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Production of targeted aromatics by using Diels–Alder classes of reactions with furans and olefins over ZSM-5 \dagger

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In this paper we study the co-feeding of olefins (ethylene and propylene) with a series of furanic compounds (furan, 2-methylfuran, furfural, and furfuryl alcohol) over ZSM-5 catalyst in a continuous flow fixed-bed reactor at a temperature range of 450–600 °C. We show the importance of Diels–Alder cycloaddition reactions when olefins are co-fed with furanics over ZSM-5. Co-feeding propylene with furan (C_4 diene) increased the toluene aromatic selectivity from 22% to 59%. Similarly, co-feeding propylene with 2-methylfuran (C_5 diene) increased the xylenes aromatic selectivity from 9% to 27%. Co-feeding of ethylene with furans did not change the aromatics selectivity. The increase of toluene selectivity was also observed in the co-feeding of propylene with furfural and furfuryl alcohol. Furfural and furfuryl alcohol both underwent decarbonylation reactions to produce CO and furan. The reaction conditions that maximize Diels–Alder products were a propylene to 2MF molar ratio of 1 at 450 °C. Increasing the temperature to 600 °C increased the selectivity of benzene, toluene and CO. Decreasing the temperature to 300 °C increased the coke yield and decreased the xylene yield. The xylene selectivity went through a maximum at a propylene to 2-methylfuran molar ratio of 1 : 1.

1 Introduction

Lignocellulosic biomass has attracted significant attention worldwide as a feedstock for renewable liquid fuels and chemical production due to its low cost and availability.¹⁻⁹ However, it is not currently used as a feedstock to make liquid fuels due to technological and economic challenges.^{1,4,9} Several processes for obtaining biofuels from biomass are currently under development.9,10 The ideal process to produce biofuels and biochemicals from lignocellulosic biomass would be a single step reactor where solid biomass is directly converted into a liquid fuel at short residence times. Catalytic fast pyrolysis (CFP) is such a process for the production of renewable aromatics including benzene, toluene, and xylenes (BTX).¹¹⁻¹³ In this single step process biomass, including wood, agricultural wastes, or fastgrowing energy crops is fed into a fluidized-bed reactor with zeolite catalysts. During CFP biomass is rapidly heated (>500 °C s⁻¹) to intermediate temperatures (400-600 °C) where the biomass decomposes into oxygenated pyrolysis vapors.¹⁴⁻¹⁶ The pyrolysis vapors then enter the zeolite pores where they are converted into aromatics and light olefins, as well as CO, CO2, water, and dehydrated oxygenates.^{11,17-25} The advantages of CFP are: (1) all the reaction chemistry occurs in a single reactor; (2)

inexpensive silica-alumina catalysts are used; (3) fungible liquid aromatics (BTX) and light olefins (C_2-C_6 olefins) are produced that fit into the existing petrochemical infrastructures; (4) water is not required for this process; (5) CFP can be used to convert a range of different lignocellulosic feedstocks; (6) the pretreatment of biomass is simple (drying and grinding); and (7) the process uses fluidized-bed reactors that are already commercially used today in the petroleum refinery.

We have recently shown that aromatics and olefins can be directly produced from wood *via* CFP in a bubbling fluidizedbed reactor using zeolite catalyst.¹² The lignin fraction of the biomass primarily forms coke and carbon dioxide through free radical chemistry.^{26–30} Some lignin can also form monomeric compounds.²⁶ The cellulose and hemicellulose in the biomass form anhydrosugars.^{12,14,31} These anhydrosugars undergo dehydration reactions and form furanic compounds, such as furan, 2-methylfuran, fufural, and furfuryl alcohol.³² The furanic compounds enter zeolite pores and undergo a series of acid-catalyzed oligomerization, decarbonylation, decarboxylation, and de-hydration reactions producing aromatics, olefins, CO, CO₂, water, and coke.^{33,34} The aromatics + olefins yield is a function of hydrogen to carbon effective ratio (H/C_{eff}) of the feedstocks, which is defined as eqn (1), where C, H, and O are the moles of carbon, hydrogen, and oxygen, respectively.^{35,36}

$$H/C_{eff} = \frac{H - 2O}{C}$$
(1)

It was found that the yield of desired products (aromatics + olefins) increased with the increase of $\rm H/C_{eff}$ ratios but undesired

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products (coke) decreased. One method to increase H/C_{eff} ratios in the feedstock is to co-feed hydrogen-rich hydrocarbons such as olefins. In our previous study we fed ethylene and propylene with biomass feedstocks into a bubbling fluidized-bed reactor and obtained improved aromatics yield.¹²

We have used furan (C_4H_4O) as a probe molecule to identify some of the key classes of reactions that occur during biomass CFP.^{12,33,37} In this model reaction a wide distribution of aromatics were obtained including BTX, and smaller amount of undesired styrene, indene, and naphthalene. The ratio of benzene to toluene to xylenes (BTX ratio) is typically 6 to 5.5 to 1.33 It would be highly desirable to be able to tune this ratio for several reasons: (1) the ratio is far from the market demands in petrochemical industry (55 to 11 to 34);³⁸ (2) xylenes are the most valuable aromatic and the xylene selectivity is low; and (3) each of the aromatics has different uses in the petrochemical industry.³⁸⁻⁴² For example, benzene is alkylated with olefins to make alkylbenzenes for production of polystyrenes.^{40,41} Benzene is also used as a feedstock to make polycarbonates and polyurethanes.^{40,41} Toluene is a molecule with high octane number that can be blended into gasoline (>20 wt%).43,44 Toluene can also be converted into benzene and xylenes by disproportionation reactions, or used to make TDI (toluene diisocyanate) for production of polyurethanes.^{39–42} p-Xylene is the precursor to make terephthalic acid which is then used to make PET (polyethylene terephthalate).^{39,40} Xylenes can also be blended into gasoline and are a good octane enhancer.^{43,44} Due to the diversity of these three basic aromatics (BTX), their market demands are increasing, especially in *p*-xylene.^{38,45}

