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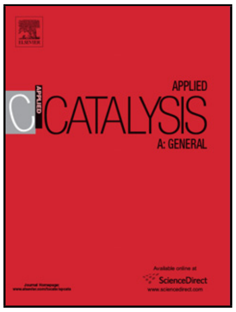

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Catalytic Fast Pyrolysis of Cellulose in a Microreactor System Using Hierarchical ZSM-5 Zeolites Treated with Various Alkalis

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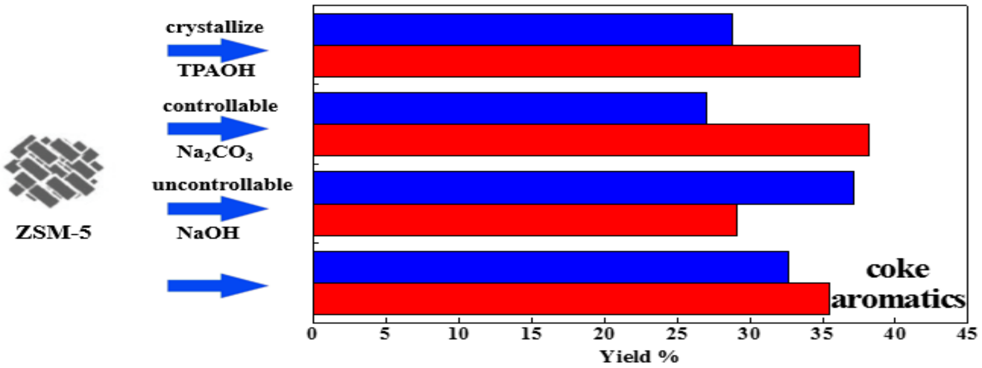
Graphical Abstract



Highlights:

1. The catalytic fast pyrolysis of cellulose to aromatics was studied over the hierarchical ZSM-5 catalysts prepared by three different alkalis.
2. Alkali treatment with Na_2CO_3 was highly controllable, resulting in an increase of the Brønsted acidity and the formation of hierarchical structures.
3. The highest aromatic and lowest coke yield were obtained over the hierarchical ZSM-5 treated by 0.6 M Na_2CO_3.
4. The hierarchical ZSM-5 treated with Na_2CO_3 increased the selectivity of benzene, toluene, and xylene.

ABSTRACT

Hierarchical ZSM-5 catalysts were prepared by desilication using NaOH, Na_2CO_3 and TPAOH with different concentrations under the same treatment conditions. Their structures and acidities were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), N_2 adsorption and desorption (N_2-BET) and ammonia temperature-programmed desorption (NH_3-TPD). The catalytic fast pyrolysis (CFP) of cellulose to produce aromatics over the hierarchical ZSM-5 catalysts prepared using different alkali treatments was investigated. The alkali treatment by Na_2CO_3 (0.4~0.8 M) was much milder than treatment by NaOH, which allowed the desilication process to be highly controllable, resulting in an increase of both the amount and strength of the strong acid sites, and the formation of hierarchical structures combining micro- and mesoporosity. The organic hydroxide TPAOH did not change the pore structure of ZSM-5, but it greatly increased the relative crystallinity. The CFP of cellulose with HZSM-5 produced 35.5 % liquid aromatic hydrocarbons and 32.7 % coke. The yield of aromatics increased after Na_2CO_3 treatment but decreased after NaOH treatment. In addition, the yield of coke showed the opposite trend. The highest aromatic yield (38.2 %) and lowest coke yield were obtained in the CFP of cellulose with the desilicated zeolite treated with 0.6 M Na_2CO_3. The increased acidity in hierarchical ZSM-5 treated with Na_2CO_3 increased the selectivity of highly valuable aromatics, such as benzene, toluene, and xylene, and decreased the selectivity of large aromatics. TPAOH-treated HZSM-5 showed a slightly increased yield of aromatics due to the repair effect of TPAOH, but this treatment did not form a mesoporous structure.

KEYWORD: Catalytic fast pyrolysis; aromatic; hierarchical HZSM-5; Brønsted acidity; microreactor system

1. Introduction

The demand for benzene, toluene, and xylene (BTX) in 2012 was up to 106.5 million tons, which evidenced the importance of aromatic hydrocarbons on the global market [1]. The production of more than 85 % of aromatics has traditionally depended on the catalytic reforming of petroleum resources. With the increasing scarcity of fossil resources and the steadily growing market demand for aromatics, traditional aromatic production technology is facing severe challenges. The development of renewable and environmentally friendly aromatic production technologies has gradually attracted wide attention. Lignocellulosic biomass is being studied worldwide as a sustainable energy source for biofuel production due to its low cost and large availability [2]. Catalytic fast pyrolysis (CFP) is a promising technology for the direct conversion of solid biomass into valuable aromatic compounds, such as BTX [3-4]. Biomass first thermally decomposes to form pyrolysis vapors, which then are converted into aromatics via a series of reactions, such as cracking, deoxygenation, oligomerization, and aromatization in the presence of a catalyst [5, 6]. The entire conversion process can occur in a single reactor with short reaction times, which is advantageous compared to gasification and fermentation technologies [5, 7].

Several catalysts have been investigated for their function in catalytic pyrolysis of biomass, including alkali and alkaline earth metals [8, 9], metal oxides [10, 11], and zeolites [12-14]. ZSM-5 zeolite has been shown to be the most active and selective catalyst to produce aromatics from various biomass feedstocks owing to its moderate pore structure, strong acidity and high hydrothermal stability. ZSM-5 has a three-dimensional microporous structure with average pore dimensions of 5.5-5.6 Å, which are similar to the kinetic diameters of benzene, toluene, p-xylene, indene, furfural and 2-methylfuran [14]. However, ZSM-5 is limited by low reactant and product mass-transfer rates for large molecules, such as most phenolic molecules and anhydrosugars produced during pyrolysis. The large molecules are limited by diffusion into the micropores, which cause coke formation at continuous elevated temperatures [14, 15]. Mesoporous zeolites with large pores, which provide a good spatial structure for the reaction of large molecules and improve the diffusion rates of reactants and products to reduce coke formation, have good deoxygenation performances, but aromatic production in the mesoporous zeolites is limited by their low acidity and hydrothermal stability.

