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In order to promote hydrocarbon production and catalyst stability in catalytic fast pyrolysis (CFP) of biomass, HZSM-5 catalysts were treated by alkali solution to introduce mesopores into microporous system. Parent and hierarchical catalysts were tested in the catalytic conversion of furan as an important intermediate from biomass fast pyrolysis (BFP). Controlled desilication with mole concentration of NaOH of 0.3 M (HZSM-5-0.3M) resulted in sheet-like mesopores on the external sphere, enhancing mass transferring in catalyst, and it specifically promoted the carbon yield of hydrocarbons by 21.6%. Though coke content on HZSM-5-0.3M catalysts increased gradually by 11.6%, its tolerance toward deactivation by coke deposition was improved. Cyclic tests of catalysis-regeneration process over hierarchical HZSM-5-0.3M with 20 cycles revealed that it can withstand long-running with a stable yield of hydrocarbons being achieved. Thus, hierarchical HZSM-5 is a suitable catalyst for CFP of biomass and its derivates to hydrocarbons for its simple synthetic process.

# Introduction

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Catalyst deactivation is the biggest barrier in CFP of biomass for hydrocarbons that can be great sources of most liquid and gaseous fuels.<sup>1-3</sup> A high carbon yield (23.7%) of olefins and aromatic hydrocarbons from pine wood catalytic pyrolysis in a fluidized bed reactor has been achieved, but actually it is much lower than the theoretical yield (more than 60%), which is mainly due to catalyst deactivation caused by coke deposition.<sup>4</sup> Among all studied catalysts, ZSM-5, a three-dimensional micropore system that consists of two perpendicularly intersecting channels of 10membered rings, i.e., straight channels (5.5 Å×5.1 Å) and zigzag channels (5.6 Å×5.3 Å), is a well known catalyst in CPF because it has moderate pore openings, internal pore space (i.e., pore intersection, d=6.36 Å) and steric hindrance, all that favors aromatic production.<sup>5, 6</sup> In biomass zeolite-catalyzed hydrocarbon formation reactions, loss of ZSM-5 catalyst activity is mainly due to coke formation. Some high molecular weight oxygenates larger than pore opening of ZSM-5 (like levoglucosan) cannot enter the pores of microporous catalysts, and will polymerize and form coke on the surfaces. Some small-molecule oxygenates with high activity (like furans) can also polymerize and form coke in the presence of external acid sites of the catalyst.<sup>7, 8</sup> Coke deposition may result in changes in pore structure and acid property. On one hand, it will increase the effective diffusion length, block the pore mouth on the surface of ZSM-5 and then inhibit the entering of pyrolysis vapor. On the other hand, coke species will cover lots of active sites, namely it leads to decrease of acid strength and amount.9, 10 To

Key Laboratory of Energy Thermal Conversion and Control, Ministry of Education, Southeast University, Nanjing 210096, P.R. China Email: hyzhang@seu.edu.cn, ruixiao@seu.edu.cn recover the activity of catalysts, the deactivated catalysts are usually regenerated in air atmosphere in which the combustion temperature determines the result of regeneration. Regeneration at low temperature may not remove the coke completely, while higher temperature may bring about overheating and furthermore break down the catalysts structure.<sup>11</sup>

Thanks to some developed effective methods, they can be used to decrease the effective diffusion length and also increase the specific surface area, improve the mass transfer ability of catalysts and thus promote the production of hydrocarbons.<sup>12, 13</sup> To shorten diffusion pathways, nano-sized zeolites were proposed, thus improving the mass transport in the zeolite channel.<sup>14, 15</sup> Another popular method is to introduce mesopores into microporous zeolite catalysts, the diffusivity of the microporous channel and the accessibility of the active sites are also greatly promoted.<sup>16-18</sup> There are usually two methods to introduce mesopores into the original microporous system by desilication, namely templating and alkaline treatment. A carbon source is impregnated with a zeolite precursor solution after which the material is subject to a hydrothermal treatment to grow the zeolite crystals, subsequently the carbon and the template are burned away resulting in intracrystalline mesopores in the zeolite<sup>19</sup>. Some templates are very expensive, which determines its limited application in industry. Removal of silica from the crystal framework with alkali solutions is an easily operated method that may cause the appearance of mesoporosity.<sup>20-22</sup> Selective dissolve and remove of silica from the zeolite framework can be realized by alkaline treatment. Silica extraction leads to the formation of structural defects in the lattice.<sup>23, 24</sup> Thus, desilication by alkaline treating is a preferential method to introduce mesopores. These hierarchical zeolites enhance the utilization of their active volume, and have attained superior yield of targeted products in lots of catalysis reaction.25

