A review on the role of hierarchical zeolites in the production of transportation fuels through catalytic fast pyrolysis of biomass

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ABSTRACT

Design of highly active catalysts plays a critical role in catalytic fast pyrolysis (CFP) of lignocellulosic biomass. Advanced catalysts can improve the deoxygenation rate of pyrolysis vapors and boost the production of fuel precursors. Zeolites are suitable frameworks for catalyzing pyrolysis vapors into species of transportation fuel value. However, their nano-sized structure limits the diffusion of reactants into pores and over active sites. Consequently, the aggregation of large molecules outside micropores leads to a massive coke formation, blocking pore channels, and thus, preventing the accessibility to acid sites. This could cause quick deactivation and instability of the catalyst, necessitating frequent catalyst regeneration and replenishment. Hierarchical micro/mesopore-structured zeolites are promising candidates to cope with the mentioned challenges. In addition to their adjusted pore structure and increased accessibility of acid sites, the formation of mesoporosity in zeolites provides an adequate room for the deposition of additional active phases such as metal nanoparticles, further boosting the catalytic activity. Different strategies used for preparing hierarchical zeolites can tremendously alter their attributes, and consequently affect product selectivity during CFP of biomass. Focusing on the precursors of transportation fuels (i.e., aromatic hydrocarbons and olefins), the present paper critically reviews the impacts of methods used for synthesizing hierarchical zeolites, on CFP of bio-based feedstocks. Moreover, the role of metal addition to hierarchical zeolites in biomass catalytic pyrolysis is also discussed briefly. Among the different synthesis techniques, desilication treatment using alkaline solutions is the most promising owing to its simplicity, high productivity, and scalability. In terms of product selectivity, the addition of Ga species to hierarchical zeolites can increase aromatic hydrocarbons while Ce incorporation can increase the yield of valuable oxygenates such as furan. Despite the advantages of mono-metallic hierarchical zeolites in producing cherished chemicals, future studies should scrutinize the influence of bi-metallic hierarchical zeolites in bio-based CFP processes.

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1. Introduction

Global modernization, urbanization, and industrialization are accompanied by a substantial expansion of the transportation network and consequently, massive increases in energy demands, mainly met by fossil fuels (Soltanian et al., 2019). These, in turn, have led to increasing emissions of greenhouse gases (mainly carbon dioxide) and the resultant unfavorable phenomena, i.e., global temperature rise and climate change (Soltanian et al., 2020). In this regard, an urgent transition from powering vehicles by fossil-based fuels to more environmentally-friendly alternatives such as electricity generated by wind, solar, and hydro technology is of crucial importance. However, the apparent shortcomings of battery technologies in terms of capacity and charging time hinder the reliable use of clean electricity in vehicles. Hence, liquid biofuels are still considered as promising options for substituting fossil fuels in the transportation sector (Abdollahi et al., 2019).

There are three main strategies for converting biomass into fuel precursors including chemical routes (e.g., transesterification), biological routes (e.g., aerobic digestion, anaerobic digestion, fermentation), and thermochemical routes (e.g., hydrothermal liquefaction, fast/slow pyrolysis, gasification) (Tabatabaei et al., 2019). Among all conversion methods, fast pyrolysis is a highly reliable approach for transforming low-grade biomass into liquid bio-oil (up to 75 wt%) with a higher energy density (Aghbashlo et al., 2019). Fast pyrolysis refers to the thermal degradation of biomass into condensable vapors at temperatures ranging between 400-600 °C in the limited presence of oxygen for short residence times of 1-2 seconds (Álvarez-Chávez et al., 2019). Then, the pyrolytic vapors are immediately cooled down to obtain a thermally unstable black liquor also known as bio-oil (Aghbashlo et al., 2019).

It should be noted that the bio-oil derived from fast pyrolysis is not suitable to be used directly as transportation fuel and is not miscible to be blended partially either (Liu et al., 2014). Table 1 proves the dissimilarities between fossil crude oil and bio-oil. Pure bio-oil suffers from high viscosity, intense corrosivity, poor chemical stability, and relatively low heating value (Tabatabaei et al., 2019). Many undesirable compounds are to blame for these adverse attributes primarily including oxygenates (e.g., aldehydes, ketones), carboxylic acids (e.g., acetic acid, propionic acid), unsaturated species, oligomers, and water (Liu et al., 2014). Figure 1 shows the typical chemical constituents of bio-oil and their relative contents along with their classifications according to functional groups. Overall, it has been reported that bio-oil encompasses more than 300 unfavorable species (Tan et al., 2018). In this regard, it is imperative to deoxygenate and stabilize the produced bio-oil before further processing for the production of on-specified transportation fuels.

Compared to non-catalytic fast pyrolysis, catalytic fast pyrolysis (CFP) is a promising technique resulting in improved bio-oil characteristics. Through CFP, hot pyrolytic vapors meet a catalyst bed before condensing into the liquid phase. The advantages and disadvantages of CFP over non-catalytic fast pyrolysis are presented in Table 2. Generally, the CFP technologies are categorized into ex-situ CFP or in-situ CFP; the former is a strategy in which the pyrolysis and upgrading stages are separated by using the catalyst bed at the downstream of the pyrolysis reactor while the latter is a technique in which the pyrolysis process is interwoven with an upgrading step by mixing the feedstock with catalyst before heating (Zhang et al., 2016). Table 3 presents the merits and drawbacks of these CFP types.

A major problem associated with using catalyst in biomass fast pyrolysis is the massive coke deposition on the surface of the catalyst causing its rapid deactivation. Thus, it is of crucial significance to design suitable catalysts leading to increased yields of aromatics while reducing coke formation. In light of that, substantial efforts have been put into exploring high-performance catalysts for the CFP of biomass, among which, zeolites have gained a particular prominence. As an important attribute, zeolitic materials possess a high level of crystallinity imparting a high thermal/hydrothermal stability to them. Typically, the structures of zeolites are composed of cavities and channels, 0.3 and 1.5 nm in size (Groen et al., 2007).
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It is important to note that zeolites are shape-selective as they have uniform passages within the micropore range. Thus, they are capable of separating different molecules according to their shapes and sizes. This characteristic of zeolites renders them suitable adsorbents in separation processes. In addition, zeolites possess a high ion-exchange capability owing to the presence of aluminium atoms in their structure which impose negative charges on the framework that could be compensated by external cations. This feature of zeolites is well exploited in different industries such as water treatment and detergent manufacturing. It is worthwhile to note that the transferable cations

Fig. 1. Chemical composition of bio-oil from lignocellulosic biomass along with the most abundant molecules found in bio-oil. Redrawn with permission from Huber et al. (2006). Copyright© 2006 American Chemical Society.

Table 2.
Merits and drawbacks of catalytic fast pyrolysis compared to its non-catalytic counterpart*.

| Advantages                                      | Disadvantages                                      |
|------------------------------------------------|---------------------------------------------------|
| • Single reactor                               | • High energy consumption                         |
| • High compatibility of the produced bio-oil   | • Catalyst cost                                   |
| with existing infrastructures                  | • Need for catalyst regeneration                  |
| • Lower reaction temperature                   | • Unreliable re-usage of deactivated catalyst      |
| • High-grade bio-oil and its diverse applications |                                                   |
| • High stability and energy density of final liquid products |                                                   |
| • High adsorption properties of the produced char for removing heavy metals, contaminants, pollutants, and odor from wastewater/polluted air |                                                   |
| • Decreased impurities (e.g., solid residue, sulfur, nitrogen, phosphorous) in the produced liquid oil |                                                   |

* Source: Cheng et al. (2012)

Table 3.
The pros and cons of different types of CFP, i.e., in-situ CFP and ex-situ CFP*.

| CFP type | Merits                                                                 | Drawbacks                                                                 |
|----------|------------------------------------------------------------------------|--------------------------------------------------------------------------|
| In-situ CFP | • Intimate contact between feedstock and catalyst                      | • Catalyst deterioration due to its exposure to char and ash             |
|          | • Higher rate of biomass conversion into liquid products (especially aromatics) | • Complex separation of catalyst from char and ash                      |
|          | • Lower capital cost owing to the simpler process configuration         | • Higher poisoning of the catalyst through the accumulation of metals   |
| Ex-situ CFP | • Ability to keep the catalyst separate from contaminants              | • Higher minimum fuel-selling price compared to in-situ CFP              |
|          | • Simple regeneration and reuse of catalyst                            |                                                                          |
|          | • Ability to perform thermal and catalytic stages at different temperatures |                                                                          |
|          | • Superior control on bio-oil yield and its composition                |                                                                          |
|          | • Higher deoxygenation activity compared to in-situ pyrolysis          |                                                                          |
|          | • Lower techno-economic risk compared to in-situ                       |                                                                          |

* Source: Li et al. (2015); Murugappan et al. (2016); Isa et al. (2016); Kumar et al. (2019)
of zeolites could be replaced by protons, acting as robust Brønsted acid sites. On the other hand, Lewis acid sites could be formed through dehydroxylation of these protons. In this regard, the high and tunable acidity of zeolites makes them highly attractive as catalyst in petrochemical and oil industries (Primo and Garcia, 2014). In addition, zeolites are good candidates to be used as support for additional active phases based on which advanced bifunctional catalysts could be prepared through metal incorporation.

