<u>Supplementary Information</u>: Kinetic Regimes in the Tandem Reactions of H-BEA Catalyzed Formation of *p*-Xylene from Dimethylfuran

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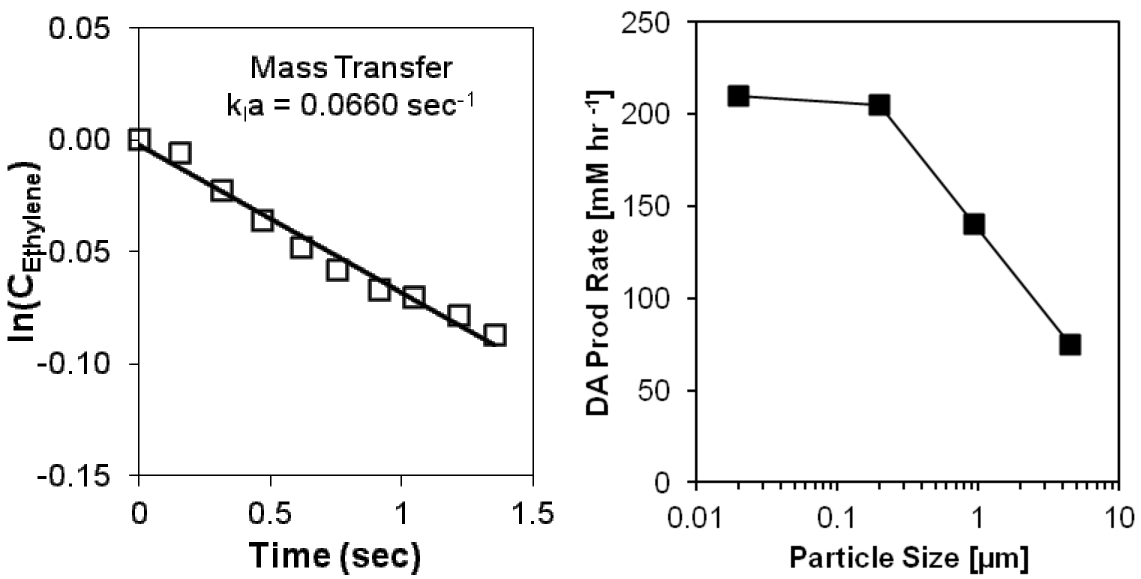

Figure S1. Characterization of Reactor Transport. A. Ethylene Interphase Mass Transfer Ethylene gas pressure in the headspace of the batch reactor containing heptane at 200 °C, measured as a function of time, is fit to determine $k_L a$= 0.066 sec^{-1}. **B. Intraparticle Mass Transfer.** Rate of production of Diels-Alder products (mmol/hr) relative to H-BEA particle size, using 1.38M DMF at 250 °C and 37.4 atm (550 psi) ethylene.

A. Synthesis of 3DOm-i zeolite BEA. The three dimensionally ordered imprinted zeolite BEA (3DOm-i BEA) was prepared by a seeded growth method using a mesoporous carbon (3DOm carbon with 35 nm cage size) as a hard template according to literature.[1] The 35nm 3DOm carbon was prepared from 35 nm colloidal silica nanoparticles based on previous report.[2, 3] Briefly, a zeolite BEA synthesis solution was prepared by dissolving 0.1 g of sodium hydroxide (Fisher) in 11.83 g of tetraethylammonium hydroxide solution (TEAOH, 35wt%, Alfa Aesar). 17.85 g of Ludox HS-30 (Aldrich) was dropwise added into the above solution under stirring, and 0.365 g of aluminum isopropoxide (Aldrich) was then added into the clear solution. The composition of the solution was 25 SiO_2: 0.25 Al_2O_3: 9 TEAOH: 0.35 Na_2O: 331 H_2O. The final solution was aged for one day with stirring before use. The resulting clear solution was filtered with a 200 nm syringe filter. An amount of 0.4 g of 3DOm carbon was immersed in 25 mL of zeolite BEA synthesis solution and enclosed in a Teflon-lined stainless steel autoclave and heated at 120 °C for three days in a preheated oven. The solid product was then washed by filtration with 1 L deionized water. In subsequent cycles, the washed solid was immersed in fresh synthesis solution and hydrothermally treated at the 120 °C for 3 days. The hydrothermal process was repeated four times. The final product was calcined in a tube furnace with flowing air (~250 cc/min) with a ramping rate of 1 °C/min to 550 °C for 12 hours to remove carbon and organic structure directing agent occluded in the zeolite structure. The ion-exchange process was carried out by contacting sample with 1 M NH_4NO_3 (ammonium nitrate, Macron) solution (1 g vs. 25 mL) and treated in 80 °C oil bath for two hours with magnetic stirring. The slurry was centrifuged and the solid was re-dispersed into the ammonium nitrate to repeat the process. After centrifuged and dried in 80 °C oven overnight, the sample was calcined in a tube furnace with flowing air (~250 cc/min) with a ramping rate of 1 °C/min to 550 °C for 12 hours to yield proton form of the zeolite.