To improve carbon yield of hydrocarbons in CFP of biomass and

#### ARTICLE

promote the catalyst stability, alkali treatment was carried out on HZSM-5 catalysts to introduce some mesopores into the microporous catalyst system. The hierarchical HZSM-5 catalyst showed better mass transfer. In our study, N<sub>2</sub> adsorption and transmission electron microscopy were used to investigate the existence of mesopores, and the morphology was greatly dependent on the treating conditions. The parent and hierarchical HZSM-5 catalysts were employed in the catalytic conversion of furan as an important intermediate from biomass fast pyrolysis. The effect on the hydrocarbon production was studied and the catalyst performance in cycle runs of catalysis-regeneration process was discussed.

# Experimental

#### Catalyst and desilication procedure

In this study, two series of HZSM-5 catalyst samples were compared: A commercial catalyst (purchased from catalyst plant of Nankai University, stated Si/Al ratio 25) and its hierarchical counterpart. The hierarchical catalyst was prepared by desilication according to the following procedure. 2 g parent sample was treated in stirred aqueous NaOH solutions (0.1-1 M, 70 °C, 30 min, 33 mL solution per gram catalyst material). Mixture were washed and filtered for times until neutral, and the isolated solids were dried at 110 °C for 12 h. All modified zeolites were converted to the protonic form by ion exchange in aqueous NH<sub>4</sub>Cl solution (1 M, 80 °C, 4 h, 10 mL solution per gram catalyst material, 3 consecutive treatments) and washed for several times followed by calcination in air at 600 °C for 5 h. These catalysts will be referred to as HZSM-5-P and HZSM-5-X, respectively. X stands for the mole concentration of NaOH solutions. It should be mentioned that Cl content of final modified catalysts has been tested in the following section to eliminate the influence of CI on the catalytic performance.

#### **Catalyst characterization**

The parent and desilicated samples were characterized by several techniques.

The structure of the ZSM-5 samples was determined through X-ray powder diffraction (XRD) from Bruker using Cu Ka radiation at 40 kV and 40 mA with a scanning speed of 0.02 °/min in the range of 5 ° $\leq \theta$ ≤80 °.

Energy Dispersive Spectrometer (EDS) was used to determine the element content, and then Si/Al was obtained. Cl content helps to make sure that little CI was left. It was performed on a Vantage IVsystem, Thermo Fisher Scientific, USA.

Nitrogen physisorption isotherms were measured using a AutosorbiQ gas adsorption analyzer (Quantachrome, USA) at -196 °C. Each sample was outgassed at 200 °C for 6 h before measurement. The specific surface area (S<sub>BET</sub>) was calculated by using the Brunauer-Emmett-Teller equation ( $P/P_0=0.05\sim0.20$ ). The total pore volume  $(V_{total})$  is taken as the total uptake at P/P<sub>0</sub>=0.995. The Barrett-Joyner-Halenda (BJH) method was used to determine the micropore volume and micropore size distribution. And the mesoporous volume was obtained by subtracting the micropore volume from the overall pore volume.

Scanning electron microscopy (SEM) experiments were performed to obtain the morphology of the fresh and modified catalysts. The measurements were performed with a FEI Inspect F50 system at 10kV. Prior to each measurement, the samples were prepared 36 ha carbon pad and sputtered with gold to obtain the necessary conductivity. The morphology and pore size of zeolites were also examined by transmission electron microscopy (TEM) on a Tecnai G2 microscope operated at an electron acceleration voltage of 200 kV. A small amount of catalyst was dispersed in ethanol, sonicated, and dispersed over a micrograte.

