Anchoring Effect of Organosilanes on Hierarchical ZSM-5 Zeolite for Catalytic Fast Pyrolysis of Cellulose to Aromatics

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ABSTRACT: As an essential chemical feedstock, aromatics can be obtained from biomass by catalytic fast pyrolysis (CFP) technology, in which diffusion limitation is still a problem. In this study, several ZSM-5 zeolites with intercrystal stacking macropores were synthesized by adding organosilanes (OSAs) with different alkyl chain groups. Due to the structure-directing effect of the OSA, the prepared ZSM-5 zeolites possess a larger external surface area and pore volume than Blank-Z5. Moreover, the pore size is related to the extent of anchoring of the OSA and silicon−aluminum species in the zeolite precursor. Pyridine Fourier transform infrared (Py-FTIR) and NH3-temperature-programmed desorption (TPD) analyses show that the obtained ZSM-5 zeolites have a higher Brønsted acidity and total number of acid sites. In addition, excessive addition of OSA is not conducive to the growth of ZSM-5 zeolites. The catalytic performance of the synthesized ZSM-5 zeolites was evaluated by Py-GC/MS. The larger external surface area and pore volume improve the accessibility of the acid sites and thus promote the conversion of biomass into aromatics.

1. INTRODUCTION

With the shortage of fossil resources and increasing carbon emissions, biomass energy, as the only renewable carbon source, has gradually attracted attention to replace traditional fossil resources.1−5 Catalytic fast pyrolysis (CFP) is a promising technology for producing aromatics directly from biomass that integrates fast pyrolysis and catalytic cracking technology.6,7 In recent years, extensive research into the reaction mechanism8−11 and catalysts12−15 for CFP has been reported. Aromatization is the main pathway for small-molecule oxygenates and olefins to form aromatics through the "hydrocarbon pool mechanism," activated by the shape-selective effect of ZSM-5 zeolite channels.16

The average pore dimensions of ZSM-5 are close to the kinetic diameter of aromatic products, and ZSM-5 zeolite exhibits favorable aromatization capacity, shape selectivity, and tunable acidity.17 Therefore, ZSM-5 zeolite is considered a suitable catalytic pyrolysis catalyst for the CFP process. However, conventional ZSM-5 zeolite microporous channels can only accommodate the transfer of small-molecule organics. Primary pyrolysis oxygen compounds are prone to occur polymerization and condensation reactions on the outer surface of the zeolite and inside the micropores to form coke.18 Thus, it is necessary to improve the diffusion of macromolecule substances and increase the accessibility of acid sites in the pores of the zeolite.19,20

Hierarchical ZSM-5 zeolite has been verified to be an effective material for solving the above problem.21 Qiao et al. reported a 41.8% aromatic yield for CFP of cellulose with hierarchical ZSM-5 zeolite.22 There have been some reports on the preparation of hierarchical ZSM-5 zeolites by alkaline treatment. Appropriate treatment conditions can effectively introduce interconnected mesopores in parent zeolites.23,24 In addition, mesopores or macropores can be introduced by adding organosilanes (OSAs) to the zeolite precursor. However, the OSA might prolong the crystalization time and reduce the crystallinity and acidity, such as for bipedal OSAs with the structure of (OR2)3SiR1Si(OR2)3, which can strongly impede the aggregation of nanounits, leading to a partially amorphous material.25 Nonetheless, the mesopore diameter can be tailored by altering the OSA group or adding a hydrophobic swelling agent to modulate the interaction of OSA with silicon−aluminum species.26−28 For instance, a new structure-directing agent was used to prepare single-walled zeolitic nanotubes, presumably a long-chain agent containing π-stacking interactions that forms a template for nanotube zeolites.29 The presence of an amine moiety in OSA increases the extent of anchoring of OSA to the primary zeolite

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nanounits in the gel, resulting in more mesopores. Therefore, the effect of the OSA structure on the physicochemical properties of zeolites should be considered for designed reactions.

