

Heterogeneous & Homogeneous & Bio- & Nano-

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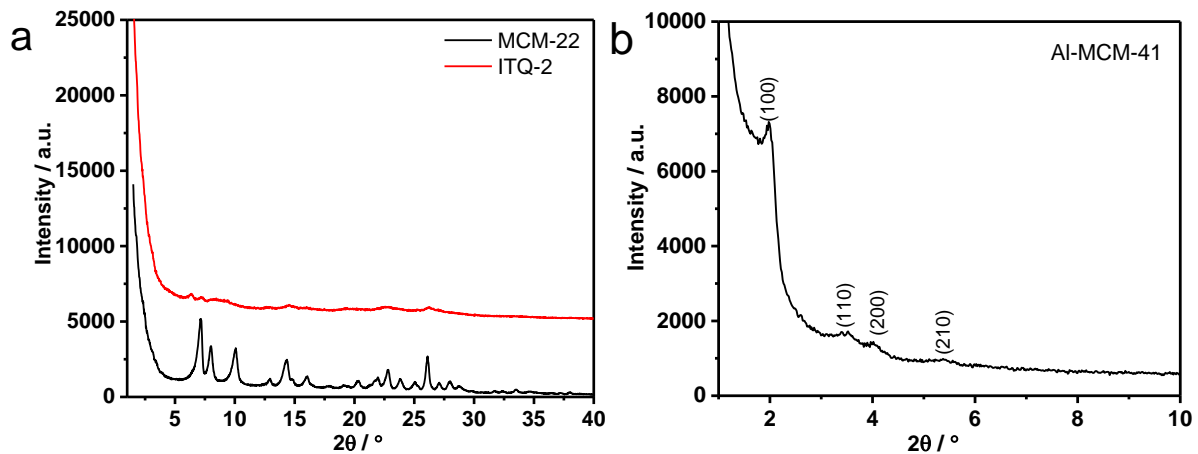
CATALYSIS

## Supporting Information

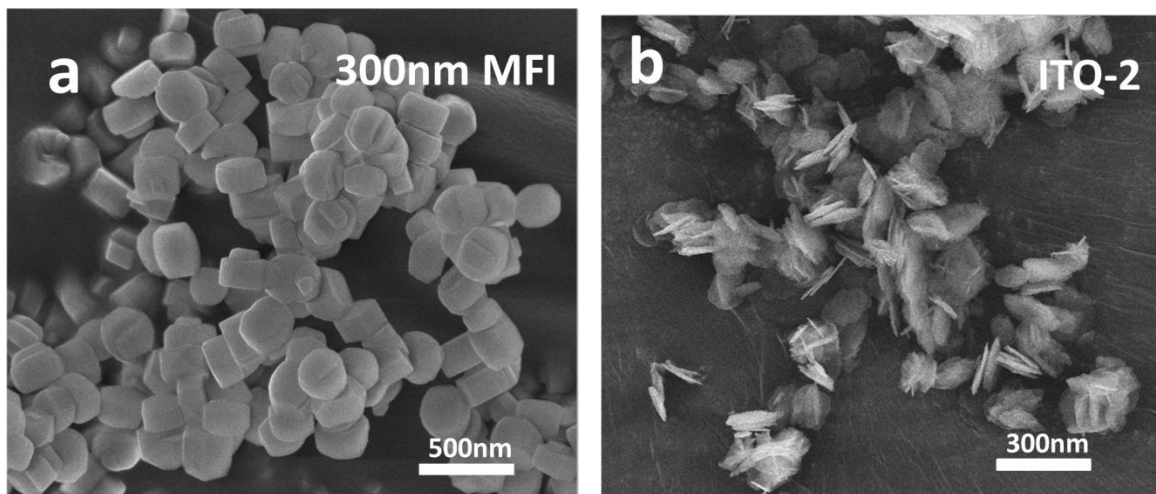
### Effects of the Framework and Mesoporosity on the Catalytic Activity of Hierarchical Zeolite Catalysts in Benzyl Alcohol Conversion