The acidity of the catalysts was estimated by the  $\mathsf{NH}_3$  temperature programmed desorption (TPD) technique. The sample was pretreated at 600 °C in flowing He for 0.5 h. After pretreatment, the sample was cooled to 100 °C and saturated with NH<sub>3</sub> gas. The physical absorbed NH<sub>3</sub> was then blown out. Finally, NH<sub>3</sub>-TPD was carried out under a constant flow of He (20 mL/min). The temperature was raised from 100 to 600 °C at a heating rate of 15 °C/min.

Deactivated catalysts were regenerated in air atmosphere of 50 mL/min in a thermogravimetric analyzer to determine coke content by the weight loss during oxidation. Typically, 15 mg of sample was placed in the alumina crucible and heated from ambient temperature to 800 °C at a rate of 15 °C/min.

#### **Catalyst tests**

All catalytic tests were performed in a quartz glass fixed-bed reactor described elsewhere.<sup>26</sup> The catalyst bed was activated in a pure air flow (200 mL/min) at 600 °C for 1 h prior to each run. Then, the nitrogen flow was mixed with 1.68 g/h furan via a spring pump, resulting in a weight hourly space velocity (WHSV) of 11.2 g furan per gram catalysts per hour. All experiments were carried out under atmospheric pressure and a furan partial pressure of P<sub>furan</sub>=12.30 Torr. After 20 minutes of catalysis reaction, furan feeding was stopped and air was introduced into the reactor with flow rate of 500 mL/min for 30 minutes and it should be ensured the coke was removed completely. During the coke combustion process, CO was converted into CO<sub>2</sub> in the copper converter which was full of copper oxide and then trapped by the ascarite. The coke amount was measured by the weight increase in the CO<sub>2</sub> capturer. Product analysis was performed using gas chromatography. The product composition was determined with gas chromatography/mass spectrometry (GC/MS) (Agilent, 7890A-5975C) equipped with HP-5 capillary column (30 m×0.25 mm×0.25  $\mu$ m), and then quantified by GC-Flame-ionisation detector/thermal-conductivity (FID/TCD) with a Restek Rtx-VMS capillary column to qualify olefins and aromatics. Coke content is the proportion between weight of coke and weight of fresh catalyst.

# **Results and Discussion**

#### Physicochemical characterization

The XRD powder pattern of parent and desilicated HZSM-5 are shown in Fig. 1. Both types of catalysts displayed two diffraction peaks in the range of 8~10 ° and 20~25 °, which are the characteristic reflection of MFI topology. The intensity of refection peaks decreased at higher NaOH concentration, while no big difference of intensity can be found when NaOH concentration was lower than 0.5 M. It suggested that effective size of the crystalline has changed after severe alkali treatment.

Journal Name

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

The nitrogen adsorption-desorption isotherms of HZSM-5-P and its hierarchical counterparts are recorded in Fig. S1. The isotherm of type I, characteristic of microporous structure, was presented in parent HZSM-5, namely, high uptake was evident at low P/P<sub>0</sub>. The hierarchical samples exhibited the characteristic of type IV isotherms, obvious hysteresis loop corresponded to a gradual uptake over the  $P/P_0$  range of 0.4~0.9, which revealed the presence of mesopores especially for HZSM-5-1M.27 It can be furtherly verified by the pore size distribution as shown in Fig. 2. For these samples treated with NaOH concentration lower than 0.3 M, mesopores with diameter size lower than 5 nm were produced, while larger mesopores appeared with NaOH concentration higher than 0.3 M. The BET surface area, total pore volume and micropore volume derived from the isotherms are summarized in Table 1. The BET surface area increased from 239 m<sup>2</sup>/g to 312 m<sup>2</sup>/g. Moreover, the total pore volume increased by alkali treatment caused by the presence of mesopores, and it is at the expense of micropore volume because of the partial damage of micropore framework.