B. Synthesis of 200 nm zeolite BEA. To synthesize 200 nm zeolite BEA, the synthesis solution for preparing 3DOm-i BEA was used. The hydrothermal treatment condition is 120 °C for three days. The formed zeolite nanocrystals were collected by centrifugation and washed extensively by deionized water. The calcination and ion-exchange procedures followed the same procedures described above.

C. Synthesis of 1 μm zeolite BEA. The synthesis of 1 μm zeolite BEA was prepared according to a seeded growth method in a fluoride medium.[4, 5] The seed solution was prepared according to the previous section (200 nm zeolite BEA) without calcination. The washed solids were dispersed into DI for later use. The concentration of the solid is 0.175 g/mL.

In a typical run, 10 g of tetraethylorthosilicate (TEOS, Alfa Aesar) was added into 11.46 g of TEAOH solution, and stirred at room temperature until it became a homogeneous solution (about 1.0-1.5 hours). Then, 0.211 g of anhydrous aluminum chloride (Alfa Aesar) was added under stirring. The solution was stirred in a hood until ethanol generated from the hydrolysis of TEOS and some water was evaporated. The final weight loss was 11.34 g (8.74 g of ethanol and 2.60 g of water). Then, 0.652 mL of zeolite beta seed solution (0.175 g/mL) was added into the solution (4.0 wt% with respect to the silica content) and mix by plastic spatula. Finally, 0.968 mL of hydrofluoric acid (Alfa Aesar, 49%) was added into the solution, and homogenized by using a plastic spatula for 10 minutes. The composition of the final gel was SiO_2: 0.573 TEAOH: 0.573 HF: 0.0167 Al_2O_3: 7.03 H_2O. The obtained solid-like hard gel was then loaded into a Teflon-lined stainless steel autoclave. The autoclave was heated at 140 °C with a rotation of 2 rpm for four days. The product was filtered, thoroughly washed by deionized water, and dried in an 80 °C oven overnight. The as-made solid was calcined with a ramping rate of 1 °C/min to 550 °C for 12 hours to remove the organic structure directing agent and fluoride ions.

D. Synthesis of 4.5 μm zeolite BEA. Synthesis of large crystal of zeolite BEA was accomplished by modifying the recipe of synthesis gel for preparation of 1 μm zeolite BEA, particularly higher hydrothermal temperature and more water in the gel. Typically, 10 g of tetraethylorthosilicate (TEOS, Alfa Aesar) was added into 11.46 g of TEAOH solution, and stirred at room temperature until it became a homogeneous solution (about 1.0-1.5 hours). Then, 0.211 g of anhydrous aluminum chloride (Alfa Aesar) was added under stirring, and 0.52 g of DI was added. The solution was stirred in a hood until ethanol generated from the hydrolysis of TEOS evaporated. The final weight loss was 8.74 g (ethanol). Finally, 0.968 mL of hydrofluoric acid (Alfa Aesar, 49%) was added into the solution, and homogenized by using a plastic spatula for 10 minutes. The composition of the final gel was SiO_2: 0.573 TEAOH: 0.573 HF: 0.0167 Al_2O_3: 10 H_2O. The obtained solid-like hard gel was then loaded into a Teflon-lined stainless steel autoclave. The autoclave was heated at 170 °C with a rotation of 2 rpm for 6 days. The product was filtered and thoroughly washed by deionized water, and dried in an 80 °C oven overnight. The as-made solid was calcined with a ramping rate of 1 °C/min to 550 °C for 12 hours to remove the organic structure directing agent and fluoride ions.

Supplementary References

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