In this research, three OSAs with different alkyl chain groups were used to prepare hierarchical ZSM-5 zeolites to investigate the anchoring effect of OSAs on hierarchical ZSM-5 zeolite. The obtained ZSM-5 zeolites form a special morphology and possess a large pore volume and relatively high crystallinity. The prepared zeolites were used to produce aromatics through CFP of cellulose. The results indicate that a better balance between acidity and the pore structure can be achieved by selecting an appropriate OSA to prepare hierarchical ZSM-5 zeolites. The ZSM-5 zeolite with the highest acidity and moderate pore volume shows the highest aromatic yield (42.2%) and a lower coke yield (29.3%).

2. RESULTS AND DISCUSSION

2.1. Characterization. The X-ray diffraction (XRD) patterns for Blank-Z5 and catalysts with different OSAs added are shown in Figure 1. Figure S1 shows the XRD characterization of ZSM-5 zeolites with a varying amount of ODDMMS addition. All synthesized ZSM-5 zeolites show an MFI topological structure (JCPDS: 01-087-1527). The intensity of the peak varies with the type and amount of OSA, indicating that the type and amount of OSA affect the ZSM-5 zeolite crystallinity. The calculation of crystallinity is based on the sum of the diffraction peak areas in the range of 2θ = 22°−25°. The relative crystallinity based on Blank-Z5 is displayed in Table S1. ODMDES(0.05)-Z5 shows the lowest relative crystallinity, while the relative crystallinity of ODTMS(0.05)-Z5 and ODDMMS(0.05)-Z5 is only slightly lower than that of Blank-Z5. This result suggests that the addition of ODTMS and ODDMMS can overcome the problem of significantly decreased crystallinity for hierarchical ZSM-5 zeolite. However, the relative crystallinity of ZSM-5 zeolite distinctly decreases with increasing addition of ODDMMS. This proves that excessive addition of ODDMMS can suppress the crystallization process of zeolites.

Figure 2. $^{27}$Al MAS NMR spectra of the ZSM-5 zeolites.

$^{27}$Al MAS NMR spectra characterizing the environment of Al atoms in zeolites are shown in Figures 2 and S2. The chemical shifts observed at 55 and 0 ppm represent the tetrahedral Al in the zeolite framework (FAI) and extraframework octahedral Al (EFAI) atoms, respectively. It can be observed that the proportion of FAl in all prepared ZSM-5 zeolites is close to that in the standard ZSM-5 zeolite (in the range 5−10%). The FAl content in the three zeolites synthesized with OSA is slightly lower than that in Blank-Z5, indicating that Al atoms tend to form EFAI when preparing zeolite using OSA. When ODDMMS/SiO$_2$ = 0.15, the EFAI content reaches up to 10.4%. This may be related to the significant decrease in the relative crystallinity of ODDMMS(0.15)-Z5.

Figure 3 displays the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of ODDMMS(0.05)-Z5 and Blank-Z5 zeolites. As clearly shown in Figure 3D, Blank-Z5 is composed of aggregates of loose small particles. ODDMMS(0.05)-Z5 shows a cactus-like morphology. Many small particles are attached to the surface of large particles of approximately 300 nm in size. As shown in Figure 3A, the small particle size of ODDMMS(0.05)-Z5 mainly ranges from 30 to 50 nm. Based on the TEM images and our previous work, the possible mechanism of OSA affecting the morphology of ZSM-5 can be explained as follows. First, protозеолитic nanounits formed in the precrystallization process in the presence of the microporous template tetrapropyl ammonium hydroxide (TPAOH). Then, the RO−Si− moieties of OSA hydrolyzed to produce the −Si−OH structure and formed −Si−O−Al− and −Si−O−Si− linkages that anchored the OSA in the zeolite framework. ZSM-5 zeolites prepared with OSA show a similar morphology, which is different from Blank-Z5, indicating that the long carbon chain group in OSA plays a major role in the morphology of ZSM-5 zeolites. The long carbon chain adsorbed more silicon–aluminum species and restrained the accumulation of nanoparticles. Therefore, molecular addition became the predominant mechanism involving two-dimensional (2D) layer nucleation and stepwise advancement of layers, resulting in the formation of large particles. Later, silicon–aluminum species adsorbed by the carbon chain of OSA gave another 2D layer and small particles continued to grow one by one by a second 2D layer growth pathway. Finally, the morphology of small particles attached to the surface of large particles was formed. The formation of large particles may be the reason why ZSM-5 zeolites prepared with OSA still show high crystallinity. TEM images of ODDMMS(0.10)-Z5 and ODDMMS(0.15)-Z5 are shown in Figure S3C,D. As the addition of ODDMMS increases, the small particles attached to the surface of the large particles gradually become loose and even detach from the surface of the large particles. This may be because excessive ODDMMS hinders the aggregation of small particles. The morphology of ODTMS(0.05)-Z5 and...
ODMDES(0.05)-Z5 shown in Figure S3A,B shows similar characteristics, which prove the above assumption.

