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Review Paper

A Review on Zeolite Application for Aromatic Production from Non-Petroleum Carbon-Based Resources

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Abstract

The application of zeolite catalyst has been expanded to support on-purpose sustainable technology. This review focused on zeolite application to produce aromatic compounds from non-petroleum carbon-based resources, including methanol, CO_2, CO, and biomass. For COx resources, the two main routes for producing aromatics products are discussed, i.e., the olefinic and the oxygenates-mediated route. Moreover, several improvement strategies for enhancing catalytic performance are also discussed, i.e., the addition of metal components, tuning the metal and zeolite structure, and modifying the reaction process. Finally, prospects for future development are formulated.

Keywords: *aromatics; benzene, toluene, xylene (BTX); non-petroleum carbon-based resource; zeolite.*

Introduction

The pursuit toward developing environmentally sustainable technology processes to fulfil the demand for energy and chemical compounds is urgent in view of fossil energy depletion. In this case, using renewable resources and waste to produce high-value-added hydrocarbon products is an up-and-coming way to solve this problem [1]. Aromatics, especially benzene, toluene, and xylene (BTX), are important components of hydrocarbon compounds which are widely used for making many essential products. For instance, benzene and xylene are utilized for making polymer products, respectively, polystyrene (PS) via ethylbenzene and polyethylene terephthalate (PET) [2-4]. Conventionally, BTX is obtained from the steam reforming process of naphtha or thermal cracking of crude oil. However, other routes have been considered to produce aromatics with a high yield by utilizing other abundant carbon resources, such as methanol [5,6], biomass [7,8], CO [9,10], and CO_2 [11, 12], where zeolite is usually involved in catalyzing the process.

Zeolite is a microporous alumino-silicate material that has been extensively involved in many catalytic processes [13-17]. In producing aromatics from non-petroleum carbon-based resources, zeolite is used as an acid catalyst to selectively catalyze the transformation of several compounds into hydrocarbon products. Usually, other components, such as a metal or oxide, are needed to form intermediate species and/or promote a reaction that cannot proceed in a zeolite catalyst. During the conversion process, several reactions can occur in zeolite's active sites, such as oligomerization, dehydrogenation, aromatization or cracking, resulting in various hydrocarbon products, such as olefin, aromatic, paraffin, and other C1 compounds. This selectivity is directed by many factors, including topology, acid properties, crystallite size, morphology, pore structure, and reaction condition [11].

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Regardless of the complexity of zeolite catalysis, significant progress has been made in using zeolite to produce hydrocarbon products. Several reports have been published regarding the improvement of the catalytic performance of zeolite for many reactions. For instance, the breakage of the Anderson-Schulz-Flory (ASF) distribution in the Fischer Tropsch reaction (FTs) was obtained by combining a classical FTs catalyst with zeolite [18,19]. In addition, employing zeolite for biomass pyrolysis can enhance bio-oil quality due to its excellent ability in the deoxygenation process [20]. Along with these signs of progress, several reviews have also been published regarding the role of zeolite in producing either the simple C1 chemistry product [19], C_{2+} hydrocarbon [11], or biofuel [20,21] through several processes. This review focuses on recent advances in zeolite catalysts for aromatic production from non-oil-based feedstock. We also pay attention to the effect of either zeolite properties or metal components in improving the catalytic performance. At the end of the conclusion section, we also provide directions for future research.

Aromatic Production over Zeolite Catalyst

Zeolites are porous materials that are built from tetrahedra AlO_4 and SiO_4, linked by an oxygen atom. Until now, 255 zeolite frameworks have been reported. However, only few have been applied to commercial processes. In the case of aromatics production, ZSM-5 is the zeolite type that is primarily being used (Table 1). It contains pores of ca. 0.5 nm with an MFI type of framework topology. The typical morphology observed in SEM analysis is coffin-type, although other morphologies have also been reported. With respect to the average pore size, it has been found to be a suitable size with regard to the kinetic diameter of light aromatics, such as BTX compounds. Several studies have demonstrated that the selectivity of the aromatic product reached over 80% by using this type of zeolite [21,22]. In this section, the application of zeolite for aromatic production utilizing non-petroleum-based feedstock will be discussed.

Aromatic Production from Methanol

The aromatic production from methanol feedstock has almost reached industrial maturity, especially in China. Several demonstration plants have been set up for the methanol-to-aromatics (MTA) process. For instance, in 2013, Tsinghua University collaborated with China Hudian Corporation to launch the first industrial-scale MTA plant, in which 30,000 t/a (tonnes per annum) of aromatics are successfully produced. This technology contains two reactor systems that operate at 450 to 500 °C and 520 to 550 °C. The former is responsible for converting methanol to a mixture of aromatics and paraffin. Meanwhile, the latter facilitates further aromatization at a higher temperature for the non-aromatic compound (C_3-C_5 paraffin) that remains in the mixture. In 2017, this process could achieve an aromatic production of 100 t/a with approximately 83% selectivity to aromatic products [23].

The technology of the MTA process was derived from the well-known MTH (methanol-to-hydrocarbon) or MTG (methanol-to-gasoline) processes but contains dehydrogenation and cyclization steps (Figure 1). Thus, metal functionality within the zeolite catalyst is needed for the MTH reaction [1]. Also, it needs a higher reaction temperature (450 to 550 °C) [1,23] than to produce olefin (380 to 495 °C) [24, 25] or gasoline (340 to 405 °C) [26] from methanol. The first step of the reaction focuses on the build-up of hydrocarbon pool (HCP) species, called the induction period. Also, it is believed to be the steady-state period for the hydrocarbon formation in an autocatalytic process. Based on the hydrocarbon pool mechanism, the HCP species can generate alkane, light olefins, and aromatics through either the olefinic cycle (methylation and cracking of olefins) or the aromatic cycle (methylation and dealkylation of aromatics). It further proceeds to the dehydrogenation and cyclization step to finally generate the aromatic products [1].

Basically, the metal component introduced in the zeolite catalyst aims to enhance the dehydrogenation reaction rate. Thus, the aromatic selectivity can be increased. Although Ga and Zn are the most popular metals to combine with zeolite for the MTA reaction, other metals have also been reported to give a positive effect. For instance, Conte, et al. [27] evaluated several metals, i.e., Ag, Cu, Ni, Pd, Ir, and Ru, impregnated in ZSM-5 zeolite.

Table 1 Reported works on aromatic production from non-petroleum-based feedstock through various processes.