The strategies for improving the diffusion and accessibility limitations of large molecules formed are to introduce mesopores connected to micropores [16-18] and use layered and pillared ZSM-5 [19, 20]. The creation of mesopores connected to micropores could have a positive effect by providing more access to available catalytically active sites to improve the conversion of large molecules, preserve the aromatization capacity through the microporosity of ZSM-5 [14] and decrease carbon deposition [21]. Kelkar et al. [22] investigated the CFP of poplar over MSU-MFI catalysts prepared using different silane-modified polymers as mesopore-generating agents. The results showed that the MSU-MFI catalysts produced more C_8 and C_9 monoaromatics and that the yield of aromatics for MSU-MFI prepared with the smaller D400 polymer pyrogen was comparable with that of conventional ZSM-5. Park et al. [23] studied the catalytic upgrading of pyrolytic vapors derived from radiata pine sawdust with meso-MFI zeolite synthesized using an amphiphilic organosilane. The mesoporous MFI zeolite exhibited the best activity in deoxygenation and aromatization. In addition, the mesoporous MFI zeolite showed high selectivity for highly valuable BTX aromatics. Li et al. [24] investigated the effects of mesoporous ZSM-5 prepared by desilication with NaOH solutions on the CFP of beech wood. The results showed that the desilicated ZSM-5 produced higher aromatic yields and showed lower coke yield than the parent microporous ZSM-5. Alkali treatment of conventional microporous ZSM-5 is a simple and effective method to create intracrystalline mesopores in ZSM-5 [25-27]. In addition, desilication treatment can generate more open mesopores accessible for large molecules compared with templating methods [28].

In this work, a series of mesoporous ZSM-5 samples were prepared by desilication of conventional microporous ZSM-5 with three kinds of alkalis (NaOH, Na_2CO_3 and TPAOH) of varying concentrations under the same treatment conditions. The effects of the porosity, morphology, acidity and catalytic performance on the CFP of cellulose for the mesoporous and microporous zeolites were studied.

2. Experimental

2.1. Feedstocks and catalysts

The feedstock used in this study was microcrystalline cellulose powder, which was purchased from Sigma Aldrich. The elemental composition of the microcrystalline powder was 41.44 wt% carbon, 6.57 wt% hydrogen, and 51.99 wt% oxygen (by difference), as measured by an elemental analyzer (Vario Micro, Elementar, Germany).

HZSM-5 (SiO_2/Al_2O_3=38) was purchased from the Catalyst Plant of Nankai

University and used as a raw material (designated as HZ-Parent). Mesoporous ZSM-5 samples were obtained from the following procedure: first, 1 g of ZSM-5 and 50 mL of NaOH or Na_2CO_3 with different concentration (0.2-0.8 M) were mixed at 80 °C for 2 h. Then, the slurry was rapidly cooled to room temperature, filtered, washed with deionized water, and dried at 110 °C overnight. Finally, the alkali-treated zeolites were ion-exchanged with 1 M NH_4Cl at 80 °C for three times. After each exchange, the samples were filtered, washed, dried, and calcined at 550 °C for 5 h. The alkali treatment with tetrapropylammonium hydroxide (TPAOH) followed the same steps as above but without the ion-exchange process. For the following sections, alkali-treated zeolites are named as HZ-xM (A) where x represents the concentration of the alkali solution, and A represents the alkali used.

2.2. Characterization of the catalysts

Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 diffractometer with Cu-Kα radiation at 40 kV and 40 mA. The diffractions were carried out in the 2θ range of 5°-50° at a rate of 4°/min. N_2 adsorption and desorption isotherms were measured on a Micromeritics 3Flex adsorption instrument. The samples were degassed for 12 h under N_2 at 300 °C prior to the measurements. The micropore surface area and volume were determined by t-plot method, and the specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method. The total pore volume was derived from the amount of N_2 adsorbed at $p/p_0=0.99$ and the mesopore volume was calculated by subtracting the micropore volume. The size distributions of mesopore were obtained from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) method.

SEM images were obtained using a cold-field emission scanning electron microscope (FE-SEM, S-4800, Hitachi). Ammonia temperature programmed desorption (NH_3-TPD) was measured on a connected thermal conductivity detector (TCD). Typically, 50 mg of the zeolite was pretreated at 120 °C in He (20 mL/min) for 2 h and then cooled to 80 °C before ammonia adsorption for 40 min. Ammonia desorption measurements were achieved in the temperature range of 80 °C-700 °C at a ramping rate of 10 °C /min.

2.3. Catalytic fast pyrolysis of cellulose

The CFP experiments were conducted in a Tandem μ-reactor system (Rx-3050 TR, Frontier Laboratories, Japan) coupled directly to a GC/MS for identification and quantification of the pyrolysis products. The furnace consisted of two reactors (upper and lower), both of which could be individually temperature-controlled from 40 °C to 900 °C. The interface between the furnaces and the GC could be heated to 100-400 °C, which was operated at 300 °C to minimize the condensation of the pyrolysis products.

For a typical test of CFP, approximately 4 mg of a mixture with a catalyst-to-cellulose weight ratio of 20:1 was used. Helium was used as the pyrolysis gas and the carrier gas. The pyrolysis vapor was swept into a gas chromatograph (Agilent 7890 B) equipped with a three-way splitter coupled to three detectors: a mass spectrometer (5977A MSD), a flame-ionization detector (FID), and a thermal-conductivity detector (TCD). A liquid nitrogen bath (MicroJet Cryo-Trap, MJT-1030E) was used to focus the pyrolysis vapors of the volatile components, such as CO, CO_2 and olefin hydrocarbons. A good separation effect for the vapors was achieved by rapidly cooling and concentrating the vapors using liquid nitrogen at the head of the column to increase the peak resolution. The condensable pyrolysis products were separated with an Ultra alloy-5 capillary column (30 m × 0.250 mm and film thickness of 2 μm). The products were quantified by injecting calibration standards with known concentrations of the target species into the furnace at the same experimental conditions. The yields of CO and CO_2 were then quantified by TCD with external standard gas mixtures, and the other products were quantified by FID with external standard solutions. Each final product distribution was reported as the molar carbon yield, defined as the molar ratio of carbon in a specific product to the carbon in cellulose. The aromatic selectivity was defined as the ratio of the moles of carbon in a specific aromatic hydrocarbon to the total moles of carbon in the aromatic products. The unaccounted contents included small amounts of alkanes, large molecular weight compounds unidentified by GC and unrecovered coke deposited on the walls of the sample cups. All measurements were repeated three times under the same conditions to check the reproducibility of the data, and average values were calculated for each test.