Several researchers have used zeolite catalysts to produce aromatics and olefins from biomass, beginning first in the early 1980s with the work of Chen *et al.*^{25,35,46–53} For example, woods were converted by using a two-step reactor where woods were first pyrolyzed into pyrolysis vapors in a non-catalytic reactor followed by a second fixed-bed reactor with zeolite to upgrade the pyrolysis vapors.^{48–50} Olazar and coworkers reported 12% aromatic yields in a single stage reactor using ZSM-5 catalyst.⁴⁷ Corma and coworkers have converted sorbitol and glycerol to aromatics over a series of zeolite catalysts where ZSM-5 was found to be the most selective zeolite to make aromatics.⁴⁶

In addition to producing aromatics from these biomass with zeolite catalysts, recently another route to form aromatics from furanic compounds in the liquid phase has been suggested, as described in Fig. $1,^{54}$ where 2,5-dimethylfuran (DMF) reacts with an ethylene to form *p*-xylene and water. This is a typical Diels–Alder reaction followed by dehydration. The Diels–Alder reaction is a cycloaddition reaction where a conjugated diene adds to an alkene (dienephile) to yield cyclohexene derivatives.⁵⁵ The Diels–Alder reaction is desired for CFP since it takes place



Fig. 1 Cycloaddition of 2,5-dimethylfuran and ethylene over ZSM-5 catalyst forms *p*-xylene.

in one step and produces compounds with 6-membered ring structure that is favorable in the ZSM-5 pores. Brandvold obtained 30% theoretical yield of *p*-xylene by using acid-washed activated carbon or zeolite catalysts.⁵⁴ Dauenhauer *et al.* performed the same reactions (DMF + ethylene) over synthesized HY and ZSM-5 catalysts at 200–300 °C.⁵⁶ They found Brønsted acids catalyzed dehydration reaction, which is the rate-determining step, and thus promoted the Diels–Alder cycloaddition. In these studies the reactions were performed at low temperatures (100–300 °C), high pressure (10–1500 psig), and long residence time (1–48 h) that are far from CFP conditions.

These results suggest that Diels-Alder classes of reactions could be used to make tune the aromatic distribution in CFP. The required dienes (furanics, such as 2-methylfuran) can be obtained from hydrodeoxygenation of furfural in high yields.^{57–59} Furfural is now produced primarily in China with a production of 150-220 kg per metric ton of lignocellulosic biomass. Recently, improved furfural yield and process cost has been reported.^{60,61} Therefore, it is highly desirable to produce aromatics from those furanics. The objective of this paper is to demonstrate how CFP could be tuned to more selectively make targeted aromatics by adjusting the relative concentration of different reactants within the CFP process. Alternatively targeted furanic compounds could be produced from biomass and co-feed over zeolites in the gas phase to make selective aromatics. A range of furanic compounds can be produced from biomass by aqueous phase dehydration reactions. 5,62 In this paper we will report the product selectivity for conversion of different furanic compounds over ZSM-5 with the goal of showing how the aromatic selectivity could be adjusted in CFP by changing the product concentration or reaction conditions. Fig. 2 shows the different reactions we will study in this paper, where different furans (diene) react with olefins (dienephile) forming aromatics and water.











Fig. 2 Examples of cycloaddition (Diels–Alder condensation and dehydration) of furan-ring with olefins.

2 Experimental and materials

2.1 Materials

Furans, including furan (Sigma-Aldrich, liquid, $\geq 99\%$), 2-methylfuran (2MF, Sigma-Aldrich, liquid, 99%), furfural (Sigma-Aldrich, liquid, 99%), and furfuryl alcohol (FA, Sigma-Aldrich, liquid, 98%) were used as feedstocks without any pretreatment. A ZSM-5 catalyst from Zeolyst (CBV 3024E, SiO₂/Al₂O₃ = 30) was used as the catalyst for this study. Before being used, the catalyst was calcined at 600 °C in a flowing air (Airgas, breathinggrade air, dehumidified by a drierite tube, the flow rate is 60 mL min⁻¹) for 5 hours in the flow reactor described below. The following calculations were used in this paper.

$$Overall selectivity = \frac{\text{moles of carbon in a product}}{\text{moles of carbon in all products}} \times 100\%$$
(2)

Aromatic selectivity =
$$\frac{\text{moles of carbon in an aromatic product}}{\text{moles of carbon in all aromatic products}} \times 100\%$$

$$Olefin selectivity = \frac{\text{moles of carbon in an olefinic product}}{\text{moles of carbon in all olefinic products}} \times 100\%$$
(4)

Weight hourly space velocity (WHSV)

$$=\frac{\text{flow rate of a feedstock } (g h^{-1})}{\text{weight of catalyst } (g)}$$
(5)

$$Xylenes distribution = \frac{\text{moles of a xylene isomer}}{\text{moles of all xylene isomers}} \times 100\%$$
(6)

Deactivation rate =

$$\frac{\text{yield of 2MF}(t) - \text{yield of 2MF}(t = 0 - 1.5 \text{ min})}{\text{yield of 2MF}(t = 0 - 1.5 \text{ min}) \times t} \times 100\%$$
(7)

2.2 Catalytic conversion of furans in the continuous flow fixedbed reactor

Details of reactions and analyses are given in the support information. The catalytic reactions were carried out in a flow fixedbed reactor. Prior to reactions, the catalyst was calcined as described above. Helium was used as the carrier gas. Furan and 2MF were introduced into the helium stream by a syringe pump (Fisher KDS-100) and was set to bypass the reactor for 30 min before switching the helium stream to go through the reactor. An air bath condenser was used to trap the heavy products. Gas phase products were collected by air bags. All runs were done at atmospheric pressure. No pressure drop was detected across the catalyst bed.