Characteristic of the catalyst				Reactant (molar ratio)	Operation condition			Catalytic Performance				Ref.
Catalyst name	Zeolite type	Si/Al	Weight ratio of metal or oxide: Zeolite		T (°C)	P (MPa)	Space velocity (h^{-1})	Conversion	Aromatic selectivity	Other Products	Stability test	
Methanol to Aromatic (MTA.) Process												
Ag/ZSM-5	MFI	30	1% metal loading in zeolite	CH_3OH	450	0.45	0.16	~100	55.1	Ethylene, propene, C_1-C_6, higher aromatics (C_9^+)	11 h	[27]
Zn/ nano HZSM-5	MFI	100	0.5% Zn loading	CH_3OH	450	0.1	0.8	100	67.7 (B.T.X.)	$C_1^- - C_4^-$; C_5^+ non-aromatic; C_9^+ aromatics	40 h	[28]
Zn-P-ZSM-5	MFI	100	0,75% Zn loading	CH_3OH	430	atmospheric	2.0	-	84.73 (B.T.X.)	Alkanes, olefins, and higher aromatics (C_9^+)	6 cycles reactions	[22]
Zn/hollow H-ZSM-5	MFI	31.5	1% Zn loading in zeolite	CH_3OH under N_2 flow	390	0.5	3.18	~100	48,69	$C_1^- - C_4^-$; $C_2^= - C_5^=$; C_5^+ non-aromatic, others	156 h	[29]
Syngas to Aromatic Process												
Zn-ZrO2/H-ZSM-5	MFI	120	1:2	CO : H_2 (1 : 2)	400	3.0	500	20	80	CH_4, $C_{2-4}^=$, C_{2-4}^0	1000 h	[9]
Fe_2O_3-SiO_2/Ni-HZSM-5	M.F.I.	50	1:1 with 3% Ni loading	CO : H_2 (1 : 2)	330	4.0	1813	99.20	48.01	C_1~C_4, aliphatics C_5^+, CO_2.	12 h	[31]
Mo-ZrO_2/H-ZSM-5	MFI	120	1:2	CO : H_2 (1 : 2)	400	3.0	3000	22	76	CH_4, $C_{2-4}^=$, C_{2-4}^0, aliphatic C_5^+, CO_2.	100 h	[32]
$Ce_{0.2}Zr_{0.8}O_2$/ZSM-5	MFI	40	1:1	CO : H_2 (1 : 1)	380	2.0	600	8.1	83.1	CH_4, $C_{2-4}^=$, C_{2-4}^0, aliphatic C_5^+,	10 h	[10]
Fe_3O_4@MnO_2/hollow HZSM-5	MFI	27	1:4	CO : H_2 (1 : 1)	320	2.0	4000	>90	57	CH_4, olefins	180 h	[50]
Fe-$ZnCr_2O_4$/ZSM-5	MFI	-	4% of Fe content	CO : H_2 (1 : 1)	350	2.0	600	~50	~80	CH_4, C_{5+} paraffins, C_2-C_4	100 h	[51]
CO_2 to Aromatic Process												
Zn-AlO_x&HZSM-5	MFI	-	1 : 1	CO_2 : H_2 (1 : 3)	320	3.0	2000	9.1	73.9[a]	CO, CH_4	100 h	[52]
ZnZrO/HZSM-5	MFI	100	1 : 1	CO_2 : H_2 (1 : 3)	320	4.0	1200	14	73[a]	CO, CH_4	100 h	[53]
Aerogel ZnO-ZrO/ meso- H-ZSM-5	MFI	56	1 : 2	CO_2 : H_2 (1 : 3)	340	4.0	7200	16	76[a]	CO, CH_4	52 h	[54]
ZnO/ZrO_2-meso-HZSM-5	MFI	300	1 : 2	CO_2 : H_2 (1 : 3)	340	4.0	4800	6.0	55.5	CO, CH_4	100 h	[55]
$ZnCrO_x$-ZnZSM-5	MFI	140	2 : 1	CO_2 : H_2 (1 : 3)	320	5.0	2000	19.9	81.1[b]	CO, CH_4	-	[56]
$ZnFeO_x$-4.25Na/ meso-nanokristal-HZSM-5	MFI	25	1 : 2	CO_2 : H_2 (1 : 3)	320	3.0	4000	36.2	60.0	CO, CH_4	100 h	[57]
Na-Fe@C/hollow-H-ZSM-5-0.2M	MFI	32,8	1 : 3	CO_2 : H_2 (1 : 3)	320	3.0	9000	33.3	50.2[a]	CO, CH_4	60 h	[58]
Fe-K/a-Al_2O_3 & 0.8P/ZSM-5	MFI	25	1 : 1	CO_2 : H_2 (1 : 1)	400	3.0	3000	36.4	35.5	CO, CH_4	-	[12]
6,25%Cu-Fe_2O_3/HZSM-5-pt	MFI	25	1 : 1	CO_2 : H_2 (1 : 1)	320	3.0	1000	55.38	61.94	CO, CH_4	120 h	[59]
Na-Fe_3O_4/HZSM-5	MFI	25	1 : 1	CO_2 : H_2 (1 : 2)	320	3.0	4000	27.7	44.5	CO, CH_4	-	[60]
ImpNa-FeMnOx-Pmodified HZSM-5	MFI	25	1 : 1	CO_2 : H_2 (1 : 3)	400	3.0	1000	44.49	71.52	CO, CH_4	-	[61]
Kopresipitasi 2,3%Na-Cu-Fe_2O_3/HZSM-5	MFI	-	1 : 1	CO_2 : H_2 (1 : 3)	320	3.0	1000	33.26	57.7	CO, CH_4	-	[62]
Na-FeMn/HZSM-5	MFI	105	1 : 1	CO_2 : H_2 (1 : 3)	320	3.0	4000	27.0	36.5	CO, CH_4	50 h	[37]
Biomass to Aromatic Process												
Cu-HZSM-5	MFI	38	0.1 % Cu loading	Rice straw	600	-	20 : 1[c]	-	~80	Olefin, CO, CO_2	-	[63]
Ce-HZSM-5	MFI	55	1.95 wt % Ce	Glucose	600	-	1 : 9[c]	-	~40 (BTX)	CO, CO_2, light gases and coke	-	[64]
Soft templated-ZSM-5	MFI	-	-	Rice straw	300	-	20 : 1[c]	-	~60 (BTX)	CO, CO_2, olefin and coke	-	[8]
Desilicated-ZSM-5	MFI	25	-	Kraft lignin	500	-	10: 1[c]	-	-	Oxygenates, naphthalene and polycyclic aromatic hydrocarbons	-	[42]
Desilicated ZSm-5	MFI	38	-	Cellulose	300	-	20 : 1[c]	-	~40	Gaseous CO and coke	-	[41]

[a] Aromatic selectivity without CO.

[b] Aromatics selectivity in C5+ hydrocarbons

[c] Weight ratio catalyst to biomass

Surprisingly, each metal group exhibits a different selectivity to the aromatic product. The results showed that Ag generates the highest selectivity to the C_6-C_8 aromatic fraction (ca. 40%). Meanwhile, Ni and Cu produce the highest selectivity for naphthalene and C_9-C_{11} aromatics (up to 20%), respectively. These values were much higher than those for the non-impregnated ZSM-5, which had 25% and 1% selectivity to C_6-C_8 and C_9-C_{11} aromatic products. In addition, there was no effect of Pd, Ir, and Ru metal-modified zeolite on the MTA reaction. The different selectivity among these catalysts is attributed to the distinct ability of metal-modified zeolite to stabilize the olefinic intermediates. Ni, Ag, and Cu provide a more stable environment for olefinic intermediates to efficiently coordinate their metal oxide clusters on the edge of zeolites, thus enhancing the formation of aromatic compounds. Meanwhile, oxide clusters of other metals, such as Ir, Pd, and Ru, have less interaction with zeolite crystals, resulting in a smaller effect on the aromatic selectivity product.

Zhang, et al. [28] reported the enhanced catalytic performance of zeolite catalyst in the MTA reaction by reducing its crystallite size to nanometers and modifying it with Zn. The OH group in the zeolite surface could interact with Zn and changes the catalyst's acidity properties. Brønsted acid was reduced and Lewis acid was generated. The moderate Brønsted acid restricts the cracking reaction of C_{7+}-C_{9+} polymers; meanwhile, the Lewis acid promotes the dehydrogenation of C_{7+}-C_{9+} intermediates. Thus, the selectivity to BTX products could be improved. On the other hand, the nano size of the zeolites diminishes the diffusion path length and residence time of the molecules, thus enhancing the catalyst lifetime. Notably, there was no decrease in the BTX product yield up to 20 h of reaction time, and the conversion stayed at ~100% until 40 h of reaction. On the other hand, by using conventional zeolites, a sharp decrease in conversion up to ~15% was observed. Furthermore, the BTX selectivity dropped up to half from the initial reaction stage, showing the lower stability of conventional zeolite compared to nanosized zeolites.

