## Supplementary Information

# Ultra-Selective Cycloaddition of Dimethylfuran for Renewable *p*-Xylene with H-BEA<sup>†</sup>

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#### **Catalyst preparation**

CBV600 (FAU, Si/Al=2.6), CP814C (BEA, Si/Al=19), CP814E (BEA, Si/Al=12.5) and CBV3024E (MFI, Si/Al=15) were obtained from Zeolyst. Prior to reactions, the catalysts were calcined in a tube furnace under air flow with an online drierite tube to remove moisture present in the gas. The calcination was carried at 550 °C for 12h with a ramping rate of 1 °C min<sup>-1</sup>. Gamma alumina (STREM) was pretreated at 500 °C for 12h with the same ramping rate. Niobic acid (HY-340, CBMM) was pretreated for 3 h at 100 °C.

#### Brønsted acid sites and total acid sites measurement

Physiochemical properties of the catalysts are included in Talbe S1. The numbers of Brønsted acid site of the catalysts were determined by temperature programmed desorption (TPD) of isopropylamine (IPA, Aldrich) in conjunction with thermal gravimetric analysis (TGA) in a thermal analyzer (SDT600, TA instrument). Around 10 mg of catalyst was first cleaned at 550 °C for 1 h under helium flow. After the sample cooled down at 120 °C, isopropylamine was bubbled with helium at room temperature into the furnace for adsorbing on the catalysts. The stream was then switched to pure helium and kept flowing for 1 h to remove weakly adsorbed species. After that, the temperature programmed desorption/decomposition of isopropylamine was carried out with a ramping rate of 10 °C min<sup>-1</sup> to 700 °C. The Brønsted acid site concentrations were then determined by the weight difference between 300 °C and 400 °C, which is the temperature range corresponding the decomposition of isopropylamine on Brønsted acid sites.<sup>1</sup>

The numbers of total acid sites were measured by FT-IR measurement on pyridineadsorbed catalysts. The spectra were collected on Equinox 55 (Bruker) with a resolution of 2 cm<sup>-1</sup>. Briefly, the catalysts were loaded in the High Temperature Reaction Chamber (Harrrick) on Praying Mantis<sup>TM</sup> DRIFTS attachment (Harrick) and degassed at 550 °C for 1 hr under helium flow. Pyridine vapor was then bubbled into the chamber and contacted with the catalysts for 10 min. The catalysts were heated up to 150 °C and held for 1 hr under a flow of helium, and the spectra were all recorded at 120 °C. The Brønsted/Lewis acid site ratio was determined by integrating the adsorbance bands corresponding to Brønsted acid site (~1545 cm<sup>-1</sup>) and Lewis acid site (~1454 cm<sup>-1</sup>) and applications of molar extinction coefficients (1.67 cm  $\mu$ mol<sup>-1</sup> and 2.22 cm  $\mu$ mol<sup>-1</sup>, respectively). Detailed procedure can be found in the work by Emeis.<sup>2</sup> The numbers of total acid sites were calculated by using the Brønsted acid to Lewis acid site ratio and Brønsted acid site concentrations obtained from the IPA-TGA measurement,.

### **Reaction details**

The detailed schematic of the reactor design can be found in our previous work.<sup>3</sup> In dimethylfuran (DMF, Alfa Aesar or Acros Organics, >98%) reactions, 100 mL of ~1.2±0.1M of DMF in n-heptane (Alfa Aesar, 99%) with n-tridecane (Acros Organics, 99%) was enclosed in a 160 mL mini bench-top reactor (Parr) with 0.45±0.05 g of catalyst, and the reaction vessel was purged by nitrogen. For furan (Aldrich, 99%) and methylfuran (MF, Alfa Aesar, 98%) experiments, 100 mL of 1.0 M furanic feedstock in n-heptane with tridecane was used with 0.45±0.05 g of catalysts. The mixture was then stirred at 950±50 rpm with a gas entrainment impeller to ensure facile mass transfer in the system and heated up to 250 °C, controlled by 4848 control unit (Parr). The reactor was then pressurized with 14 bar (partial pressure) of ethylene gas (Airgas), and the total pressure the system was kept at ~62 bar over the reaction period. Liquid was sampled by a double block sampling system at designed reaction times. The composition of the sample was then analyzed on an Agilent 6890A or 7890A gas chromatograph with column equipped with flame ionization detector. The products were identified by comparing the retention times with standard chemicals. The concentrations of alkylated products and oligomers were estimated by using the response factor (RF) for p-xylene, toluene, or benzene and the additive RF of the aforementioned