After reaction, the reactor was purged by helium at a flow rate of 408 mL min⁻¹ for 45 s at the reaction temperature. After

reaction, the spent catalyst was regenerated at 600 °C in a 60 mL min⁻¹ flowing air. The CO formed during regeneration was converted to CO_2 by a CO converter (copper oxide, CuO, Sigma-Aldrich). CO₂ was trapped by a CO₂ trap (Ascarite, Sigma-Aldrich). The coke yield was obtained by measuring the weight change of the CO₂ trap.

Furfural and FA were fed into the reactor by using a bubbler surrounded by a water bath at 45 °C. The helium stream (408 mL min⁻¹) flowed through the bubbler and carried furfural or FA vapor into the reactor. The other operations were the same as furan or 2MF conversion.

For olefins co-feeding experiments, a 2% ethylene or a 2% propylene balanced by helium (Airgas) was co-fed into the reactor with different furans feedstocks. Different olefins/furans ratios were obtained by diluting the olefins by helium.

Products are identified by GC/MS and quantified by GC/FID/ TCD. In the entire study less than 0.05% of the carbon was obtained in the condenser. The majority of the products were in either the gas phase or coke deposited on the catalyst.

3 Results

(3)

3.1 Furan conversion

Table 1 summarizes the results for conversion of furan, olefins, and furan + olefins over ZSM-5. In the first two runs we adjusted furan conversion by changing the space velocity. The aromatic distribution (or aromatic selectivity) was not a strong function of furan conversion when only furan was used as a feed. Only naphthalene shows an increase in aromatic selectivity from 7 to 15% when increasing furan conversion. Co-feeding of 2% propylene with the furan caused a dramatic change in the distribution of aromatics. For example, at 600 °C the toluene selectivity increased from 25 to 59% by co-feeding 2% propylene with furan. The overall aromatic selectivity increased from 29.2 to 53.8% when the propylene was co-fed with furan at 600 °C. The carbon monoxide selectivity also decreased with the propylene co-feed. This means more oxygen was removed by dehydration reactions rather than decarbonylation reactions. In the Diels-Alder reactions oxygen is removed from furan through dehydration reactions producing water as opposed to decarbonylation reactions which produce CO (see the reaction (3) in Fig. 2). These results suggest that Diels-Alder reactions are important when olefins are added to the reactor feed.

Fig. 3 and Table 1 show the overall product carbon selectivity as a function of temperature with furan and propylene as the feeds. The CO and CO₂ selectivity increased with increasing temperature, suggesting the rate of decarbonylation and decarboxylation increase with temperature compared to the other reactions. This result was also seen with pure furan where the selectivity of CO and CO₂ was increased from 7 to 18% and 0 to 1% respectively when the temperature increased from 450 to 650 °C.³³ However, the CO selectivity decreased when propylene was added to the feed, suggesting that Diels–Alder reactions occurred at all of these temperatures. The change of CO₂ selectivity was smaller than the change in CO. The coke selectivity decreased with increasing temperature. The aromatic selectivity goes through a maximum at 550 °C. In contrast, the olefins selectivity goes through a minimum at 550 °C. The change of

Table 1	Products distribution	obtained from	conversions	of furan.	olefins.	and furan +	olefins mix	tures over	ZSM-5
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Feedstock	Furan	Furan	Furan 1.92%	Furan 1.94%	Furan 2%	Furan 2%	Furan 2%	Non 1.92%	Non 1.94%	Non 2%
Carrier gas	Не	Не	Ethylene	Propylene	Propylene	Propylene	Propylene	Ethylene	Propylene	propylene
Temperature (°C)	600	600	600	600	550	450	300	600	600	450
Furan WHSV $(h^{-1})^a$	10.4	5.9	10.4	10.4	10.4	10.4	10.4	10.4	10.4	9.1
Olefins WHSV $(h^{-1})^a$	—		11.1	15.6	16.0	16.0	16.0	11.1	15.6	9.1
P _{furan} (torr)	6.0	6.0	6.0	6.0	6.0	6.0	6.0	0.0	0.0	0.0
Olefins/furan mol. ratio			2.6	2.4	2.5	2.5	2.5			
Furan conversion (%)	48	64	50	65	59	54	14			
Olefin conversion (%)	_	_	1	16	25	22	2	4	14	35
Overall selectivity (%) ^b										
CO	13.9	14.1	15.0	7.5	4.4	2.8	0.3	0.0	0.0	0.0
CO ₂	1.1	1.8	1.7	1.5	0.8	0.2	0.0	0.0	0.0	0.0
Olefins	19.1	16.9	17.0	29.0	22.7	29.4	31.0	20.2	69.3	86.9
Aromatics	29.2	42.6	40.2	53.8	65.6	60.2	34.5	21.2	22.9	8.9
Coke	33.8	23.0	23.9	7.4	5.5	5.4	19.0	58.6	7.7	4.1
Oxygenates	2.9	1.6	2.1	0.7	1.1	2.0	15.3 ^c	0.0	0.0	0.0
Aromatic selectivity (%)										
Benzene	27.5	24.3	28.4	15.3	8.4	5.1	1.9	31.8	35.9	9.6
Toluene	25.1	21.8	30.1	58.6	53.7	38.9	20.9	13.4	32.7	35.1
Xylenes	4.6	3.9	7.9	13.6	18.3	35.1	47.1	3.5	14.8	43.5
Styrenes ^d	9.8	5.9	9.6	5.9	5.1	1.1	0.0	5.8	2.2	0.0
Indenes ^d	20.6	24.4	15.8	3.9	8.4	7.9	8.4	31.8	9.8	0.0
Naphthalenes ^d	11.2	19.1	6.1	0.8	2.1	1.8	1.9	12.9	3.7	0.0
Alkylbenzenes ^d	1.3	0.5	2.1	1.8	4.2	10.3	19.7	0.7	0.9	11.8
Olefin selectivity (%)										
Ethylene	38.7	41.7		56.4	47.1	29.5	10.3		53.8	29.2
Propylene	35.1	35.6	59.1					24.4		
C₄ olefins	4.3	4.6	10.4	32.3	39.6	48.2	58.9	71.9	44.8	55.9
Allene	4.6	4.3	4.5	0.7	0.1	0.0	0.0	0.6	0.7	0.0
C ₅ olefins	14.2	11.3	19.2	7.1	5.2	7.1	17.4	3.0	0.7	8.9
C_6 olefins	3.1	2.5	6.8	3.6	6.1	11.6	12.0	0.0	0.1	4.8
C ₇ olefins	0.0	0.0	0.0	0.0	1.9	3.6	1.5	0.0	0.0	1.2
Xylenes distribution (%) ^e										
<i>p</i> -Xylene	NA	36	NA	NA	NA	NA	NA	NA	NA	37
<i>m</i> -Xylene	NA	47	NA	NA	NA	NA	NA	NA	NA	47
o Vulono	NIA	17	NΛ	NIA	NA	NIA	NΙΛ	NA	NΙΛ	16