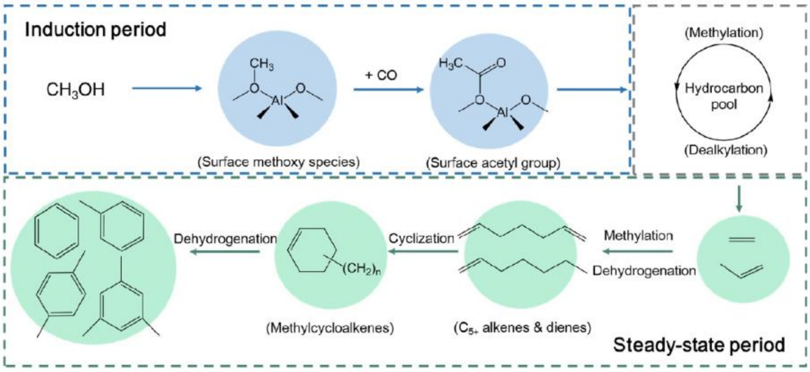

Figure 1 Schematic illustration of the methanol to aromatic route via olefin intermediate over metal-modified-zeolite catalyst. Reproduced with permission from Ref. [1], © 2021 American Chemical Society.

Further, Wang, et al. [29] investigated the effect of different zeolite morphologies in Zn/zeolite catalyst. Remarkable activity and selectivity (48.59%) of the MTA reaction were obtained when using the hollow morphology of zeolite (hollow capsule structure with mesoporous shell), while the coffin morphology had the lowest catalytic performance. This remarkable performance is attributed to the hollow morphology's ability to facilitate the uniform dispersion of $(ZnOH)^+$ sites. Meanwhile, the mesopores facilitate the diffusion and mass transfer of both reactant and product, resulting in high stability of the catalyst (187 h), which was much higher than that of the coffin-type catalyst (78 h). This stability has also been related to the ability of the hollow morphology of zeolites to reduce the carbon deposition rate by facilitating the faster removal of coke precursor from the channel through the mesopores. Moreover, the mesopores allow a higher capacity of admitting carbon deposition; thus, the lifetime of the catalyst is longer.

Instead of a zinc element, Qiao, et al. [22] used a zinc phosphate group isolated in zeolite (ZnPHZ) to enhance the BTX selectivity (up to 85%) of the MTA reaction. The strong interaction between zinc and phosphorus species with the zeolite surface generates a strong Lewis acid center, which is favorable for BTX production. Particularly the Lewis nature of the Zn ions ($ZnOH^+$, Zn^{2+}-L acid center) allows faster recombination of surface hydrogen. Moreover, the decrease of the Bronsted acid sites suppress C_3 cracking and improves the cyclization and aromatization of $C_6^{=}$-$C_9^{=}$ oligomer intermediates through dehydrogenation. In addition, the P components enhance the catalyst's stability by restricting zeolite dealumination during the process. Moreover, the isolated structure of the ZnPHZ catalyst limits the loss of zinc compounds, thus extending the regeneration cycle. Based on the catalytic test, the SnPHZ catalyst could maintain its catalytic activity after five cycles of reaction-regeneration, showing the high recoverable capability of the catalyst. Particularly, the yield and selectivity of BTX products in the first cycle was 50.59% and 84.73%, respectively, and 47.30%, and 84.01%, respectively, in the fifth cycle.

Differently, Shoinkhorova, et al. [6] used high silica ZSM-5 zeolite alone (SiO_2/Al_2O_3 = 280) to catalyze the MTA reaction. Instead of adding metal components to the zeolite, the catalytic performance was enhanced by employing a high-pressure reaction (30 bar). By applying high-pressure operation, the high partial pressure of the methanol (and that of primary olefin products) will increase, leading to favorable aromatic production through the hydrogen transfer, methylation, and oligomerization processes. At the same time, the increase of the partial pressure of water inhibits the further condensation of aromatic products due to the competitive adsorption between methanol and water on the Brønsted acid site. Thus, the catalyst's lifetime is prolonged.

Aromatic Production from Syngas

Syngas (a mixture of carbon monoxide and hydrogen) is an important resource to substitute carbon-based petroleum resources. It can be obtained from natural gas, coal, biomass, and even waste such as CO_2 through various processes, including steam reforming, pyrolysis, or dry reforming. Conventionally, the well-established production of hydrocarbon from syngas has been conducted through the Fischer-Tropsch process, in which several hydrocarbon products can be generated, i.e., gasoline, diesel, jet fuel, aromatics, and olefins. Unfortunately, the product is limited to the Anderson-Schulz-Flory (ASF) distribution, in which the straight-chain hydrocarbon product is the dominant product. In this case, combining the FTs catalyst with zeolite has been reported to successfully break the ASF distribution [10,19].

Principally, the conversion of syngas into aromatic products can be categorized into two steps, i.e., the transformation of CO into intermediates and further hydrogenation of the intermediates to generate the aromatic products. The containing Fe (carbide) based Fischer-Tropsch catalyst convert the gas into olefinic intermediates. Meanwhile, the metal oxide-containing catalyst produces oxygenate intermediates such as methanol or DME (dimethyl ether). When the intermediate is formed, it proceeds on the zeolite as a solid acid catalyst through the hydrocarbon pool mechanism [30]. Recently, several reports have been published on modifying zeolite and combining it with various metal or oxide components to enhance its catalytic properties. Yang, et al. [31] evaluated both iron-based FT catalyst (Fe_2O_3-SiO_2) and Cu-based catalyst (CuO-ZnO-Al_2O_3) as methanol catalysts combined with Nb-Ni-HZSM-5 zeolite, respectively coded as Fe-HZ and CZA-HZ. The results showed that both catalysts had different selectivity to the aromatic product. High selectivity to BTX products was shown by the Fe-HZ catalyst. Meanwhile, the CZA-HZ catalyst exhibited high selectivity to durene. Interestingly, combining these two catalysts resulted in high selectivity to trimethylbenzene (triMB) products. This difference in product selectivity is attributed to the distinct reaction route for each catalyst. On the Fe-based catalyst, the BTX was produced via cracking, cyclization, hydrogen transfer, and dehydrogenation of unsaturated aliphatic hydrocarbon. In this case, the polymetylbenzene product was generated by the alkylation between aromatics and light olefin product, which is difficult to achieve. Thus, the BTX product was favorable in the Fe-HZ catalyst. On the other hand, the mechanism of hydrocarbon production on the CZA-HZ catalyst follows the hydrocarbon pool mechanism since the methanol is formed as an intermediate reaction. Under the reaction conditions, it could reversibly transform to dimethyl ether and further convert to olefins via a dehydration reaction. Within the zeolite pores, these light olefins can transform via a hydrocarbon pool mechanism, leading to the generation of many hydrocarbon pool species such as trimethylbenzene.

Cheng et al. [9] reported 80% selectivity of aromatic products using zeolite-containing methanol catalysts (usually metals or oxides). In their work, the ZSM-5 was coupled with Zn-doped ZrO_2 nanoparticles. The evaluation of proximity between each catalyst component was investigated. It was shown that the spatial arrangement of the different active sites in the bifunctional catalyst is critical in defining conversion and selectivity. The lowest activity was produced when the two components were separated by quartz wool. By increasing the bond between both components, the selectivity to the BTX product was enhanced. This is reasonable, because the transfer of intermediate CH_3OH/DME formed on the Zn-ZrO_2 toward the zeolite catalyst will be faster if their proximity is closer, preventing the occurrence of an undesired reaction and thus enhancing the product selectivity. Moreover, the metal oxide component was well distributed on the zeolite surface catalyst, leading to activity improvement.