The textural properties including the Brunauer−Emmett−Teller (BET) surface area and pore volume for different zeolites were calculated by N2 adsorption−desorption. The isotherms and the pore size distribution are shown in Figures 4 and 5, respectively. As shown in Figure 4, the ZSM-5 zeolites contain both microporous and macroporous structures, which explains the rapid increase in the isotherms observed when P/P0 is 0 and 0.9−1.0, respectively. Mesopores and macropores with sizes larger than 10 nm are mainly generated by the accumulation of ZSM-5 zeolite particles.26,35

The BET surface area and pore volume are displayed in Table 1. Compared with Blank-Z5, the zeolites prepared with OSA show a smaller micropore surface area and micropore volume but a larger external surface area and mesopore volume, showing an increase of at least 27% from 95 m2/g (Blank-Z5) to 120 m2/g (ODMDES(0.05)-Z5), indicating that the OSA influences the crystal growth process. According to the TEM characterization (Figure 3), there are many small particles with a size of tens of nanometers on the surface of Blank-Z5 and ZSM-5 zeolites prepared with OSA, indicating that the increase in the external surface area is mainly due to the intercrystal stacking of mesopores and macropores rather than a decrease in crystal size. By increasing the external surface area, more reactive sites can be exposed, and the catalytic reaction at these active sites has a smaller steric hindrance than that in the micropores. During crystallization of zeolites, the RO−Si−moieties of OSA hydrolyzed to produce the −Si−OH structures and the OSA anchored to protozeolitic nanounits through covalent bonds. Then, OSA affected the crystallization process of zeolites, and the external surface area and pore volume increased finally.25,30,32 Interestingly, ODTMS contains three RO−Si groups, resulting in more protozeolitic nanounits anchored by ODTMS. Thus, ODTMS(0.05)-Z5 shows the largest BET surface area and mesopore volume but the smallest micropore surface area and micropore volume. This can lead to a lower acidity, which then reduces the catalytic pyrolysis activity in the CFP process.31

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However, adding ODDMMS(0.05) to the precursor not only increases the external surface area but also has a small effect on the micropore structure of the zeolite. With increasing addition of ODDMMS, the micropore surface area and micropore volume of ZSM-5 zeolites gradually decrease, indicating that...
The addition of ODDMMS hinders the formation of the microporous structure to a certain extent. The intercrystal stacking macroporous volume decreases, in good agreement with the gradual loosening of small particles as the addition of ODDMMS increases.