In the CFP process, zeolitic materials are capable of deoxygenating the vapors through dehydration, cracking, isomerization, cyclization, and aromatization reactions to produce high amounts of deoxygenated species (Mihalick et al., 2011; Isa et al., 2016). The shape selectivity and acidity of zeolites are determining factors in the thermal conversion of biomass into valuable products. Jia et al. (2011) found that the aromatic yields from the CFP of glucose over different zeolites formed a bell-shaped trend as a function of zeolite pore size. They showed that zeolites with small pores (i.e., SAPO-34, ZK-5) favored the production of oxygenates and coke instead of aromatics, while zeolites with medium pore sizes (i.e., SSZ-20, ZSM-11, ZSM-5, IM-5, TNU-9) yielded the highest amounts of aromatics. The zeolites with large pore sizes (i.e., SSZ-55, β zeolite, Y zeolite) tended to form low aromatics, high coke, and low oxygenates.

However, the small pores of microporous zeolites pose a critical problem in the CFP of biomass as they prevent the diffusion of bulky biopolymers into the micropores. In this context, the majority of active sites, that are placed inside the zeolite micropores, are barely reachable by the reactants. Even worse, the aggregation of biopolymeric molecules on the exterior surface of microporous zeolites could result in high coke formation at elevated temperatures, blocking the micropores, and consequently, limiting further access of the reactants to the acid sites inside the micropores (Chen et al., 2018a). Therefore, conventional microporous zeolites could not be exploited for their highest catalytic potentials and suffer from low activities.

It should be noted that many of the oxygen-containing volatiles produced during the biomass fast pyrolysis cannot penetrate into the zeolite micropores and as a result, they re-polymerize to form the coke precursors on the external surface of the catalyst (Stanton et al., 2018). For instance, the dimensions of the syringol and guaiacol molecules, as representatives of lignin-derived compounds, are 10.738x7.856x4.218 Å and 9.476x8.101x4.197 Å, respectively. On the other hand, ZSM-5 zeolite has a three-dimensional pore structure consisting of two perpendicularly intersecting channels of 10-membered rings, i.e., straight channels (5.5x5.1 Å) and zigzag channels (5.6x5.3 Å). Consequently, the lignin-derived bulky oxygenated compounds produced during lignin catalytic pyrolysis could not diffuse into the microporous pores of the ZSM-5 zeolite, leading to high coke formation and thus catalyst deactivation. It should be noted that although the deactivated catalyst could be regenerated through combustion in an air environment, the low-temperature combustion might not satisfactorily remove the coke while the combustion at high temperature could overheat the catalyst which might further lead to its structure collapse (Shao et al., 2016).

In the past years, hierarchical zeolites consisting of two porosity levels (i.e., microporous and mesoporous structures) have been shown as a promising remedy to address the small pore scale of conventional zeolites. These zeolites enhance the accessibility of reactants to the internal acid sites, resulting in higher catalytic activities in the reactions suffering from steric and diffusional limitations (Serrano and Pizarro, 2013). Chang et al. (2015) observed that the introduction of the mesoporosity could appreciably reduce the diffusional time constants of cyclohexane into hierarchical silicate-1, indicating facile mass transport and rapid overall adsorption/desorption.

Facilitated reachability to Brønsted acid sites on the mesopore surface promotes the rates of decarbonylation reactions to produce aromatic-enriched bio-oils (Puértolas et al., 2015). In this context, Jia et al. (2017) showed that the formation of both mono-aromatic and bi-aromatic hydrocarbons over the hierarchical zeolites are faster than over their parent zeolites. This is ascribed to the fact that the diffusion of reactants onto active sites inside the mesopores, as well as the diffusion of products out of the zeolite particles, become faster after the hierarchicalization of parent zeolite microporosity. Similarly, Stanton et al. (2018) revealed that the hierarchical mesoporous ZSM-5 could boost the formation of mono-aromatic hydrocarbon, olefins, alkanes, and normal phenol, while its microporous counterpart tended to produce poly-aromatic hydrocarbons.

It is notable that the molecular diffusion within the micropores primarily follows the configurational or restricted diffusion mechanism; whereas, the diffusion of molecules inside secondary mesopores complies with the Knudsen diffusion mechanism (Li et al., 2014b). It is important to note that the secondary mesoporosity shortens the diffusion length substantially. On another hand, the diffusion rate varies with the inverse of the square of the diffusion length. Therefore, the diffusion time in hierarchical frameworks are more than two orders of magnitude shorter than those in microporous structures (Groen et al., 2007). It is worth mentioning that temperature has a remarkable impact on the diffusivities of substrate molecules in hierarchical zeolites. Bu et al. (2018) demonstrated that the diffusion inside the microporosity and along the outer surface of hierarchical mesoporous H-ZSM-5 zeolite is favorable only at low temperatures, while the diffusion within the mesoporosity is considerably improved at typical pyrolysis temperatures. Nevertheless, it has been perceived that an appropriate trade-off between mesoporosity and microporosity is imperative for yielding high aromatics. In addition, the distribution of aromatic compounds is correlated strongly with the microporosity (Qiao et al., 2019).

The presence of mesoporous crystals interconnecting with micropores could assist with diffusing much of coke precursors out of the micropores, preventing the micropore blockage that would otherwise cause catalyst deactivation (Escola et al., 2012). Although the coke precursors might then be deposited on the mesoporous mouths or the exterior catalyst surface, they impose much less harmful effects on the stability of the catalyst (Jia et al., 2017). For this reason, unlike microporous zeolites, much of the activity could be recovered after the regeneration of hierarchical zeolites. Moreover, the hierarchical zeolites could markedly reduce the burning temperature of the regeneration, alleviating the problem of overheating in the microporous zeolites (Fig. 2).

In the CFP process, incorporating metals into the zeolitic framework is well-recognized as a successful tactic for alleviating the catalyst deactivation as a result of surface coke formation and for enhancing the selectivity towards hydrocarbons and less oxygenated chemicals. There have been plenty of studies attempting to introduce different metallic cations as non-framework species in interaction with zeolite acid sites to improve bio-oil characteristics. For example, Cheng et al. (2012) showed that bifunctional Ga-loaded HZSM-5 catalysts could produce aromatic hydrocarbons up to 40% higher compared with the conventional ZSM-5 zeolite. The increased aromatics is due to the fact that the Ga species promoted decarbonylation and olefin aromatization reactions, while the ZSM-5 fraction catalyzed the cracking and oligomerization reactions. Mullen et al. (2018) reported that Ga-doped ZSM-5 zeolites favored the production of aromatics through the olefin oligomerization and
treatment by acid solutions at high temperatures is the most familiar procedure. The framework using a hydrothermal treatment or by chemical agents. The zeolites. In this method, the aluminium atoms are removed from the zeolite in zeolites with lower Si/Al ratios, such as FAU and ultra-stable Y-type (USY) CFP of bio-based substrates are discussed.