Generally, the addition of an oxide component in the zeolite catalyst facilitates the oxygenates species in oxide vacancies. Huang, et al. [10] reported 83.1% aromatics selectivity from syngas conversion over $Ce_{0.2}Zr_{0.8}O_2$/ZSM-5 catalyst. The abundant surfaces of ceria components facilitate the C-O activation process. Meanwhile, zeolite ZSM-5 provides a moderate acidity, which is appropriate for BTX formation. Interestingly, the crystal size of zeolite has a vital role in catalytic performance, where a smaller crystallite size produces a higher selectivity. This is attributed to the increased surface area, acid density, and the enhancement of diffusion properties within the nanosized zeolite crystal, resulting in a higher selectivity product. In addition, Zhou et al. [32] demonstrated the hydrogenation ability of mixed oxide Mo-ZrO_2, resulting in 22% CO conversion and 76% selectivity to aromatics when combined with ZSM-5 zeolite catalyst. Moreover, the BTX fraction in the aromatic products could be increased by 50% after passivation of the zeolite external surfaces.

Aromatic Production from CO_2

Similar to aromatic production from syngas, the conversion of CO_2 into aromatic products needs a bifunctional catalyst responsible for the realization of the two consecutive reactions, CO_2 activation and aromatization. For this case, an Fe-based catalyst or metal oxide coupled with zeolite has been reported. During the reaction process, there are two types of intermediates that can be formed based on the catalyst used. The Fe-based catalyst usually results in a CO and/or olefin intermediate, while Cu or other metal oxide catalysts produce methanol in the intermediate reaction. These two different routes are known respectively as reverse water gas shift (RWGS) and methanol-mediated pathways. The zeolite acts as the acid catalyst for converting the intermediate to undergo further reactions, such as hydrogen cracking, dimerization, oligomerization, isomerization, cyclization, and dehydrogenation (H transfer) [33,34]

In the case of aromatic production, zeolite not only provides the active site for aromatization but also selectively directs the product to the desired product thanks to its unique micropore channel. In the study reported by Ramirez, et al. [35], the effect of the different topologies of zeolites on CO_2 hydrogenation was investigated. The catalyst used was potassium superoxide doped iron oxide and zeolite (coded as Fe_2O_3@KO_2/zeolite), in which MOR and MFI were employed. The result showed that these two different zeolites generated a difference in product selectivity. The MFI, a 10-membered zeolite with both a straight channel (5.1 x 5.5 Å) and a sinusoidal channel (5.1x 5.5 Å), demonstrated a high selectivity to the aromatic product (selectivity of Aro = 24.9%; C_2-C_4 = 12.1%). Meanwhile, the MOR, which only has a straight channel (8-ring (2.6 x 5.7 Å) and 12-ring (6.5 x 7.0 Å)), is favorable for light olefins production (selectivity of Aro = 2.6%; C_2-C_4 = 33.3%). This is attributed to the higher potential of MFI in providing a confined channel to activate the long alkanes toward the carbenium ions. However, it should be noted that the acidity properties are also a crucial aspect to be considered, since they play an important role in promoting the reaction. Therefore, the acidity of these two zeolites should be comparable. In zeolites, the acidity properties are generally proportional to the Si/Al ratio. Based on the compositional analysis, the SiO_2/Al_2O_3 of the samples was 35 and 25 for ZSM-5 and MOR, respectively. However, it was found from the NH_3-TPD analysis that there is no significant difference in acidity between these two zeolites. In their study, the linear correlation between the Si/Al ratio and the aromatic selectivity in MFI zeolite was also observed. A higher Al content was more favorable to aromatic formation.

Other than Al, other elements could also be applied to isomorphically substitute the Si components in the zeolite framework. In this case, the elements should be able to coordinate tetrahedrally. Therefore, trivalent heteroatoms, such as B, Fe, and Ga, are usually applied, where the nature of these elements affects the acidic strength of the zeolite. For instance, the order of acidity strength of MFI zeolite after isomorphic substitution is B–OH–Si < Fe–OH–Si < Ga–OH–Si < Al–OH–Si [36]. However, for the aromatic production from CO_2, a metal is usually incorporated by wet impregnation, where the metal acts as a counter ion and is located on an extra framework instead of within the framework of the zeolite. Notably, it also affects the number of acid sites and their strength. For instance, the phosphorus modification of zeolite MFI in Fe-K/alkaline-Al_2O_3-zeolite catalyst through impregnation has been reported to increase the number of medium-acid-strength acid site of zeolites due to the interaction of medium acid oxide P_2O_5 with ZSM-5. The resulting modified acid characteristic of zeolite further promotes aromatic formation with 35.5% of aromatic product selectivity [12]. On the other hand, the modification with Zn and Ga components produces a lower aromatic selectivity, i.e., 28.7% and 24.4%, respectively. This is related to the change in the acidity properties of the zeolites. After modification, the total amount of acid in the zeolite decreases because the oxide covers the acid sites of the zeolite. The NH_3-TPD analysis demonstrated a shifted peak toward a higher temperature for Ga- and Zn-modified zeolites, which indicates the formation of a new, stronger acid site. On the other hand, for P-modified catalyst, the peak shifted to a lower temperature, which represents moderate acidity of the zeolite. It further confirms that the acidity is strongly correlated to the catalytic performance of the zeolite catalyst in aromatic production from CO_2. In the case of aromatic production from CO_2, medium acid strength is needed; therefore, this issue should be considered when choosing the metal.

In particular cases, such as in para-xylene production, the acidity of the zeolite should be suppressed. Usually, SiO_2 modification is performed to achieve this objective. The zeolite-core and SiO_2-shell structure has been reported to enhance the para-xylene selectivity due to the restriction of the further alkylation and isomerization of the para-xylene product on the external surface [37]. In addition, the enhancement of para-xylene selectivity can also be obtained by engineering the morphology of the MFI zeolite catalyst, as reported by Wang, et al. [38]. They found that lengthening the nanochain morphology from 0.0 to 0.73 nm could remarkably improve the para-xylene selectivity due to the reduction of the exposed straight channel in MFI zeolite leading to the restriction of the formation of a bulkier molecule as a secondary product, such as tetramethyl benzene. Thus, the para-xylene selectivity is increased. However, limited mass transfer may occur when the b-axis of the crystal stacking morphology is longer than 0.73 nm, resulting in a decrease of para-xylene selectivity.

Aromatic Production from Biomass

The practical application of zeolites in biomass conversion is known as catalytic fast pyrolysis (CFP). It is used to produce bio-oil by conducting the reaction at relatively high temperatures (450 to 600 ℃) in the presence of a catalyst [39]. Basically, the process comprises two steps, i.e., thermal depolymerization and decomposition of biomass into vapor and further conversion of the vapor into several products such as olefin and aromatics through the deoxygenation process, where the latter process usually needs a zeolite catalyst [8]. With respect to the shape selectivity properties, using a suitable type of zeolite could selectively direct the reaction to create the desired product. In the study conducted by Yu, et al. [39], a different product selectivity from the CFP of lignin resulted when using zeolites with different topologies. In this case, the highest yields of aromatics and the lowest coke deposit were produced by ZSM-5 zeolite, followed by Beta, Mordenite, and Y zeolite, respectively, suggesting that the internal pore space (6.36 Å) and steric hindrance (CI of 6.9) of ZSM-5 are favorable for the aromatic formation and prevent the generation of large polyaromatic compounds. However, there are still many large oxygenate compounds contained in the product since the medium-size pores of ZSM-5 cannot let these large molecules through.