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Hongxia Xi,<sup>\*[a]</sup> and Wei Fan<sup>\*[b]</sup>

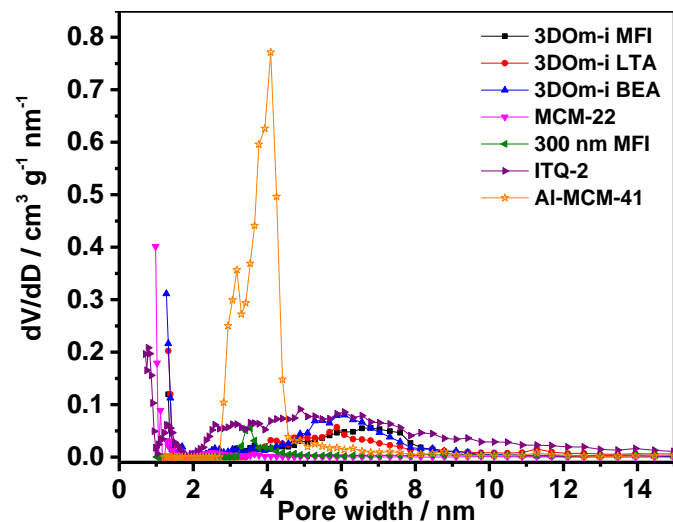
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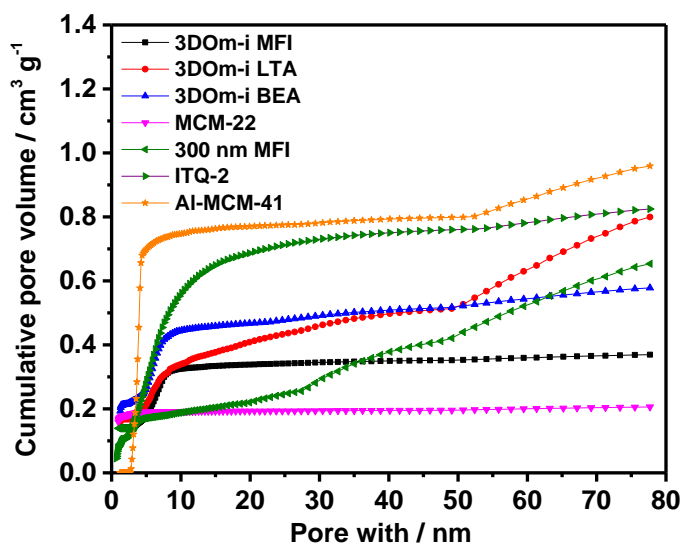
**Figure S1.** X-ray diffraction patterns of a) MCM-22, ITQ-2 and b) Al-MCM-41.



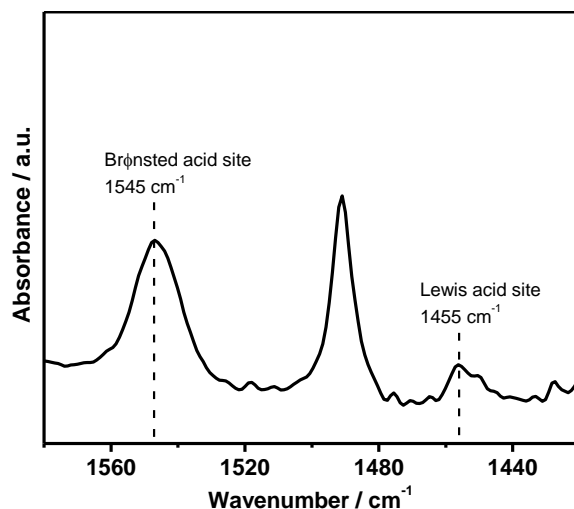
**Figure S2.** SEM images of a) 300 nm MFI and b) ITQ-2.