The removal of Si atoms from the zeolite framework creates structural defects in the lattice. However, the exact morphology of alkali-treated hierarchical zeolites is substantially dependent on the treatment conditions. As an influential factor, the concentration of alkali solution used has a striking impact on the structure of the formed mesoporosity. After treatment by an alkaline solution, the mesopore volume is largely increased at the expense of a reduction in micropore surface and volume, indicating the reform of micropores into mesopores (Table 4). For low alkaline concentrations, the surface and volume of micropores are decreased slightly, while high concentrations lead to notable reductions in microporosity.

**Table 4.**

| Catalyst type | Si/Al ratio | Specific surface area (m²/g) | Pore volume (cm³/g) | Hierarchy factor, HF a | Relative crystallinity (%) |
|---------------|-------------|----------------------------|---------------------|------------------------|---------------------------|
|               |             | S micro | S meso | S macro | V micro | V meso | V macro |
| ZSM-5 (parent) | 54.0 | 357.2 | 39.0 | 318.2 | 0.035 | 0.134 | 0.0866 | 85.70 |
| ZSM-5 (0.2 M) | 53.5 | 407.1 | 138.9 | 268.1 | 0.226 | 0.104 | 0.1075 | 100.00 |
| ZSM-5 (0.3 M) | 46.3 | 446.6 | 261.7 | 184.9 | 0.258 | 0.082 | 0.1333 | 59.29 |
| ZSM-5 (0.5 M) | 31.9 | 337.5 | 198.1 | 139.4 | 0.217 | 0.065 | 0.1353 | 64.94 |
| ZSM-5 (0.8 M) | 20.3 | 271.2 | 176.0 | 95.2 | 0.178 | 0.046 | 0.1333 | 59.29 |

a The hierarchy factor (HF)=(V micro/V macro)×(S macro/S micro).

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The desilication is an effective method for forming mesoporosity inside conventional zeolites, especially those with high Si/Al ratios such as ZSM-5 zeolite, as it preserves structural integrity. In this method, some silica atoms are removed from the crystal framework with alkali solutions. Generally, the Si–O–Al linkages are barely hydrolyzed in alkali solutions owing to the negative charge of the AlO4 − attack. As a result, the Si atoms next to the four-coordinated Al are also secured from the attack of hydroxide anions. Hence, the alkaline solutions favor the breakage of the Si–O–Si linkages not neighboring the four-coordinated Al, and form terminal Si–OH (Fig. 3) (Svelle et al., 2011). It should be noted that a small extent of dealumination is unavoidable for the zeolites with low Si/Al ratios due to their high Al content.

![NaOH desilication](image)

**Fig. 3.** Mechanism of bond scission using alkaline treatment. Redrawn with permission from Ren et al. (2018). Copyright© 2018 American Chemical Society.

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In more detail, moderate alkali concentrations generate sheet-like pores only on the outer sphere, while alkali solutions with higher intensities could simply diffuse into the internal space leading to severe corrosion and consequently, the formation of hollow mesopores (Fig. 4). Excessive alkali treatments could result in the framework collapse and uncontrolled loss of acid sites. In this context, Xiao et al. (2015) showed that the hierarchical HZSM-5 zeolites desilicated with the NaOH solutions with concentrations lower than 0.4 M generated considerable mesopores as they maintained an adequate level of microporosity. In these cases, the crystallinity of the hierarchical zeolites did not change significantly. While NaOH solutions with concentrations higher than 0.5 decreased the relative crystallinity of the zeolites, consequently shortening the lifetime of the catalysts. The decrease in relative crystallinity is likely ascribed to the decrease in bulk Si–O–Si bonds and the increase in surface atoms with growing mesoporosity (Hoff et al., 2017). Moreover, high concentrations of NaOH could break Si–O–Al bonds in addition to Si–O–Si bonds, leading to both dealumination and desilication of zeolite framework. Figure 5 displays the TEM images of parent microporous HZSM-5 zeolite and hierarchical HZSM-5 zeolites desilicated with different NaOH concentrations in order to understand the effect of alkali intensity on mesoporosity formation and mesopore size distribution.

It has been reported that alkaline desilication transforms Brønsted acid sites into Lewis acid sites meaning that alkali treatments with higher concentrations result in greater losses in Brønsted acidity (Table 5) (Xiao et al., 2015). This might be related to the elimination of internal Si–OH bonds from zeolite framework as well as the retention of extracted aluminum atoms on the outer surface of the zeolite. Therefore, product distribution and selectivity during CFP could considerably vary with alkali intensification. Table 6 tabulates the changes in yields of the main products of bio-based CFP process (i.e., oxygenates, aromatics, olefins, and coke) over different nonmetallic hierarchical zeolites (prepared by different synthesis methods) in comparison with their microporous counterparts. Li et al. (2014a) revealed that the hierarchical ZSM-5 desilicated with 0.3 M NaOH attained the highest amount of aromatics (i.e., 30.2%) and lowest coke formation (i.e., 39.9%) during the CFP of beech wood. On the contrary, the zeolite treated with the high NaOH concentration of 0.5 M remarkably reduced the aromatic production as the treatment ruined a large fraction of its microporosity. Similarly, Ding et al. (2017) confirmed that the hierarchical HZSM-5 zeolite desilicated by 0.3 M NaOH solution, as the optimal catalyst, augmented aromatic yields by 44% and mitigated coke deposition by 29% compared with the parent zeolite. Moreover, this hierarchical catalyst increased the selectivity towards BTX compounds (i.e., benzene, toluene, and xylene) by 82%. Shao et al. (2016) also evidenced that the catalytic pyrolysis of furan yielded the highest amounts of aromatic hydrocarbons and olefins over the hierarchical zeolite desilicated with 0.3

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The changes in yields of the main products of bio-based CFP process over different nonmetallic hierarchical zeolites prepared by different synthesis methods.

| Zeolite framework | Synthesis method | Si/Al of synthesized zeolite | Feedstock (s) | Operating conditions | Change in oxygenates yield | Change in aromatic hydrocarbons yield | Change in olefins yield | Change in coke formation | Reference |
|-------------------|------------------|-------------------------------|---------------|----------------------|---------------------------|--------------------------------------|------------------------|--------------------------|-----------|
| ZSM-5             | Desilication by 0.1-0.5 M NaOH solution | 21.1-25.5 | Beech wood | CTF=10 | Decreased | Decreased | Increased | NA | Li et al. (2014a) |
| ZSM-5             | Desilication by 0.3 M NaOH solution | 24.0 | Cellulose | CTF=10 | NA | Nearly unchanged | Increased | NA | Li et al. (2014a) |
| ZSM-5             | Desilication by 0.3 M NaOH solution | 24.0 | Lignin | CTF=10 | NA | Increased | Increased | NA | Li et al. (2014a) |
| ZSM-5             | Desilication by 0.2 M NaOH solution | 17 | Kraft lignin | T=600 °C | Decreased | Decreased | NA | NA | Wang et al. (2020) |
| ZSM-5             | Hybrid method using the desilication of ZSM-5 by 0.2 M NaOH and the surfactant by CTAB | 36 | Kraft lignin | T=600 °C | Increased for CTF=3 and decreased for CTF=5 | NA | NA | Wang et al. (2020) |
| ZSM-5             | Desilication by 0.2 M NaOH solution | 17 | Pyrolytic lignin | T=600 °C | Decreased | NA | Increased | NA | Wang et al. (2020) |
| ZSM-5             | Hybrid method using the desilication of ZSM-5 by 0.2 M NaOH and the surfactant by CTAB | 36 | Pyrolytic lignin | T=600 °C | Decreased | NA | Increased | NA | Wang et al. (2020) |
| HZSM-5            | Desilication by 0.2 M NaOH solution | 45 | Oak | T=500 °C | Decreased | Increased | NA | Increased | Jia et al. (2017) |
| HZSM-5            | SAC of the dry gel performed by dual templating (SDA=TPAOH, surfactant=triblock copolymer) | 49 | Glucose | T=600 °C | Increased | Decreased | NA | Decreased | Neumann and Hicks (2012b) |
| HZSM-5            | Desilication by 0.1-0.7 M NaOH solutions | NA | Waste cardboard | T=600 °C | Decreased | Increased | NA | Decreased for NaOH≤0.5 M and increased for >0.5 M | Ding et al. (2017) |
| HZSM-5            | Desilication by 0.2-0.8 M NaOH solutions | 38 | Cellulose | CTF=20 | NA | Increased | NA | Increased for NaOH≤0.4 M and decreased for >0.4 M | Qiao et al. (2017) |
| HZSM-5            | Desilication by 0.2-0.8 M NaOH solutions | 38 | Cellulose | CTF=20 | NA | Nearly unchanged | Decreased | Decreased | Qi et al. (2017) |
| HZSM-5            | Desilication by 0.2-0.8 M TPAOH solutions | 38 | Cellulose | CTF=20 | NA | Nearly unchanged | Nearly unchanged | NA | Qi et al. (2017) |
| HZSM-5            | Integrated desilication and dealumination by 0.2-1.0 M NaOH and 0.1 M HCl solutions | 15.3-26.1 | Cellulose | T=550 °C | Decreased | NA | Increased for NaOH≤0.4 M and decreased for >0.2 M | Hoff et al. (2017) |
| HZSM-5            | Desilication by 0.2 M NaOH solution while assisted by 0-1.0 piperidine | 13-20 | Lignite | T=600 °C | Decreased | NA | NA | Decreased | Ren et al. (2018) |
| HZSM-5            | Desilication by 0.2-1.0 M NaOH solutions | NA | Rice straw | T=600 °C | Increased | Increased | Increased | Decreased | Chen et al. (2018a) |
| HZSM-5            | Desilication by 0.2-1.0 M NaOH solutions and washed with 0.1 M HCl solution | NA | Rice straw | T=600 °C | Increased | Increased | Increased | Decreased | Chen et al. (2018a) |
Table 6. continued.

