Supporting Information

Catalytic self-etherification of 5-hydroxymethylfurfural to 5,5'(oxybis(methylene)bis-2-furfural over zeolite catalysts: Effect of pore structure and acidity

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HMF conversion, OBMF yield, and products selectivity were defined as follow:

HMF Conversion (mol%) =
$$\frac{\text{Moles of reacted HMF}}{\text{Moles of added HMF}} \times 100\%$$

OBMF Yield (mol%) = $\frac{\text{Moles of formed OBMF}}{\text{Moles of added HMF/2}} \times 100\%$
OBMF Selectivity (mol%) = $\frac{\text{OBMF Yield}}{\text{Moles}} \times 100\%$

BMF Selectivity (mol%) =
$$\frac{100}{\text{HMF Conversion}} \times 100$$

Sample	S _{BET}	V _{micro}	V _{meso}	Weight loss	
	$(m^2 \cdot g^{-1})^{[a]}$	$(cm^{3} \cdot g^{-1})^{[b]}$	$(cm^{3} \cdot g^{-1})^{[c]}$	(wt%) ^[d]	
ZSM-5	14	0	0.04	12.6	
HMZ	149	0.01	0.37	17.4	
Beta	87	0	0.54	22.3	
MCM-22	151	0	1.41	26.2	

Table S1. Physical properties of the used samples.

^[a] Determined by BET method. ^[b] Estimated using the t-plot method. ^[c] Determined by a subtraction of total pore volume at a relative pressure of $P/P_0 = 0.99$ from the Microporous pore volume obtained from the t-plot. ^[d] Calculated by TG.

Catalyst	Conversion of HMF (%)	Selectivity (%)					
		OBMF	THB	MF	FMF	unknown	
ZSM-5	22.5	33.3	/	/	1.53	65.17	
HMZ	96.8	95.97	0.08	/	/	3.95	
Beta	75.8	70.18	1.13	7.33	4.47	16.89	
MCM-22	84	67.86	0.66	7.71	2.92	20.85	

Table S2. Product distribution of HMF self-etherification on the different catalysts.

Reaction condition: 18 mL 4-clorotoluene, 1.0 g HMF, 0.5 g catalyst, 100°C and 8h reaction. THB: 1,2,4-Trihydroxybenzene; MF: 5,5'-Methylendi-2-furaldehyd; FMF: 5-(2-furaldehyde)methyl formate. The selectivity of other products was determined by GC with area normalization method.



Figure S1. The ¹H NMR spectrum of the HMF (solvent: CDCl₃).



Figure S2. Mass spectrum of the HMF.



Figure S3. The ¹H NMR spectrum of the OBMF (solvent: CDCl₃).



Figure S4. Mass spectrum of the OBMF product.



Figure S5. Mass spectrum of the 5,5'-Methylendi-2-furaldehyd (MF) product.



Figure S6. Mass spectrum of the 5-(2-furaldehyde)methyl formate (FMF) product.



Figure S7. Mass spectrum of the 1,2,4-Trihydroxybenzene (THB) product.



Figure S8. The initial rate of catalyst under the different agitation speed.



Figure S9. The reusability of catalysts (without of regeneration) in self-etherification of HMF to OBMF. Reaction conditions: 18 mL 4-clorotoluene, 1.0 g HMF, 0.5 g catalyst, 100°C and 2h reaction.



Figure S10. The color of fresh and used catalysts.



Figure S11. TG-DTG curves of the used catalysts.



Figure S12. Catalytic performances of the catalysts in self-etherification of HMF to OBMF (a, b) and effect of reaction temperature on the OBMF selectivity (c) and yield (d) over the different catalysts (4h reaction). Reaction conditions: 18 mL 4-clorotoluene, 1.0 g HMF, 0.5 g catalyst, 90°C.



Figure S13. NH₃-TPD curves of the Beta, HMZ, and modified catalysts.



Figure S14. The reusability of HMZ sample in self-etherification of HMF to OBMF.