

## Supporting Information

### Methylbenzenes Intermediates Equilibrium Analysis for Methanol-to-olefins Process

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#### 1 Experimental procedure and explanation

The experiment was performed on a fixed bed reactor. Catalyst of 0.3300 g was put into a quartz tube reactor. Methanol was putted into a vessel with a consistent temperature of 20.00 °C, and the saturated vapor was entrained into the reactor by nitrogen of 30.00 mL/min. The partial pressure of methanol was 13.03 kPa, and the WHSV was 1 h<sup>-1</sup>. The product was analyzed by a Gas Chromatography (GC 7890A of Agilent Technology) with 2 FID detectors. One FID for detecting light olefins and paraffins, while another for detecting aromatics species.

Commercial H-ZSM-5 were bought from the Catalyst Plant of Nankai University, and the zeolite was used as bought. We performed the experiments over both ZSM-5 and SAPO-34, and similar relationship was noticed. However, this paper was based on ZSM-5 for clearance.

Experiment for **Figure 2E** and **F** was performed over a nano ZSM-5 synthesized by ourselves. It has clear structure of ~60 nm crystals, and can be analyzed clearly. Same conditions was used and product distribution of aromatics is specially measured for “product distribution” in **Figure 2F**.

## **2 Method for capturing the hydrocarbon species by oriented blocking at b axis: a brief introduction**

Reason for changing system from commercial ZSM-5 to specially-synthesized nano ZSM-5 is here. A special phenomenon was noticed over the home-made nano ZSM-5. Coke firstly deposited at a and c axis, while almost no coke deposited at b axis at the first period of coking. We managed to deposit amorphous silica at b axis due to the limitation of carbon. Then carbon was removed by calcination, and we got a nano ZSM-5 with b-axis blocked. Aromatics can only diffuse along straight channels (b-axis) and cannot diffuse out along zigzag channels (c-axis), so we limit the aromatic production in MTO process. Product of pristine nano ZSM-5 included 12% of aromatics, and after special treatment, less than 4% of aromatics was found. With this method, we can measure the HP species captured and it fits the model well.

We coked the nano ZSM-5 with methanol at 475 °C for 20 h, WHSV of methanol is 0.7 h<sup>-1</sup>, and then the coked was treated with TEOS, dissolved in hexane. After continuous stirring, it is calcined at 550 °C for 6 h to remove the coke. Reactions was performed at 450 °C, the same condition with commercial ZSM-5 experiment.

## **3 Detailed description of MIEA**

We performed the Methylbenzene Intermediate Equilibrium Analysis (MIEA) with HSC Chemistry 6.0. We used “equilibrium composition”, and added one phase to continue the calculation. Then we added the components mentioned in the main text and set the temperature and pressure. Then we normalized the concentration of olefins and get the

result of ASF distribution. In order to compare with the experimental results, we also normalized the concentration of olefins from experiments.

In fact, some branched olefins such as isobutylene can diffuse from the channels of ZSM-5, but it won't change the result if you add them into the model, for their similar energy to their n-isomers. So we didn't include them into the model in the main text, in order to clarify the importance of steric factors in MIEA.

#### 4 Details description of energy barrier in Figure 2B

We calculated the chain growth probability  $\alpha$  under different temperature, and did a nonlinear regression of the model in Figure 3B to get the energy barrier.

Model in Figure 3B was derived from the definition of chain growth probability  $\alpha$ :

$$\alpha = \frac{k_g}{k_g + k_t}$$

We combined the formula with Arrhenius Equation:

$$k = Ae^{\frac{E_a}{RT}}$$

And collected some parameters, to get the model:

$$\alpha = \frac{1}{1 + Ae^{\frac{\Delta E}{RT}}}$$