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of the HZ-xM (NaOH), HZ-xM (Na_2CO_3) and HZ-xM (TPAOH) samples are shown in Fig. 1. For the Na_2CO_3- and TPAOH-treated samples, all the hierarchical samples showed the same characteristic peaks in the ranges of 7° to 9° and 22.5° to 25.0° as the original sample. This meant that the morphology of the ZSM-5 sample did not change after the desilication [29]. The intrinsic lattice structure of the original sample was preserved. However, the peak intensities and the relative crystallinity of HZ-xM (NaOH) decreased to some extent for the hierarchical samples treated with much higher alkali concentrations (0.4 M-0.8 M). This was due to the collapse of the zeolite framework as silica was removed. The relative crystallinities of the zeolite samples were calculated using the peak area of the five characteristic diffraction peaks, and the relative crystallinity of HZ-Parent was denoted as 100 %. With an increase of the NaOH concentration, the relative crystallinity of the zeolite decreased rapidly. The amorphous materials were removed in the process of Na_2CO_3 treatment, leading to an increase of the relative crystallinity of the zeolites. After treatment with TPAOH, the relative crystallinity of the zeolite greatly increased, which was mainly because the TPAOH solution acted as a template, leading to the secondary crystallization of amorphous and non-framework materials and exhibiting a protective effect on the skeleton of the zeolite [30].

The N_2 adsorption-desorption isotherms and pore-size distributions, measured by the BJH method, of the samples are illustrated in Fig. 2. The original ZSM-5 sample presented a type I isotherm with a plateau starting at a very low relative pressure, which was characteristic of the microporous zeolite structure without any mesopores. However, a type IV isotherm with a remarkable hysteresis loop, a known fingerprint of a hierarchical porous system [31], appeared after NaOH or Na_2CO_3 treatment (see Fig. 2 (a) and (b)), indicating the formation of mesopores and even macropores. The isotherms of the hierarchical ZSM-5 samples presented a rapid increase of adsorption. This suggested that the internal pores of the ZSM-5 samples were destroyed and that capillary condensation occurred on the surfaces and intracrystalline portions of the zeolites [32]. The mesopore sizes for the obtained HZ-0.2M (Na_2CO_3) samples were centered uniformly at approximately 10 nm, indicating that larger mesopores were formed and that the framework collapsed and micropores were destroyed [32]. Thus, a two-gradient porous structure was formed. The HZ-0.2M (NaOH) samples showed complex mesopore distribution due to the collapse of the zeolite framework treated with NaOH. In addition, mesopores were not found in the HZ-0.2M (TPAOH) sample, indicating that the weak base TPAOH did not influence ZSM-5 to form a hierarchical structure.

The textural properties of all supports from the N_2-BET measurements are summarized in Table 1. For the hierarchical samples treated with NaOH, the mesopore surface area and volume increased with an increase of the alkali concentration because of the development of the mesopores [29, 33] and then decreased when the alkali concentration increased higher than 0.4 M. The micropore surface area and volume decreased at these high alkali concentrations due to the alkali treatment consuming the microporous. For the HZ-xM (TPAOH) samples, the surface areas and volumes for the micropores and mesopores showed only minor changes as the TPAOH concentration increased, which further proved that TPAOH had a negligible effect on the desilication of ZSM-5. The total and micropore surface area and volume of HZ-xM (Na_2CO_3) consistently decreased, and the mesopore surface area and volume increased as the Na_2CO_3 concentration increased due to the development of the mesopores [29, 33]. It was found that the NaOH treatment was severe and hard to control, while the TPAOH treatment did not have a significant effect on the desilication of ZSM-5 because the alkalinity of TPAOH is too weak [27]. Na_2CO_3 was a suitable desilication medium to treat ZSM-5 to develop a hierarchical structure, showing a highly controllable demetallation process. The alkali pretreatment reaction involved alkali modification with a critical range of alkali concentrations and alkali dissolution with a high alkali concentration [32].

The morphologies of HZ-Parent and the alkali-treated samples studied by SEM are shown in Fig. 3. For the HZ-0.6M (NaOH) and HZ-0.8M (NaOH) samples, the typical ZSM-5 morphology was destroyed by the NaOH treatment. However, the morphology of ZSM-5 was maintained after Na_2CO_3 and TPAOH treatment. For the HZ-0.6M (Na_2CO_3) and HZ-0.8M (Na_2CO_3) samples with smaller crystal sizes, the surfaces of the crystals eroded, showing many pores and amorphous materials. The edges of the ZSM-5 particles appeared melted and became very irregular. The TPAOH-treated samples showed uniform crystalline morphologies with smooth crystalline surfaces, which indicated that TPAOH helps repair the crystal structure of ZSM-5 to some extent. This was corroborated with the XRD and N_2 adsorption and desorption results.

The acidity of the hierarchical ZSM-5 samples was studied by NH_3-TPD. As shown in Fig. 4, HZ-Parent exhibited two peaks at approximately 200 °C and 450 °C, which represented weak and strong acidity, respectively [34]. The first peak is attributed to the desorption of ammonia from the Lewis acid sites, and the second desorption peak, present at a higher temperature, is related to the desorption of ammonia from the Brønsted acid sites [35]. For the HZ-xM (NaOH) samples, the weak acid peak decreased to a lower temperature, indicating a lower acid strength. The Brønsted acidity decreased dramatically, and the Lewis acidity increased after desilication. This suggested that the alkaline treatment converted some Brønsted acid sites into Lewis acid sites due to the removal of silica [36, 37]. Thus, the Brønsted acid sites of the hierarchical samples treated with NaOH almost disappeared, as shown in Fig. 4 (a). Although the NaOH treatment removed Si, resulting in a decrease of the Si/Al ratio, the acid site density decreased due to the collapse of the zeolite framework, the presence of Al atoms in non-accessible positions and/or the presence of non-framework octahedral Al on the pore walls [38]. The number of acid sites in the hierarchical HZ-xM (Na_2CO_3) samples was slightly higher than that of the parent sample, and the number of Brønsted acid sites and Lewis acid sites were preserved. This was attributed to the higher Al contents in the alkali-treated zeolites, which gave higher densities of acid sites. In addition, the formation of mesopores upon the consumption of micropores might contribute to a decrease of the Brønsted acid sites [34]. In addition, for the HZ-xM (TPAOH) samples, the Brønsted acidity and Lewis acidity slightly decreased compared with HZ-Parent.