Several efforts to modify the zeolite pore structure have been reported to enhance the aromatic yield. In this case, the synthesis of hierarchical structure zeolite has been successfully reported with several techniques. For instance, the post-synthesis with a strong/medium inorganic/organic base, e.g., NaOH [40], Na_2CO_3, TPAOH [41], and TMAOH [42], has been revealed to increase the aromatic yield in CFP of various biomass feedstock such as, cardboard waste, kraft lignin, and cellulose. On the other hand, creating hierarchical zeolite during the synthesis process has also been reported, using mesoporogen as a template. Zhang et al. [8] reported the use of hexadecyl trimethyl ammonium bromide (CTABr) as template, resulting in zeolite with additional mesopores with a size of 2 to 8 nm [8]. In another work, the same authors applied an organosilane with a different carbon chain length to create mesopores in zeolite for CFP of rice straw. The results showed that hexadecyltrimethoxysilane ($C_{19}H_{42}O_3Si$) gave the highest aromatic yield (25.6%) with the lowest coke yield (43.3%), having the highest total acidity and crystallinity with intracrystalline mesopores [7]. In addition, Che, et al. [43] used starch as a green template to introduce additional mesopores on ZSM-5 zeolite. The results showed that the increase of mesopore volume in the zeolite samples was followed by an increased amount of aromatic product. The highest yield obtained from the CFP of wood sawdust using this catalyst sample reached 91.84 mg/g, i.e., much higher than that of a conventional catalyst (62.32 mg/g).

Figure 2 Illustration of the catalytic fast pyrolysis (CFP) of biomass over conventional zeolite vs. hierarchical zeolites. Reproduced with permission from Ref. [43]. © 2019 Elsevier.

From everything mentioned in the previous paragraph, it can be seen that the addition of mesopores in the zeolite structure exhibits activity and selectivity enhancement for aromatic production. This is expected since there are many bulky oxygenates compounds in pyrolysis vapors, such as syringol, guaiacol, and their derivative compounds, that have a larger kinetic diameter than the ZSM-5 zeolite pores. Thus, they cannot be accommodated by the zeolite micropores [20]. In that sense, the presence of mesopores provides more open space for those molecules to access the zeolite active sites, leading to enhanced selectivity and aromatic yield (Figure 2). Moreover, with respect to the reduced diffusional limitation, the formation of coke is also prevented, resulting in high stability of the catalyst.

In contrast to creating a more accessible catalyst to enhance aromatic production, Cheng, et al. [44] reduced pore opening to focus on para-xylene as the target of the aromatic product through chemical liquid deposition (CLD) of tetraorthosilicate (TEOS). This modification enhanced the para-xylene selectivity from 32% to 92% from the CFP of 2-methylfuran + propylene compound. Furthermore, the addition of Ga components in sylilated zeolite catalyst boosted para-xylene selectivity up to 96% due to its higher space confinement effect on the zeolite catalyst. It is believed that Ga in zeolite is responsible for promoting the decarbonylation and the aromatization of olefin intermediates. Meanwhile, the zeolite component acts as an acid catalyst for other reactions, such as oligomerization, cyclyzation, and dehydrogenation [45]. Regarding the effect of metals on zeolite catalyst in biomass conversion, Che et al. [46] evaluated various metals, i.e., Zn, Fe, Ca, Ce, and La. The results showed that incorporating Zn in zeolite resulted in the highest total yield of BTX product. This is attributed to the very strong acidity provided by Zn species. However, excessive metal components (10%) lead to a decrease in BTX yield due to a decrease in acidity and poor reactant diffusion.

Conclusion and Outlook

The utilization of non-petroleum carbon-based resources is a promising method to solve current issues related to fossil energy depletion. In this case, zeolite plays a vital role in realizing the transformation process from renewable and waste feedstock into high-added value hydrocarbon products. In aromatic production, ZSM-5 zeolite is the most popular and most suitable for catalyzing this process (Table 1). Mostly, it has to be combined with other treatments or catalyst components such as a metal or metal oxide to realize the transformation of feedstock into aromatic product. In the production of aromatics from methanol, the addition of a metal aims to increase the dehydrogenation and aromatization reaction. Meanwhile, in CO_x conversion, metal or metal oxide is used to produce an intermediate reaction through the CO_x activation process. Differently, aromatic production from biomass usually uses zeolite alone to catalyze the reaction. However, the biomass should be previously converted into pyrolysis vapors by applying extreme reaction conditions.

Currently, numerous reports have been published on optimizing zeolite as catalyst for this conversion reaction. Several metals or oxides from several different elements, such as Fe, Zn, Zr, Ga, Ce, Mo, have been investigated to improve zeolite activity by providing oxygen vacancies or hydrogenation ability. Moreover, the modification of the zeolite structure itself can also enhance catalytic performance. For instance, the modification of the pore structure with mesopores results in increased diffusion and mass transfer properties, leading to improved product selectivity. Although several enhancements of the catalytic performance of zeolite-based catalysts on aromatic production are attributed to one specific structural, textural, or physicochemical property, such as the topology, crystallite size, morphology, pore architecture, or acidity, it should be noted that during catalytic evaluation, other properties should also be considered. Sometimes, modifying a certain feature of zeolite also affects other zeolite properties. Thus, the improved catalytic performance may result from a cumulative effect of the modified zeolite properties.

In view of the many advances that have been made in this field, several things can be considered. Exploring other types of zeolite catalysts for aromatic production is still possible, although using ZSM-5 zeolite has shown excellent results. Zeolites that are synthesized via a green route [47-49] remains unexplored. Also, the investigation of the appropriate state of metal components must be considered. In this case, a thorough study on the kinetic aspect of the reaction as well as the catalyst’s state during the reaction should be conducted. From another point of view, computational study and machine learning may help to predict and predesign either the catalyst or the reaction process. To this end, the development of mature technology for realizing this process should also be prioritized.

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References

[1] Li, T., Shoinkhorova, T., Gascon, J. & Ruiz-Martinez, J., *Aromatics Production via Methanol-Mediated Transformation Routes*, ACS Catal*.,* **11**, pp. 7780–7819, 2021. doi:10.1021/acscatal.1c01422.

[2] Perego, C. & Pollesel, P., *Advances in Aromatics Processing Using Zeolite Catalysts*. In Advances in Nanoporous Materials, Elsevier, **1**, pp. 97-149, 2010. doi:10.1016/S1878-7959(09)00102-9.

[3] Huang, M., Xu, J., Ma, Z., Yang, Y., Zhou, B. & Wu, C.*, Bio-BTX Production from the Shape Selective Catalytic Fast Pyrolysis of Lignin Using Different Zeolite Catalysts: Relevance between the Chemical Structure and the Yield of Bio-BTX*, Fuel Process. Technol., **216**, 106792, 2021. doi: 10.1016/j.fuproc.2021.106792.

[4] Mruthyunjaya, V., *Catalysis for Bio-BTX (Benzene, Toluene, and Xylene) Synthesis*, in Advanced Catalysis for Drop-in Chemicals, Elsevier, pp. 223–256, 2022. doi:10.1016/B978-0-12-823827-1.00003-1.

[5] Gong, Q., Fang, T., Xie, Y., Zhang, R., Liu, M., Barzagli, F., Li, J., Hu, Z., & Zhu, Z., *High-Efficiency Conversion of Methanol to BTX Aromatics over a Zn-Modified Nanosheet-HZSM-5 Zeolite*, Ind. Eng. Chem. Res*.,* **60**, pp. 1633–1641, 2021. doi: 10.1021/acs.iecr.0c06342.

