

Supplementary Materials

for

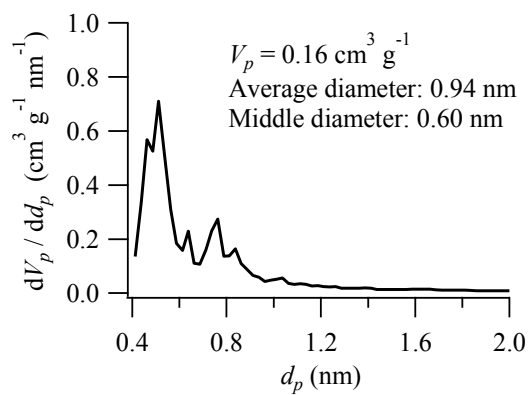
**Hydroxymethylation of Furfural to HMF with
Aqueous Formaldehyde over Zeolite Beta Catalyst**

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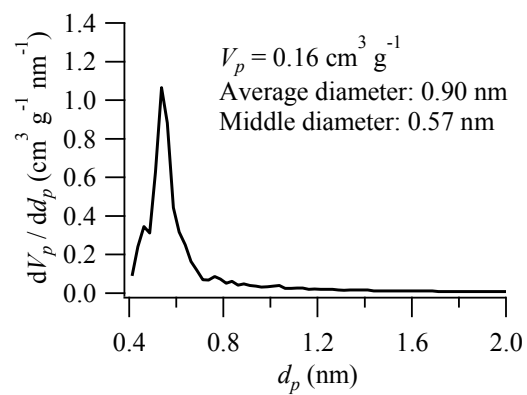
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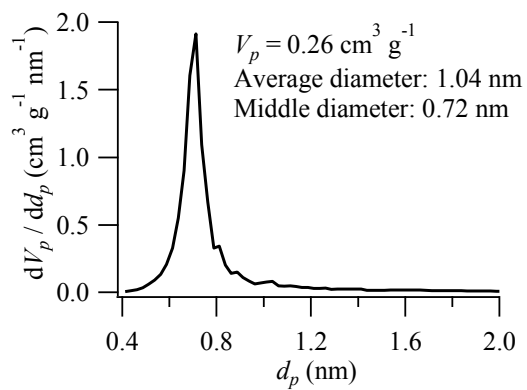
(a) ZSM-5



(b) Mordenite



(c) Y



(d) $\text{SiO}_2\text{-Al}_2\text{O}_3$

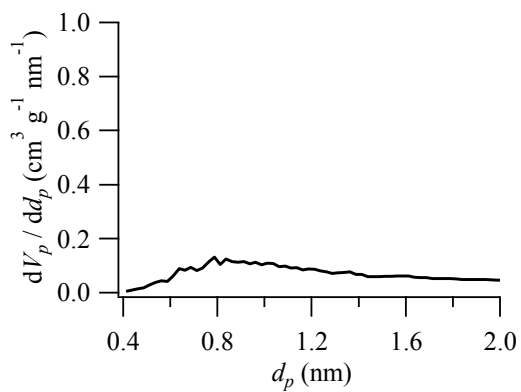
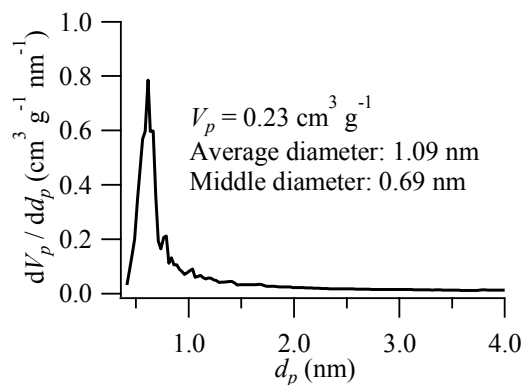
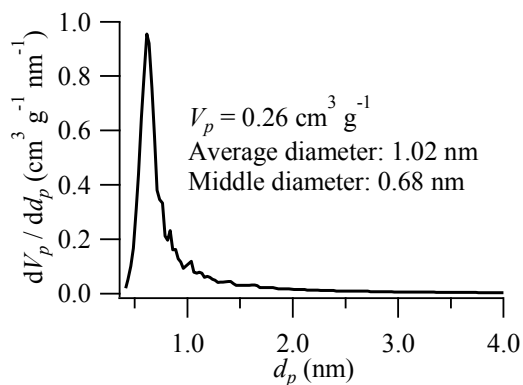


Figure S1. Pore size distributions of ZSM-5, mordenite, zeolite Y and normal $\text{SiO}_2\text{-Al}_2\text{O}_3$ determined by Ar adsorption.