3.2. Effects of desilication of ZSM-5 on the CFP of biomass

The pyrolysis of cellulose without a zeolite catalyst was conducted. The products were all oxygenated products without any aromatics. In addition, the CFP of cellulose with HZSM-5 produced mainly liquid aromatic hydrocarbons (35.5 %), gaseous CO (21.8 %) and coke (32.7 %). In the presence of ZSM-5, the oxygenates formed from the initial thermal decomposition of biomass are converted into aromatics via a series of zeolite-catalyzed reactions at the Brønsted acid sites on both the external surface and internal surface of ZSM-5 [24, 39]. Compared with HZ-Parent, the yields of aromatics and CO_2 decreased over desilicated zeolite HZ-xM (NaOH) as the NaOH treatment concentration increased, while the yield of coke increased. The yields of aromatics decreased to 2.8 % and 1.6 % for HZ-0.6M (NaOH) and HZ-0.8M (NaOH), respectively, while the yields of coke increased to 74.3 % and 80.1 %. In this work, the hierarchical ZSM-5 samples prepared by NaOH were measured under the following treatment conditions: 1: 50 mL of microporous ZSM-5 (g)/NaOH solution (ml), 0.2~0.8 M of NaOH concentration, and 80 °C of treating temperature for 2 h. Chen et al. [36] reported that the removal of Si from the framework of ZSM-5 without complete destruction of the crystal lattice occurred at a low alkaline concentration, but the structure was destroyed at a high alkaline concentration. Therefore, the treatment condition in this work was much stronger for NaOH treating, resulting in destroying the structure of the zeolite, and lowering the relative crystallinity, mesoporosity and acidity of the ZSM-5. The NH_3-TPD results showed that the Brønsted acid sites in HZSM-5 decreased significantly for HZ-0.2M (NaOH) and disappeared when the NaOH concentration was above 0.2 M. The XRD, TEM and N_2 adsorption and desorption results showed that the zeolite framework collapsed as silica was removed. The surface area and volume decreased, indicating that the pore structure collapsed. Huber et al. [3] reported that silicalite, without Brønsted acid sites, and silica-alumina, with Brønsted acid sites but without pore structure, produced primarily coke. HZSM-5 with both Brønsted acid sites and pore structure produced primarily aromatics. Thus, the Brønsted acid sites and pore structure are both needed for aromatic production. The ZSM-5 samples after NaOH treatment, particularly when the NaOH concentration was higher than 0.4 M, showed nearly zero Brønsted acid sites, which are the major catalytic sites for converting biomass-derived oxygenates into aromatics. Additionally, the pore structure, where the aromatization reaction occurs, collapsed without the morphology of ZSM-5 [24]. Thus, using these samples as catalysts did not convert the cellulose to aromatics because the zeolite-catalyzed reactions at the Brønsted acid sites did not occurred.

The aromatic distributions for the catalytic fast pyrolysis of cellulose with the various HZ-xM (NaOH) catalysts is shown in Fig. 6. For the HZ-Parent catalyst, large aromatics (C_{10-15} aromatics) were the major fraction of aromatic production, and the selectivity was 43.4 %. The selectivity of BXT reached 51.4 % (14.8 % benzene, 24.2 % toluene and 12.4 % xylene). For the HZ-xM (NaOH) catalysts, the selectivity of C_{10-15} aromatics decreased as the NaOH concentration increased due to the lack of Brønsted acid sites and lack of pore structure to convert cellulose to aromatics. Although the selectivity of toluene and xylene increased as the NaOH concentration increased, the yield of total aromatics was low (2.8 % and 1.6 % for HZ-0.6M (NaOH) and HZ-0.8M (NaOH), respectively).