products and the furanic feedstock (based on the reaction scheme).<sup>4</sup> The conversion of furanic compounds and selectivity to the products are defined as following:

$$X_{\text{furans}} (\%) = 100 \times \frac{C_{\text{furans},t_0} - C_{\text{furans}}}{C_{\text{furans},t_0}}$$
  
Selectivity<sub>product i</sub>(%) =  $100 \times \frac{C_i}{\sum_i C_i}$   
Carbon balance(%) =  $100 \times \frac{C_{\text{furans}} + \sum_i C_i}{C_{\text{furans},t_0}}$ 

where C is concentration of the chemicals. The conversion of DMF, selectivity to *p*-xylene, and carbon balance for each catalyst are included in Table S2. The concentration profiles of the products for each catalyst are included in Figure S1-S4.

| Catalyst                                 | Si/Al<br>Ratio <sup>[a]</sup> | surface<br>area <sup>[a]</sup><br>$(m^2 g^{-1})$ | Na <sub>2</sub> O content <sup>[a]</sup><br>(wt.%) | Brønsted acid<br>sites <sup>[c,d]</sup><br>(mmol g <sup>-1</sup> ) | Total acid<br>sites <sup>[d]</sup><br>(mmol g <sup>-1</sup> ) |
|--|-------------------------------|--|--|--|---|
| H-BEA<br>(CP814E)                        | 12.5                          | 680  | 0.05   | 0.70   | 1.12 <sup>[e]</sup>   |
| H-BEA<br>(CP814C)                        | 19                            | 710  | 0.05   | 0.56   | 1.21  |
| H-Y<br>(CBV600)                          | 2.6                           | 660  | 0.2  | 0.36   | 0.99  |
| H-ZSM-5<br>(CBV3024E)                    | 15                            | 405  | 0.05   | 0.71   | 1.10  |
| Niobic Acid                              | NA                            | $118^{[b]}$                                      | -  | $0.05^{[b]}$   | 0.13 <sup>[b]</sup>   |
| $\gamma$ -Al <sub>2</sub> O <sub>3</sub> | NA                            | 200 <sup>[b]</sup>                               | -  | -  | 0.21 <sup>[b]</sup>   |

Table S1. Physicochemical properties of the catalysts

[a] Zeolyst; [b] D. Wang et al.<sup>5</sup>; [c] measured by isopropylamine TPD-TGA; [d] C. L. Williams et al.<sup>3</sup> [e] pyridine FT-IR.

| Catalyst              | DMF<br>Conversion <sup>[a]</sup><br>(%) | <i>p</i> -Xylene<br>selectivity <sup>[a]</sup><br>(%) | Carbon balance <sup>[b]</sup><br>(%) |
|-----------------------|---|---|--------------------------------------|
| H-BEA<br>(CP814E)     | 99±0.1                                  | 90±1  | 90±4                                 |
| H-BEA<br>(CP814C)     | 78±2                                    | 80±1  | 97±5                                 |
| H-Y<br>(CBV600)       | 52±2                                    | 74±4  | 81±7                                 |
| H-ZSM-5<br>(CBV3024E) | 54±6                                    | 70±1  | 94±3                                 |
| Niobic Acid           | 45±8                                    | 76±4  | 90±9                                 |

 $58\pm2$ 

78±3

Table S2. Summary of the results of DMF cycloaddition reaction with ethylene (62 bar)

[a] after 24 hours,  $250^{\circ}$ C; [b] based on C<sub>DMF, t0</sub>.