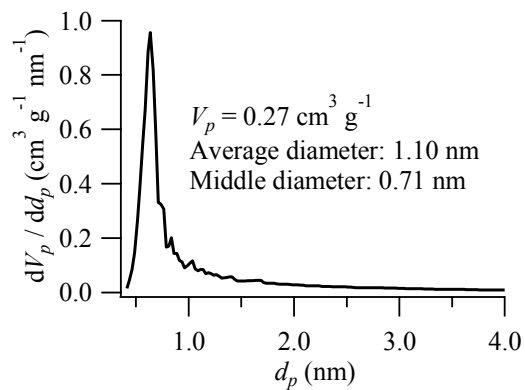
(a) $\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$



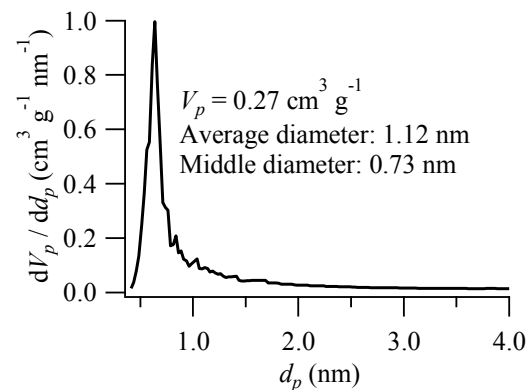
(b) $\text{SiO}_2/\text{Al}_2\text{O}_3 = 42.2$



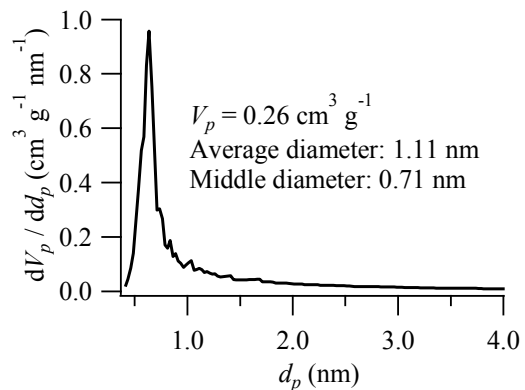
(c) $\text{SiO}_2/\text{Al}_2\text{O}_3 = 104$



(d) $\text{SiO}_2/\text{Al}_2\text{O}_3 = 150$



(d) $\text{SiO}_2/\text{Al}_2\text{O}_3 = 440$



(e) $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1700$

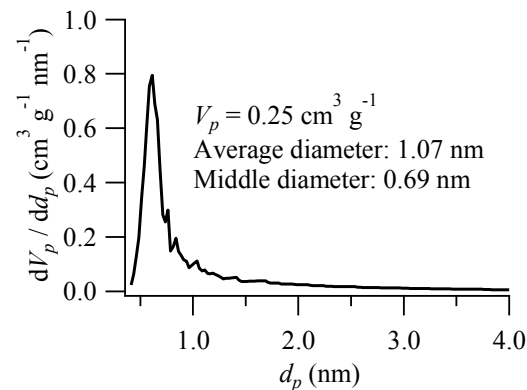


Figure S2. Pore size distributions of zeolite beta with various $\text{SiO}_2/\text{Al}_2\text{O}_3$ determined by Ar adsorption.