| Zeolite framework | Synthesis method | Si/Al of synthesized zeolite | Feedstock(s) | Operating conditions | Change in yields | Change in aromatic hydrocarbons yield | Change in olefins yield | Change in coke formation | Reference |
|-------------------|------------------|-----------------------------|--------------|---------------------|-----------------|-------------------------------------|------------------------|--------------------------|-----------|
| HZSM-5            | Desilication by 0.1-0.9 M NaOH solutions | NA | Cellulose | • T=500 °C | *Increased for NaOH≥0.5 M and increased for >0.5 M | *Increased for NaOH≥0.3 M and decreased for >0.3 M | NA | *Decreased for NaOH≥0.3 M and increased for >0.3 M | Dai et al. (2018) |
| HZSM-5            | Dual templating by the SDA of TPAOH and surfactant of CTAB (CTAB/SiO2=0.01-0.05) | NA | Rice straw | • T=5°C | *Increased for CTAB/SiO2≥0.01 and decreased for >0.01 | *Increased | *Increased for CTAB/SiO2≥0.01 and increased for >0.01 | Zhang et al. (2018a) |
| HZSM-5            | Hard templating by sucrose with Sucrose/Si ratios of 0.15-0.6 | NA | Cellulose | • T=600 °C | *Increased for Sucrose/Si≥0.3 and decreased for >0.3 | *Increased | *Decreased for Sucrose/Si≥0.3 and increased for >0.3 | Chen et al. (2018b) |
| HZSM-5            | Desilication by 0.3, 0.5 M NaOH solutions | 17.9-25.5 | Lignin (mixed Guaiacyl/Syringyl type) | • T=600 °C | *Decreased | *Increased | *Decreased | *Decreased | Tang et al. (2019) |
| HZSM-5            | Desilication by 0.3 M NaAlO2 solution | 17.9 | Lignin (mixed Guaiacyl/Syringyl type) | • T=600 °C | *Decreased | *Increased | *Decreased | *Decreased | Tang et al. (2019) |
| HZSM-5            | Desilication by 0.3 M Na2CO3 solution | 30.3 | Lignin (mixed Guaiacyl/Syringyl type) | • T=600 °C | *Decreased | *Increased | *Increased | *Decreased | Tang et al. (2019) |
| HZSM-5            | Desilication by 0.3 M TPAO solution | 30.2 | Lignin (mixed Guaiacyl/Syringyl type) | • T=600 °C | *Nearly unchanged | *Decreased | *Increased | *Decreased | Tang et al. (2019) |
| HZSM-5            | Silanization using PHAPTMS (OTS≤5-15 wt.%) | 37.8-38.2 | Cellulose | • T=600 °C | *Increased | *Nearly unchanged | *Decreased | Qiao et al. (2019) |
| HZSM-5            | Silanization using APTMS (OTS≤5-15 wt.%) | 40.3-42.8 | Cellulose | • T=600 °C | *Decreased | *Increased | *Increased | *Decreased | Qiao et al. (2019) |
| HJ                 | Desilication by Na2CO3 solution | NA | Lignin | • T=500 °C | *Decreased | *Increased | *Decreased | NA | Bi et al. (2018) |
| HJ                 | Desilication by NaOH solution | NA | Lignin | • T=500 °C | *Decreased | *Increased | *Increased | NA | Bi et al. (2018) |
| HJ                 | Desilication by NaOH/TPAOH solution | NA | Lignin | • T=500 °C | *Decreased | *Increased | *Increased | NA | Bi et al. (2018) |
| HZSM-5/MCM-41      | Hybrid method using the desilication of ZSM-5 by 1.5-3.0 M NaOH and the surfactant by CTAB | 27 | Poultry litter | • T=500 °C | *Decreased for NaOH≥2.5 M and increased for >2.5 M | *Increased for NaOH≥2.0 M and decreased for >2.0 M | NA | *Decreased | Zhang et al. (2018a) |
| HZSM-5/MCM-41      | Hybrid method using the desilication of ZSM-5 by 2.0 M NaOH and the surfactant by CTAB | 27 | Co-feed distillers dried grains with soluble (D) and waste agricultural plastic mulching films (W) | • T=600 °C | *Increased | *Increased | *Decreased | Zhang et al. (2018b) |
| HZSM-5/MCM-41      | Hybrid method using the desilication of ZSM-5 by 2.0 M NaOH and the surfactant by CTAB | 27 | Co-feed Waste greenhouse plastic films (F1) and rice husk (F2) | • T=600 °C | *Increased | *Increased | *Decreased | Li et al. (2020) |

* Change in yield compared to parent microporous zeolite.

** Abbreviations:** AP: (3-aminopropyl)trimethoxysilane; CT: Catalyst-to-feed ratio; CTAB: hexadecyltrimethylammonium bromide; HR: Heating rate; NA: Not available; OTS: Organosilane-to-silica ratio; P: Pressure; PHAPTMS: 3-(Phenylamino)propyltrimethoxysilane; RT: Residence time; SAC: Steam assisted crystallization; SDA: Structure-directing agent; T: Temperature; TPAOH: Tetrapropylammonium hydroxide; VRT: Vapor residence time.

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It is of paramount importance that different types of alkali solutions used for the desilication process could also impose distinct morphologies on zeolites, varying the product distribution and selectivity of the CFP process. Qiao et al. (2017) conducted the CFP of cellulose to produce aromatics over the mesoporous hierarchical ZSM-5 zeolites desilicated using various alkali solutions of NaOH, Na$_2$CO$_3$, and tetrapropylammonium hydroxide (TPAOH) with different concentrations under fixed treatment conditions. They found that the desilication process with Na$_2$CO$_3$ solution was more controllable than that with NaOH solution. Thus, the former synthesized the micro/mesoporous hierarchical catalysts with higher acid sites. In terms of product selectivity, the CFP over Na$_2$CO$_3$-treated catalyst increased the aromatic production, while the NaOH-treated counterpart tended to decrease the amount of aromatics. The amount of coke formation followed opposite trends. Due to the increased acidity of the Na$_2$CO$_3$-treated ZSM-5 zeolites, they had a high tendency to form valuable mono-aromatics (i.e., benzene, toluene, and xylene) rather than large poly-aromatics. Interestingly, the TPAOH did not have a considerable impact on the parent ZSM-5 pore structure, whereas it substantially improved the relative crystallinity. It was noticed that the TPAOH treatment had a repairing ability during the desilication process of HZSM-5 zeolite, slightly improving the aromatic formation in the CFP process.