**Figure S3.** The NLDFT pore size distribution of 3DOm-i MFI, 3DOm-i LTA, 3DOm-i BEA, MCM-22, 300 nm MFI, ITQ-2 and Al-MCM-41.



**Figure S4.** The NLDFT cumulative pore volume plots over the entire pore width range for 3DOm-i MFI, 3DOm-i LTA, 3DOm-i BEA, MCM-22, 300 nm MFI, ITQ-2 and Al-MCM-41.



**Figure S5.** FTIR spectrum of pyridine adsorbed on 3DOM-i MFI at 523 K. The calculated Brønsted acid site density and Lewis acid site density are 0.108 mmol g<sup>-1</sup> and 0.012 mmol g<sup>-1</sup>, respectively.

### Synthesis of 3DOM Carbon

A hard template, 3DOM carbon, was made by following the method reported in our previous studies.<sup>[1]</sup> In a typical synthesis, a precursor solution made of furfuryl alcohol (Aldrich) and oxalic acid (Aldrich) with a weight ratio of 200/1 was impregnated within the silica colloidal crystal templates composed of highly monodisperse 35 nm silica nanoparticles. The resulting samples were heated to 343 K for 2 days to polymerize furfuryl alcohol, and then placed in flowing N<sub>2</sub>, first at 473 K for 3 h to cure the polymer, and then heated at 1173 K for another 2 h to carbonize the samples. The silica nanoparticles were dissolved in 6 M KOH solution (Aldrich) at 423 K for 2 days to yield 3DOM carbon replica. The resulting carbon material was then thoroughly washed with DI water to near-neutral pH. Finally, the 3DOM carbon was dried at 343 K for 24 h.

### Synthesis of 3DOM-i MFI

For the synthesis of 3DOM-i MFI, a clear synthesis solution with a molar composition of 1 SiO<sub>2</sub>: 0.25 TPAOH: 0.00625 Al<sub>2</sub>O<sub>3</sub>: 0.014 Na<sub>2</sub>O: 16.44 H<sub>2</sub>O was prepared by mixing TPAOH (Sigma

Aldrich), sodium hydroxide (Sigma Aldrich), silica sol (Ludox HS-40, Sigma Aldrich) and aluminum isopropoxide (98%, Aldrich). For the confined synthesis of MFI in the 3DOm carbon with a mesopore size of 35 nm, 0.2 g of 3DOm carbon was added to 10 g of the clear synthesis solution. Hydrothermal synthesis was conducted in a Teflon-lined autoclave at 373 K for 1 day with a rotation rate of 3 rpm. The hydrothermal treatment was repeated 3 times. A freshly made synthesis solution was used for each cycle. The solid sample was collected by filtration and dried at 373 K. 3DOm carbon was removed by calcination at 823 K for 24 h under air.

### **Synthesis of 3DOm-i BEA**

3DOm-i zeolite beta (3DOm-i BEA) was synthesized using a synthesis solution with a composition of 25 SiO<sub>2</sub>: 0.25 Al<sub>2</sub>O<sub>3</sub>: 4.5 (TEA)<sub>2</sub>O: 0.35 Na<sub>2</sub>O: 330 H<sub>2</sub>O. 0.1 g of NaOH was dissolved in 13.51 g of tetraethylammonium hydroxide (TEAOH, 35 wt% Alfa Aesar), followed by dropwise adding 17.85 g of LUDOX HS-30 colloidal silica (30 wt% Aldrich). After dissolving LUDOX HS-30 at room temperature, 0.366 g of aluminum isopropoxide (98%, Aldrich) was added to the solution. The mixture was aged for 24 h at room temperature and filtered using a 200 nm syringe filter to obtain a clear solution. The clear solution was used for the synthesis of 3DOm-i BEA. Typically, 0.4 g of 35 nm 3DOm carbon was immersed in 25 ml of the synthesis solution. After sealing in a Teflon-lined stainless steel autoclave, the mixture was heated at 373 K for 4 days. Thereafter, the samples were taken out of the autoclaves and washed by filtration with DI H<sub>2</sub>O before putting into a freshly prepared synthesis solution for the second cycle of the hydrothermal synthesis. The growth process was repeated 4 times.