The Py-FTIR results are shown in Figure 6. The peak located at \( \sim 1460 \text{ cm}^{-1} \) corresponds to Lewis acid sites. The peak at \( \sim 1545 \text{ cm}^{-1} \) is attributed to Brønsted acid sites. The peak at \( \sim 1490 \text{ cm}^{-1} \) corresponds to the interaction of Brønsted acid and Lewis acid sites. The results obtained from a quantitative analysis of acidity are displayed in Table 2. Table 2 shows that ODDMMS(0.05)-Z5 has the highest concentration of Brønsted acid sites. ODTMS(0.05)-Z5 shows the lowest concentration of Brønsted acid sites compared with other zeolites with the addition of OSA, which may be related to the low microporosity of the structure. The NH3-TPD results for different zeolites are shown in Figure 7. The two main characteristic peaks are located at 150−300 and 300−500 °C, representing the weak acid sites and strong acid sites of zeolites, respectively. The total acid amounts for ODTMS(0.05)-Z5, ODMDES(0.05)-Z5, and ODDMMS(0.05)-Z5 are all increased compared with Blank-Z5, and ODDMMS(0.05)-Z5 shows the highest total acid amount among all samples. This result is consistent with the Py-FTIR results.

The Py-FTIR and NH3-TPD profiles of ZSM-5 zeolites prepared with different ODDMMS addition amounts are shown in Figures S4 and S5. With increasing ODDMMS addition, the Brønsted acid amount and the total acid amount of the zeolite decrease, which may be related to the decrease in micropore surface area and crystallinity. Compared with the lower Brønsted acid sites of the hierarchical ZSM-5 zeolite prepared by alkaline treatment, the addition of OSA can reduce the damage to the structure and acid amount of the ZSM-5 zeolite. Thus, it is practical to prepare hierarchical ZSM-5 zeolite by adding a suitable amount of ODDMMS to the precursor gel.

The 29Si MAS NMR spectra characterizing the environment of Si atoms in zeolites are shown in Figure 8. The chemical shifts at \( \sim 102, \sim 107, \) and \( \sim 110 \) ppm can be assigned to SiOH, Si(1Al,3Si), and Si(4Si), respectively. It is generally accepted that the SiOHAl groups (corresponding to Si(1Al,3Si)) can offer Brønsted acid sites and strong acid sites for zeolites and increase the acidity of the zeolite.

Table 1. Textural Properties of the ZSM-5 Zeolites

| catalysts      | \( S_{BET} \) (m²/g) \(^a\) | \( S_{mic} \) (m²/g) | \( S_{ext} \) (m²/g) | \( V_{tol} \) (cm³/g) \(^b\) | \( V_{mic} \) (cm³/g) | \( V_{mes} \) (cm³/g) |
|---------------|------------------|----------------|----------------|-----------------|----------------|----------------|
| Blank-Z5      | 371              | 276            | 95            | 0.311           | 0.163           | 0.148           |
| ODTMS(0.05)-Z5| 385              | 250            | 135           | 0.349           | 0.136           | 0.213           |
| ODMDES(0.05)-Z5| 384              | 264            | 120           | 0.321           | 0.152           | 0.169           |
| ODDMMS(0.05)-Z5| 384              | 261            | 123           | 0.329           | 0.152           | 0.177           |
| ODDMMS(0.10)-Z5| 375              | 256            | 119           | 0.278           | 0.156           | 0.122           |
| ODDMMS(0.15)-Z5| 377              | 252            | 125           | 0.305           | 0.145           | 0.160           |

\(^a\)BET method. \(^b\)Volume adsorbed at \( P/P_0 = 0.99 \).

Table 2. NH3-TPD Data and Acid Amount of the Prepared ZSM-5 Zeolites

| catalysts      | \( T_{peak} \) (°C) | LT peak | HT peak | total acidity | weak acidity | strong acidity | B \(^+\) | L \(^+\) |
|---------------|----------------|--------|--------|---------------|--------------|---------------|--------|--------|
| Blank-Z5      | 207.0          | 390.3  |        | 921           | 406          | 515           | 902    | 258    |
| ODTMS(0.05)-Z5| 209.1          | 402.4  |        | 1002         | 508          | 494           | 966    | 293    |
| ODMDES(0.05)-Z5| 204.7          | 389.1  |        | 1015         | 503          | 512           | 1047   | 312    |
| ODDMMS(0.05)-Z5| 212.7          | 416.7  |        | 1262         | 621          | 641           | 1140   | 236    |
| ODDMMS(0.10)-Z5| 202.2          | 383.5  |        | 1048         | 515          | 533           | 1005   | 259    |
| ODDMMS(0.15)-Z5| 202.8          | 385.9  |        | 1028         | 496          | 532           | 957    | 254    |