^{*a*} Weight hourly space velocity (WHSV) is defined as flow rate of furan, ethylene, or propylene (g h⁻¹) divided by weight of the catalyst (g). ^{*b*} For conversion of mixtures, ethylene or propylene are excluded. ^{*c*} Oxygenates includes 86% C₇ oxygenates formed directly by addition of furan and propylene. In the other runs most oxygenates are benzofuran (>50%). ^{*d*} Styrenes include styrene and methylstyrenes; indenes include indene, indan and methylindenes; naphthalenes include naphthalene, dihydronaphthalene, and methylnaphthalenes. Alkylbenzenes includes ethylbenzene, 1,2,4-trimethylbenzene, 4-ethyltoluene, and propylbenzene. ^{*e*} NA: not analyzed.



Fig. 3 (a) Overall products selectivity and (b) aromatics distribution as a function of reaction temperature obtained from conversion of furan + 2% propylene over ZSM-5 catalyst; reaction conditions: temperature 300-600 °C, WHSV 10.4 h⁻¹, and furan partial pressure 6 torr.

coke and aromatics selectivity with temperature was similar to pure furan.³³ However, for pure furan conversion the selectivity of benzene was comparable with toluene at 450–600 °C. The relatively high toluene selectivity in Fig. 3(a) was due to Diels–Alder reactions where toluene should be the major product, as shown in reaction (3) in Fig. 2.

As shown in Fig. 3(b), the benzene, toluene and styrene selectivity increased with increasing temperature. The xylenes and other alkylbenzenes selectivity decreased with increasing temperature. These results suggest that at low temperatures, hydrocarbon pool products are more favourable than Diels-Alder reaction type products (toluene). It has been found that at high temperatures dealkylation of alkylbenzenes occurs, implying that alkylation reactions are suppressed at high temperatures.^{63,64} Another interesting result is that in our previous study, at 450 °C furan conversion produced mostly benzofuran and coke with 18 and 47% overall selectivity, respectively.³³ However, with the existence of propylene in the feedstocks, benzofuran (oxygenates) shows less than 2% overall selectivity, and coke shows only 5% overall selectivity. This is consistent with our previous study that co-feeding of molecules that have a high H/C_{eff} ratio with furan could reduce coke and make more aromatics. $\frac{36,65}{36}$ As shown in Table 1, when ethylene was fed into the reactor, only 4% conversion was observed. Similarly, co-feeding of furan with ethylene, only 1% ethylene conversion was observed. The furan conversion only showed a slightly increase from 48 to 50% when ethylene was co-fed with furan. The carbon monoxide selectivity did not decrease and the aromatics distribution did not change significantly with ethylene co-feeding. It is suggested that the reaction (1) in Fig. 2 did not occur since benzene did not increase its selectivity by ethylene co-feeding. These results suggest that ethylene is not a good dienephile due to its low reactivity. Other types of catalysts should be introduced for ethylene conversion.66

3.2 2-Methylfuran (2MF) conversion

Table 2 summarizes the results for the conversion of 2MF and 2MF + propylene over ZSM-5 catalyst. 2MF was more reactive than furan. At 600 °C, 2MF was completely converted at a WHSV with only 64% of furan converted at this same condition. About 50% of the oxygen was removed as CO (theoretical CO selectivity is 20%) with the remaining oxygen being removed as water. More olefins and aromatics, and less coke were obtained from 2MF than with furan. As has been previously discussed the hydrogen to carbon effective ratio (H/Ceff) of a biomass derived feedstock can be used to predict the amount of olefins and aromatics that can be produced.^{36,65} The aromatic + olefin yield increases with increasing H/Ceff ratio. 2MF and furan have H/Ceff ratios of 0.8 and 0.5 respectively. 2MF also has a higher aromatic + olefin yield than furan. The selectivity of different aromatics is similar for both 2MF and furan. 2MF had a higher xylenes selectivity and lower naphthalene selectivity than furan.