Fig. 2 BJH mesopore size distribution of parent and hierarchical HZSM-5 catalysts

The morphology of parent and alkali treated HZSM-5 are scanned as show in Fig. S2 by SEM. The surface of parent HZSM-5 was quite smooth, while lots of gullies appeared due to alkali corrosion. And partial catalysts framework collapsed at some extremely treating conditions such HZSM-5-1M. To furtherly understand the the influence of alkali treatment on the mesopore formation in catalysts crystals and size distribution of pores, TEM images were

Table 1 Textural properties of parent and hierarchical HZSM-5 catalysts

Sample	S <sub>BET</sub> (m²/g)	V <sub>micro</sub> ª (cm³/g)	DQV <sub>tota</sub> @.1039 (cm³/g)	/C6RA05356E Si/AI <sup>b</sup>
HZSM-5-P	239	0.11	0.14	22.28
HZSM-5-0.1M	244	0.12	0.16	21.13
HZSM-5-0.3M	262	0.11	0.17	21.89
HZSM-5-0.5M	271	0.10	0.2	19.45
HZSM-5-0.8M	291	0.09	0.23	17.67
HZSM-5-1M	312	0.08	0.25	15.31
<sup>a</sup> Calculated by t-plo	ot method			

<sup>b</sup> calculated from EDS analysis

recorded to see the changes of crystals after treatment (see Fig. 3). The parent HZSM-5 showed uniform micropore distribution, whereas it consists of sheet-like materials on the outer sphere of HZSM-0.3M. For these samples treated with higher concentration of NaOH solution, TEM images revealed clearly the appearance of intracrystalline mesopores marked as the arrows. The morphology of catalysts is greatly dependent on the treating conditions of HZSM-5 catalysts. It has been widely accepted that when different treating conditions are used, the grown sites, shape and size are quite different, leading to catalyst crystals with different morphology.<sup>28</sup> Moderate alkali treating produced sheet-like pores only on the outer sphere, and larger concentration of NaOH concentration makes it easy to diffuse into the internal space for serious corrosion and hollow mesopores creation, verified by BET and TEM characterization.



Fig. 3 TEM images of parent and hierarchical HZSM-5

It has been tested in Table 1 that Si/Al ratio showed a very slight decrease for HZSM-5-0.1M and HZSM-5-0.3M, and then decreased sharply for samples with higher treating concentration of NaOH, which proves that serious dealumination should be happening accompanied with desilication by alkali treatment.<sup>29</sup> The total acid

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amount is proportional to the frammework Al content. Then the hierarchical HZSM-5 catalyst was supposed to present very different acid properties. To validate the above hypothesis, NH<sub>3</sub>-TPD was conducted as shown in Fig. 4 finding the typical profiles with two peaks from NH<sub>3</sub>-TPD analysis, of which the peak at low temperature  $(P_{LT})$  was around 200 °C and that at high temperature  $(P_{HT})$  was around 400 °C. Fig. 4(b) shows the area ratio between modified samples and original catalyst  $(S_M/S_P)$  and area ratio between  $P_{HT}$  and P<sub>HT</sub> (S<sub>LT</sub>/S<sub>HT</sub>). P<sub>LT</sub> can be attributed to weak Lewis acid sites (e.g. extra framework aluminum)<sup>30</sup>. The amount of PLT for HZSM-5-0.3M decreased to 91% of parent HZSM-5, then decreased sharply for HZSM-5-0.5M and HZSM-5-0.8M, and HZSM-5-1M finally showed quite weak intensity of  $P_{LT}$ . And  $P_{HT}$  is usually related to ammonia interacting with Brønsted type acid sites (e.g. framework aluminum)<sup>30</sup>. An obvious gradual decrease of P<sub>HT</sub> indicated that alkali treatment mainly brings about the decrease of acid strength and amount of Brønsted aid sites. It indicated that alkali treatment may damage not only Si but also frammework Al. For HZSM-5-0.3M, the characteristic MFI topology did not change, which can be found by XRD analysis. Though frammework Al was partially deprived, the acid amount and strength is well kept for its catalysis for hydrocarbons. Thus, it can be assumed that hierarchical HZSM-5 catalyst presented relatively weaker Brønsted acid sites rather than Lewis acid sites compared with parent catalyst.