As shown in Fig. 7, the desilicated zeolites treated with Na_2CO_3 converted the cellulose-derived oxygenates into aromatics effectively. The yield of aromatics increased after the Na_2CO_3 treatment and consistently increased as the Na_2CO_3 concentration increased (a small decreased was observed for HZ-0.8M (Na_2CO_3)). The yield of aromatics increased from 35.5 % for HZ-Parent to 37.8 %, 38.2 % and 37.1 % for HZ-0.4M (Na_2CO_3), HZ-0.6M (Na_2CO_3) and HZ-0.8M (Na_2CO_3), respectively. In contrast, the coke yield showed the opposite trend. It decreased to 27.0 % for HZ-0.6M (Na_2CO_3) and slightly increased to 28.9 % for HZ-0.8M (Na_2CO_3). Thus, the Na_2CO_3 treatment of ZSM-5 enhanced the yield of aromatics and inhibited coke formation under the same condition compared with NaOH treatment in this work. As shown in Table 2 and Fig. 2, the total surface areas of HZ-xM (Na_2CO_3) samples increased in the order of HZ-0.2M (326 m^2/g) ≈ HZ-0.4M (326 m^2/g) < HZ-0.8M (331 m^2/g) < HZ-0.6M (336 m^2/g), and the yields of aromatics also increased in the order of HZ-0.2M (36.9%) < HZ-0.4M (37.8%) ≈ HZ-0.8M (37.1%) < HZ-0.6M (38.2%). The mesopore surface area and volume increased as the Na_2CO_3 concentration increased due to the development of the mesopores as shown in Table 2. This increased surface area offered sufficient catalytic sites for effectively converting oxygenates into aromatics. The size distributions of mesopore in hierarchical ZSM-5 treated by Na_2CO_3 were very uniform which centered at 10 nm. The size distribution of mesopore did not change but the mesopore surface area increased, meaning that the amount of mesopores increased as the Na_2CO_3 concentration and the Na_2CO_3 treatment was very mild and controllable, which did not cause the collapse of framework. Therefore, the yield of aromatics increased due to the increased amount of catalytic sites and improved mass transfer of reactants. However, the surface areas of HZ-xM (NaOH) samples increased first but decreased sharply as the concentration of NaOH further increased, and the surface areas of HZ-xM (TPAOH) samples did not change much as the concentration of TPAOH increased from 0.2 to 0.8 M. The size distributions of mesopore for HZ-xM (NaOH) samples increased from 7 nm for HZ-0.2M (NaOH) to 20 nm for HZ-0.4M (NaOH), and then the framework collapsed when the NaOH concentration was higher than 0.4 M. It can be found that the formation of mesopores in ZSM-5 benefited the yield of aromatics from CFP of cellulose, but the HZ-0.2M (NaOH) and HZ-0.4M (NaOH) also exhibited a desired size distribution of mesopore which gave lower yields of aromatics than that obtained over the HZ-Parent. Thus, the acidity of the hierarchical ZSM-5 influenced the catalytic conversion simultaneously. The NH_3-TPD results showed that the acidity, particularly the Brønsted acidity, increased after the Na_2CO_3 treatment to provide catalytic sites for converting biomass-derived oxygenates into final aromatics. The Na_2CO_3 treatment did not result in the collapse of the pore structure, and the morphology of ZSM-5 was preserved after desilication. But the Brønsted acidity decreased sharply after the NaOH treating. Compared with HZ-Parent, the desilicated HZ-xM (Na_2CO_3) zeolites containing considerable mesopores increased the numbers of accessible Brønsted sites on their external surfaces for cracking bulky molecules. As a result, the acid sites in the desilicated zeolites were more efficiently used in the conversion of cellulose-derived oxygenates, particularly bulky oxygenates, than HZ-Parent, resulting in an increase of the aromatic yield. The mesopores also inhibited coke formation from secondary reactions, such as polymerization of monoaromatics inside the micropores [40, 41]. Perez-Ramirez et al. [42] reported that the HZSM-5 produced mainly the internal coke and hierarchical ZSM-5 produced mainly the external coke during the conversions of methanol to hydrocarbons. From the distribution results of the aromatics, although the yield of aromatics increased, the selectivity of large aromatics (C_{10-15} aromatics) decreased, and the toluene and xylene fractions increased as the concentration increased. Thus, the acidity in ZSM-5 enhanced the production of aromatics and improved the selectivity of large aromatics. The yield and selectivity of BTX both increased after the Na_2CO_3 treatment.

The results from the HZ-xM (NaOH) and HZ-xM (Na_2CO_3) catalysts indicated that the severity of the desilication must be controlled carefully, as a decrease of the severity of the desilication conditions had a beneficial effect. To evaluate the effect of the desilication conditions on the zeolite-catalyzed CFP, another weaker base, TPAOH, was used as desilication medium to treat ZSM-5. The CFP results are shown in Fig. 9 and Fig. 10. The yield and distribution of aromatics did not change after the alkali treatment with TPAOH because the ZSM-5 pore structure did not significantly change compared with that of HZ-Parent, as shown in Fig. 2 (c) and Table 2; however, the treatment decreased the acidity, particularly the Brønsted acidity.

4. Conclusions

Three kinds of alkalis, NaOH, Na_2CO_3 and TPAOH, were used for the desilication of

ZSM-5 to obtain hierarchical ZSM-5 catalysts. A comparison of the catalytic fast pyrolysis of cellulose to produce aromatics using the ZSM-5 catalysts prepared with different alkali treatments was investigated. Alkali treatment with Na_2CO_3 was much milder than treatment with NaOH, which allowed the desilication process to be highly controllable, resulting in an increase of both the amount and strength of the strong acid sites, and the formation of hierarchical structures combining micro- and mesoporosity. Thus, the yield of aromatics increased to 38.2 %, and the yield of coke decreased to 27.0 % compared with the original HZSM-5 (35.5 % aromatic yield and 32.7 % coke yield). The organic hydroxide TPAOH did not change the pore structure of ZSM-5 and decreased the Brønsted acidity. Thus, TPAOH treatment did not influence the catalytic fast pyrolysis of cellulose. Increasing the acidity in hierarchical ZSM-5 increased the selectivity of BTX but decreased the selectivity of C_{10-15} aromatics.

Acknowledgments

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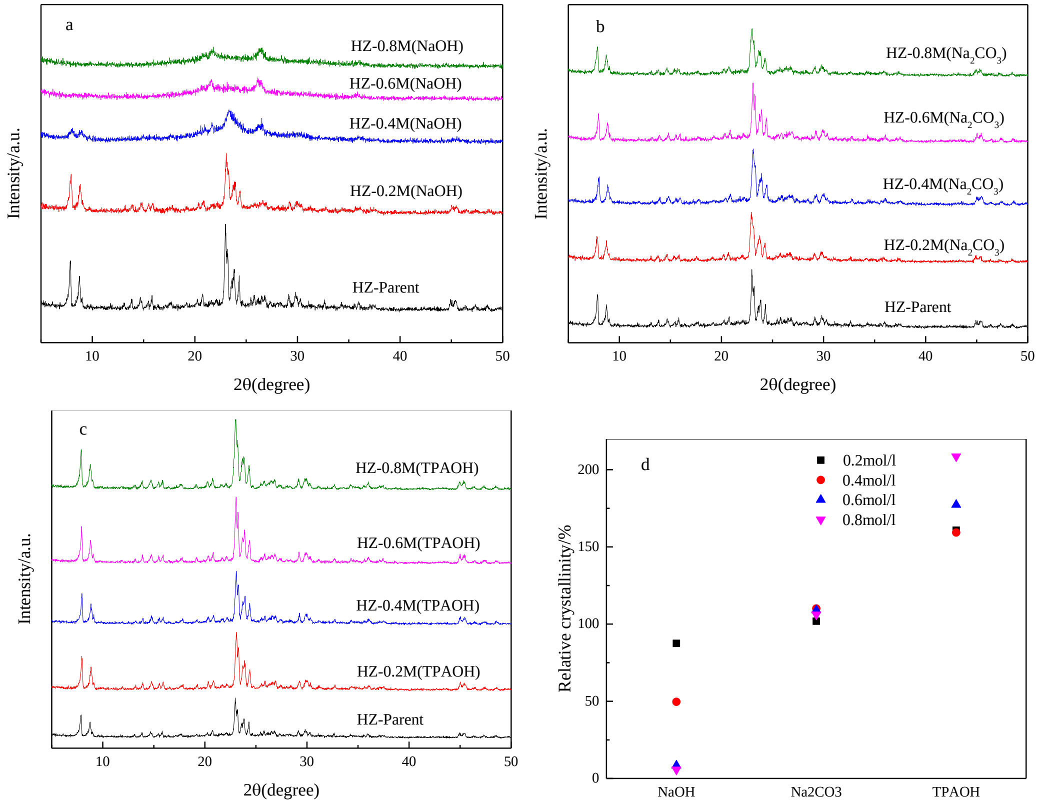


