Angewandte
International Edition Chemie

DOI: 10.1002/anie.201107390

Biomass Conversion

Production of Renewable Aromatic Compounds by Catalytic Fast Pyrolysis of Lignocellulosic Biomass with Bifunctional Ga/ZSM-5 Catalysts**

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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.[1] In this single-step process, biomass including wood, agricultural wastes, and fast-growing energy crops is fed into a fluidized-bed reactor where the biomass first thermally decomposes to form pyrolysis vapors. These pyrolysis vapors then enter the zeolite catalysts, which are also inside the fluidized-bed reactor, and are converted into the desired aromatic compounds and olefins along with CO, CO_2, H_2O, and coke.[1c,2] The spent catalyst and coke are then sent to a regenerator where they are burned to provide process heat. The advantages of CFP are: 1) all the desired chemistry occurs in one single reactor, 2) the process uses an inexpensive silica–alumina catalyst, and 3) fungible aromatics and olefins are produced that fit easily into existing infrastructures. Several researchers have used zeolites to convert pyrolysis vapors inside the pyrolysis reactor[2i,3] as well as outside the pyrolysis reactor.[4] While previous studies have shown that aromatics can be produced from pyrolysis vapors, they have produced low yields of the desired aromatics and high yields of coke. Herein we show how bifunctional Ga/ZSM-5 catalysts can be used to increase the yield of aromatics by CFP by 40% compared to that with the standard ZSM-5 catalyst. Ga/ZSM-5 is most likely a bifunctional catalyst where Ga promotes both the desired decarbonylation reactions and olefin aromatization while the ZSM-5 portion of the catalyst catalyzes the remaining reactions for the production of aromatics (e.g. oligomerization and crackings).

We have recently shown that aromatics and olefins can be directly produced from wood by CFP.[1d] The biomass first thermally decomposes into vapors. The cellulose and hemicellulose in the biomass form anhydrosugars upon pyrolysis.[5] These anhydrosugars then undergo dehydration to form furans.[5] The furans then enter the zeolite pores where they undergo a series of reactions to form aromatics, olefins, coke, CO, CO_2, and H_2O. The lignin fraction of the biomass primarily forms coke.[6] The aromatic selectivity in CFP is a function of the pore size, internal pore volume, and structure of the zeolite.[7] Our previous studies indicate that ZSM-5 has the optimal zeolite structure to produce the highest yield of aromatics from biomass. The previous highest carbon yield of aromatics from wood by CFP is 14%.[1d]

We have used furan as a model compound for wood to identify the key reactions occurring inside a zeolite catalyst.[8] The proposed reaction pathway for furan conversion is shown in Scheme 1. Furan initially undergoes either decarbonylation to form allene (C_3H_4) and CO or Diels–Alder condensation to form benzofuran (C_8H_6O) and water. The allene can undergo either oligomerization to form a series of olefins, or alkylation with other aromatics to form heavier aromatics and ethylene. The olefins can react with the furan to form aromatics and water. The benzofuran can also undergo decarbonylation to form benzene, CO, and coke. The olefins produced during CFP can be recycled to the reactor to form more aromatics.[1d] For example, co-feeding of propylene with furan increases the production of toluene. However, co-feeding of ethylene with furan does not change the rate of aromatic production with ZSM-5. This suggests that it would be highly desirable to have a catalyst that has high rates of decarbonylation and high rates of olefin aromatization (particularly ethylene). Ga-promoted zeolite catalysts have been shown to increase the rate of olefin oligomerization and subsequent conversion into aromatics.[9] Furthermore, Ga-promoted catalysts have also shown to have high rates of dehydrogenation and aromatization of alkanes.[9,10] Recently Ga-promoted zeolites have been used to upgrade bio-oils and pyrolysis vapors.[4d,11] In these studies BTX production from biomass was promoted by using Ga/ZSM-5 catalysts. These previous results suggest that Ga promotion of ZSM-5 may be able to increase the rate of aromatics production for the CFP of biomass.