Fig. 4 NH<sub>3</sub>-TPD analysis of parent and hierarchical HZSM-5 catalysts: (A) HZSM-5-P, (B)HZSM-5-0.1M, (C)HZSM-5-0.3M, (D)HZSM-5-0.5M, (E)HZSM-5-0.8M, (F)HZSM-5-1M,



Mechanism of desilication and mesopore creation

Fig. 5 Formation process of mesopores in HZSM-5 by alkaline treatment

Si-O-Al bond is usually thought to be weaker than Si-O-Si bond and vulnerable to be attacked and hydrolyzed, yet it only applies to acid treatment. In alkaline solutions, because of the negative charge of AlO<sub>4</sub><sup>-</sup> tetrahedron, the four-coordinated Al is protected from the attack of OH<sup>-</sup>, and Si-O-Al is not easy to hydrolyze. Each fourcoordinated AI can protect four adjacent Si atoms from attack, thus these Si-O-Si bonds without adjacent AlO<sub>4</sub><sup>-</sup> tetrahedron are easily to break, and then desilication happens with terminal Si-OH formation during which coordination environment is steady.<sup>31</sup> For these ZSM-5 catalysts with low Si/Al ratio, Al content and acid strength/amount are high, and the inevitable dealumination is accompanied by loss of four-coordinated Al. On one hand, when high concentration of NaOH solution is used, both Si-O-Al bond and Si-O-Si bond break, namely dealumination and desilication of framework both happens. On the other hand, excessive alkali treatment may lead to direct falling off of the integral Al quadridentate. Therefore, alkali treatment of HZSM-5 is a selective desilication process at moderate conditions, while Si-O-Al may also be cut when severe treating condition is used. The bond breaking process of alkali treatment is described in detail in Fig. 5(a). The schematic diagram of formation process of mesopores in HZSM-5 is presented in Fig. 5(b). Alkali corrosion begins from the outer sphere of HZSM-5 following the guide of Si atoms. The sheet-like pores were firstly formed, indicated by TEM images.<sup>32</sup> Further diffusion of OH<sup>-</sup> will permeate into the inner micropores and result in alkali corrosion around

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#### Journal Name ARTICLE

them.<sup>33</sup> Hollow mesopores with average diameter around 8 nm were formed when the concentration of NaOH solutions was 0.5 M. Finally, excessive treating led to framework collapsing and involuntary loss of acid sites. The average diameter of HZSM-5-1M is mainly around 10 nm. Thus, the degree of alkali treatment must be well controlled and the targeted mesopore shape can be realized, sheet-like or hollow.

# Catalytic conversion of biomass derivates over hierarchical HZSM-5 catalyst

Catalytic conversion of furan as an important biomass-derived compound was investigated over parent and desilicated HZSM-5 catalysts to find out the optimal post-treating condition for maximizing the production of hydrocarbons. Fig. 6 shows the results of catalytic tests for the parent and hierarchical HZSM-5 catalysts performed at the pyrolysis temperature of 600 °C. Fig. 6(a) presents the general olefins and aromatic hydrocarbon yield and distribution with the change of concentration of NaOH solution in desilication. Moderate alkaline treating will lower diffusion limitation, decrease the strong acid and increase the concentration of acid sites on the external level.<sup>34</sup> Carbon yield of olefins and aromatic hydrocarbons reached a maximum of 23.3%. It showed an improvement of 21.6% compared with the parent HZSM-5 catalyst. The excellent performance of hierarchical HZSM-5 may be attributed to the synthesis of mesopore that will promote the diffusion of reactants and products, and get easier access to acid sites in the micropores.<sup>35</sup> However, too severe desilication produced redundant mesopores, led to bad selectivity and less acid sites to meet the fundamenal catalysis reaction. The framework even collapsed at extreme treating conditions. In Fig. 6(b), the curves describe carbon yield of olefins as a function of time over the treated catalysts and also a comparison with the parent catalyst. It is obvious that the initial carbon yield increased with the increasing concentration of NaOH solution in desilication, accompanied by higher surface area and acid density on the external sphere. Carbon yield of olefins increased to a maximum value in a short time which is usually name "induction period" and then decreased sharply due to coke deposition. It is found that the length of induction period is closely related to alkali treating conditions. The presence of mesopore, the shape and size of mesopores as well may influence the formation of active sites. Unfortunately, the detailed mechanism of the relationship is still unknown.