Fig. 1 XRD patterns of the hierarchical ZSM-5 samples prepared using different alkalis: (a) NaOH; (b) Na_2CO_3; (c) TPAOH.

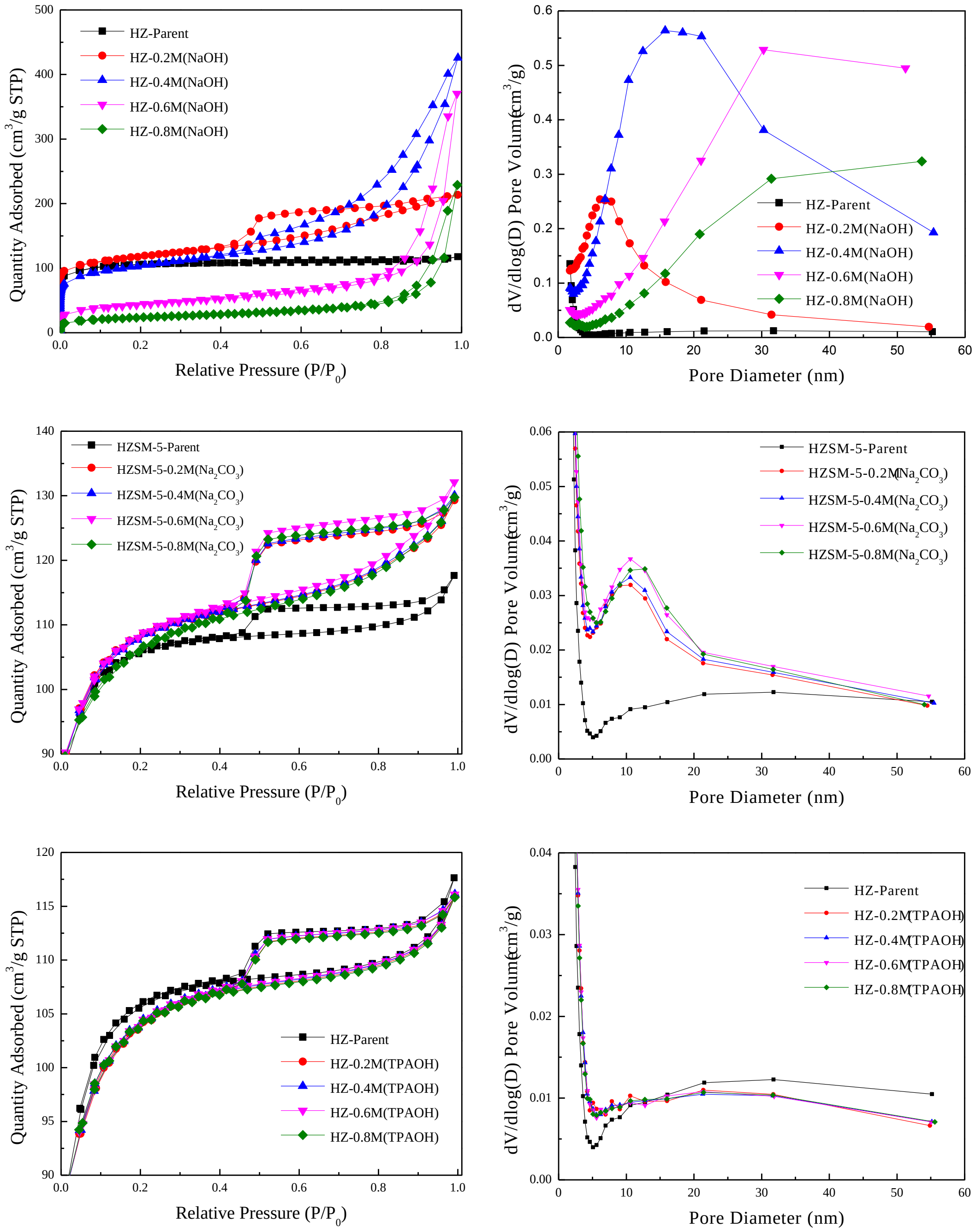


Fig. 2 N_2 adsorption-desorption isotherms and pore-size distributions of the hierarchical ZSM-5 samples prepared using different alkalis.