We prepared a series of Ga-promoted catalysts to test this hypothesis. We synthesized the Ga catalysts by four different methods: 1) ion-exchange (Ga1/HZSM-5), 2) incipient wetness (Ga2/HZSM-5), 3) modified ion-exchange (Ga3/HZSM-5), and 4) a hydrothermal synthesis method where the Ga was incorporated directly into the ZSM-5 framework (GaF4–GaF7/ZSM-5). All of the zeolites we synthesized had MFI (mordenite framework inverted) structure (see Figure S1 in the Supporting Information). We also prepared a Ga/SiO_2 catalyst by the incipient-wetness method. Ga was also added to a commercially available spray-dried (SD) catalyst as well (GaSD). Table S1 in the Supporting Information shows the

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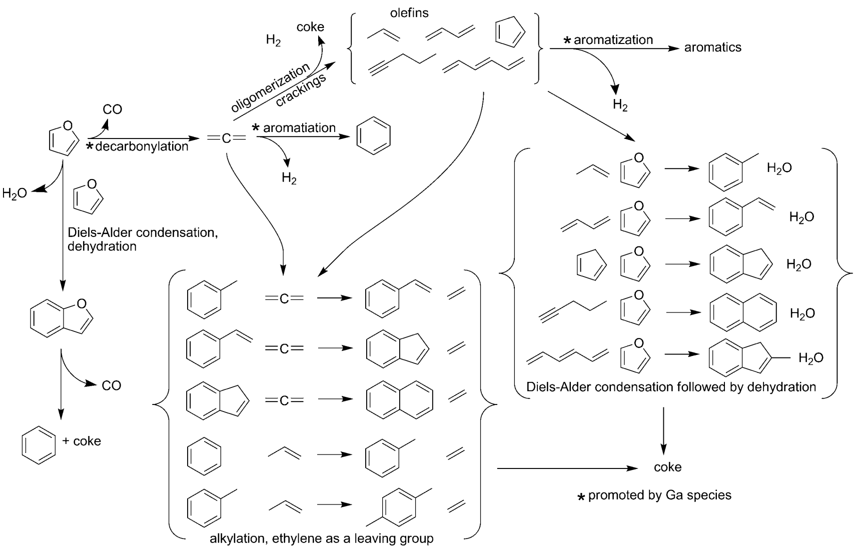
[**] This work was supported as part of the Catalysis Center for Energy Innovation, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under award number DE-SC0001004.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201107390.



Scheme 1. Reaction network of furan conversion into aromatics over ZSM-5 at 600 °C.

results of the elemental analysis of all catalysts. Table 1 and Table 2 show the product distribution for furan conversion over the different zeolite catalysts in a flow fixed-bed reactor, and for pinewood conversion over spray-dried catalysts in a fluidized-bed reactor, respectively. Experimental details are given in the Supporting Information.

Table 1: Summary of furan conversion and carbon selectivity of the products obtained by using ZSM-5 and Ga-promoted ZSM-5 as the catalyst; reaction conditions: temperature 600 °C, weight hourly space velocity (WHSV) 10.4 h^{-1}, and furan partial pressure 6 Torr.

