

Supplementary Information

Catalytic upgrading of carboxylic acid as bio-oil models over hierarchical ZSM-5 obtained via an organosilane approach

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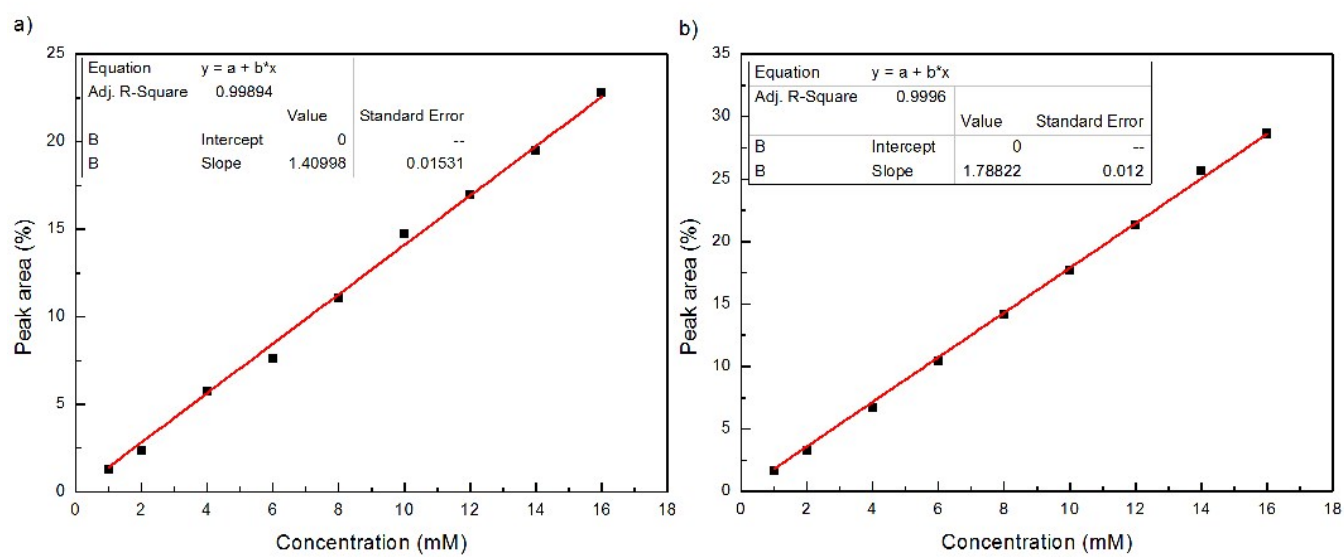


Figure S1. Calibration curves of a) Benzyl alcohol and b) Benzyl acetate by using decane as an internal standard.