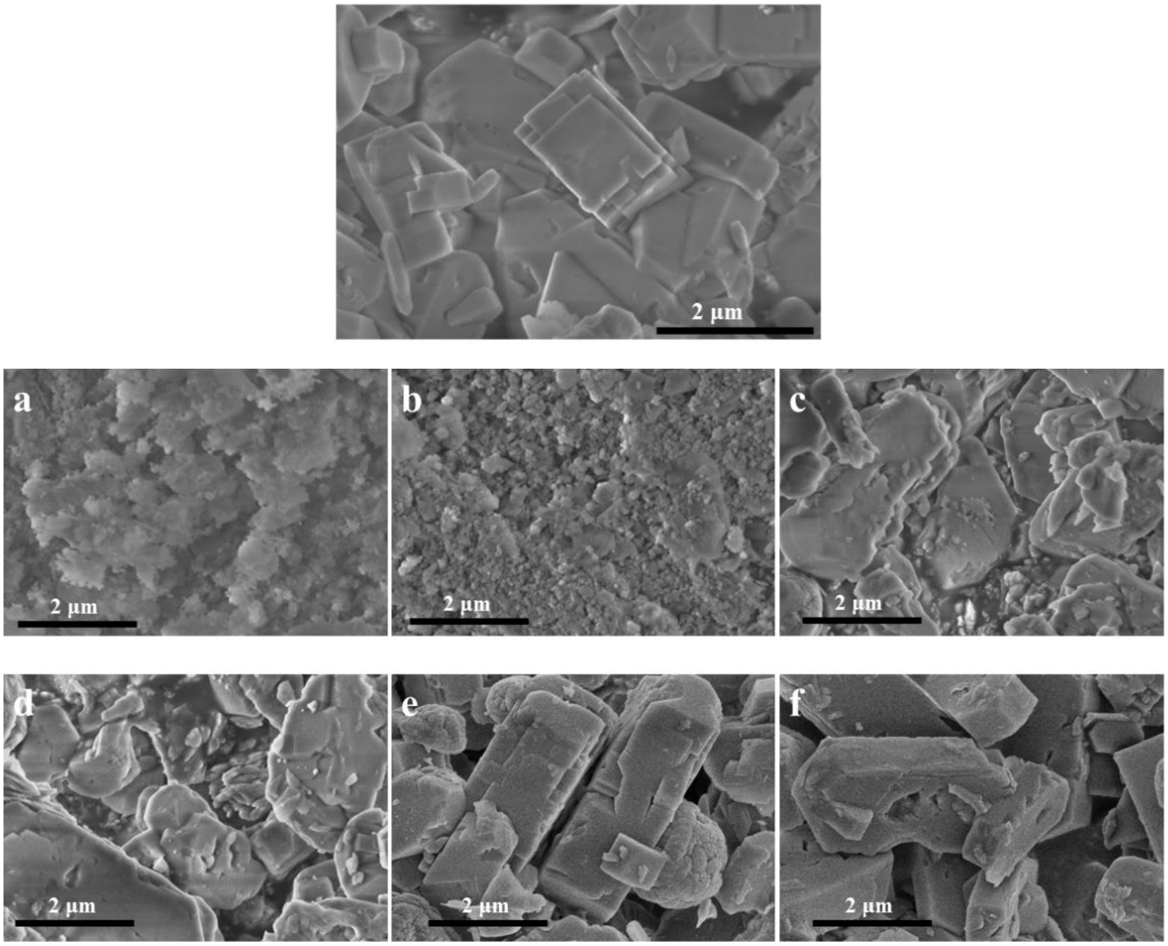
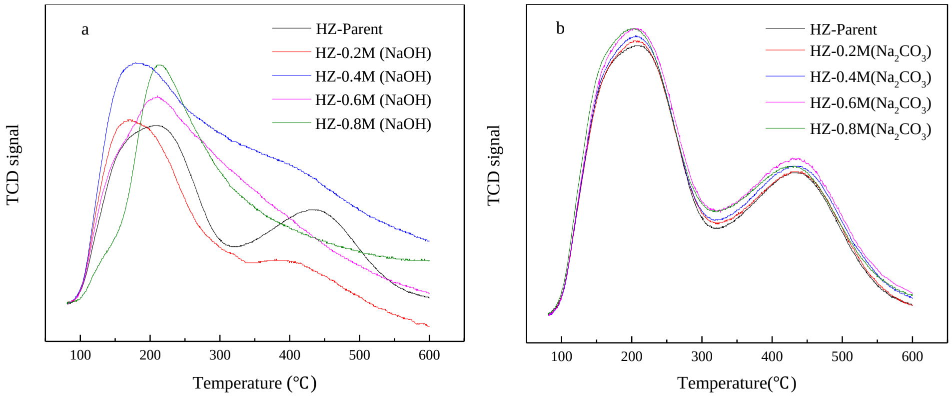


Fig. 3 SEM images of HZ-Parent, (a) HZ-0.6M (NaOH), (b) HZ-0.8M (NaOH), (c) HZ-0.6M (Na_2CO_3), (d) HZ-0.8M (Na_2CO_3), (e) HZ-0.6M (TPAOH), and (f) HZ-0.8M (TPAOH)



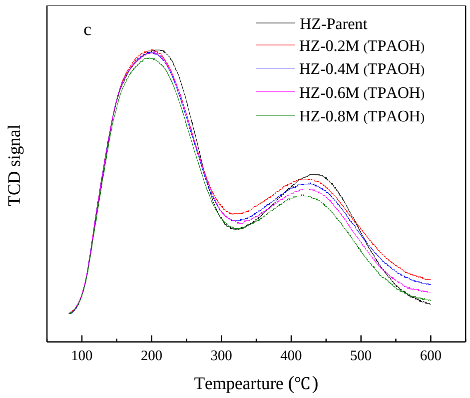


Fig. 4 NH_3-TPD patterns of the hierarchical ZSM-5 samples prepared with different alkalis: (a) NaOH; (b) Na_2CO_3; (c) TPAOH.

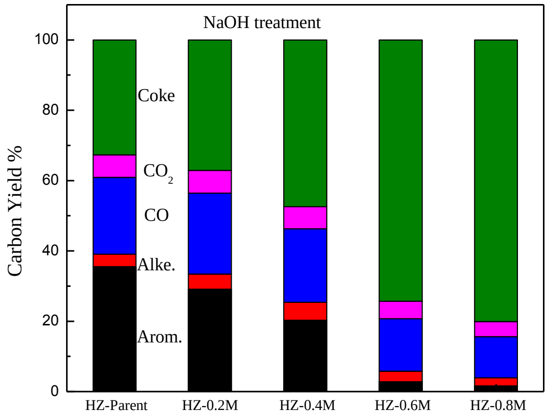


Fig. 5 Catalytic fast pyrolysis of cellulose with various HZ-xM (NaOH) catalysts.