Catalyst	ZSM-5	Ga1/ HZSM-5	Ga2/ HZSM-5	Ga3/ HZSM-5	Ga4F /ZSM-5	Ga5F/ ZSM-5	Ga6F/ ZSM-5	Ga7F/ ZSM-5	Ga/ SiO$_2$
Furan conversion [%]	48	53	50	47	28	15	28	33	14
Overall selectivity [%]									
aromatics	31.0	37.8	39.7	43.5	28.3	23.0	35.5	24.8	17.8
olefins	19.1	16.0	14.0	13.2	17.5	19.9	17.9	16.3	27.7
aromatics + olefins	50.1	53.9	53.7	56.8	45.8	42.8	53.4	41.1	45.6
CO	13.9	16.8	16.8	17.2	14.9	13.0	16.1	18.6	9.3
CO$_2$	1.1	1.7	2.0	1.8	0.7	0.0	0.5	1.0	4.6
coke	33.8	26.9	27.1	23.8	38.3	43.7	28.9	38.6	39.9
oxygenates	1.0	0.6	0.5	0.5	0.4	0.4	1.1	0.7	0.7
Aromatics selectivity [%]									
benzene	25.9	38.8	35.6	33.7	45.4	40.5	38.1	53.8	16.5
toluene	23.6	21.2	17.5	15.1	16.1	13.3	16.1	17.5	12.3
xylenes[a]	4.3	3.1	1.9	1.5	2.4	1.5	2.6	1.9	2.5
benzofuran	5.9	4.0	3.2	3.4	7.3	11.6	5.5	4.6	13.3
indenes[b]	19.3	10.4	11.6	11.5	15.1	19.0	13.8	10.7	19.2
naphthalenes[c]	10.6	13.6	23.5	28.1	6.4	9.4	14.8	6.0	30.8
alkylbenzenes[d]	1.2	0.6	0.4	0.3	0.5	0.3	0.6	0.5	0.3
styrenes[e]	9.2	8.3	6.4	6.3	6.8	4.4	8.5	5.0	5.2
Olefin selectivity [%]									
ethylene	38.7	39.9	40.4	39.6	18.2	13.6	34.1	41.6	18.7
propylene	35.1	27.4	27.6	24.8	11.8	7.9	17.5	22.0	14.4
allene	4.6	15.8	16.7	20.2	53.1	60.3	30.6	23.9	50.2
C$_4$ olefins	4.3	5.0	4.9	5.2	7.4	10.3	5.8	4.2	7.2
C$_5$ olefins	14.2	9.5	8.2	7.8	8.0	5.1	9.4	6.7	6.1
C$_6$ olefins	3.1	2.3	2.3	2.3	1.5	2.8	2.6	1.6	3.4

[a] Xylenes include *p*-, *m*-, and *o*-xylenes. [b] Indenes include indene, methylindenes, and indane. [c] Naphthalenes include naphthalene and methylnaphthalene. [d] Alkylbenzenes include ethylbenzene and trimethylbenzene. [e] Styrenes include styrene and methylstyrenes.

The Ga-promoted catalysts that were prepared by the ion-exchange and incipient-wetness methods had comparable catalytic activity (based on furan conversion) to ZSM-5. The aromatics selectivity increased from 31 % for ZSM-5 up to 44 % for Ga3/HZSM-5. The addition of Ga also caused the olefin selectivity to decrease, the CO selectivity to increase, and the coke selectivity to decrease. These same Ga-promoted catalysts also had a higher benzene and naphthalene selectivity than the unpromoted ZSM-5. The allene selectivity increased from 5 to 20 % when Ga was added to ZSM-5. These results suggest that Ga increases the rates of both decarbonylation (to form allene and CO) and also olefin aromatization (to convert more olefins into aromatics).

The catalysts that had Ga inside the zeolite framework (GaF/ZSM-5) had a lower catalytic activity than ZSM-5. The GaF/ZSM-5 catalysts also had lower aromatics selectivity and higher coke selectivity than ZSM-5 (with the exception of Ga6F/ZSM-5), suggesting that framework Ga is undesirable for aromatics production. The Ga-framework catalysts had very high allene selectivity, especially those lacking the strong Brønsted acid sites provided by SiO$_2$/Al$_2$O$_3$ (Ga4F and Ga5F/ZSM-5). This suggested that strong Brønsted acid sites are required for allene conversion into olefins and the subsequent aromatization. The high benzene selectivity could be attributed to allene dimerization catalyzed by Ga species (Scheme 1).

The Ga/SiO$_2$ catalyst had very low activity for furan conversion and formed large amounts of coke. It also had very high allene and CO selectivity. The aromatics the Ga/SiO$_2$ catalyst produced were primarily indenes and naphthalenes. The BTX selectivity was low (17, 12, and 3 %, respectively) with Ga/SiO$_2$.