Ren et al. (2018) evidenced that the presence of piperidine solutions with concentrations <0.3 M could prevent the 0.2 M NaOH solution from deep destruction of the HZSM-5 structure. In terms of zeolite acidity, the hierarchical HZSM-5 structure prepared by 0.2 M NaOH+0.1 M piperidine had a higher amount of acid sites (i.e., 0.88 mmol/g) compared with its non-desilicated counterpart (0.75 mmol/g). Mechanistically, owing to its hydrophobicity, piperidine tends to interact with the hydrophobic Si–OH terminals through electrostatic connections and subsequently stops more desilication of the zeolite structure (Wang et al., 2017). However, it has been pointed out that it is necessary to comprehend the scope of piperidine’s influence as excessive concentrations of piperidine could exert adverse effects by attacking the lattice Al atoms during the extraction of the Si atoms by the alkaline solution. Overall, desilication assisted by 0.3 M piperidine has been found ideal because of attaining the highest selectivity towards light aromatics (i.e., benzene, toluene, ethylbenzene, xylene, and naphthalene) (Ren et al., 2018).

It is worth mentioning that the time of desilication treatment could considerably affect the morphology of hierarchical zeolites and subsequently change product selectivity of the CFP process. Wang et al. (2017) indicated that alkali treatment times longer than 4 h damaged the crystallinity of HZSM-5 zeolite. Furthermore, an increase in desilication time decreased the number of active acid sites. From the product selectivity point of view, the modest time of 4 h improved aromatic yields.

Another fundamental factor is the Si/Al atomic ratio of the parent zeolite which could substantially impact the desilicated mesoporosity. It has been shown that the desilication treatment of the ZSM-5 generates hierarchical mesopores with the highest surface areas for Si/Al atomic ratios within the range of 25–50 (Groen et al., 2004). For lower ratios, the high amount of aluminum prevents the removal of silica from the framework, generating a relatively low mesoporosity in ZSM-5 (Groen et al., 2006). For higher ratios, excessive silica is dissolved, resulting in the generation of larger mesopores.
pores of lower mesopore surface areas (Serrano and Pizarro, 2013). Kim et al. (2012) reported that through Na\(_2\)CO\(_3\)-assisted desilication, the parent ZSM-5 zeolites with Si/Al ratio of 42 could establish a bimodal mesoporous zeolitic system (intraparticle mesoporosity, i.e., cylinders and cavities). The cylindrical mesopores connected internal micropores to external surface of the catalyst. This structure showed an increase in the stability of the catalyst during the conversion of olefins (i.e., 2-methyl-2-butenes) to aromatic hydrocarbons (Kim et al., 2012).

### 2.2. Dual templating using surfactants

Dual templating strategy is applied to prepare ordered mesoporous zeolites. This strategy integrates a structure-directing agent synthesizing the main structure of the zeolite and a surfactant forming the mesoporous phase. The surfactant breeds the micelles acting as template for the mesoporous structure while the structure-directing agent forms the crystal phase around the walls of mesoporous configuration (Serrano and Pizarro, 2013). Zhang et al. (2018a) prepared hierarchical HZSM-5 zeolites through the dual templating method in which TPAOH was employed as the structure-directing agent and hexadecyltrimethylammonium bromide (CTAB) was used as the mesopore template with the CTAB/SiO\(_2\) ratios of 0.01-0.05. It was revealed that the incorporation of the CTAB template did not ruin the crystallinity of the microporous HZSM-5. Moreover, as the CTAB/SiO\(_2\) ratio increased in the synthesis process, the mesopore surface area and volume steadily increased at the expense of micropore surface and volume. On the contrary, the total acidity of the catalyst peaked at the lowest CTAB/SiO\(_2\) ratio of 0.01. Therefore, the hierarchical zeolite associated with this CTAB/SiO\(_2\) ratio attained the maximum aromatic yield (i.e., 26.8%) and the minimum coke formation (39.2%) (Fig. 9). Unlike aromatics, the optimal CTAB/SiO\(_2\) ratio for the production of olefins was 0.03.

![Fig. 9. Effect of CTAB/SiO\(_2\) ratio used for synthesizing hierarchical HZSM-5 zeolites on product distribution of the CFP of rice straw. Adapted from Zhang et al. (2018a).](image)

### 2.3. Hard templating

In the hard templating strategy, solids with certain porosity are used as template to confine aluminosilicate species among their pore spaces in order to form mesoporous zeolites after the removal of the template (Fig. 10). This technique can facilitate the formation of ordered mesoporous structure and offers a precise control over the size of mesopores (Chen et al., 2011). Basically, the desired configuration of hard template can lead to the formation of mesoporosity with the anticipated structure. However, the hard templating method requires complex multiple steps due to the possible mismatches between the aluminosilicate species and the hard template (Zhou et al., 2011).

![Fig. 10. A Schematic presentation of synthesizing hierarchical zeolites using the hard templating technique (by carbonaceous template). Reprinted and modified with permission from Chen et al. (2011). Copyright© 2011 American Chemical Society.](image)

Moreover, the destruction of the hard template for achieving the hierarchical mesoporosity needs severe conditions which could be harmful to the zeolite microporosity (Serrano and Pizarro, 2013).

There is a broad range of hierarchical zeolites synthesized by different types of carbonaceous materials such as glucose and sucrose (Serrano and Pizarro, 2013). Chen et al. (2018b) used the hard templating method utilizing sucrose (with sucrose/SiO\(_2\) ratios of 0.15-0.6) as the meso-template to prepare hierarchical HZSM-5 zeolites. Increased addition of sucrose led to an increase in both mesopore surface area and volume at the expense of a decrease in the micropore surface area and volume. The authors observed that the CFP of cellulose over the hierarchical catalyst prepared from sucrose (sucrose/SiO\(_2\) ratio of 0.15) yielded the maximum amount of aromatics (i.e., 37.0%) and the minimum coke (i.e., 30.4%) (Fig. 11). However, the highest olefin yield was attained over the hierarchical zeolites fabricated by hard templating using sucrose and with a sucrose/SiO\(_2\) of 0.6.

![Fig. 11. Effect of sucrose/SiO\(_2\) ratio used for synthesizing hierarchical HZSM-5 zeolites (via hard templating method) on product distribution during the CFP of cellulose. Adapted from Chen et al. (2018b).](image)

### 2.4. Zeolitization of raw solid gel

Unlike the conventional hydrothermal routes, the main concept of zeolitization technique is based on the crystallization of a prepared aluminosilicate dry-gel using vapors. This strategy can be generally classified into two procedures of vapor phase transport (VPT) and steam-assisted conversion (SAC). In the former, the prepared dry gel is crystallized by a vapor consisting of water and structure-directing agents. In the latter, water vapor alone is involved in the crystallization of the dry gel and the structure-directing agents are contained in the solid phase (Li et al., 2014a). Jia et al. (2018) proved that the hierarchical ZSM-5 zeolite
made by the SAC method showed more favorable catalytic lifetime and selectivity toward mono-aromatic hydrocarbons in methanol aromatization reaction compared with its mesoporous counterpart prepared by the conventional hydrothermal procedure. Zang et al. (2018) applied the SAC method to synthesize the hierarchical HZSM-5 zeolites with low Si/Al ratios (<30). In preparing the solid gel, they tested different templates including sucrose, polyethylene glycol, and Pluronic P123 along with TPAOH as the structure-directing agent. Among them, sucrose was found as a suitable option for creating the hierarchical HZSM-5 zeolites with meso/macroporosity. Neumann and Hicks (2012a) conducted the CFP of glucose over the hierarchical HZSM-5 zeolites synthesized by the SAC process. The dry gel of this catalyst was prepared by the dual templating method using a solution of triblock copolymer (as the surfactant) and TPAOH (as the structure-directing agent). Compared to the parent HZSM-5 zeolite, the hierarchical catalyst led to an increase in the oxygenate yield and a decrease in the aromatic production.