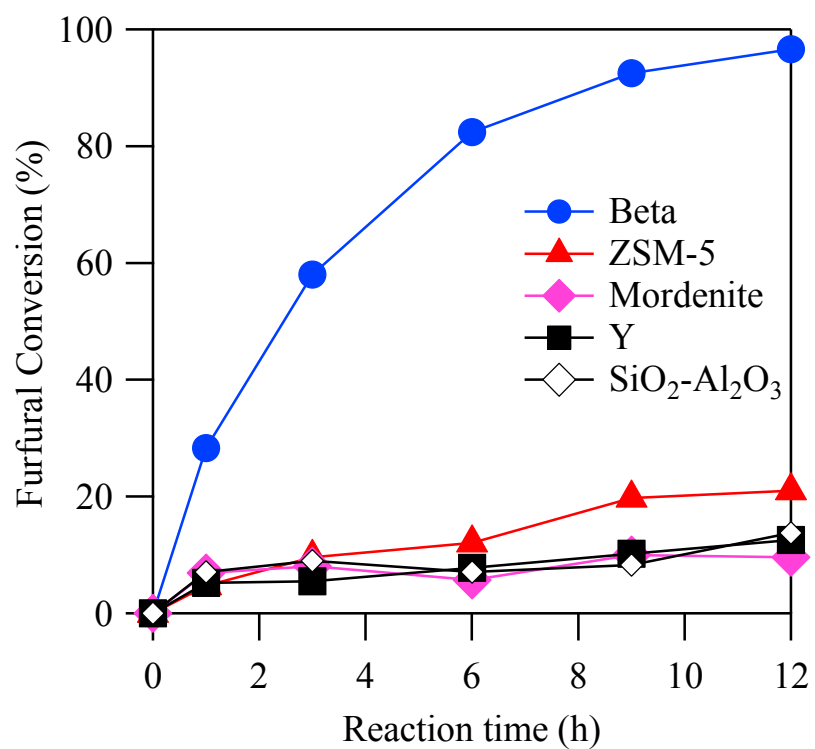


Figure S3. Time based reaction progression of the furfural conversion for hydroxymethylation among four zeolites and normal SiO₂-Al₂O₃ over in a batch reactor.

Reaction conditions: furfural (1 mmol), formalin (5 mL), catalyst (200 mg), temp. (363 K), stirring (500 rpm).

Table S1. Recycling experiments on the zeolite beta ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 150$) in a batch reactor.^{a,b}

	Conversion (%)	Yield (%)	Selectivity (%)
Fresh	80.2	27.3	34.0
Reuse 1	76.8	27.2	35.4
Reuse 2	78.3	26.9	34.3
Reuse 3	70.3	26.2	37.2

^aReaction conditions: furfural (1-3 mmol), formalin (5-15 mL), catalyst (600-200 mg), temp. (363 K), time (6 h), stirring (500 rpm). The catalyst was re-calcined at 823 K before each reuse.

^bReaction scale for each run (furfural/formaline/catalyst): fresh run - 3 mmol/15 mL/600 mg; 1st reuse - 2 mmol/10 mL/400 mg, 2nd reuse – 1.5 mmol/7.5 mL/300 mg, and 3rd reuse - 1 mmol/5 mL/200 mg.

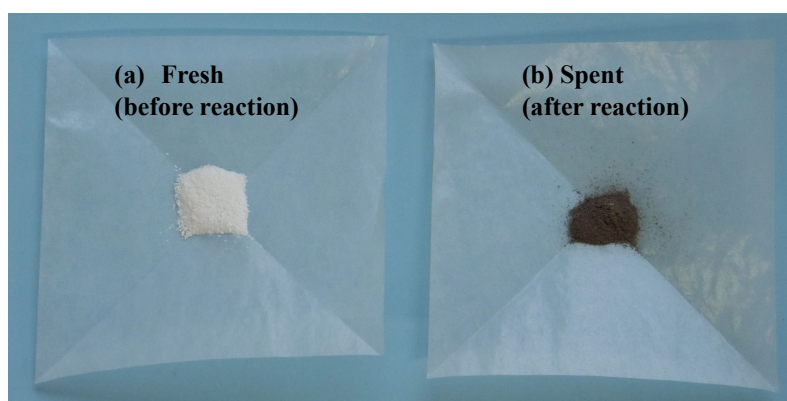


Figure S4. Photographs of (a) fresh and (b) spent zeolite beta catalyst ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 150$).