A spray-dried Ga-promoted catalyst was prepared and also tested for the CFP of pinewood sawdust in a bubbling fluidized-bed reactor (Table 2). The addition of Ga increased the aromatics yield from 15 to 23 %. These results confirm that the Ga-promoted catalyst is able to convert not only model compounds but real wood into aromatics in higher yields. As

Table 2: Summary of the conversion of pinewood sawdust with SD and GaSD catalysts.[a]

Catalyst	ZSM-5	GaSD	ZSM-5	GaSD
T/°C	550	550	600	600
Overall carbon yield [%]				
aromatics	15.4	23.2	11.5	17.5
olefins	7.1	8.9	8.8	6.6
methane	2.0	1.5	2.0	2.8
CO_2	7.7	5.4	4.7	4.5
CO	20.3	17.1	24.9	17.2
coke	42.1	33.3	34.0	37.6
total	94.7	89.4	85.8	86.3
Aromatic carbon selectivity [%]				
benzene	12.4	19.6	25.6	33.0
toluene	31.2	34.3	37.8	33.7
xylenes	22.4	18.9	16.9	10.2
ethylbenzene	1.6	2.7	1.4	0.8
styrene	2.5	2.4	1.1	0.6
phenol	4.8	5.2	4.0	2.0
benzofuran	6.2	1.8	1.6	3.2
indene	0.9	1.2	0.9	0.1
naphthalenes	18.2	14.0	10.7	0.6
Olefin carbon selectivity [%]				
ethylene	34.3	42.5	42.4	43.7
propylene	51.9	49.1	44.4	41.7
C_4 olefins	13.7	8.3	13.2	7.6
Aromatics + olefin carbon yield/theor. aromatics + olefin carbon yield [%]				
	29.3	42.7	23.8	32.5

[a] Reactions were run at 550 and 600 °C, WHSV 0.35 h^{-1}, and gas flow rate 1000 mL min^{-1}. Reaction time was 30 min.

we have previously demonstrated, it is possible to convert the olefins into aromatics by recycling the olefins to the reactor.[1d] Assuming that the olefins are converted into aromatics, then the total aromatics yield would be 32 % carbon. Thus 55 gallons of aromatics can be produced from one ton of wood by CFP using the Ga catalyst. On an energy basis, 41 % of the energy of the wood is converted into fungible products that fit into existing petrochemical or fuels markets. The other 59 % of the wood's energy can be used to provide process heat for CFP. In competing technologies like gasification followed by Fischer–Tropsch synthesis (FTS), and production of ethanol from cellulose by hydrolysis/fermentation, 20 and 49 % of the energy of the biomass feed is converted into diesel fuel and ethanol, respectively.[12] These technologies are significantly more complicated than the single-step process of CFP, and therefore requiring higher capital costs. Aromatics are more valuable than diesel fuel or ethanol because they can be used as octane enhancers or as petrochemicals.[13]

The Ga-promoted ZSM5 catalyst was tested for 28 reaction-regeneration cycles. No significant deactivation was observed during the testing of this catalyst, indicating that the minerals in the biomass do not poison this catalyst. In the temperature-programmed desorption of ammonia (NH_3-TPD; Figure S2) we found that after 28 reaction-regeneration cycles, the acidity corresponding to weak acid (250 °C) slightly decreased and the acidity corresponding to strong acid (400–600 °C) increased. No major change was observed, suggesting that the active sites on GaSD were stable during the 28 reaction-regeneration cycles.

The CFP of wood is not as selective towards aromatics as the CFP of furan (Tables 1 and 2). As we have previously demonstrated, the yield of aromatics for CFP of maple wood decreases with the increasing content of the lignin in the maple wood.[6] The lignin in the wood primarily produces coke on the catalyst surface.[6] Thus one possible reason for the difference between the aromatics yield from wood and from furan is the lignin present in the wood.