### **Synthesis of 3DOm-i LTA**

3DOm-i LTA was synthesized using a synthesis solution with a composition of 11.25 SiO<sub>2</sub>: 1.8 Al<sub>2</sub>O<sub>3</sub>: 13.4 (TMA)<sub>2</sub>O: 0.6 Na<sub>2</sub>O: 700 H<sub>2</sub>O, 13.29 g of tetramethylammonium hydroxide

(TMAOH, 25 wt% Aldrich), 7.05 g of NaOH solution (Aldrich) was dissolved in 14.28 g of DI water), and 1.2 g of silicic acid (98%, Aldrich) were mixed together. After dissolving silicic acid at 343 K, 1.0 g of aluminum isopropoxide (98%, Aldrich) was added to the solution. This mixture was aged for 1 h at room temperature and filtered using a 200 nm syringe filter to obtain a clear solution. The clear solution was used for the synthesis of 3DOm-i LTA in 3DOm carbon. Typically, 0.4 g of 35 nm 3DOm carbon was added into 25 ml of the synthesis solution and aged for 1 h at room temperature before heated to 343 K for zeolite growth. After heating for 12 h, the samples were washed by filtration with DI H<sub>2</sub>O. Thereafter, the samples were put into a freshly prepared synthesis solution and aged for 1 h at room temperature, and then hydrothermal synthesis was carried out again at 343 K. The growth process was repeated 6 times.

### **Synthesis of 300 nm MFI**

The ZSM-5 nanocatalyst with a crystallite size of 300 nm was prepared by following the method in a published paper.<sup>[2]</sup> Typically, 5.261 g of tetraethyl orthosilicate (TEOS, 98%, Alfa-Aesar) was added into a mixture containing 17.25g of DI water and 6.325 g of tetrapropylammonium hydroxide (TPAOH, 1M aqueous solution, Sigma-Aldrich) under stirring at a speed of 1000 rpm. After stirring at 353 K for 24 h, and cooling down the mixture, a clear solution was obtained. Thereafter, a solution containing 1.274 g of DI water, 0.1914 g of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (98%, Alfa-Aesar) and 0.25 ml of 10 M NaOH aqueous solution were added to the mixture. The molar composition of the final gel was 1 SiO<sub>2</sub>: 0.01 Al<sub>2</sub>O<sub>3</sub>: 0.25 TPAOH: 0.05 Na<sub>2</sub>O: 35 H<sub>2</sub>O. Subsequently, this prepared synthesis gel was transferred to a Teflon-lined stainless-steel autoclave and hydrothermally treated at 443 K for 24 h. The solid product was collected by centrifugation and washed with DI water several times. After drying in 343 K overnight, the Na-

type 300 nm ZSM-5 samples were obtained by calcination of the as-synthesized sample in a furnace at 823 K with a ramp of 1 K min<sup>-1</sup>.

### **Syntheses of MCM-22 and ITQ-2**

For comparison, conventional MCM-22 and its delaminated sample were prepared in this study following a method reported in literature.<sup>[3]</sup> Aluminosilicate MCM-41 was purchased from Aldrich. After ion-exchange, H-form Al-MCM-41 was finally obtained.