\(^+\)Measured at 150 °C.
Figure 8. $^{29}$Si MAS NMR spectra of prepared zeolites. (A) Blank-Z5, (B) ODTMS(0.05)-Z5, (C) ODMDES(0.05)-Z5, and (D) ODDMMS(0.05)-Z5.

Figure 9. Product yield and aromatic distributions obtained for the catalytic fast pyrolysis of cellulose over the synthesized ZSM-5 zeolites. (A) Yield of products for CFP of cellulose over ZSM-5 zeolites prepared with different OSAs; (B) aromatic selectivity for CFP of cellulose over ZSM-5 zeolites prepared with different OSAs; (C) yield of products for CFP of cellulose over ZSM-5 zeolites prepared with different amounts of ODDMMS; and (D) aromatic selectivity for CFP of cellulose over ZSM-5 zeolites prepared with different amounts of ODDMMS.
SiOH can offer weak acid sites. It is interesting to note that zeolites prepared with OSA show a higher content of Si(1Al,3Si) and SiOH sites (Figure S1) compared with Blank-Z5, leading to the increase of acid amount. According to $^{29}$Si MAS NMR spectra, we can conclude that OSA can modulate the coordination environment of Si in zeolites and thus promote the formation of acid sites.

### 2.2. Catalytic Performance

A microreactor directly connected to a gas chromatography/mass spectrometry (GC/MS) system was used for the qualitative and quantitative analyses of the pyrolysis products for the catalytic pyrolysis of cellulose, and the yields of the main products are shown in Figure 9A. A 37.0% yield of aromatics, a 14.4% yield of CO, an 8.4% yield of CO$_2$, a 2.8% yield of short-chain alkanes and olefins, and a 36.7% coke yield were obtained when catalyzed by Blank-Z5, which is consistent with the reported results. For CFP of cellulose over ODDMMS(0.05)-Z5, the yields of aromatics and coke are 42.2 and 29.3%, respectively. The formation of CO, CO$_2$, and H$_2$O is mainly derived from the primary pyrolysis of oxygenated compounds. Decarboxylation, decarbonylation, and dehydration concurrently occur on the acid sites of ZSM-5 zeolites. The yield of CO is much higher than that of CO$_2$, indicating that the oxygen atom in the primary pyrolysis products tends to be more easily removed by decarbonylation.

Many studies have proven that Brønsted acid sites can promote the conversion of primary pyrolysis products of biomass into final aromatics. Meanwhile, Lewis acid sites can inhibit side reactions in the Diels−Alder reaction. ODMDES(0.05)-Z5 (aromatic yield of 40.2%) and ODDMMS(0.05)-Z5 (aromatic yield of 42.2%) possess similar porous parameters while the latter shows more Brønsted acid sites and therefore higher yield for aromatics during the CFP process. This result proves the importance of Brønsted acid sites in the CFP process. In addition, we should note that ODTMS(0.05)-Z5 (aromatic yield of 40.6%) shows fewer Brønsted acid sites and a larger external surface area than ODMDES(0.05)-Z5 (aromatic yield of 40.2%). The two zeolites show a similar yield of aromatics, which can prove that an increase in the external surface area can improve the accessibility of acid sites and make up for a slight lack of acidity.

A comprehensive consideration of the Brønsted acid sites and pore structure can explain why zeolites prepared with OSA reflect a higher yield for aromatics and the production of less coke compared with Blank-Z5. Interestingly, although ODTMS(0.05)-Z5 shows a larger external surface area and mesoporous pore volume, it possesses the smallest micropore area, resulting in a lower aromatic yield than ODDMMS(0.05)-Z5. This proves the importance of the micropore structure and acid sites in the CFP process. Thus, a balance between the proportion of micropores and macropores is essential to obtain a higher aromatic yield.