2.5. Silanization

In the silanization technique, some kinds of organosilanes are utilized to produce a secondary mesoporosity in zeolites. These materials have a propensity to interact with the aluminosilicate and silicate fractions of the solid phase gel, and are anchored by silanol functional groups to form various organofunctionalized silica configurations. In this regard, the organosilane fractions do not allow the gel to be crystallized in the normal way conventional zeolites are. As a consequence, the crystallization process develops organic-mesoporous configurations. In this case, the dissolution of silica happens locally and the surfactant micelles rearrange the zeolitic units to form the mesoporosity. Zhang et al. (2018a) utilized 1.5-3.0 M NaOH for the desilication and CTAB as surfactant to synthesize the hierarchical ZSM-5/MCM-41 catalyst. In this catalyst, the MCM-41 moiety was formed as an external shell layer stuck onto the ZSM-5 moiety at the core. The authors evaluated this catalyst in the microwave-assisted CFP of poultry litter. They observed that the lowest bio-oil was produced by using the catalyst prepared with the NaOH concentration of 2 M. However, the highest quantity of aromatic hydrocarbons was also generated using the same catalyst overshadowing its low bio-oil yield (Fig. 13). In addition to the concentration of NaOH solution, Li et al. (2019) argued that the mass-fraction of the surfactant used for preparing the hierarchical HZSM-5/MCM-41 zeolite was also instrumental. They reported that 10 wt% of CTAB led to the production of the highest amounts of aromatic hydrocarbons and olefins during the CFP of rice husk (totally 54%) (Fig. 14).

Using a hierarchical HZSM-5/MCM-41 catalyst, Li et al. (2020) assessed the synergetic effects between two feedstocks (rice husk and waste greenhouse plastic films) in the CFP. They showed that the maximum hydrocarbon yield of 71.1% was achieved from rice husk to waste greenhouse plastic films of 1:1.5. In a microwave-assisted co-pyrolysis over the hierarchical HZSM-5/MCM-41 zeolite, Zhang et al. (2018b) used distillers dried grains with solubles (D) and waste agricultural plastic mulching films (W) as feedstocks and SiC as microwave absorbent. They revealed that the integrated hierarchical catalyst and

![Fig. 12. Effects of different organosilanes used for synthesizing hierarchical HZSM-5 zeolites on product distribution of the CFP of rice straw. Redrawn with permission from Zhang et al. (2018b). Copyright © 2018 American Chemical Society.](image1)

In addition, it was discovered that the presence of ammonium ion inside organosilanes hindered the formation of aromatics and increased the coke deposition, while it augmented olefin production. Qiao et al. (2019) investigated the CFP of cellulose over two series of hierarchical ZSM-5 zeolites synthesized using two different organosilanes 3-(phenylamino)propyltrimethoxysilane (PHAPMS) and (3-aminopropyl)trimethoxysilane (APMS) as the mesopore-directing agents. NH3-TPD analysis exhibited that the strength and amounts of the acid sites in the hierarchical HZSM-5 zeolites were nearly unchanged as the organosilane/silica ratios were varied. This study reported that the maximum aromatic yield of 41.8 was achieved for the CFP over the hierarchical ZSM-5 catalyst synthesized by PHAPMS with the organosilane/silica ratio of 10 wt%.

2.6. Hybrid

Hybrid methods refer to the combination of different approaches to achieve a favorable control over producing hierarchical micro-mesoporosity. One of the hybrid strategies applied for the formation of hierarchical zeolites is the post-synthesis treatment using both alkaline solution and surfactants. In this case, the dissolution of silica happens locally and the surfactant micelles rearrange the zeolitic units to form the mesoporosity. Zhang et al. (2018a) utilized 1.5-3.0 M NaOH for the desilication and CTAB as surfactant to synthesize the hierarchical ZSM-5/MCM-41 catalyst. In this catalyst, the MCM-41 moiety was formed as an external shell layer stuck onto the ZSM-5 moiety at the core. The authors evaluated this catalyst in the microwave-assisted CFP of poultry litter. They observed that the lowest bio-oil was produced by using the catalyst prepared with the NaOH concentration of 2 M. However, the highest quantity of aromatic hydrocarbons was also generated using the same catalyst overshadowing its low bio-oil yield (Fig. 13). In addition to the concentration of NaOH solution, Li et al. (2019) argued that the mass-fraction of the surfactant used for preparing the hierarchical HZSM-5/MCM-41 zeolite was also instrumental. They reported that 10 wt% of CTAB led to the production of the highest amounts of aromatic hydrocarbons and olefins during the CFP of rice husk (totally 54%) (Fig. 14).
microwave absorbent increased the yields of aromatics and olefins remarkably. Their findings showed that the optimal temperature of the microwave-assisted catalytic fast co-pyrolysis for the production of aromatics was around 650 °C. Moreover, the mass ratio (W/D) of 1.0 was found to be the best mixture to yield the highest hydrocarbons.

3. Effects of metal-loaded hierarchical zeolites in catalytic pyrolysis

Due to the presence of secondary mesoporosity in the hierarchical zeolites, they can be used in the preparation of catalysts with higher dispersion of additional active phases (e.g., metal nanoparticles), compared with their microporous counterparts in which active sites are only localized on the external surface (Serrano and Pizarro, 2013). Moreover, the application of hierarchical zeolites as catalyst framework could reduce the propensity for sintering and forming large metal nanoparticles (Puértolas et al., 2014). However, the loading of metals into hierarchical zeolites could decrease the number of Brønsted acid sites and increase the amount of Lewis acid sites (Table 7). This could be ascribed to the incorporation of metal cations into the ion-exchange positions during impregnation. In addition, the surface area is slightly reduced since the zeolite pores might be blocked by metal species (Table 7). Table 8 presents the changes in yields of the main products of biomass-based CFP process (i.e., oxygenates, aromatics, olefins, and coke) over different metallic hierarchical zeolites (prepared by different synthesis methods) in comparison with their microporous and nonmetallic hierarchical counterparts.

3.1. Nickel loading

The presence of Ni metal on hierarchical zeolites, such as bimodal micro-mesoporous β zeolite, leads to a high selectivity toward producing gasoline-range products. Moreover, it could promote olefin conversion through olefin aromatization and hydroisomerization reactions (Escola et al., 2012). However, the extent of olefin conversion considerably depends on the type of hierarchical zeolite. It has been observed that olefins were completely converted through the hydrogenation reaction over the hierarchical Ni/β zeolite, whereas around 30% of the olefins remained unconverted by using the hierarchical Ni/ZSM-5 because of an insufficient balance between the acid and metal functions (Escola et al., 2011).

It should be noted that the incorporation of metallic species significantly reduces the Brønsted acidity of hierarchical zeolites. In this regard, Veses et al. (2016) showed that the decreased amount of Brønsted acidity in the hierarchical ZSM-5 zeolites loaded by different metals (i.e., Ni, Sn, Cu, and Mg) led to lower production of aromatic hydrocarbons. On the contrary, Dai et al. (2019) achieved different results during the CFP of torrefied corn cob over a Ni-modified hierarchical ZSM-5 catalyst and recorded improved yields of aromatic hydrocarbons.

3.2. Iron loading

Dai et al. (2018) observed that the addition of Fe to hierarchical HSM-5 had an inverse impact on aromatic yields during the CFP of cellulose. Furthermore, Fe modification tended to produce mono-aromatics, especially BTX compounds, while reducing the poly-aromatics.