Co-feeding of propylene with 2MF at 600 °C dramatically increases the xylenes selectivity as shown in Table 2. This increase in xylene selectivity is expected due to an increase in Diels–Alder reactions as shown in Fig. 1 reaction (5). The CO selectivity decreased from 11% to 6% when propylene was

co-fed with the 2MF. The xylenes was a mixture of all three isomers: *p*-xylene, *m*-xylene, and *o*-xylene. Table 2 also shows the distribution of the xylene isomers. At 600 °C *m*-xylene is the most favourable isomer with or without propylene co-feeding. According to the reaction (5) in Fig. 2, *m*-xylene should dominate xylene isomers for 2MF + propylene reaction. Isomerization between xylenes inside ZSM-5 pores may also be occurring in this reaction.^{67,68}

The ratio of the xylene distribution is a function of reaction temperature as shown in Table 2. Lower temperatures led to an increase in *p*-xylene and decreases in *m*-xylene and *o*-xylene. This might be attributed to the formation of coke inside the ZSM-5 catalyst that can slightly block the pore and modify the diffusivity of the different xylene isomers. Researchers have found that the diffusion rate of *p*-xylene inside ZSM-5 is at least 1000 times faster than *o*- and *m*-xylenes.^{38,69} The increasing diffusion resistance by pre-coking zeolites will create more diffusion difference between *p*-xylene and the other xylene isomers.³⁸ The coke yield was similar at 600 and 450 °C, but *m*-xylene and *o*-xylene have lower diffusivity at 450 °C due to lower temperature. Therefore, *p*-xylene increased its selectivity among xylene isomers. This suggests that the coke induces space confinement that causes the *p*-xylene selectivity to further increase.

Fig. 4(a) shows the overall products carbon selectivity as a function of temperature for conversion of 2MF + propylene. Details are shown in Table 2. Similar to the conversion of furan + propylene the CO selectivity increases with temperature indicating that decarbonylation reactions increase with temperature. Aromatics went through a maximum at 450 °C. The olefins and CO2 selectivity did not change much with temperature. The distribution of aromatics formed was a strong function of temperature as shown in Fig. 5(b). The xylenes and higher alkylbenzenes decreased with increasing temperature, that was similar to furan + propylene reactions. However, the increase of temperature from 300 to 450 °C did not change xylenes selectivity. The 2MF conversion was low (13%) at 300 °C with the propylene conversion being 20% at this same temperature. This suggests that more of the aromatics were formed from propylene aromatization instead of 2MF at this temperature. Table 1 also shows that propylene has a high aromatic selectivity towards xylenes and alkylbenzenes at 450 °C. These results suggest that 450-600 °C is the best temperature for Diels-Alder reaction of furanics with olefins over ZSM-5.

3.3 2MF conversion: olefins/2MF ratios

We also carried out the 2MF + propylene reactions at 450 °C with different olefins to 2MF molar ratios (Ole/2MF). As shown in Table 2, the 2MF conversion increased with an increase in the Ole to 2MF ratio. This suggests that propylene helps convert the 2MF into aromatics. Fig. 5(a) shows the overall products carbon selectivity as a function of Ole/2MF ratio. The CO selectivity decreased with an increase in propylene concentration. The coke and CO₂ selectivity decreased with increasing Ole to 2MF ratio. These suggest that the existence of hydrogen-rich reactants like propylene reduced coke formation during furans CFP, and shifted the method of oxygen removal to a dehydration route instead of decarbonylation or decarboxylation. The aromatic

Feedstock Carrier gas	2MF	2MF 2% Propylene						
	IIC	270110pytene	270110pytene	270110pytene	270110pytene	270110pytene	27011009910110	
Temperature (°C)	600	600	450	300	200	450	450	
2MF WHSV $(h^{-1})^d$	5.7	5.7	5.7	5.7	5.7	5.7	5.7	
Propylene WHSV $(h^{-1})^a$		9.1	9.1	9.1	9.1	2.9	1.0	
P _{2MF} (torr)	4.9	4.9	4.9	4.9	4.9	4.9	4.9	
Olefins/2MF molar ratio		3.09	3.09	3.09	3.09	1.00	0.35	
2MF conversion (%)	98	99	92	13	0	86	79	
Propylene conversion (%)	—	31	42	20	14	43	35	
Overall selectivity $(\%)^b$								
CO	11.0	5.9	1.2	0.0	0.0	3.0	4.8	
CO2	0.5	0.1	0.2	0.0	0.0	0.8	1.5	
Olefins	23.3	27.8	27.5	23.5	14.4	11.7	8.9	
Aromatics	47.3	59.6	66.1	51.7	20.6	71.1	60.4	
Coke	16.6	62	5.0	24.8	65.0	12.1	21.6	
Oxygenates ^c	1.4	0.4	0.0	0.0	0.0	1.3	2.8	
Aromatic selectivity (%)								
Benzene	23.8	24.4	6.8	0.9	1.8	69	74	
Toluene	24.5	28.6	17.5	9.2	5.1	17.1	17.3	
Xylenes	9.2	26.0	48.9	51.3	35.7	46.5	35.7	
Styrenes ^d	4.8	26.9	0.8	0.0	0.5	2.2	41	
Indenes ^e	25.4	10.3	6.8	3.4	10.9	9.4	18.7	
Nanhthalanas ^e	10.1	3.1	1.0	1.0	11.7	1.6	17	
Alkylbenzenes ^e	2.2	4.0	18.2	34.2	34.4	16.4	15.1	
Olatin salactivity (%)								
Ethylene	28.7	61.6	30.4	0.1	0.0	47.1	567	
Propulana	25.0	01.0	50.4	9.1	0.0	4/.1	50.7	
C olofing	15.6	28.0	40.2	61.2	61.0	40.3	20.1	
Allono	13.0	20.0	49.5	01.2	01.9	40.5	50.1	
Calafina	17.4	0.1	0.0	20.2	18.2	0.0 5 7	5.2	
C_5 olemns	17.4	7.5	0.0	20.2	10.5	5.7	5.2	
C_6 olenns	3.0	3.0	8.6	9.5	19.9	5.2	0./	
C ₇ olefins	0.0	0.0	3./	0.0	0.0	1./	1.3	
<i>Xylenes distribution (%)^e</i>								
<i>p</i> -Xylene	36	32	43	54	NA	41	43	
<i>m</i> -Xylene	46	49	42	37	NA	45	43	
o-Xylene	17	19	14	9	NA	14	13	