 $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

52±3



**Fig. S1** Concentration of products as a function of time for the reaction of DMF over H-FAU (Si/Al=2.6).



**Fig. S2** Concentration of products as a function of time for the reaction of DMF over H-ZSM-5 (Si/Al=15).



Fig. S3 Concentration of products as a function of time for the reaction of DMF over niobic acid.



Fig. S4 Concentration of products as a function of time for the reaction of DMF over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.



**Fig. S5** Concentration of products as a function of time for the reaction of 2, 5 hexanedione, water, and ethylene (62bar) over H-BEA (Si/Al=12.5) at 250  $^{\circ}$ C.

The experiment to confirm the formation of *p*-xylene from 2,5-hexanedione was carried out by using 100 mL of reactant containing 0.12 M of 2, 5-hexanedione and 1.0 M of water in heptane with 0.5 g of H-BEA (Si/Al=12.5) at 250 °C. As shown in Figure S5, 2, 5-hexanedione undergoes cyclization to form DMF even with presence of water during the heating process (point "RT" to time = 0), similar to diketone cyclization described in literature,<sup>6</sup> and the composition did not change significantly after held at 250 °C for about 4 hrs. Once ethylene was introduced into the reactor (at 3.8 hours), the formed DMF started to be converted into *p*-xylene, and it supports the postulation that 2, 5-hexanedione, the product from hydrolysis of DMF, can be cyclized back to DMF during the reaction and subsequently form *p*-xylene.

H-BEA also had high activity for the conversion of MF to toluene. Figure S6 shows that MF conversion reaches 90% in 20 hours and 99% in 30 hours when using H-BEA. However, H-Y only achieves 85% MF conversion in 50 hours. The difference between the activity of H-BEA and H-Y in the cycloaddition of MF and ethylene is not as pronounced as in the cycloaddition of DMF and ethylene. Figure S7 depicts selectivity to toluene as a function of MF conversion for H-BEA and H-Y. Initially, cycloaddition of MF with H-Y produces a higher selectivity to toluene. However, H-BEA achieves almost 50% selectivity to toluene at >90% MF conversion. Only cycloaddition with H-BEA was found to attain >90% conversion in less than 24 hours.



**Fig. S6** Conversion of MF as a function of time for the reaction of MF and ethylene over H-BEA (Si/Al = 12.5) and H-Y (Si/Al = 2.6) at  $250^{\circ}$ C.



**Fig. S7** Selectivity to toluene as a function of MF conversion for the reaction of MF and ethylene over H-BEA (Si/Al = 12.5) and H-Y (Si/Al = 2.6) at  $250^{\circ}$ C.



**Fig S8** Conversion of furan as a function of time for the reaction of furan and ethylene over H-BEA (Si/Al = 12.5) and H-Y (Si/Al = 2.6) at  $250^{\circ}$ C.

H-BEA exhibited almost the same activity as H-Y for the conversion of furan to benzene. Figure S8 shows that furan conversion is only marginally higher for H-BEA, and that both catalysts depict the same trend of increasing conversion with time. Additionally, H-BEA is seen to produce the same selectivity to benzene as H-Y in Figure S9.



**Fig S9** Selectivity to benzene as a function of time for the reaction of furan and ethylene over H-BEA (Si/Al = 12.5) and H-Y (Si/Al = 2.6) at  $250^{\circ}$ C.



Scheme S1 Proposed recycle process for *p*-xylene production from DMF

A proposed recycle process is included in Scheme S1. In this process, excess DMF, ethylene and the hydrolysis product 2,5-hexanedione are recycled from the product mixture. As shown in Fig. S5, the 2,5-hexanedione will convert back to DMF and thereby contribute to the formation of p-xylene. The utilization of 2,5-hexanedione can reduce the carbon loss in the process and increase the yield of p-xylene, and the operational cost on starting materials can be further reduced.

### References

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