In desilication process, the introduction of mesopores will also change the shape selectivity of catalysts dependent on the size of gate between mesopore and micropore and the change of diffusion limitation. The detailed product distribution was listed in Table 2, in which HZSM-5-0.3M showed larger selectivity to ethylene and smaller selectivity to naphthene. When using concentration of NaOH solution lower than 0.3 M, the sheet-like channels will shorten the diffusion pathway. The contact time of furan in the catalyst decreased, which is insufficient for olefin aromatization, and thus the selectivity to olefins increased. For these hierarchical HZSM-5 catalysts like HZSM-0.5M, HZSM-0.8M and HZSM-1M, the hollow mesopores provided enough space for aromatization. Therefore, alkali treatment is a useful method for promotion of olefins in catalytic conversion of furan.



Fig. 6 Catalytic performance of hierarchical HZSM-5 catalysts

Table 2 Product distribution in the catalytic conversion of furan over HZSM-5

	Parent	0.1M	0.3M	0.5M	0.8M	1M			
Carbon yield (mol%)									
Olefins	5.41	6.74	8.78	7.10	5.12	3.82			
Aromatic hydrocarbons	13.79	14.25	14.57	15.65	14.66	13.31			
Coke content (wt%)	7.07	7.43	7.89	7.99	8.53	9.91			
Ethylene	10.13	15.72	19.81	12.58	8.18	6.85			
Propylene	7.41	9.06	8.63	9.04	7.91	2.76			
Butylene	9.57	5.22	5.56	5.38	4.91	1.99			
Benzene	8.25	9.19	15.32	9.84	7.35	12.52			
Toluene	12.47	10.47	16.93	14.17	14.27	14.31			
Xylene	4.21	3.55	5.64	4.32	6.06	5.06			
Benzofuran	3.40	7.20	10.20	13.20	17.60	20.10			
Indene	5.62	6.44	6.12	5.92	6.41	6.32			

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To understand coking behavior of hierarchical HZSM-5, coke content of deactivated catalysts were analyzed by thermal analysis as shown in Fig. 7. It showed mass loss of deactivated catalysts during coke combustion. First of all, total coke content of catalysts are of some differences among all catalysts. Compared with the parent one, the treated catalysts almostly had more coke content, and this observation can also be found in other coked catalyst with hierarchical structure.<sup>36, 37</sup> This suggests that the mesopores may act as space for coke to form and accumulate.<sup>38</sup> Though more coke were deposited on the hierarchical catalysts, carbon yield of hydrocarbon was higher compared with parent catalyst, which indicated its higher tolerance toward coke deposition. Actually, not only the coke content of all catalysts differed from each other, but also the combustion temperature ranges were different as shown in Fig. S3. Major coke was deprived from 400 °C to 800 °C, while some weak peaks appeared at the temperature range of 100~400 °C for HZSM-5-0.5M, HZSM-5-0.8M, HZSM-5-1M. It means that either the location of coke or the chemical species of coke were different from three other catalysts. Kaskel found that deactivated hierarchical materials showed higher porosities, and assumed that coke in the mesoporous area was more loose and porous.<sup>39</sup>



Cycle run of catalysis-regeneration process

To determine the cycle performance of hierarchical catalysts, cyclic tests were conducted with 20 catalysis-regeneration cycles consisting of 20 min catalytic reaction followed by 30 min catalyst regeneration. The catalytic condition was the same as section 3.3, and the regeneration was performed with air flow rate of 200 mL/min. The variation of carbon yield of hydrocarbons as a function of cycle number for the catalyst HZM-5-P and HZSM-5-0.3M is shown in Fig. 8.