^{*a*} Weight hourly space velocity (WHSV) is defined as flow rate of 2MF or propylene (g h^{-1}) divided by weight of the catalyst (g). ^{*b*} For conversion of mixtures, ethylene or propylene are excluded. ^{*c*} Oxygenates contain furan and furylethylene. ^{*d*} Styrenes include styrene and methylstyrenes; indenes include indene, indan and methylindenes; naphthalenes include naphthalene, dihydronaphthalene, and methylnaphthalenes. Alkylbenzenes includes ethylbenzene, 1,2,4-trimethylbenzene, 4-ethyltoluene, and propylbenzene. ^{*e*} NA: not analyzed.



Fig. 4 (a) Overall products selectivity and (b) aromatics distribution as a function of reaction temperature obtained from conversion of 2MF (2-methylfuran) + 2% propylene over ZSM-5 catalyst; reaction conditions: temperature 300–600 °C, WHSV 5.7 h⁻¹, and 2MF partial pressure 4.9 torr.



Fig. 5 (a) Overall products selectivity and (b) aromatics distribution as a function of olefins/2MF (2-methylfuran) ratios obtained from conversion of 2MF + propylene over ZSM-5 catalyst; reaction conditions: temperature 450 °C, WHSV 5.7 h^{-1} , and 2MF partial pressure 4.9 torr.



Fig. 6 (a) Selectivity of *p*-, *m*-, and *o*-xylenes, and (b) total xylenes yield as a function of reaction time on stream, obtained from 2MF (2-methyl-furan) + 2% propylene conversion. Reaction conditions: temperature 600 (#) and 450 (*) °C, 2MF WHSV 5.7 h⁻¹, and 2MF partial pressure 4.9 torr.

selectivity goes through a maximum with the Ole to 2MF ratio. When pure propylene is used the aromatics selectivity is 8.9%. The aromatics had a maximum selectivity at an Ole to 2MF ratio of 1, suggesting that bimolecular reactions were favored for aromatics production. This is consistent with Diels–Alder reaction as shown in Fig. 2. Fig. 5(b) shows the aromatic distribution as a function of Ole to 2MF ratio. When 2MF was in the feed, the xylene selectivity increased when the Ole/2MF ratio increased from 0.35 to 1.0, and did not change at higher Ole/2MF ratio. Pure propylene conversion shows more toluene but less xylenes.

3.4 2MF conversion as a function of time on stream

Fig. 6(a) shows the xylene isomers distribution as a function of reaction time on stream obtained for conversion of 2MF + pro-pylene at 450 and 600 °C. *p*-Xylene selectivity went through a maximum of 60% and 55% at around 20 min time on stream for reactions at 450 and 600 °C, respectively. The *m*-xylene went through a minimum of 30% for both temperatures at 20 min time

on stream. The *p*-xylene selectivity then decreased to a steady state value of 40% and 50% at 450 and 600 °C, respectively. The overall *p*-xylene yield rapidly decreased within 50 min time on stream as shown in Fig. 6(b). This deactivation is due to coking on the catalyst surface. The rates of catalyst deactivation at 600 and 450 °C initially are 334 and 218 h⁻¹ respectively, and are 10 and 0 h⁻¹ respectively at 50 min time on stream. The deactivation rates for 2MF + propylene were faster than pure furan conversion over ZSM-5 where its deactivation rate was 126 h⁻¹ in the beginning and was 5.5 h⁻¹ at 1 hour time on stream.³³

3.5 Furfural and furfuryl alcohol (FA) conversion

Fig. 7 shows the overall products carbon selectivity and aromatics distribution obtained from different furanic feedstocks (including furan, furfural, furfuryl alcohol (FA) and 2MF) with and without co-feeding of propylene at 600 °C. Furfural had a higher CO selectivity than the other furans. However, the Published on 21 August 2012. Downloaded by New York University on 13/10/2014 22:58:13.



Fig. 7 (a) and (b) Overall selectivity of products; (c) and (d) their aromatics distribution obtained from conversion of different feedstocks; reaction conditions: temperature 600 °C; WHSV 10.4 h^{-1} for furan, 5.7 h^{-1} for 2MF (2-methylfuran), 9.0 h^{-1} for furfural, and 3.3 h^{-1} for FA (furfuryl alcohol); partial pressure 6 torr for furan, 7 torr for furfural, 2.5 torr for FA, and 4.9 torr for 2MF.

aromatic distribution (BTXN selectivity) for furfural and furan was similar. The furfural conversion also showed high selectivity of furan in the products (15%). These suggest that the first step for furfural conversion is decarbonylation to form furan and CO. The produced furan then enters the furan conversion network as shown in Fig. 8. When co-feeding propylene, oxygenates (furan) showed low selectivity. This suggests that the propylene helps convert the produced furan by Diels-Alder reactions. 2MF formed more aromatics than furan and furfural. Furan and furfural have lower H/Ceff ratios than 2MF. FA has H/Ceff ratio 0.4 that is lower than furan (0.5) but higher than furfural (0). Although FA showed higher aromatics selectivity than furan, it produced more undesired polycyclic aromatics (Fig. 7(c)) such as indenes and naphthalenes, than the other feeds. 2MF showed a similar aromatics distribution as furan and furfural, suggesting that 2MF may be involved in similar reaction mechanisms.