At first, MCM-22 precursor (MCM-22(P)) was synthesized using the method described by Corma *et al.*<sup>[3a, 4]</sup> 0.122 g of sodium aluminate (56% Al<sub>2</sub>O<sub>3</sub>, 37% Na<sub>2</sub>O, Sigma-Aldrich) and 967.9 μl g of 10 M sodium hydroxide solution were added into 50 ml of DI water. Subsequently, 3.07 g of hexamethyleneimine (HMI) (99%, Aldrich) and 3.79 g of fumed silica (Cab-o-sil M5) were added. The mixture with molar composition of 1 SiO<sub>2</sub>: 0.49 HMI: 0.01 Al<sub>2</sub>O<sub>3</sub>: 0.09 Na<sub>2</sub>O: 44 H<sub>2</sub>O was formed, and then stirred at room temperature for 5 h with a magic stir bar at 500 rpm. The mixture was transferred into Teflon-lined steel autoclave and loaded into rotation oven at 408 K for 11 days with a rotating speed of 10 rpm. The crystalline power was collected by centrifugation, washed with DI water throughly and dried in oven at 353 K overnight. The MCM-22 sample was obtained by calcination of MCM-22(P) at 823 K under air for 12 h to remove the structure directing agent HMI. ITQ-2 was obtained from the delamination of swollen MCM-22. MCM-22(P) was first swollen by following procedure.<sup>[5]</sup> A mixture of 9.0 g of aqueous slurry of MCM-22(P) (20 wt% solids) was refluxed with 35.0 g of an aqueous solution of 29 wt% hexadecyltrimethylammonium bromide (CTAB, Aldrich) and 11.0 g of an aqueous solution of 40 wt% tetrapropylammonium hydroxide (TPAOH, Alfa Aesar) for 16 h at 353 K. After collecting swollen MCM-22 sample, the layers of MCM-22 were forced apart by placing the slurry in an ultrasound bath (50W, 40 kHz) for 1 h. Finally, isolated solid phase was gained

by adding a few drops of concentrated hydrochloric acid until the  $\text{pH} < 2$ , after centrifuging, drying and calcining, the final product ITQ-2 was yielded.

### **Ion-Exchange of Catalysts**

Ion-exchange was performed three times with 1 M aqueous solution of  $\text{NH}_4\text{NO}_3$  at 353 K for 2 h, the final products were converted to H-form by calcination at 823 K for 8 h with a ramp of 1 K  $\text{min}^{-1}$  in air flow.

### **$\text{N}_2$ physisorption isotherms data analysis**

Prior to the analysis, all catalysts were degassed at 573 K for 12 h. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation based on the adsorption branch curve in a relative pressure ( $P/P_0$ ) range of 0.05 - 0.3. The pore size distributions were estimated from the entire adsorption branch, based on a non-localized density functional theory (NLDFT) method which describes  $\text{N}_2$  adsorbed onto silica with cylindrical pores at 77 K (Versawin™ 1.0, Quantachrome).

### **IPA or CLD-TPD experiment**

Prior to the analysis, the catalysts (10 - 15 mg) were pre-treated at 773 K for 1 h in a helium flow to clean the catalyst surface. After the samples cooled down to 393 K, an isopropylamine (IPA)/He gas mixture passed through the sample at 100  $\text{ml min}^{-1}$ . After the adsorption of IPA reaches to equilibrium onto the catalysts, the temperature was raised from 393 K to 1023 K with a ramping rate of 10  $\text{K min}^{-1}$ . The decomposition of IPA into ammonia and propene on the Brønsted acid sites of zeolite catalysts occurring between 575 K and 650 K was used to calculate the total amount of Brønsted acid sites of the catalysts. 2,4,6-collidine (CLD, 99%, Alfa-Aesar) which is too bulky to diffuse into MFI pores was used to quantify acid sites on the external surface of 3DOm-i ZSM-5<sup>[6]</sup> and MCM-22.<sup>[7]</sup> A typical CLD-TPD experiment was run on the