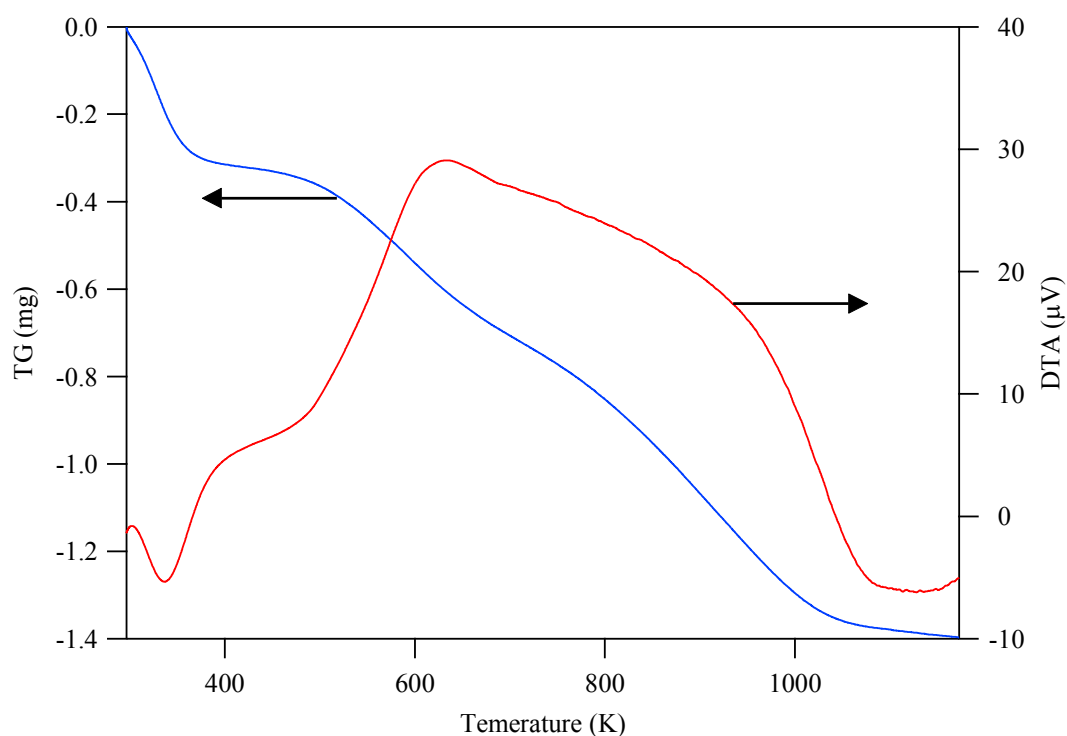


Figure S5. TG-DTA curves of spent zeolite beta ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 150$) in a batch reaction.

Operation conditions: TG-DTA (Rigaku; Thermoplus EV02, TG8121), sample (10 mg), 293-1173 K at a ramping rate of 20 K min^{-1} , Ar flow (100 mL min^{-1})

Note: Gradual decreases in weight with broad exotherm peaks suggested that the heating treatment induced the combustion of carbon decomposed on the catalyst surface, and then the surface of catalyst was refreshed and cleaned.

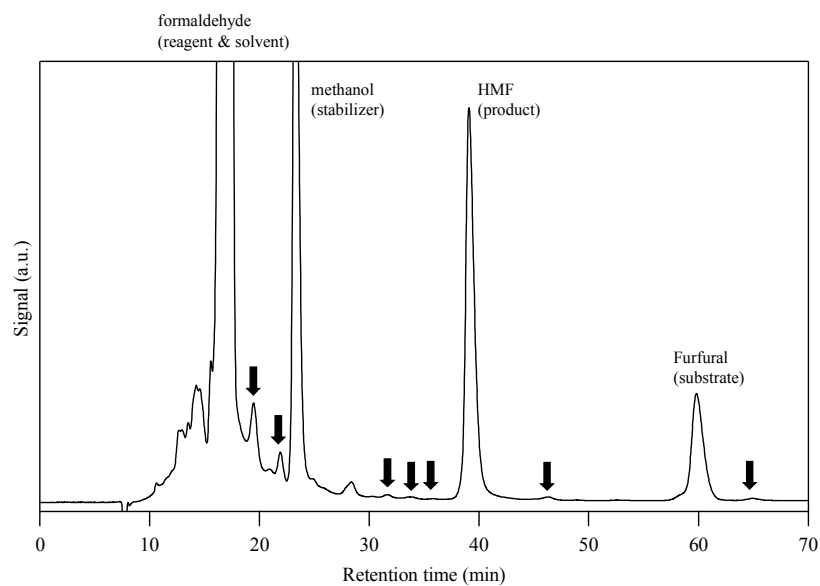


Figure S6. Example of HPLC chromatograph for hydroxymethylation of furfural to HMF in aqueous formaldehyde over zeolite beta.