3.3. Copper loading

Chen et al. (2018a) compared the yields of aromatics produced from the CFP of rice straw over the hierarchical HZSM-5 zeolites modified by different metals (i.e., Ni, Cu, Zn, and Ga). They observed that the Cu-incorporated hierarchical zeolite showed the highest performance in the production of aromatics (Fig. 15). Based on their finding, the incorporation of Zn and Ga affected the formation of aromatics insignificantly. It was also

![Fig. 15. Aromatic yields produced from the CFP of rice straw over the 0.2 M-NaOH desilicated hierarchical HZSM-5 zeolites modified with different metals and at various metal loadings. Adapted from Chen et al. (2018a).](image)

Table 7. Porous and acidic features of nonmetallic and metal-loaded hierarchical zeolites*.

| Mesoporous zeolite | Loaded metal | Si/Al | S BET (m²/g) | V mic (cm³/g) | V mes (cm³/g) | Acid properties |
|--------------------|--------------|-------|--------------|---------------|---------------|----------------|
| HZSM-5             | –            | 40    | 528          | 0.12          | 0.51          | C 200 (μmol/g) |
| HZSM-5             | Sn           | 40    | 518          | 0.13          | 0.53          | 163            |
| HZSM-5             | Cu           | 40    | 471          | 0.13          | 0.41          | 108            |
| HZSM-5             | Ni           | 40    | 500          | 0.13          | 0.54          | 148            |
| HZSM-5             | Mg           | 40    | 456          | 0.13          | 0.33          | 75             |

* Source: Reproduced with permission from Veses et al. (2016). Copyright© 2016 American Chemical Society.
Table 8. The changes in yields of the main products of bio-based CFP process over different metallic hierarchical zeolites prepared by different synthesis methods.

| Metal(s) (wt%) | Zeolite framework | Synthesis method | Si/Al of synthesized zeolite | Feedstock (s) | Operating conditions | Change in oxygenates yield | Change in aromatic hydrocarbons yield | Change in olefins yield | Change in coke formation | Reference |
|---------------|------------------|------------------|-----------------------------|---------------|----------------------|---------------------------|-------------------------------|------------------------|-------------------------|-----------|
| Mg (1.0) [WI] | HZSM-5           | Destillation by 0.2 M NaOH solution | 40                       | Bio-oil from woody biomass | T=450 °C, P=1.013 bar | **Decreased** | **Decreased** | NA | **Decreased** | Veses et al. (2016) |
| Mg (8.4) [WI] | HZSM-5           | Silanization using PHAPTMS*** | 58                       | Eucalyptus woodchips | T=500 °C, P=1.013 bar, CTF=0.2 | **Decreased** | NA | NA | **Decreased** | Hernandez et al. (2017) |
| Mg (8.7) [WI] | HB               | Silanization using PHAPTMS       | 24                       | Eucalyptus woodchips | T=500 °C, P=1.013 bar, CTF=0.2 | **Decreased** | NA | NA | **Decreased** | Hernandez et al. (2017) |
| Fe (1.0) [WI] | HZSM-5           | Destillation by 0.2 M NaOH solution | NA                       | Cellulose      | T=500 °C, P=1.013 bar, RT=30 s, VRT=1.5 | Increased | Increased | **Decreased** | **Decreased** | NA | Dai et al. (2018) |
| Cu (3) [WI]  | HZSM-5           | Destillation by 0.2 M NaOH solution while assisted by 0.3 piperidine | 20                       | Lignite        | T=600 °C, P=1.013 bar, VRT=1.5 | Nearly unchanged | Increased | NA | NA | **Decreased** | Ren et al. (2018) |
| Ni (1.0) [WI] | HZSM-5           | Destillation by 0.2 M NaOH solution | 40                       | Bio-oil from woody biomass | T=450 °C, P=1.013 bar | **Decreased** | **Decreased** | NA | **Increased** | Veses et al. (2016) |
| Ni (0.1-1.0) [WI] | HZSM-5          | Destillation by 0.2-1.0 M NaOH solutions and washed with 0.1 M HCl solution | NA                       | Rice straw     | T=600 °C, P=1.013 bar, CTF=20 | Nearly unchanged | Increased | **Decreased** | **Increased** | **Decreased** | Chen et al. (2018a) |
| Ni (2-10) [WI] | ZSM-5           | Destillation by 0.2 M NaOH solution | NA                       | Torrefied corn cob | T=550 °C, P=1.013 bar, CTF=2 | Decreased | Increased | **Increased** | **Increased** | NA | Dai et al. (2019) |
| Cu (1.0) [WI] | HZSM-5           | Destillation by 0.2 M NaOH solution | 40                       | Bio-oil from woody biomass | T=450 °C, P=1.013 bar | **Decreased** | **Decreased** | NA | **Decreased** | Veses et al. (2016) |
| Cu (0.1-1.0) [WI] | HZSM-5          | Destillation by 0.2-1.0 M NaOH solutions and washed with 0.1 M HCl solution | NA                       | Rice straw     | T=600 °C, P=1.013 bar, CTF=20 | Increased for the metal loadings ≤0.5 wt% and decreased for >0.5 wt% | **Decreased** | **Decreased** | **Increased** | **Decreased** | Chen et al. (2018a) |
| Zn (9.7) [WI] | HZSM-5           | Silanization using PHAPTMS       | 58                       | Eucalyptus woodchips | T=500 °C, P=1.013 bar, CTF=0.2 | **Decreased** | NA | NA | **Decreased** | Hernandez et al. (2017) |
| Zn (10) [WI] | HB               | Silanization using PHAPTMS       | 24                       | Eucalyptus woodchips | T=500 °C, P=1.013 bar, CTF=0.2 | **Decreased** | NA | NA | **Decreased** | Hernandez et al. (2017) |
| Zn (0.1-1.0) [WI] | HZSM-5          | Destillation by 0.2-1.0 M NaOH solutions and washed with 0.1 M HCl solution | NA                       | Rice straw     | T=600 °C, P=1.013 bar, CTF=20 | **Decreased** | NA | NA | **Decreased** | Chen et al. (2018a) |
| Ga (1.0) [WI] | HZSM-5           | Destillation by 0.2 M NaOH solution | NA                       | Cellulose      | T=500 °C, P=1.013 bar, RT=30 s, VRT=1.5 | Increased | **Increased** | **Increased** | **Increased** | NA | Dai et al. (2018) |
| Ga (0.1-1.0) [WI] | HZSM-5          | Destillation by 0.2-1.0 M NaOH solutions and washed with 0.1 M HCl solution | NA                       | Rice straw     | T=600 °C, P=1.013 bar, CTF=20 | Increased for the metal loadings ≤0.5 wt% and decreased for >0.5 wt% | **Decreased** | **Decreased** | **Increased** | **Decreased** | Chen et al. (2018a) |
| Zr (5) [WI] | HZSM-5           | Destillation by 0.2 M NaOH solution while assisted by 0.3 piperidine | 20                       | Lignite        | T=600 °C, P=1.013 bar, VRT=1.5 | **Decreased** | **Decreased** | **Decreased** | **Increased** | Ren et al. (2018) |
found that the aromatic yield decreased as the metal loading increased. This could be ascribed to the metal atoms exchange with H⁺ on the catalyst surface at higher metal loadings, leading to decreases in the acidity and cracking capability of the catalyst.

3.4. Gallium loading

Dai et al. (2018) proved that the impregnation of hierarchical HSM-5 zeolites with Ga species imparted a positive effect on aromatic yields. They found that this metal-modified hierarchical zeolite tended to form BTX compounds and alkylbenzenes at the expense of reducing poly-aromatic hydrocarbons.

3.5. Lanthanum loading

Li et al. (2018) conducted vacuum pyrolysis of rape straw over La-modified hierarchical HZSM-5 zeolites desilicated by a 3 M Na₂CO₃ solution. Compared to the parent HZSM-5 and nonmetallic hierarchical HZSM-5 zeolites, the metal-incorporated catalyst yielded the largest quantity of hydrocarbons (i.e., ~50%) while showed the lowest tendency toward carbon species (about 11%). Moreover, it had the highest selectivity toward mono-aromatic hydrocarbons, while generating the minimum amount of coke (~11%).

3.6. Cerium loading

One of the potential incentives for cerium introduction in a catalytic framework is to mitigate coke formation. Nevertheless, it should be noted that the incorporation of cerium into the zeolite structure shifts product selectivity from aromatic hydrocarbons toward oxygenated compounds. Neumann and Hicks (2012b) used a Ce-incorporated hierarchical HZSM-5 zeolite in the CFP of lignocellulosic biomass. They figured out that the catalyst had a shifted tendency toward valuable oxygenates (i.e., furans, ketones, and aldehydes) compared with the parent hierarchical HZSM-5 framework. Ce-incorporated hierarchical HZSM-5 zeolite could nearly promote the ketonization of acetic acid to yield much higher quantities of acetone compared to both parent microporous HZSM-5 zeolite and nonmetal-containing hierarchical HZSM-5 zeolite (Fig. 16).