same thermogravimetric analysis instrument as IPA-TPD, except for using CLD as the adsorbate. Triphenylphosphine (TPP, 99%, Alfa-Aesar), a larger basic molecule was used to evaluate the acid sites on the external surface of BEA zeolite, as suggested by literature.<sup>[8]</sup> [ENREF 32](#) In this experiment, 3DOM-i BEA was first calcined at 823 K for 8 h in an air flow to remove the adsorbed impurities. 1 ml of CH<sub>2</sub>Cl<sub>2</sub> solution containing 10<sup>-7</sup> M of TPP was added into the calcined BEA zeolite. The sample was washed with an excess amount of CH<sub>2</sub>Cl<sub>2</sub> to remove the weakly adsorbed TPP. Finally, it was dried in an oven at 393 K overnight to remove CH<sub>2</sub>Cl<sub>2</sub>. The subsequent procedure was the same as described above for IPA-TPD and CLD-TPD measurements. In the case of Al-MCM-41, IPA-TPD was used to measure the amount of acid sites on the surface.

### **FT-IR measurement**

The numbers of total acid sites were measured by FT-IR measurement on pyridine-adsorbed 3DOM-i MFI. The spectrum was 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 (Harrick) on Praying Mantis<sup>TM</sup> DRIFTS attachment (Harrick) and degassed at 823 K for 1 h 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 423 K and held for 1 h under a flow of helium, and the spectra were all recorded at 523 K. The Brønsted/Lewis acid site ratio was determined by integrating the absorbance 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 μmol<sup>-1</sup> and 2.22 cm μmol<sup>-1</sup>, respectively).

### **Benzyl alcohol self-etherification in presence of DTBP (in internal micropores)**

In the calculation, the etherification rate is assumed to be proportional to the concentration of the

adsorbed benzyl alcohol and the Brønsted acid site inside the micropores of zeolite catalyst. The effective diffusivity for benzyl alcohol in the micropores is considered constant, the differential equation that describes steady state diffusion and reaction of benzyl alcohol is,

$$D_A \frac{d^2 \bar{C}_A}{dx^2} - k_{\text{int}} C_{\text{H}^+} \bar{C}_A = 0 \quad (\text{Equation S1})$$

where  $D_A$  is the effective diffusion coefficient of benzyl alcohol in the catalyst ( $\text{m}^2 \text{s}^{-1}$ );

$\bar{C}_A$  is the adsorbed benzyl alcohol concentration on the catalyst ( $\text{mol L}^{-1}$ );

$x$  is the radius of catalyst particle size (m);

$C_{\text{H}^+}$  is the Brønsted acid site concentration inside the catalyst ( $[\text{mol H}^+] \text{L}^{-1}$ );

$D_A$  in Equation S1 is determined by using large ZSM-5 catalyst ( $17 \mu\text{m}$ ,  $x_p = 8.5 \mu\text{m}$ ) have a severe diffusion limitation for the etherification reaction ( $D_A = 6.15 \times 10^{-20} \text{m}^2 \text{s}^{-1}$ ).<sup>[6]</sup>

The Equation S2 presented as follows was used to calculate the apparent rate constant of the self-etherification reaction,  $k_{\text{eth,app,int}}$ .

$$\frac{V_{\text{sol.}}}{C_{\text{H}^+} V_{\text{cat.}}} \frac{1}{K \bar{C}_A^{\text{max}}} \left[ \ln \frac{C_A^0}{C_A} + K (C_A^0 - C_A) \right] = k_{\text{eth,app,int}} t \quad (\text{Equation S2})$$

where  $V_{\text{sol.}}$  is the total volume of solution present in the batch reactor (L);

$V_{\text{cat.}}$  is the volume of catalyst used in the reaction (L);

$K$  is the adsorption equilibrium constant ( $K = 62 \text{L mol}^{-1}$ );

$\bar{C}_A^{\text{max}}$  is the maximum adsorbed concentration of benzyl alcohol in the catalyst ( $\bar{C}_A^{\text{max}} = 1.35 \text{mol L}^{-1}$ );<sup>[6, 9]</sup>

$k_{\text{eth,app,int}}$  is determined from the experimental data  $\ln \frac{C_A^0}{C_A} + K (C_A^0 - C_A)$  vs.  $t$  for each catalyst, as

shown in Figure 6a.