The aromatic and olefin selectivity increased and the coke and CO selectivity decreased when propylene was added to the feeds. The toluene selectivity increased by 34 and 29% when propylene was co-fed with furan and furfural, respectively. The xylene selectivity increased by 18% when propylene was co-fed with 2MF. The toluene and benzene selectivity did not change much when propylene was co-fed with 2MF (\leq 4%). The

benzene, toluene and xylenes selectivity increased when propylene was co-fed with FA. The Diels–Alder reaction effect was not significant for FA + propylene but we still can see that the toluene increased its selectivity more than benzene and xylenes. This suggested that FA was firstly converted into furan and then furan reacted with propylene that formed toluene.

4 Discussion

4.1 Reaction network

We have described the overall reaction network for furan conversion at 600 °C in our previous work.^{33,66} In this paper we have shown the importance of Diels–Alder reactions between different furanic species and olefins within this network. Fig. 8 summarizes this chemistry. Furan (C_4H_4O) first undergoes one of three reactions: (1) decarbonylation to form allene (C_3H_4) and CO, (2) Diels–Alder reaction with another furan followed by dehydration forming benzofuran and water or (3) Diels–Alder reaction with propylene (or another olefin) to produce toluene (or another aromatic) and water. The allene undergoes oligomerization and cracking reactions to produce a series of olefins. Benzene can be produced either from benzofuran decarbonylation or



Fig. 8 Overall reaction network for conversion of furan and furan + propylene over ZSM-5 catalyst at elevated temperatures.

allene dimerization/dehydrogenation. There are two possible routes to form the other aromatics. The first route is alkylation and cracking of an aromatic with allene or another olefin forming ethylene and another aromatic. The second route is a Diels–Alder reaction between olefins and furan. For example, propylene reacts with furan producing toluene and water. Polycyclic aromatics can also be formed *via* Diels–Alder reaction between aromatics and furan. For example, the benzene can react with furan and form naphthalene and water. By adjusting the concentration of olefin to furan in the reactor the rate of this second pathway can be increased causing the selectivity to toluene or other targeted aromatics to increase.

The addition of propylene to the reactor increases the rate of furan conversion. This suggests that the Diels–Alder reactions are faster than the decarbonylation reactions. For example, at 450 °C without propylene co-feeding, the furan conversion was only 22% and the aromatics selectivity was 20%.³³ Benzofuran (18% carbon selectivity) and coke (47% carbon selectivity) were the products produced in highest yield. However, as shown in Table 1, at 450 °C and with the existence of propylene, 54% furan was converted and only 5% converted carbon formed coke at the same furan partial pressure and space velocity.

4.2 Maximizing *p*-xylene selectivity

p-Xylene is a large volume commodity chemicals that is used as a starting material to produce PET. Here we would like to suggest reaction conditions for maximizing *p*-xylene selectivity. Xylenes are produced during biomass CFP.^{12,33,36,66} According to Tables 1–3 and Fig. 2, 2MF is the best starting furanic

compound for xylenes production. The reaction of 2MF with propylene at 600 °C can produce xylenes with selectivity comparable to benzene and toluene (the BTX ratio is 0.9:1:1.1).

The xylene selectivity is also a strong function of temperature. Fig. 3(b) and 4(b) show that the xylenes and alkylbenzene selectivity decreased with increasing temperature. This suggests that at higher temperatures dealkylation reactions begin to dominate.^{63,64} The overall aromatic selectivity however goes through a maximum with temperature at 450 °C for the reaction of 2MF and propylene.

The *p*-xylene selectivity (this selectivity only includes *p*-xylene, *m*-xylene, and *o*-xylene) was a function of temperature (Table 2). The *p*-xylene selectivity increased with decreasing temperature (Table 2). A similar temperature-dependence of xylene isomers was also seen by S. Al-Khattaf for the reaction of *m*-xylene transformation using pre-coked ZSM-5 catalyst.⁶⁷ In Al-Khattaf's study the ratio of *p*-xylene to *o*-xylene was increased by decreasing the temperature from 500 to 400 °C in both fresh and pre-coked ZSM-5 catalysts. p-Xylene has a higher diffusivity than the other two isomers and thus it's selectivity increases with decreasing temperatures.38,67 At high temperatures the effect of the diffusivity is reduced so that all isomers can easily diffuse out from the ZSM-5 pores. At lower temperatures the space confinement imposed by ZSM-5 pores is more important. It has been suggested that coking of the zeolite pores will decrease the pore volume and cause a change in diffusivity of the different xylene isomers.⁶⁷ In the reactions studied in this paper coke builds up on the catalyst surface with time on stream and causes an increase of *p*-xylene selectivity, as shown in Fig. 6(a). This suggests that small amounts of coke can help maximize the *p*-xylene selectivity. However, too much coke

Table 3	Products	distribution	obtained	from	conversion	of	furfural,	furfural	+	propylene	mixtures,	FA	(furfuryl	alcohol),	and	FA	+ p	ropylene
mixtures	over ZSM-	-5															-	