3.7. Magnesium loading

Veses et al. (2016) compared different hierarchical ZSM-5 zeolites modified with metal cations such as Sn, Cu, Ni, and Mg in the upgrading

| Metal(s) (wt%) [Loading method] | Zeolite framework | Synthesis method | Si/Al of synthesized zeolite | Feedstock (s) | Operating conditions | Change in | Change in | Change in | Change in | Reference |
|-------------------------------|-------------------|------------------|----------------------------|---------------|---------------------|-----------|-----------|-----------|-----------|-----------|
| Sn (1.0) [WI]                 | HZSM-5            | Desilication by 0.2 M NaOH solution | 40 | Bio-oil from woody biomass | • T=450 °C • P=1.013 bar  | **Nearly unchanged** | **Decreased** | NA         | **Nearly unchanged** | Veses et al. (2016) |
| La (5.0) [WI]                 | HZSM-5            | Desilication by 3.0 M Na₂CO₃ solution | NA | Rape straw | • T=500 °C • Po=5 kPa (vacuum) • HR=20 °C/min • RT=45 min • CTF=20 | **Decreased** | **Increased** | NA         | **Decreased** | Li et al. (2018) |
| Ce (1.92) [DG]                | HZSM-5            | SAC of the dry gel performed by dual templating (SDA=TPAOH, surfactant=tribloc k copolymer) | 55 | Glucose | • T=600 °C • RT=360 s • CTF=9.0 | **Increased** | **Decreased** | **Decreased** | NA         | Neumann and Hicks (2012b) |
| Ce (2.75) [IW]                | HZSM-5            | SAC of the dry gel performed by dual templating (SDA=TPAOH, surfactant=tribloc k copolymer) | 49 | Glucose | • T=600 °C • RT=360 s • CTF=9.0 | **Increased** | **Decreased** | **Decreased** | NA         | Neumann and Hicks (2012b) |
| Ce (1.05) [IEEx]              | HZSM-5            | SAC of the dry gel performed by dual templating (SDA=TPAOH, surfactant=triblock copolymer) | 50 | Glucose | • T=600 °C • RT=360 s • CTF=9.0 | **Increased** | **Decreased** | **Increased** | NA         | Neumann and Hicks (2012b) |
| Zr (1-15) and Co(3) [WI]      | HZSM-5            | Desilication by 0.2 M NaOH solution while assisted by 0.3 piperidine | 20 | Lignite | • T=600 °C • P=1.013 bar • VRT=1.5 s | **Increased** | **Increased** | NA         | NA         | Ren et al. (2018) |

* Change in yield compared to parent microporous zeolite.
** Change in yield compared to nonmetallic hierarchical zeolite.
*** Abbreviations: CFT: Catalyst-to-feed ratio; CTAB: hexadecyltrimethylammonium bromide; DG: Dry-gel method; HR: Heating rate; IEEx: Ion-exchange method; IW: Incipient wetness method; NA: Not available; P: Pressure; PHAHTMS: 3-(Phenylamino)propyltrimethoxysilane; RT: Residence time; SAC: Steam-assisted crystallization; SDA: Structure-directing agent; T: Temperature; TPAOH: Tetrapropylammonium hydroxide; VRT: Vapor residence time; WI: Wet impregnation method.

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3.9. Bi-metal loading

Hunns et al. (2016) explored the influence of mesoporosity and acidic strength of bifunctional hierarchical Pd/ZSM-5 catalysts on the hydrodeoxygenation of m-cresol. These catalysts exhibited high activity and selectivity values toward the production of methylecyclohexane aliphatic compounds. Based on mass normalized acid site densities obtained by the NH3 chemisorption analysis, it was revealed that the hierarchical mesoporous Pd/ZSM-5 with the Si/Al ratio of 30 possessed a slightly higher acid loading compared to its conventional microporous counterpart (i.e., 0.35 against 0.3 mmol g\(^{-1}\)). However, further increases in the Si/Al atomic ratio diminished the acid sites to about one third (i.e., 0.13). It was perceived that varying the Si/Al atomic ratio only influenced the number of acid sites, whereas their strength remained unaffected (Hunns et al., 2016).

3.8. Palladium loading

Ren et al. (2018) observed that the bi-metallic Zr-Co/hierarchical HSZM-5 had a higher total acidity than the Co/hierarchical HSZM-5. The incorporation of the bimetallic Zr-Co species facilitated the transfer of hydrogen from pyrolysis intermediates and increased the pace of the cracking and deoxygenation reactions. The co-loading of 5 wt% Zr and 3 wt% Co on the hierarchical HSZM-5 zeolite treated by 0.2 M NaOH+0.3 M piperidine was found to result in the most favorable performance. More specifically, this catalyst increased the selectivity toward light aromatics, while it mitigated the deoxygenation reactions. The co-loading of 5 wt% Zr and 3 wt% Co on the hierarchical HSZM-5 zeolite treated by 0.2 M NaOH+0.3 M piperidine was found to result in the most favorable performance. More specifically, this catalyst increased the selectivity toward light aromatics, while it mitigated the deoxygenation reactions.

3.7. Bi-metal loading

Microporous zeolites are known as reliable frameworks in designing advanced catalysts used for upgrading pyrolytic vapors. These materials can promote the reactions of cracking, aromatization, alkylation, and hydrodeoxygenation. However, the nano-size scale of microporous zeolites limits the diffusion of the molecules which are larger than the channel size of micropores. To address this challenge, hierarchical zeolites have emerged as a “trump card” for converting oxygen-rich bio-oils to valuable products by serving two levels of porosity, i.e., micropore and mesopore structures. In fact, the secondary mesoporosity of hierarchical zeolites is seen as “hitting two birds with one stone”, i.e., enhancing the accessibility to acid sites and decreasing coke formation with a single modification. However, the principal obstacles to using hierarchical zeolites in large scale is the complexity and cost of the synthesis process. Nonetheless, the capability of hierarchical zeolites for massive production of valuable chemicals can alleviate their high fabrication costs. Among the different synthesis methods applied for zeolite modification, the desilication using alkaline solutions is a promising technique to form a micro-mesoporous hierarchical network in zeolites. Unlike other hierarchicalization methods, this approach is highly advantageous due to its simplicity, efficiency, cost-effectiveness, and scalability.

Fig. 16. The yields of acetone through the ketonization of acetic acid over hierarchical HZSM-5 zeolites with and without cerium. Redrawn with permission from Neumann and Hicks (2012b). Copyright © 2012 American Chemical Society.

Fig. 17. Changes in the percentage of deoxygenation during the upgrading of wood-based bio-oil as a function of (a) Brønsted acidity and (b) Lewis acidity of metal-loaded/nonmetallic hierarchical ZSM-5 zeolites. Redrawn with permission from Veses et al. (2016). Copyright © 2016 American Chemical Society.
In the alkali-based desilication process, the hydroxide anions leach out of the Si atoms contained in zeolite structure to facilitate the formation of intracrystalline mesoporosity. However, the synthesis conditions have remarkable impacts on the acidity and textural properties of the final hierarchical zeolites, significantly affecting their catalyzing characteristics. For instance, there is a consensus among researchers that the optimal concentration of NaOH solution should be 0.3 M since this can preserve the crystalinity of parent zeolite and increase the mesopore surface and volume. Moreover, in terms of product distribution in the CFP process, the desilication technique using 0.3 M NaOH can synthesize hierarchical zeolites favoring the production of mono-aromatic hydrocarbons. It should be noted that there is a lack of research works with a focus on the influence of advanced synthesis procedures on the performance of biomass CFP. Therefore, a proportion of future studies should be dedicated to analyzing these effects.

It is important to note that the formation of secondary mesoporosity in hierarchical zeolites can provide a befitted room for the deposition of additional mono- and bi-metals. As a final suggestion, future research works should also be directed toward the assessment of the CFP performance in the presence of hierarchical zeolites impregnated by different mono- and bi-metals.

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