The catalytic performance of ODDMMS(0.10)-Z5 and ODDMMS(0.15)-Z5 is shown in Figure 9C. With increasing ODDMMS addition, the yield of aromatics is reduced, which shows the same tendency as the acid amount for the zeolites. This proves the above conclusion. In addition, the yield of aromatics decreases to its lowest value of 38.1% when ODDMMS/SiO$_2$ = 0.15. This may be related to the obvious decrease in crystallinity and micropore surface area. The external framework silicon−aluminum species are easily dissolved under biomass reaction conditions. These dissolved species are catalytically active and can lead to undesirable side reactions, thereby resulting in loss of aromatic selectivity and yield.

The distribution of components in the aromatic products is shown in Figure 9B−D. Based on the carbon number in aromatics, the products are divided into benzene (B), toluene (T), xylenes (X), trimethylbenzene (C9A), C10 aromatics (C10A), and C11 and C11+ aromatics (C11A+). The distribution of products under different zeolite-catalyzed CFP processes is similar. Compared with Blank-Z5, the BTX selectivity in other ZSM-5-catalyzed cellulose pyrolysis processes slightly decreases. This might be due to the larger external surface area and pore volume making it easier to generate polycyclic aromatics and the undesirable side reactions caused by the increase in EFAl.

### 3. CONCLUSIONS

Three organosilanes with different alkyl chain groups were used to prepare hierarchical ZSM-5 zeolites. ODTMS with three RO−Si groups can be more easily anchored to protozoelic nanounits, resulting in a larger external surface area and pore volume while also reducing the micropore area of ZSM-5 zeolites. However, there are three alkyl chain groups in ODDMMS that act as a hydrophobic swelling agent, which increases the external surface area and pore volume while reducing the impact on the micropore structure and showing the highest acidity. In addition, the influence of the OSA addition amount on the physicochemical properties of ZSM-5 zeolites was studied. Excessive addition of OSA is not beneficial to the growth of zeolites. As the addition of ODDMMS is increased, the FAI content, acid amount, and aromatic yield decrease. Compared with the catalytic activities of different ZSM-5 zeolites on CFP of cellulose to aromatics, sufficient acid sites and suitable pore structures are conducive
to the formation of aromatics. The ODDMMS (0.05)-ZS zeolite shows the largest acid amount and a larger external surface area and total pore volume, thereby showing the highest aromatic yield of 42.2% for CFP of cellulose to aromatics.

4. EXPERIMENTAL SECTION

4.1. Materials. Sodium aluminate (NaAlO₂), octadecyl trimethoxysilane (ODTMS, >90%), benzene (>99%, GC), xylene (>99%, GC), 1,3,5-trimethylbenzene (>99%, GC), and naphthalene (>99.7%, GC) were purchased from Aladdin Chemicals, Shanghai, China. Tetraethyl orthosilicate (TEOS, AR), tetrapropyl ammonium hydroxide (TPAOH, 25 wt % in water), methylvbenzene (>99.5%, GC), 1-methyl naphthalene (>99%, GC), ammonium chloride (NH₄Cl, AR), and acetone (AR) were obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Octadecyl dimethoxysiloxane (ODDMMS, >90%) was obtained from TCI, Japan. Octadecyl methyl diethoxysilane (ODMDES, >97%) was obtained from Acme, China. Microcrystalline cellulose was obtained from Sigma-Aldrich.