Feedstock Corrier gas	Furfural	Furfural	Furfural	FA	FA 2% Propulana
	пе	2% Propylelle	2% Propylelle	пе	2% Propylene
Temperature (°C)	600	600	450	600	600
Furans WHSV $(h^{-1})^a$	9.0	9.0	9.0	3.3	3.3
Propylene WHSV $(h^{-1})^a$	_	9.1	9.1	9.1	9.1
P_{furfural} or P_{FA} (torr) ^b	7.0	7.0	7.0	2.5	2.5
Furfural and FA conversion (%)	100	100	100	100	100
Propylene conversion (%)		53	64		29
Overall selectivity $(\%)^c$					
CO	29.3	11.3	7.3	13.0	2.0
CO ₂	3.3	1.9	0.1	1.5	0.0
Olefins	18.8	38.7	46.6	14.7	58.5
Aromatics	16.7	42.7	38.6	42.4	34.4
Coke	16.6	3.4	2.9	25.8	4.8
Oxygenates ^d	15.2	2.0	4.5	2.6	0.3
Aromatic selectivity (%)					
Benzene	35.5	21.0	6.1	9.1	23.4
Toluene	28.6	57.9	38.5	13.1	38.2
Xvlene	6.9	14.2	38.5	13.3	21.7
Styrenes ^e	6.9	2.1	0.6	9.6	3.5
Indenes ^e	11.3	2.3	5.3	33.4	6.2
Naphthalenes ^e	10.3	1.6	0.9	17.1	3.7
Alkylbenzenes ^e	0.6	1.0	10.2	4.4	3.3
Olefin selectivity (%)					
Ethylene	38.1	58.3	28.6	43.5	55.8
Propylene	42.8			36.1	_
C ₄ olefins	8.2	35.6	55.4	12.5	40.9
Allene	4.5	0.0	0.0	3.2	0.0
C ₅ olefins	5.8	5.1	7.9	4.7	2.4
C ₆ olefins	0.62	1.0	6.0	0.0	0.9
C ₇ olefins	0.0	0.0	2.07	0.0	0.0
<i>Xylenes distribution (%)</i>					
<i>p</i> -Xylene	37	32	40	40	31
<i>m</i> -Xylene	46	51	46	43	49
o-Xylene	17	18	14	17	20

^{*a*} Weight hourly space velocity (WHSV) is defined as flow rate of furfural or propylene (g h⁻¹) divided by weight of the catalyst (g). The amount of furfural was estimated by Antoine Equation at 45 °C. ^{*b*} The vapor pressure of furfural was estimated by Antoine equation at 45 °C. ^{*c*} For conversion of mixtures, ethylene or propylene are excluded. ^{*d*} Oxygenates contain 97–99% furan and 1–3% 2MF. ^{*e*} Styrenes include styrene and methylstyrenes; indenes include indene, indan and methylindenes; naphthalenes include naphthalene, dihydronaphthalene, and methylnaphthalenes. Alkylbenzenes includes ethylbenzene, 1,2,4-trimethylbenzene, 4-ethyltoluene, and propylbenzene.

deposition will deactivate the catalyst and decrease the p-xylene yield as shown in Fig. 7(b).

The third parameter which affects the xylene selectivity is the ratio of propylene to 2MF. The xylene selectivity increases with increasing propylene to 2MF molar feed ratio. However the xylene selectivity decreased when pure propylene was fed into the reactor. The ratio of *p*-xylene, *m*-xylene, and *o*-xylene was not a function of the olefin to 2MF feed ratio as shown in Table 2. This indicated that the xylene isomers distribution more likely was controlled by temperature and the zeolite structure (*e.g.* the space confinement imposed by the zeolites) rather than Ole/2MF ratios. The Ole/2MF ratios simply changed the overall selectivity of xylenes.

4.3 Aromatics are produced from renewable biomass

This paper thus shows two different routes to make aromatics from biomass using zeolite catalysts. The first route is where

biomass is directly fed into a fluidized bed reactor with a zeolite catalysts to produce aromatics and olefins by CFP.¹² Ethylene and propylene are produced in this CFP reaction and can be recycled back into the reactor to produce more aromatics.^{12,33} The second route is where biomass is selectively dehydrated to form furanic compounds. These furanic compounds then are converted into aromatics *via* Diels–Alder reactions. As discussed in the Introduction, furanic compounds are produced from furfural that is produced from biomass with low cost. Therefore, our results show these other routes to convert the furanics into targeted aromatics may become commercially viable.

5 Conclusions

Furan, furfural, and 2MF produced aromatics, olefins, CO, CO_2 , coke and water over ZSM-5. The addition of propylene to the feed increased the aromatics selectivity and the selectivity of

toluene and xylenes due to the increase in the Diels–Alder reactions. The toluene selectivity increased by the reaction of furan (a C_4 diene) with propylene (a C_3 dienephile). Xylenes selectivity increased by reaction of 2-methylfuran (2MF, a C_5 diene) with propylene (a C_3 dienephile). The reaction of propylene with furfural and furfuryl alcohol produces more toluene than xylene because furfural and furfuryl alcohol are converted into furan and CO inside the catalyst before they undergo conversion into aromatics.

When furan, furfural and 2MF were fed by themselves the aromatic distribution was similar (benzene, toluene, xylene and naphthalene distribution) for all three feeds, suggesting they all produce common intermediates that are converted into aromatics in this process. We have previously shown that these furanic compounds are good model compounds for conversion of solid lignocellulosic biomass into aromatics by catalytic fast pyrolysis (CFP). The amount of aromatics produced did depend on the feed. 2MF produced more aromatics and olefins than furan and furfural. Furfuryl alcohol produced more aromatics than furan. However, furfural alcohol also produced more polycyclic aromatics than furan. Co-feeding of the propylene with furan, 2MF, furfural and furfuryl alcohol increased the rate of toluene or xylene production depending on the diene that was fed. This illustrates that Diels-Alder reactions are important reactions in the conversion of lignocellulosic biomass into aromatics by CFP.

The reaction conditions that maximize xylene production were a propylene to 2MF molar ratio of 1 at 450 °C. The xylene distribution is a function of temperature and zeolite structure. Lower temperature (*e.g.* 450 °C) and more space confinement (*e.g.* precoked zeolites) caused the increase of *p*-xylene. In general, the Diels–Alder reactions provide an alternative route to produce targeted aromatics from renewable biomass.

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