[6] Shoinkhorova, T., Cordero-Lanzac, T., Ramirez, A., Chung, S.H., Dokania, A., Ruiz-Martinez, J. & Gascon, J., *Highly Selective and Stable Production of Aromatics via High-Pressure Methanol Conversion*, ACS Catal. **11**, pp.3602–3613, 2021. doi:10.1021/acscatal.0c05133.

[7] Zhang, Z., Cheng, H., Chen, H., Li, J., Chen, K., Lu, X., Ouyang, P. & Fu, J., *Catalytic Fast Pyrolysis of Rice Straw to Aromatics over Hierarchical HZSM-5 Treated with Different Organosilanes.*,Energy and Fuels, **33**, pp. 307-312, 2019. doi: 10.1021/acs.energyfuels.8b03213.

[8] Zhang, Z., Cheng, H., Chen, H., Chen, K., Lu, X., Ouyang, P. & Fu, J.*, Enhancement in the Aromatic Yield from the Catalytic Fast Pyrolysis of Rice Straw over Hexadecyl Trimethyl Ammonium Bromide Modified Hierarchical HZSM-5,* Bioresour. Technol., **256**, pp. 241–246, 2018. doi: 10.1016/j.biortech.2018.02.036.

[9] Cheng, K., Zhou, W., Kang, J., He, S., Shi, S., Zhang, Q., Pan, Y., Wen, W. & Wang, Y., *Bifunctional Catalysts for One-Step Conversion of Syngas into Aromatics with Excellent Selectivity and Stability*, Chem, **3**, pp. 334–347, 2017. doi: 10.1016/j.chempr.2017.05.007.

[10] Huang, Z., Wang, S., Qin, F., Huang, L., Yue, Y., Hua, W., Qiao, M., He, H., Shen, W. & Xu, H., *Ceria-Zirconia/Zeolite Bifunctional Catalyst for Highly Selective Conversion of Syngas into Aromatics*, ChemCatChem, **10**, pp. 4519-4524, 2018. doi:10.1002/cctc.201800911.

[11] Azhari, N.J., Nurdini, N., Mardiana, S., Ilmi, T., Fajar, A.T.N., Makertihartha, I G.B.N., Subagjo & Kadja, G.T.M, *Zeolite-Based Catalyst for Direct Conversion of CO2 to C2+ Hydrocarbon: A Review*, J. CO2 Util*.* ***59***, 101969, 2022**.** doi: 10.1016/j.jcou.2022.101969.

[12] Dai, C., Zhao, X., Hu, B., Zhang, J., Hao, Q., Chen, H., Guo, X. & Ma, X., *Hydrogenation of CO2 to Aromatics over Fe-K/Alkaline Al2O3and P/ZSM-5 Tandem Catalysts*, Ind. Eng. Chem. Res., **59**, pp.19194-19202, 2020. doi: 10.1021/acs.iecr.0c03598.

[13] Firmansyah, M.L., Jalil, A.A., Triwahyono, S., Hamdan, H., Salleh, M.M., Ahmad, W.F.W. & Kadja, G.T.M., *Synthesis and Characterization of Fibrous Silica ZSM-5 for Cumene Hydrocracking*, Catal. Sci. Technol*.,* **6,** 5178–5182, 2016. doi:10.1039/c6cy00106h.

[14] Puspitasari, T., Ilmi, M.M., Nurdini, N., Mukti, R.R., Radiman, C.L., Darwis, D. & Kadja, G.T.M., *The Physicochemical Characteristics of Natural Zeolites Governing the Adsorption of Pb2+ from Aqueous Environment*, Key Eng. Mater, **811** KEM, pp. 92–98, 2019. doi: 10.4028/www.scientific.net/KEM.811.92.

[15] Wardani, M.K., Kadja, G.T.M., Fajar, A.T.N., Subagjo, Makertihartha, IGBN, Gunawan, M.L., Suendo, V. & Mukti, R.R., *Highly Crystalline Mesoporous SSZ-13 Zeolite Obtained via Controlled Post-Synthetic Treatment.* RSC Adv., ***9***, pp. 77-86, 2019. doi:10.1039/C8RA08979E.

[16] Puspitasari, T., Kadja, G.T.M., Radiman, C.L., Darwis, D. & Mukti, R.R., *Two-Step Preparation of Amidoxime-Functionalized Natural Zeolites Hybrids for the Removal of Pb2+ Ions in Aqueous Environment*, Mater. Chem. Phys. **216**, pp. 197-205, 2018. doi: 10.1016/j.matchemphys.2018.05.083.

[17] Yulizar, Y., Kadja, G.T.M. & Safaat, M., *Well-Exposed Gold Nanoclusters on Indonesia Natural Zeolite: A Highly Active and Reusable Catalyst for the Reduction of p-Nitrophenol*, React. Kinet. Mech. Catal., **117**, pp. 353–363, 2016. doi:10.1007/s11144-015-0916-2.

[18] Wang, X., Yang, G., Zhang, J., Song, F., Wu, Y., Zhang, T., Zhang, Q., Tsubaki, N. & Tan, Y., *Macroscopic Assembly Style of Catalysts Significantly Determining Their Efficiency for Converting CO2 to Gasoline*, Catal. Sci. Technol., **9**, pp. 5401-5412, 2019. doi:10.1039/c9cy01470e.

[19] Zhang, Q., Yu, J. & Corma, A., *Applications of Zeolites to C1 Chemistry: Recent Advances, Challenges, and Opportunities.* Adv. Mater., **32**, pp. 1-31, 2020. doi:10.1002/adma.202002927.

[20] Mardiana, S., Azhari, N.J., Ilmi, T. & Kadja, G.T.M., *Hierarchical Zeolite for Biomass Conversion to Biofuel: A Review.* Fuel., **309**, pp. 122119, 2022. doi: 10.1016/j.fuel.2021.122119.

[21] Makertihartha, I.G.B.N., Kadja, G.T.M., Gunawan, M.L., Mukti, R.R. & Subagjo, *Exceptional Aromatic Distribution in the Conversion of Palm-Oil to Biohydrocarbon Using Zeolite-Based Catalyst*, J. Eng. Technol. Sci., **52**, pp. 584-597, 2020. doi: 10.5614/j.eng.technol.sci.2020.52.4.9.

[22] Qiao, J., Wang, J., Frenkel, A.I., Teng, J., Chen, X., Xiao, J., Zhang, T., Wang, Z., Yuan, Z. & Yang, W., *Methanol to Aromatics: Isolated Zinc Phosphate Groups on HZSM-5 Zeolite Enhance BTX Selectivity and Catalytic Stability*, RSC Adv., pp. 5961-5971, 2020. doi:10.1039/c9ra09657d.

[23] Xu, X., Liu, Y., Zhang, F., Di, W. & Zhang, Y., *Clean Coal Technologies in China Based on Methanol Platform*. Catal. Today, **298**, pp. 61-68, 2017, doi: 10.1016/j.cattod.2017.05.070.

[24] Tian, P., Wei, Y., Ye, M. & Liu, Z., *Methanol to Olefins (MTO): From Fundamentals to Commercialization.* ACS Catal. **5**, pp. 1922-1938, 2015. doi:10.1021/acscatal.5b00007.

[25] Yarulina, I., Goetze, J., Gücüyener, C., van Thiel, L., Dikhtiarenko, A., Ruiz-Martinez, J., Weckhuysen, B.M., Gascon, J. & Kapteijn, F., *Methanol-to-Olefins Process over Zeolite Catalysts with DDR Topology: Effect of Composition and Structural Defects on Catalytic Performance*, Catal. Sci. Technol., **6**, pp. 2663-2678, 2016. doi:10.1039/C5CY02140E.

