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Heterogeneous Catalysis

Production of *p*-Xylene from Biomass by Catalytic Fast Pyrolysis Using ZSM-5 Catalysts with Reduced Pore Openings**

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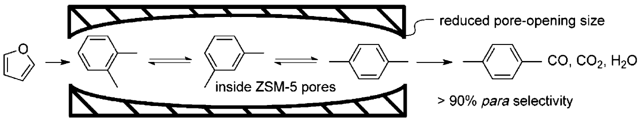
As a consequence of its low cost and availability, lignocellulosic biomass is receiving significant attention worldwide as a feedstock for renewable liquid fuels and chemical production.[1] Lignocellulosic biomass is not currently used as a feedstock to make liquid fuels because of technological and economic challenges.[1a,d,i] Several processes for obtaining biofuels from biomass are currently under development.[1i,2] Catalytic fast pyrolysis (CFP) is a promising technology for the production of renewable aromatic compounds including benzene, toluene, and xylenes (BTX) directly from solid biomass.[1i,2,3] In this single-step process, lignocellulosic biomass is fed into a fluidized-bed reactor, where the biomass first thermally decomposes to form pyrolysis vapors, which then enter zeolite catalysts that are also inside the reactor, and are converted into desired aromatic compounds and olefins along with CO, CO_2, H_2O, as well as undesired coke.[3a,b,4] The advantages of CFP are: 1) all the desired reactions occur in one single-step reactor, 2) the process uses an inexpensive silica–alumina catalyst, and 3) fungible aromatic compounds and olefins are produced that fit easily into existing infrastructures.

We have recently shown that aromatic compounds can be directly produced from wood by CFP in a bubbling fluidized-bed reactor by using a ZSM-5 catalyst.[3b,d] During CFP, cellulose and hemicellulose in the biomass form anhydrosugars,[4e] which then undergo dehydration reactions and form furanic compounds, including furan and its derivatives with appended side groups, such as 2-methylfuran (2MF) and furfural.[3a,b,4e] The furanic compounds enter the zeolite pores and undergo a series of acid-catalyzed oligomerization, decarbonylation, decarboxylation, and dehydration reactions to form aromatic compounds, olefins, CO, CO_2, water, and coke.[5] We have used furan as a probe molecule to identify key reactions occurring during CFP.[3b,d,5a,6] In this model reaction, a wide distribution of aromatic compounds was obtained, including BTX and undesired polycyclic aromatic compounds. An important class of reaction to form these aromatic compounds is the Diels–Alder reaction between furan and olefins.[5a,6] This cycloaddition was first suggested by Brandvold, with 2,5-dimethylfuran reacting with ethylene to form *p*-xylene and water over zeolite catalysts.[7]

p-Xylene, for which there is an increasing market demand in the petrochemical industry, is a precursor of terephthalic acid, which is used to make polyethylene terephthalate (PET).[8] Currently, 98% of commercially produced *p*-xylene is used to produce PET, and *p*-xylene is produced by the catalytic reforming of petroleum naphtha.[8c] Technologies to produce renewable *p*-xylene, including Virent's catalytic bioforming technology and Gevo's process to convert isobutanol into *p*-xylene, are still being developed.[8c] However, these methods do not use lignocellulosic biomass as the feedstock. We have found that *p*-xylene can be produced in low yield (<3% carbon) during the CFP of furanic compounds.[6] The total selectivity for xylene can be increased to 27% carbon by co-feeding propylene with 2MF, which is a typical Diels–Alder cycloaddition/dehydration reaction.[6] All three xylene isomers are formed in this process. However, the initial isomer formed—in a yield of 13%—from the reaction is *m*-xylene. The yield of *p*-xylene is 9%.[6,9] One option to improve the yield of *p*-xylene would be to design a zeolite catalyst that allows only *p*-xylene but not *m*- and *o*-xylenes to diffuse out of the pores (Scheme 1).



Scheme 1. A schematic diagram showing the diffusion limitations of xylene isomers inside zeolite pores.

Researchers have used ZSM-5 catalysts with finely tuned pore-opening sizes that imposed greater space confinement to increase the selectivity for *p*-xylene over the other isomers (*para* selectivity) in the toluene alkylation and toluene disproportionation reactions beginning in the late 1970s with the work of Kaeding et al.[9b,10] Impregnating phosphorus on ZSM-5 was found to provide superior *para* selectivity of the xylenes by supposedly narrowing the pore opening of the zeolites.[10b,c] By using these surface-modified ZSM-5, the *para* selectivity can be increased from 46% to 97% for toluene

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alkylation and toluene disproportionation reactions. Later in the 1980s, the chemical vapor deposition (CVD) of silicon alkoxides onto ZSM-5 catalysts was found to have the same effect, with the *para* selectivity increasing up to 98% by repeating the CVD process a couple of times.[10a,d] Similar to CVD, the chemical liquid deposition (CLD) of silicon alkoxides was introduced in the 1990s and also showed good *p*-xylene selectivity.[11] In addition to these methods, a precoked ZSM-5 catalyst can also increase the *para* selectivity for the same reactions.[9b] It has been suggested that all these techniques improve the *p*-xylene selectivity by reducing the pore-opening size of the zeolite. This previous research suggests that we should be able to improve the *p*-xylene selectivity in CFP by using zeolite catalysts that have smaller pore openings.