It is obvious that reaction stability of HZSM-5-0.3M was much better than parent HZSM-5 catalyst, in particular, carbon yield of hydrocarbons almost kept constant after 10 cycles while it decreased continuously for parent one. The highest temperature the thermocouple detected after air flowed in was named burning temperature. Burning temperature of each cycle was also recorded in Fig. 8, in which burning temperature of parent HZSM-5 was around 645 ° C, while that of HZSM-5-0.3M was 40 °C lower than parent HZSM-5 catalyst. First, it is understandable that carbon yield of hydrocarbons of HZSM-5-0.3M was higher than that of HZSM-5-P



Fig. 8 Cycle performance of parent and hierarchical HZSM-5 catalyst

because of the appearance of mesopores in HZSM-5, which provided more chances for the contact between reactant and catalysts acid sites. The parent HZSM-5 catalyst showed more serious overheating than HZSM-5-0.3M. On one hand, the loose and porous coke determines its relatively lower burning temperature.39 Svelle and Schmidt reported that coke distribution of microporous HZSM-5 showed a gradient over the catalyst particle and the carbonaceous molecules mainly deposited in the microporous nearsurface area that led to the rapid deactivation of catalysts, while hierarchical HZSM-5 catalysts showed a homogeneous distribution over the whole particle due to the improved accessibility of active sites and higher catalyst utilization.<sup>19, 40</sup> Therefore, the more uniform deactivation of the desilicated catalyst due to a complex interplay among alterations of porosity, activity, and rate of deactivation upon desilication, makes combustion gas easily diffuse out of catalysts channels.<sup>40</sup> Actually, accurate temperature within the catalyst particle was much higher than the detected value. Thus, lots of heat during coke combustion resulted in extraction of the framework AI to generate octahedrally coordinated AI species out of the zeolite framework.<sup>41</sup> Dealumination happened, and deprived aluminum retained in the pores. Generally, the mesopores in treated HZSM-5 catalyst will decrease the burning temperature and also the particle interior temperature, weaken the dealumination effect, and finally promote the stability via cycles. Coke content was also recorded online during regeneration. The coke amount determined by combustion online only includes carbon, while TG analysis of deactivated catalysts in air can determine the amount of full composition including carbon, hydrogen and oxygen. Previous study revealed that coke species at high temperature (>400 °C) are mainly hydrogen-poor carbon species with no oxygen<sup>42</sup>. Therefore, coke amount obtained by the above method may be just a little smaller than TG analysis. Coke content of original catalysts and those used for cycles has been added in Fig. S4. It is obvious that coke content decreased with the increasing cycle numbers, and the decrease rate of parent ZSM-5 catalysts seems higher. For parent ZSM-5, high burning temperature leads to hotspot in catalyst particles and then dealumination may happen<sup>43, 44</sup>. Dealumination is usually accompanied by the decrease of strong acid sites which easily causes serious coke formation<sup>41</sup>. Thus the decrease of coke content with cycle numbers is understandable. Hierarchical catalyst (HZSM-5-0.3M) showed relatively combustion temperature and thus lower degree of dealumination, which determines its slighter

decrease of coke content.

## Conclusion

Catalytic conversion of furan as an important intermediate from BFP was conducted on a micro-mesoporous HZSM-5 catalyst by alkali treatment for hydrocarbons. The prepared sample of HZSM-5-0.3M with sheet-like mesopores presented the best catalytic performance with carbon yield of hydrocarbons boosted to 21.6%. The appropriate desilicated HZSM-5 catalyst showed higher selectivity to olefins, and more serious coke deposition but higher tolerance toward coking. Moreover, the cyclic tests of catalysis-

regeneration process indicated that hierarchical HZSM-5 zeolites are potentially suitable for long-term operation. The hierarchical HZSM-5 catalyst successfully combined the high selectivity of microporous system and promoted mass transfer of mesopores in CFP of biomass for hydrocarbon production.

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Alkali treated ZSM-5 with sheet-like mesopores showed higher yield of hydrocarbons in CFP of biomass, withstanding long-running over catalysis-regeneration cycles.