Note: The peaks detected at around 19.5 min, 21.9 min, 30.3 min, 31.7 min, 33.7 min, 46.3 min and 64.6 min (described with black arrows in the chart) increase in intensity with reaction progress, in particular, after 6 h reaction in a batch reaction system. Accordingly, these are derived from by-products generation.

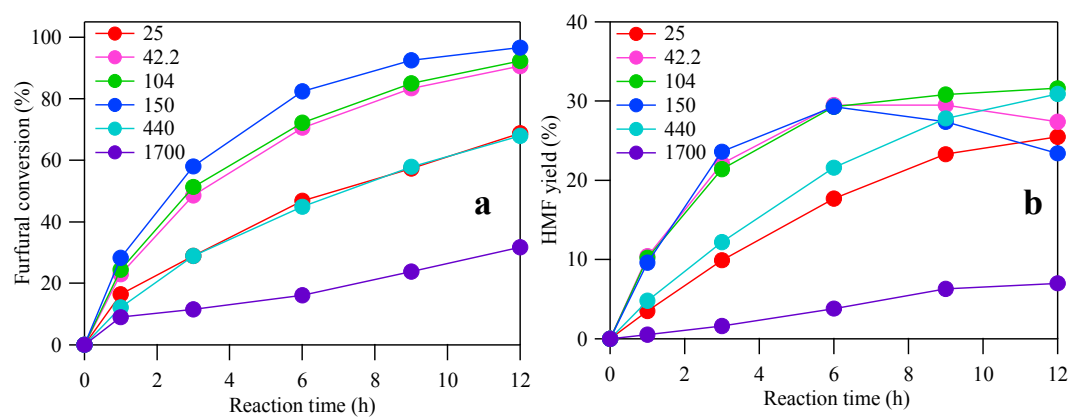


Figure S7. Time based reaction progression of the hydroxymethylation of furfural to HMF among zeolite beta samples composed of different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios in a batch reactor: (a) furfural conversion and (b) HMF yield.

Reaction conditions: furfural (1 mmol), formalin (5 mL), catalyst (200 mg), temp. (363 K), stirring (500 rpm).

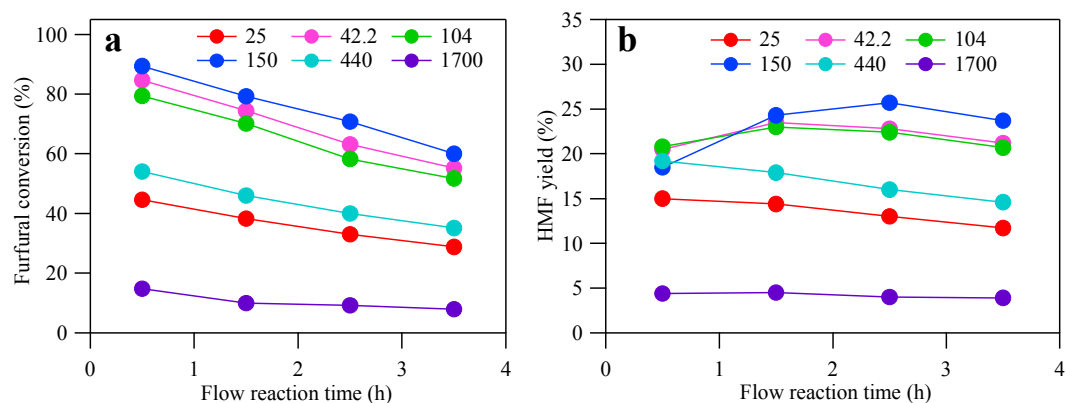


Figure S8. Time-based reaction for HMF production in a flow reactor by using f zeolite beta samples composed of various $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios: (a) furfural conversion and (b) HMF yield. Reaction conditions: furfural (10 mmol), formalin (50 mL), catalyst (500 mg), temp. (363 K), flow rate (0.2 mL min^{-1}).