[26] Mirshafiee, F., Khoshbin, R. & Karimzadeh, R. A Green Approach for Template Free Synthesis of Beta Zeolite Incorporated in ZSM-5 Zeolite to Enhance Catalytic Activity in MTG Reaction: Effect of Seed Nature and Temperature. J. Clean. Prod. **361**, 132159, 2022. doi:10.1016/j.jclepro.2022.132159.

[27] Conte, M., Lopez-sanchez, J.A., He, Q., Morgan, D.J., Ryabenkova, Y., Bartley, J.K., Carley, A.F., Taylor, S.H., Kiely, C.J. & Hutchings, G.J. *Modified Zeolite ZSM-5 for the Methanol to Aromatics Reaction,* Catal. Sci. Technol*.,* **2**, pp. 105-112, 2012. doi:10.1039/c1cy00299f.

[28] Zhang, G.Q., Bai, T., Chen, T.F., Fan, W.T. & Zhang, X., *Conversion of Methanol to Light Aromatics on Zn-Modified Nano-HZSM-5 Zeolite Catalysts.* Ind. Eng. Chem. Res*.,* **53**, pp. 14932-14940, 2014. doi:10.1021/ie5021156.

[29] Wang, K., Dong, M., Niu, X., Li, J., Qin, Z., Fan, W. & Wang, J., *Highly Active and Stable Zn/ZSM-5 Zeolite Catalyst for the Conversion of Methanol to Aromatics: Effect of Support Morphology*, Catal. Sci. Technol. **8**, pp. 5646-5656, 2018. doi:10.1039/c8cy01734d.

[30] Weber, J.L., Martínez del Monte, D., Beerthuis, R., Dufour, J., Martos, C., de Jong, K.P. & de Jongh, P.E., *Conversion of Synthesis Gas to Aromatics at Medium Temperature with a Fischer Tropsch and ZSM-5 Dual Catalyst Bed*, Catal. Today, **369**, pp. 175-183, 2021. doi: 10.1016/j.cattod.2020.05.016.

[31] Yang, T., Cheng, L., Li, N. & Liu, D., *Effect of Metal Active Sites on the Product Distribution over Composite Catalysts in the Direct Synthesis of Aromatics from Syngas*, Ind. Eng. Chem. Res., **56**, pp. 11763-11772, 2017. doi: 10.1021/acs.iecr.7b03450.

[32] Zhou, W., Shi, S., Wang, Y., Zhang, L., Wang, Y., Zhang, G., Min, X., Cheng, K., Zhang, Q., Kang, J. & Wang Y., *Selective Conversion of Syngas to Aromatics over a Mo−ZrO2 /H-ZSM-5 Bifunctional Catalys,.* ChemCatChem, **11**, pp.1681-1688, 2019. doi:10.1002/cctc.201801937.

[33] Nezam, I., Zhou, W., Gusmão, G.S., Realff, M.J., Wang, Y., Medford, A.J. & Jones, C.W., *Direct Aromatization of CO2 via Combined CO2 hydrogenation and Zeolite-Based Acid Catalysis.* J. CO2 Util., **45**, 2021. doi: 10.1016/j.jcou.2020.101405.

[34] Xu, Y., Wang, T., Shi, C., Liu, B., Jiang, F. & Liu, X., *Experimental Investigation on the Two-Sided Effect of Acidic HZSM-5 on the Catalytic Performance of Composite Fe-Based Fischer-Tropsch Catalysts and HZSM-5 Zeolite in the Production of Aromatics from CO2/H2*, Ind. Eng. Chem. Res., **59**, 8581-8591, 2020. doi: 10.1021/acs.iecr.0c00992.

[35] Ramirez, A., Dutta Chowdhury, A., Dokania, A., Cnudde, P., Caglayan, M., Yarulina, I., Abou-Hamad, E., Gevers, L., Ould-Chikh, S., De Wispelaere, K., Speybroeck, V. & Gascon, J., *Effect of Zeolite Topology and Reactor Configuration on the Direct Conversion of CO_2 to Light Olefins and Aromatics,* ACS Catal. **9**, pp. 6320-6334, 2019. doi:10.1021/acscatal.9b01466.

[36] Boronat, M. & Corma, A. *Factors Controlling the Acidity of Zeolites*. Catal. Letters, **145**, pp. 162-172, 2015. doi:10.1007/s10562-014-1438-7.

[37] Gao, W., Guo, L., Wu, Q., Wang, C., Guo, X., He, Y., Zhang, P., Yang, G., Liu, G., Wu, J. & Tsubaki N.*, Capsule-like Zeolite Catalyst Fabricated by Solvent-Free Strategy for Para-Xylene Formation from CO2 Hydrogenation*, Appl. Catal. B Environ*,* **303**, 120906, 2022. doi: 10.1016/j.apcatb.2021.120906.

[38] Wang, T., Yang, C., Gao, P., Zhou, S., Li, S., Wang, H. & Sun, Y., *ZnZrOx Integrated with Chain-like Nanocrystal HZSM-5 as Efficient Catalysts for Aromatics Synthesis from CO_2 Hydrogenation*. Appl. Catal. B Environ*,* **286**, 119929, 2021. doi: 10.1016/j.apcatb.2021.119929.

[39] Yu, Y., Li, X., Su, L., Zhang, Y., Wang, Y. & Zhang, H., *The Role of Shape Selectivity in Catalytic Fast Pyrolysis of Lignin with Zeolite Catalysts.* Appl. Catal. A Gen*.,* **447-448**, pp. 115-123, 2012. doi: 10.1016/j.apcata.2012.09.012.

[40] Ding, K., Zhong, Z., Wang, J., Zhang, B., Addy, M. & Ruan, R., *Effects of Alkali-Treated Hierarchical HZSM-5 Zeolites on the Production of Aromatic Hydrocarbons from Catalytic Fast Pyrolysis of Waste Cardboard*, J. Anal. Appl. Pyrolysis, **125**, pp. 153-161, 2017. doi: 10.1016/j.jaap.2017.04.006.

[41] Qiao, K., Shi, X., Zhou, F., Chen, H., Fu, J., Ma, H. & Huang, H., *Catalytic Fast Pyrolysis of Cellulose in a Microreactor System Using Hierarchical Zsm-5 Zeolites Treated with Various Alkalis*, Appl. Catal. A Gen., **547**, pp. 274-282, 2017. doi: 10.1016/j.apcata.2017.07.034.

[42] Bi, Y., Lei, X., Xu, G., Chen, H. & Hu, J., *Catalytic Fast Pyrolysis of Kraft Lignin over Hierarchical HZSM-5 and Hβ Zeolites.* Catalysts, **8**, 2018. doi:10.3390/catal8020082.

[43] Che, Q., Yang, M., Wang, X., Yang, Q., Chen, Y., Chen, X., Chen, W., Hu, J., Zeng, K., Yang, H. & Chen H., *Preparation of Mesoporous ZSM-5 Catalysts Using Green Templates and Their Performance in Biomass Catalytic Pyrolysis*, Bioresour. Technol*.,* **289**, 121729, 2019. doi:10.1016/j.biortech.2019.121729.

[44] Cheng, Y.T., Wang, Z., Gilbert, C.J., Fan, W. & Huber, G.W., *Production of P-Xylene from Biomass by Catalytic Fast Pyrolysis Using ZSM-5 Catalysts with Reduced Pore Openings*, Angew. Chemie - Int. Ed*.,* **51**, pp.11097-11100, 2012. doi:10.1002/anie.201205230.