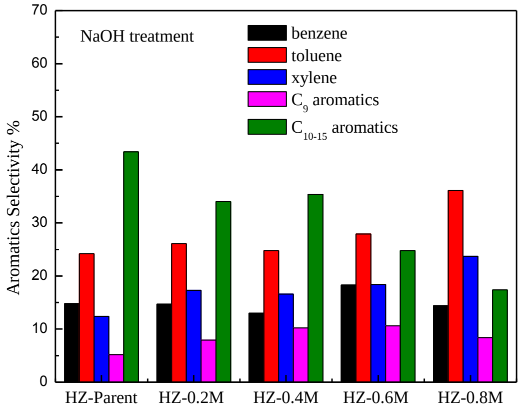


Fig. 6 Aromatic selectivity in the catalytic fast pyrolysis of cellulose with various HZ-xM

(NaOH) catalysts.

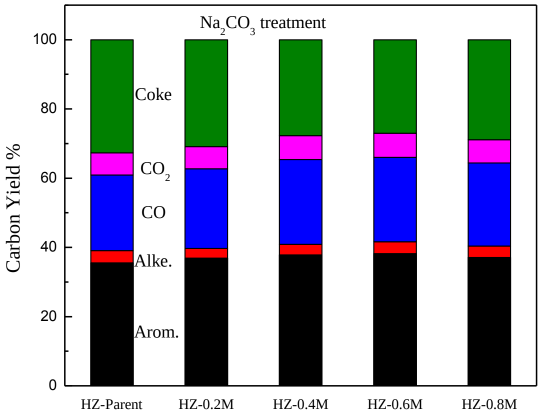


Fig. 7 Catalytic fast pyrolysis of cellulose with various HZ-xM (Na_2CO_3) catalysts.

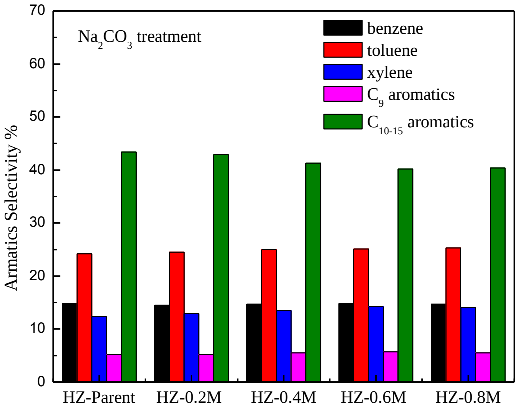


Fig. 8 Aromatic selectivity in the catalytic fast pyrolysis of cellulose with various HZ-xM (Na_2CO_3) catalysts.

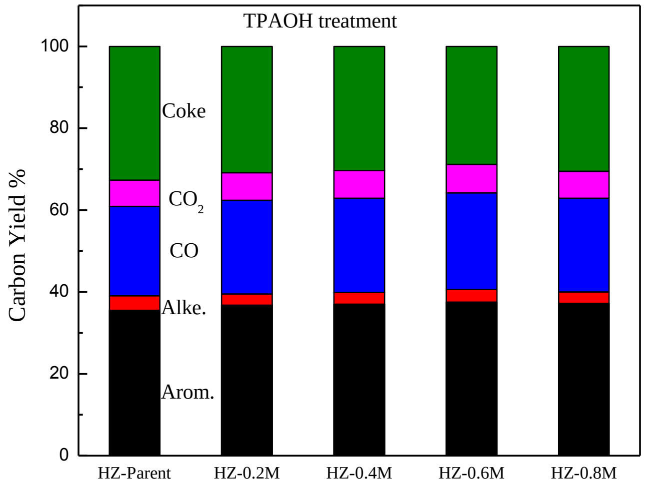


Fig. 9 Catalytic fast pyrolysis of cellulose with various HZ-xM (TPAOH) catalysts.

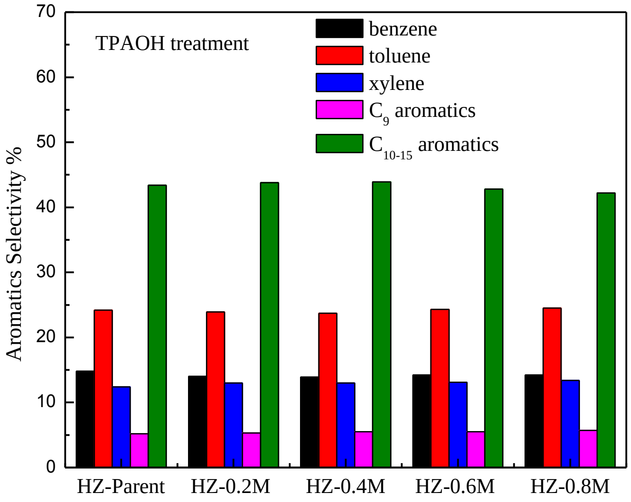


Fig. 10 Aromatic selectivity in the catalytic fast pyrolysis of cellulose with various HZ-xM (TPAOH) catalysts.

Table. 1 Physical properties of the hierarchical ZSM-5 samples prepared using different alkalis.

Samples	S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{ext} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
HZ-Parent	326	255	70	0.182	0.132	0.050
HZ-0.2M (NaOH)	379	206	173	0.331	0.107	0.224
HZ-0.4M (NaOH)	333	135	198	0.656	0.073	0.583
HZ-0.6M (NaOH)	147	34	113	0.574	0.017	0.557
HZ-0.8M (NaOH)	80	17	63	0.354	0.009	0.345
HZ-0.2M (Na_2CO_3)	326	236	90	0.200	0.127	0.073
HZ-0.4M (Na_2CO_3)	326	232	94	0.201	0.125	0.076
HZ-0.6M (Na_2CO_3)	336	239	97	0.204	0.124	0.080
HZ-0.8M (Na_2CO_3)	331	225	106	0.201	0.117	0.084
HZ-0.2M (TPAOH)	322	240	82	0.179	0.124	0.055
HZ-0.4M (TPAOH)	322	238	84	0.180	0.123	0.057
HZ-0.6M (TPAOH)	321	237	84	0.180	0.123	0.057
HZ-0.8M (TPAOH)	321	240	81	0.179	0.124	0.055