubroycharoen:** Investigation. **Guoqing Guan:** Conceptualization, Methodology, Validation, Supervision, Project administration, Writing - review & editing.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

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