[45] Cheng, Y.T., Jae, J., Shi, J., Fan, W. & Huber, G.W., *Production of Renewable Aromatic Compounds by Catalytic Fast Pyrolysis of Lignocellulosic Biomass with Bifunctional Ga/ZSM-5 Catalysts,* Angew. Chemie - Int. Ed., **51**, pp. 1387-1390, 2012. doi:10.1002/anie.201107390.

[46] Che, Q., Yang, M., Wang, X., Yang, Q., Rose Williams, L., Yang, H., Zou, J., Zeng, K., Zhu, Y., Chen, Y. & Chen H., *Influence of Physicochemical Properties of Metal Modified ZSM-5 Catalyst on Benzene, Toluene and Xylene Production from Biomass Catalytic Pyrolysis*, Bioresour. Technol., **278**, pp. 248-254, 2019. doi: 10.1016/j.biortech.2019.01.081.

[47] Maghfirah, A., Ilmi, M.M., Fajar, A.T.N. & Kadja, G.T.M., *A Review on the Green Synthesis of Hierarchically Porous Zeolite*. *Mater. Today Chem.,* **17**, 2020. doi: 10.1016/j.mtchem.2020.100348.

[48] Kadja, G.T.M., Azhari, N.J., Mukti, R.R. & Khalil, M.*, A Mechanistic Investigation of Sustainable Solvent-Free, Seed-Directed Synthesis of ZSM-5 Zeolites in the Absence of an Organic Structure-Directing Agent*, ACS Omega, **6**, pp. 925-933, 2021. doi:10.1021/acsomega.0c05070.

[49] Kadja, G.T.M., Rukmana, M.D., Mukti, R.R., Mahyuddin, M.H., Saputro, A.G. & Wungu, T.D.K., *Solvent-Free, Small Organic Lactam-Assisted Synthesis of ZSM-5 Zeolites*, Mater. Lett*.,* **290**, 129501, 2021. doi: 10.1016/j.matlet.2021.129501.

[50] Xu, Y., Liu, J., Wang, J., Ma, G., Lin, J., Yang, Y., Li, Y., Zhang, C. & Ding, M., *Selective Conversion of Syngas to Aromatics over Fe3O4@MnO2 and Hollow HZSM-5 Bifunctional Catalysts.* ACS Catal*.,* **9**, pp. 5147-5156, 2019. doi:10.1021/acscatal.9b01045.

[51] Tian, G., Liu, X., Zhang, C., Fan, X., Xiong, H., Chen, X., Li, Z., Yan, B., Zhang, L., Wang, N., Peng H.-J. & Wei, F., *Accelerating Syngas-to-Aromatic Conversion via Spontaneously Monodispersed Fe in ZnCr2O4 Spinel*, Nat. Commun*.* **13**, 5567, 2022. doi:10.1038/s41467-022-33217-9.

[52] Ni, Y., Chen, Z., Fu, Y., Liu, Y., Zhu, W. & Liu, Z., *Selective Conversion of CO2 and H2 into Aromatics,* Nat. Commun*.,* **9**, pp. 1-7, 2018. doi:10.1038/s41467-018-05880-4.

[53] Li, Z., Qu, Y., Wang, J., Liu, H., Li, M., Miao, S. & Li, C., *Highly Selective Conversion of Carbon Dioxide to Aromatics over Tandem Catalysts*, Joule, **3**, pp. 570-583, 2019. doi: 10.1016/j.joule.2018.10.027.

[54] Zhou, C., Shi, J., Zhou, W., Cheng, K., Zhang, Q., Kang, J. & Wang, Y., *Highly Active ZnO – ZrO 2 Aerogels Integrated with H-ZSM-5 for Aromatics Synthesis from Carbon Dioxide,* ACS Catal., **10**, pp. 302–310, 2020. doi: 10.1021/acscatal.9b04309.

[55] Zhang, X., Zhang, A., Jiang, X., Zhu, J., Liu, J., Li, J., Zhang, G., Song, C. & Guo, X., *Utilization of CO2 for Aromatics Production over ZnO/ZrO2-ZSM-5 Tandem Catalyst*, J. CO2 Util*.,* **29**, pp. 140-145, 2019. doi: 10.1016/j.jcou.2018.12.002.

[56] Zhang, J., Zhang, M., Chen, S., Wang, X., Zhou, Z., Wu, Y., Zhang, T., Yang, G., Han, Y. & Tan, Y., *Hydrogenation of CO2 into Aromatics over a ZnCrO: X-Zeolite Composite Catalyst*, Chem. Commun*.,* **55**, pp. 973-976, 2019. doi:10.1039/c8cc09019j.

[57] Cui, X., Gao, P., Li, S., Yang, C., Liu, Z., Wang, H., Zhong, L. & Sun, Y., *Selective Production of Aromatics Directly from Carbon Dioxide Hydrogenation*, ACS Catal*.* **9**, pp. 3866-3876, 2019. doi:10.1021/acscatal.9b00640.

[58] Wang, Y., Kazumi, S., Gao, W., Gao, X., Li, H., Guo, X., Yoneyama, Y., Yang, G. & Tsubaki, N., *Direct Conversion of CO2 to Aromatics with High Yield via a Modified Fischer-Tropsch Synthesis Pathway,* Appl. Catal. B Environ*.,* **269**, 118792, 2020. doi: 10.1016/j.apcatb.2020.118792.

[59] Song, G., Li, M., Yan, P., Nawaz, M.A. & Liu, D., *High Conversion to Aromatics via CO2-FT over a CO-Reduced Cu-Fe2O3Catalyst Integrated with HZSM-5*, ACS Catal*.,* **10**, pp. 11268-11279, 2020. doi:10.1021/acscatal.0c02722.

[60] Wei, J., Yao, R., Ge, Q., Xu, D., Fang, C., Zhang, J., Xu, H. & Sun, J., *Precisely Regulating Brønsted Acid Sites to Promote the Synthesis of Light Aromatics via CO2 Hydrogenation*, Appl. Catal. B Environ*.,* **283**, 119648, 2021. doi: 10.1016/j.apcatb.2020.119648.

[61] Song, G., Li, M., Xu, L., Yang, X., Nawaz, M.A., Yuan, H., Zhang, Z., Xu, X. & Liu, D., *Tuning the Integration Proximity between Na Promoter and FeMnOxCoupled with Rationally Modified HZSM-5 to Promote Selective CO2 Hydrogenation to Aromatics,* Ind. Eng. Chem. Res., **61**, pp. 6820-6830, 2022. doi: 10.1021/acs.iecr.2c00647.

[62] Yang, X., Song, G., Li, M., Chen, C., Wang, Z., Yuan, H., Zhang, Z. & Liu, D., *Selective Production of Aromatics Directly from Carbon Dioxide Hydrogenation over nNa-Cu-Fe2O3/HZSM-5.* Ind. Eng. Chem. Res. 2022. doi: 10.1021/acs.iecr.2c00622.

[63] Chen, H., Cheng, H., Zhou, F., Chen, K., Qiao, K., Lu, X., Ouyang, P. & Fu, J., *Catalytic Fast Pyrolysis of Rice Straw to Aromatic Compounds over Hierarchical HZSM-5 Produced by Alkali Treatment and Metal-Modification*, J. Anal. Appl. Pyrolysis, **131**, pp. 76-84, 2018. doi: 10.1016/j.jaap.2018.02.009.

[64] Neumann, G.T. & Hicks, J.C., *Novel Hierarchical Cerium-Incorporated MFI Zeolite Catalysts for the Catalytic Fast Pyrolysis of Lignocellulosic Biomass*, ACS Catal., **2**, pp. 642-646, 2012. doi:10.1021/cs200648q.

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