To test the hypothesis, we prepared a series of ZSM-5 catalysts with smaller pore opening by using the CLD method described in the Experimental Section;[11c] the silylated catalysts are marked throughout by "*" (i.e. ZSM-5*). Catalysts with and without silylation treatments were used in the CFP of furan and 2MF + propylene in a fixed-bed reactor (see the Experimental Section). Figures 1 and 2 show the overall *p*-xylene selectivity and distribution of xylenes obtained from conversion of 2MF + propylene and from furan, respectively, over various ZSM-5 catalysts. In Figure 1, the overall selectivity for *p*-xylene obtained with ZSM-5 was 5%. This value was increased to 15% by using silylated ZSM-5 (ZSM-5*). The silylation dramatically increased the *para* selectivity from 32% to 92%. Similarly, the silylated GaZSM-5* also showed a significant increase in *para* selectivity—from 58% (GaZSM-5) to 96%. However, the overall selectivity for *p*-xylene with GaZSM-5* is slightly lower than with GaZSM-5. The conversion of 2MF obtained using GaZSM-5* (74%) is lower than that using GaZSM-5 (98%; see Table S1 in the Supporting Information). In addition, the conversion of 2 MF obtained using ZSM-5* (89%) is also lower than with ZSM-5 (99%). The decrease in activity can be explained by some active sites in the external surface and in the surface near the pore openings being eliminated by silica deposition. Deposition of Ga on ZSM-5 has been proven to have the ability to increase the overall selectivity of the aromatic compounds.[3d] This is also the case with 2MF + propylene (see Table S1 in the Supporting Information), where the selectivity for aromatic compounds is 60% with ZSM-5 and 69% with GaZSM-5. However, the decrease in activity caused by the silylation in GaZSM-5* is more severe than in ZSM-5*, for the conversion of 2MF. This result suggests that both silylation and deposition of Ga decrease the number of acid sites. The Ga species may also impose a space confinement that caused an increase in the *para* selectivity (Figure 1, 58% for GaZSM-5 and 32% for ZSM-5). The silylation of GaZSM-5 further imposed more space confinement and, thus, gave the best *para* selectivity (96%).

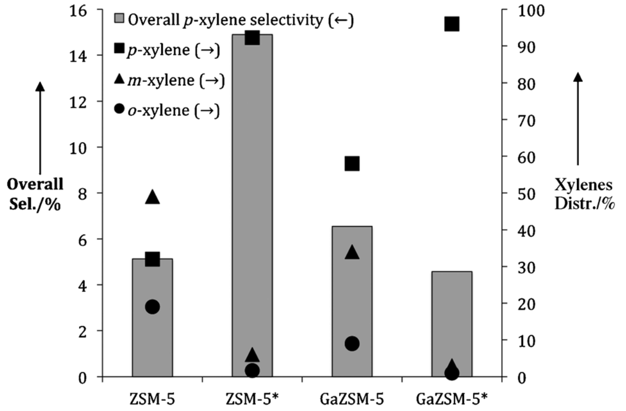

Figure 1. Overall *p*-xylene selectivity (left axis) and xylenes distribution (right axis) obtained in the conversion of 2MF + propylene over various ZSM-5 catalysts (*surface modified by CLD).

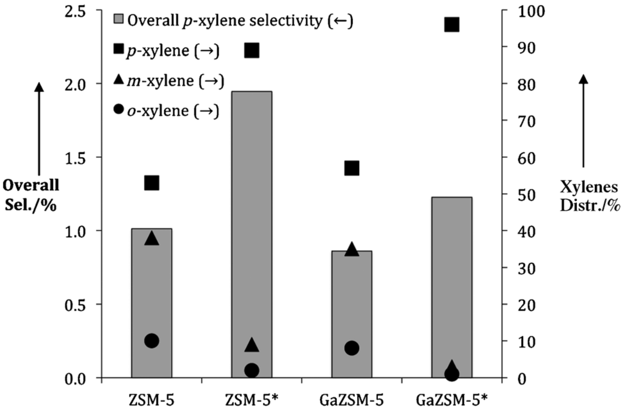

Figure 2. Overall *p*-xylene selectivity (left axis) and xylenes distribution (right axis) obtained in the conversion of furan over various ZSM-5 catalysts (*surface modified by CLD).