4.2. Catalyst Synthesis. The catalyst was synthesized by a hydrothermal synthesis method (Scheme 1), using NaAlO₂ as the aluminum source, TEOS as the main silicon source, TPAOH as the microporous template, and a certain amount of OSA. Typically, a known quantity of NaAlO₂ was dissolved in deionized water and stirred until the solution was clear. Then, a certain amount of TPAOH was added with continuous stirring. Following this, TEOS was added drop by drop until it reached a certain amount of TPAOH was added with continuous stirring. Then, the precursor was kept at 400 °C for 2 h to remove impurities. Then, the calcined solid was added to the reactor and the cold trap and a thermal conductivity detector (TCD) were used to calculate the amount of acid based on the pulse integral area.

Brominated acid sites and Lewis acid sites were measured using an FTIR spectrometer (Py-FTIR, frontier FTIR spectrometer from PerkinElmer) with the adsorption of pyridine. The sample was kept at 400 °C for 2 h to remove impurities. Then, pyridine was introduced into the sample until the absorption was saturated. The infrared spectrum was recorded when the temperature dropped to 150 °C. After subtracting the background peak, the amount of Brominated acid and Lewis acid was calculated quantitatively according to the area, and the extinction coefficients for Brominated acid sites and Lewis acid sites are 1.67 and 2.22 cm/μmol, respectively.²⁸ Si MAS NMR spectroscopy was performed using a Bruker Avance III HD spectrometer.²⁹ Si MAS NMR spectra were recorded using single-pulse sampling with 10 s recycle delay and 600 scans.

4.4. Catalytic Performance Evaluation. The catalytic pyrolysis of cellulose to produce aromatics was carried out in a tandem microreaction system (Rx-3050 TR, Frontier Laboratories, Japan). This reaction system was composed of upper and lower reactors with heater temperatures ranging from 40 to 900 °C. The reaction was conducted in the upper reactor at 600 °C. The system was directly connected to a GC-MS system (Agilent GC7890B/MS5977A) equipped with a mass spectrometer detector (MSD), a hydrogen flame ionization detector (FID), and a thermal conductivity detector (TCD).

In a typical CFP reaction experiment, 4 mg of cellulose was added into a weighing bottle (30 mm × 60 mm) with a certain amount of zeolite screened less than 400 meshes. The mass ratio of catalyst to cellulose was 20:1, which was selected from our earlier research.¹⁵ After the mixture in the bottle was vibrated and mixed thoroughly, 4 mg of the mixture was charged into a stainless steel sample cup. Then, the cup was put into the reactor once the temperature reached the set value. The reaction was carried out under high-purity helium. The pyrolysis products passed through the reactor and the cold trap and finally entered the chromatographic column Ultra.
Alloy-5 (30 m × 0.25 mm × 2 μm). The qualitative and quantitative analyses for the product were completed using the MSD, FID, and TCD. The heating procedure is described as follows: hold at 35 °C for 5 min, ramp to 280 °C at 10 °C/min, and then hold for 10 min. For the gas products, CO and CO2 were analyzed by TCD, and C2H6, C2H4, C3H8, C3H6, and aromatics were analyzed by FID. The coke was quantitatively determined by elemental analysis (Elemental Vario Micro cube, Germany). All product yields were finally calculated based on the carbon yield (the molar ratio of carbon in the product to that in the reactant). The aromatic selectivity was defined as the ratio of the number of moles of carbon in a particular aromatic component to the total number of moles of carbon in all aromatics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c00983.

XRD patterns of zeolites with different ODDMMS addition amounts (Figure S1); relative crystallinity of prepared ZSM-5 zeolites (Table S1); 27Al MAS NMR spectra of ZSM-5 zeolites with different amounts of ODDMMS (Figure S2); TEM images of ODTMS(0.05)-Z5 (Figure S3(A)); TEM images of ODMDES(0.05)-Z5 (Figure S3(B)); TEM images of ODDMMS(0.10)-Z5 (Figure S3(C)); TEM images of ODDMMS(0.15)-Z5 (Figure S3(D)); Py-FTIR profiles of zeolites with different addition amounts of ODDMMS (Figure S4); and NH3-TPD profiles of zeolites with different addition amounts of ODDMMS (Figure S5) (PDF)

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Notes
The authors declare no competing financial interest.

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