We studied the temperature-programmed desorption of ammonia and of isopropylamine (NH_3-TPD and IPA-TPD) for the ZSM-5 and Ga-promoted catalysts (Ga2 and Ga3/HZSM-5; Figure S3 in the Supporting Information). Table S2 shows the acid density of the three zeolites where the total and Brønsted acid densities were calculated from the NH_3-TPD and IPA-TPD experiments, respectively. The ratio of Brønsted to total acid densities decreased with the increase of Ga content. There is no peak shift in NH_3 and IPA desorption between catalysts, suggesting that some protons were replaced by Ga species and the remaining protons were not affected.

These results suggest that Ga species replaced protons in the ZSM-5 catalysts and that the catalysts show a bifunctional character. Furan decarbonylation and olefin aromatization are promoted by Ga species. However, in the absence of strong Brønsted acid sites, the furan conversion and the aromatics selectivity were low. Furan TPD on ZSM-5 and Ga-promoted ZSM-5 (Figure S4) shows that the temperature at which the products were formed with the promoted and unpromoted catalysts was similar. This suggests that Ga modification did not change the overall reaction mechanism. Another possibility for the catalyst improvements observed is that the Ga species decreases the strength of the acid sites causing less coke formation during CFP. While we cannot discount this hypothesis, we think it is more plausible that this catalyst is bifunctional. We have tested CFP with ZSM5 catalysts having different SiO_2/Al_2O_3 ratios and observed that the optimal value for CFP was 30.[14] Adjusting the SiO_2/Al_2O_3 ratio can also be used to modify the strength of the acid sites of the catalyst. Since the Ga-promoted ZSM-5 already has the optimal SiO_2/Al_2O_3 ratio we believe that the effect with Ga is more than just to adjust the acid strength of the catalyst. These results suggest that there is a complex interplay between the Ga species and the Brønsted acid sites that promotes aromatics formation.

Our results show that the addition of Ga to ZSM-5 can increase the rate of aromatics production during CFP. This catalyst appears to be a bifunctional catalyst where the Ga species increase the rate of decarbonylation and olefin aromatization, whereas the zeolite catalyzes other reactions such as oligomerization. Our results suggest that new types of bifunctional catalysts can be developed for more selectively converting our biomass resources into useable fuels and chemicals.

Received: October 20, 2011

Keywords: arenes · biomass · catalytic fast pyrolysis · fuels · zeolites

[1] a) G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **2006**, *106*, 4044–4098; b) Y. C. Lin, G. W. Huber, *Energy Environ. Sci.* **2009**, *2*, 68–80; c) T. R. Carlson, T. R. Vispute, G. W. Huber, *ChemSusChem* **2008**, *1*, 397–400; d) T. R. Carlson, Y.-T. Cheng, J. Jae, G. W. Huber, *Energy Environ. Sci.* **2011**, *4*, 145–161; e) J. P. Diebold, J. W. Scahill, *Abstr. Pap. Am. Chem. Soc.* **1987**, *193*, 70.

[2] a) H. B. Goyal, D. Seal, R. C. Saxena, *Renewable Sustainable Energy Rev.* **2008**, *12*, 504–517; b) A. Demirbas, *Energy Sources Part A* **2007**, *29*, 753–760; c) T. R. Carlson, G. A. Tompsett, W. C. Conner, G. W. Huber, *Top. Catal.* **2009**, *52*, 241–252; d) S. Czernik, J. Scahill, J. Diebold, *J. Sol. Energy Eng.* **1995**, *117*, 2–6; e) J. Adam, E. Antonakou, A. Lappas, M. Stocker, M. H. Nilsen, A. Bouzga, J. E. Hustad, G. Oye, *Microporous Mesoporous Mater.* **2006**, *96*, 93–101; f) M. Olazar, R. Aguado, M. J. San Jose, J. Bilbao, *J. Chem. Technol. Biotechnol.* **2001**, *76*, 469–476; g) D. Fabbri, C. Torri, V. Baravelli, *J. Anal. Appl. Pyrolysis* **2007**, *80*, 24–29; h) D. Fabbri, F. Fabbri, G. Falini, V. Baravelli, A. Magnani, C. Torri, H. Maskrot, Y. Leconte, *J. Anal. Appl. Pyrolysis* **2008**, *82*, 248–254; i) A. Aho, N. Kumar, K. Eranen, T. Salmi, M. Hupa, D. Y. Murzin, *Fuel* **2008**, *87*, 2493–2501.