### Mesitylene alkylation in absence of DTBP (on external surface)

Alkylation of benzyl alcohol with mesitylene occurs exclusively on these active sites located on the external surface of the zeolite catalysts. The alkylation reaction,  $A + B \rightarrow C$ , ( $A$ ,  $B$  and  $C$  refer to benzyl alcohol, mesitylene and 1, 3, 5-trimethyl-2-benzylbenzene, respectively.) can be approximated as pseudo-first order reaction, because of the excessive amount of mesitylene existing in the reaction.<sup>[10]</sup> The rate equation can be written as

$$\frac{dC_C}{dt} = k_{\text{alk,ext}} M_B f_{\text{B,ext}} C_A \quad (\text{Equation S3})$$

where  $C_A$  is the concentration of benzyl alcohol ( $\text{mol L}^{-1}$ ),  $C_C$  is the concentration of 1, 3, 5-trimethyl-2-benzylbenzene ( $\text{mol L}^{-1}$ ),  $t$  is the reaction time (s),  $k_{\text{alk,ext}}$  is the specific rate constant ( $[\text{mol H}^+]^{-1} \text{s}^{-1}$ ),  $M_B$  is the total number of Brønsted acid sites present in the reaction ( $\text{mol H}^+$ ), and  $f_{\text{B,ext}}$  is the fraction of external Brønsted acid site over  $M_B$  (%).

In a batch reactor, self-etherification can take place to produce dibenzyl ether simultaneous with alkylation reaction,  $A + A \rightarrow E$ , ( $A$  and  $E$  refer to benzyl alcohol and dibenzyl ether, respectively.) This reaction can also be approximated as the pseudo-first order reaction, and the selectivity for both reactions,  $\alpha = 2C_E/C_C$ , is nearly constant for all the zeolite catalysts we used (shown in Table 4), where  $C_E$  is the concentration of dibenzyl ether ( $\text{mol L}^{-1}$ ). Finally,  $C_C$  can be described as a function of benzyl alcohol concentration ( $C_A$ ) and selectivity ( $\alpha$ ),

$$C_C = \frac{C_A^0 - C_A}{1 + \alpha} \quad (\text{Equation S4})$$

where  $C_A^0$  is the initial concentration of benzyl alcohol ( $\text{mol L}^{-1}$ ). Substituting Equation S4 into Equation S3, the rate equation becomes

$$\frac{dC_A}{dt} = -k_{\text{alk,ext}} M_B f_{\text{B,ext}} (1 + \alpha) C_A \quad (\text{Equation S5})$$

Integration of Equation S5 gives the concentration of benzyl alcohol ( $C_A$ ) as a function of

reaction time ( $t$ ),

$$\ln \frac{C_A^0}{C_A} = k_{\text{alk,ext}} M_B f_{\text{B,ext}} (1 + \alpha) t = k_{\text{alk,app}} t \quad (\text{Equation S6})$$

where  $k_{\text{alk,app}}$  is the apparent alkylation rate constant of the reaction ( $\text{s}^{-1}$ ). Thus,  $k_{\text{alk,app}}$  can be determined from the slope of the plot of  $\ln \frac{C_A^0}{C_A}$  vs.  $t$  for each catalyst, as shown in Figure 5a.

Finally,  $k_{\text{alk,ext}}$  was determined from Equation S7,

$$k_{\text{alk,ext}} = \frac{k_{\text{alk,app}}}{M_B f_{\text{B,ext}} (1 + \alpha)} \quad (\text{Equation S7})$$

After calculation, the values of  $k_{\text{alk,ext}}$ ,  $k_{\text{alk,int}}$ ,  $k_{\text{eth,app,int}}$ ,  $\alpha$  and  $f_{\text{B,ext}}$  are summarized in Table 4.

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