In terms of the conversion of furan (Figure 2), increases in the overall *p*-xylene selectivity and *para*-xylene distribution are also observed with the silylated catalysts. The *para* selectivity increased from 53% for ZSM-5 to 89% for ZSM-5*, and from 57% for GaZSM-5 to 96% for GaZSM-5*. Silylation also caused the activity to decrease (see Table S1 in the Supporting Information), with furan conversion being lower with the silylated catalysts. The increased activity with GaZSM-5 (41%) compared to ZSM-5 (33%) was due to Ga species.[3d] However, the lowest conversion of furan observed on GaZSM-5* (24%) was again due to the decrease in the number of active sites probably through the silyation treatment and Ga deposition. We also tested the furan conversion using a silylated spray-dried ZSM-5 catalyst (GaSD*).[3d] The *para* selectivity observed from this catalyst is 87% (see Table S1 in the Supporting Information), which suggests that the silylation can be used for spray-dried catalysts. This catalyst was then used for the CFP of pine wood in a bubbled fluidized-bed reactor (see Table S2 in the Supporting Information). An increase in the *para* selectivity from 51% with GaSD to 72% with GaSD* was observed, thus indicating that the silylation can also be used to fine-tune spray-dried ZSM-5 catalysts and increase the *para* selectivity. However, the overall aromatic selectivity decreased with the silylated catalyst. This finding suggests that more work is needed to optimize this catalyst for the CFP of real biomass.

The CLD treatment with tetraorthosilicate (TEOS, 10.3 Å) has been shown to poison acid sites mostly on the external surface and the surface near pore openings of ZSM-5 (pore opening size: 5.3 × 5.6 Å).[11c,12] However, a certain amount of silicon species enter the micropores during the modification, which causes the number of internal acid sites, the micropore volume, and the pore diameter to decrease.[11c,12] The lower activity of the silylated catalysts observed in this study is probably due to the loss of acid sites, as measured by isopropylamine temperature-programmed desorption (IPA-TPD) (see Table S3 in the Supporting Information), where the number of Brønsted and total acid sites were reduced by 37–40 % and 33–49 %, respectively, by silylation. The total number of acid sites in the external surface measured by collidine-TPD were reduced by 37–57 %. The deposition of silica near pore openings and internal micropores imposed more space confinement on the products and caused the diffusivity of *o*- and *m*-xylene to decrease and, thus, enhanced the *para* selectivity.[13] The Ga species have been shown to replace protons in ZSM-5.[3d] According to the results (Figure 1 and Figure 2), the Ga species blocked the pores in ZSM-5, thereby leading to increases in the *para* selectivity compared to pure ZSM-5. After silylation, more protons were poisoned by silica deposition, which caused a significant decrease in the activity. The incorporation of Ga has been shown to improve aromatization and decarbonylation reactions during the CFP of furan.[3d] However, the Ga species might be poisoned by silylation, thus resulting in the decrease in the selectivity of the aromatic compounds from 69 % to 32 % (see Table S1 in the Supporting Information) for the 2 MF + propylene conversion, and the decrease of CO selectivity from 14 % to 10 % for the furan conversion.

In our previous work, we suggested that the best route to form *p*-xylene is a Diels–Alder reaction between 2 MF and propylene at a 1:1 molar ratio in the feedstock at 450–600 °C. Higher temperatures resulted in dealkylation and lowered the *para* selectivity. Lower temperatures led to poor activity.[3d] The pore size was also found to be important, since the partially coked ZSM-5 showed better *para* selectivity. The best *para* selectivity was obtained at 450 °C from partially coked ZSM-5, but was still only 60 %. In the present study we fine-tuned the pore structure by TEOS CLD, which most likely reduced the pore-opening size, thereby imposing more space confinement on the products. Therefore, the *para* selectivity for the same reactions (2 MF + propylene) was dramatically increased to > 90 %. The surface modification then makes it possible to produce *p*-xylene from furanic compounds.

We have presented a simple zeolite surface modification method for increasing *p*-xylene selectivity in the products from biomass CFP. We performed TEOS CLD to narrow the pore openings of ZSM-5 catalysts, which caused more space confinement and, thus, increased the *para* selectivity from 32 % to 96 %. The surface modification can also be used for spray-dried catalysts. This study opens a door to the inexpensive production of renewable *p*-xylene from lignocellulosic biomass.

Experimental Section

Experimental details are given in the Supporting Information. In brief, Ga/HZSM-5 (GaZSM-5, 3.8 % Ga determined by induction-coupled plasma (ICP) analysis) was prepared by ion exchange of commercial ZSM-5 (ZSM-5). The spray-dried Ga catalyst (GaSD, 2 % Ga determined by ICP) was prepared by the incipient wetness method from commercial spray-dried ZSM-5 (SD). The surface modification (reducing the pore-opening sizes) was made by chemical liquid deposition (CLD) of tetraorthosilicate (TEOS), where the catalyst (1 g) was dispersed in hexanes (25 mL, Fisher) and TEOS (0.15 mL) was added. The solution was then heated to reflux at 90 °C for 1 h. The catalyst was recovered from the solution by centrifugation and was dried at 100 °C for 1 h before being calcined at 500 °C for 4 h. The CLD process was repeated twice. The conversions of furan and 2 MF were carried out in a continuous-flow fixed-bed reactor, with ZSM-5 and GaZSM-5 used as the catalysts, and helium used as a carrier gas. Pine wood conversion was carried out in a bubbling fluidized-bed reactor, with SD and GaSD used as the catalysts, and helium used as a carrier gas.

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