[3] a) M. Olazar, R. Aguado, J. Bilbao, A. Barona, *AICHE J.* **2000**, *46*, 1025–1033; b) A. A. Lappas, M. C. Samolada, D. K. Iatridis, S. S. Voutetakis, I. A. Vasalos, *Fuel* **2002**, *81*, 2087–2095.

[4] a) J. Diebold, J. Scahill, *Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem.* **1987**, *32*, 297; b) P. A. Horne, P. T. Williams, *Fuel* **1996**, *75*, 1043–1050; c) P. A. Horne, N. Nugranad, P. T. Williams, *J. Anal. Appl. Pyrolysis* **1995**, *34*, 87–108; d) A. Ausavasukhi, T. Sooknoi, D. E. Resasco, *J. Catal.* **2009**, *268*, 68–78; e) T. Q. Hoang, X. L. Zhu, T. Sooknoi, D. E. Resasco, R. G. Mallinson, *J. Catal.* **2010**, *271*, 201–208.

[5] Y. C. Lin, J. Cho, G. A. Tompsett, P. R. Westmoreland, G. W. Huber, *J. Phys. Chem. C* **2009**, *113*, 20097–20107.

[6] J. H. Jae, G. A. Tompsett, Y. C. Lin, T. R. Carlson, J. C. Shen, T. Y. Zhang, B. Yang, C. E. Wyman, W. C. Conner, G. W. Huber, *Energy Environ. Sci.* **2010**, *3*, 358–365.

[7] J. Jae, G. A. Tompsett, A. J. Foster, K. D. Hammond, S. M. Auerbach, R. F. Lobo, G. W. Huber, *J. Catal.* **2011**, *279*, 257–268.

[8] Y.-T. Cheng, G. W. Huber, *ACS Catal.* **2011**, *1*, 611–628.

[9] a) Y. Ono, *Catal. Rev. Sci. Eng.* **1992**, *34*, 179–226; b) G. Krishnamurthy, A. Bhan, W. N. Delgass, *J. Catal.* **2010**, *271*, 370–385; c) V. R. Choudhary, A. K. Kinage, T. V. Choudhary, *Science* **1997**, *275*, 1286–1288; d) A. Bhan, W. N. Delgass, *Catal. Rev. Sci. Eng.* **2008**, *50*, 19–151.

[10] a) V. R. Choudhary, P. Devadas, S. Banerjee, A. K. Kinage, *Microporous Mesoporous Mater.* **2001**, *47*, 253–267; b) V. R. Choudhary, S. Banerjee, D. Panjala, *Microporous Mesoporous Mater.* **2002**, *51*, 203–210.

[11] H. J. Park, H. S. Heo, J. K. Jeon, J. Kim, R. Ryoo, K. E. Jeong, Y. K. Park, *Appl. Catal. B* **2010**, *95*, 365–373.

[12] a) H. Boerrigter, "*Green*" *Diesel Production with Fischer–Tropsch Synthesis*; Report No. ECN-RX-03–014; Energy Research Centre of The Netherlands, Petten, **2003**; http://www.ecn.nl/docs/library/report/2003/rx03014.pdf; b) A. Aden, M. Ruth, K. Ibsen, J. Jechura, K. Neeves, J. Sheehan, B. Wallance, L. Montague, A. Slayton, J. Lukas, *Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover*; Report No. NREL/TP-510-32438; National Renewable Energy Laboratory, Golden, CO, **2002**; http://www1.eere.energy.gov/biomass/pdfs/32438.pdf.

[13] ICIS Pricing, http://www.icispricing.com/il_home.asp.

[14] A. J. Foster, J. Jae, Y.-T. Cheng, G. W. Huber, R. F. Lobo, *Applied Catalysis A*, under reviewed, **2011**.