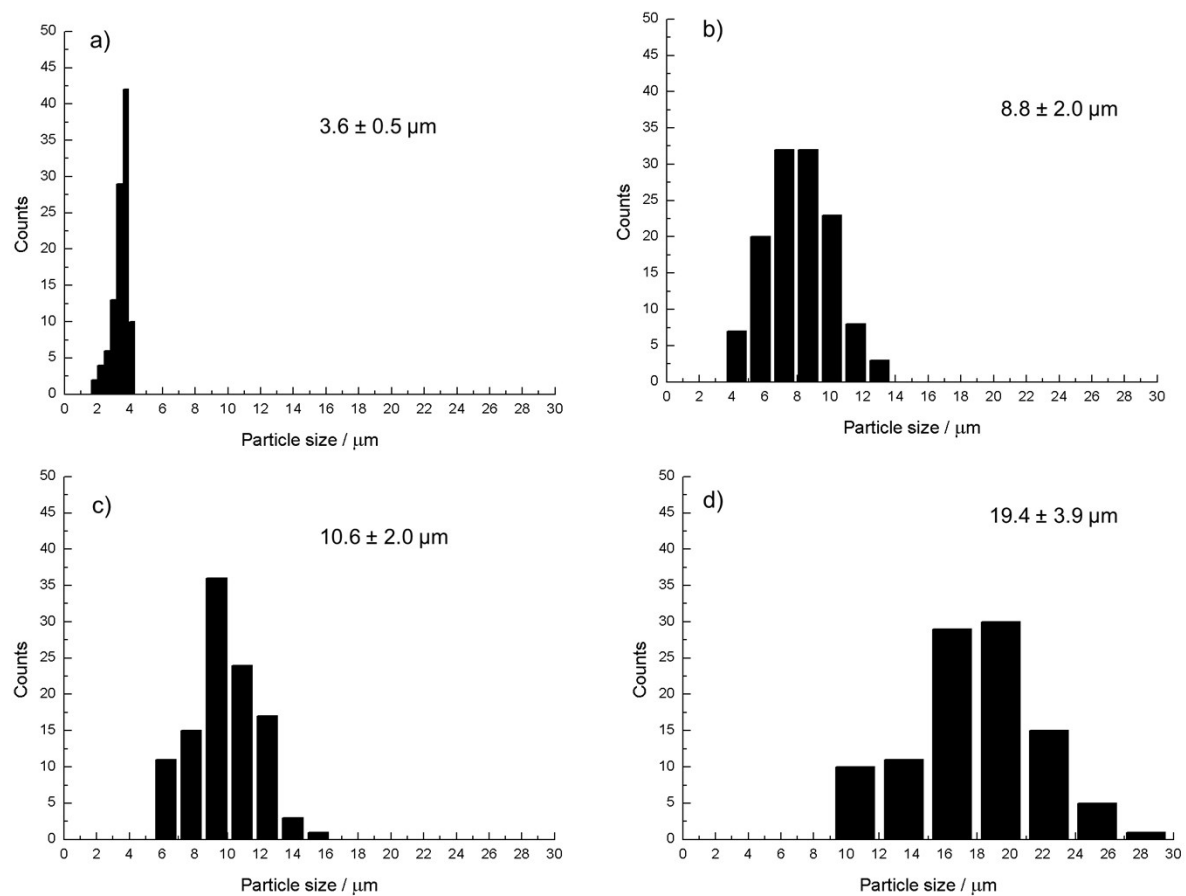


Figure S2. Particle size distribution of (a) C_ZSM-5, (b) ZSM-5_(4.8)TPOAC, (c) ZSM-5_(9.6)TPOAC, and (d) ZSM-5_(38.4)TPOAC.

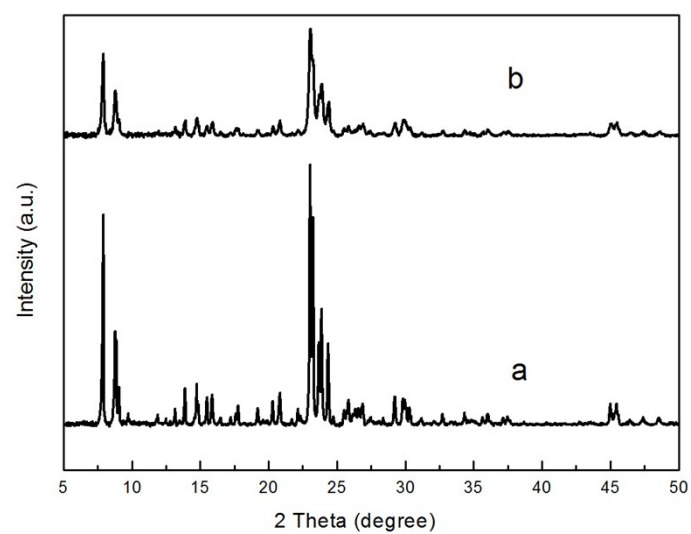


Figure S3. XRD patterns of samples with low Si/Al ratio: (a) Commercial ZSM-5, and (b) Hierarchical ZSM-5(34).

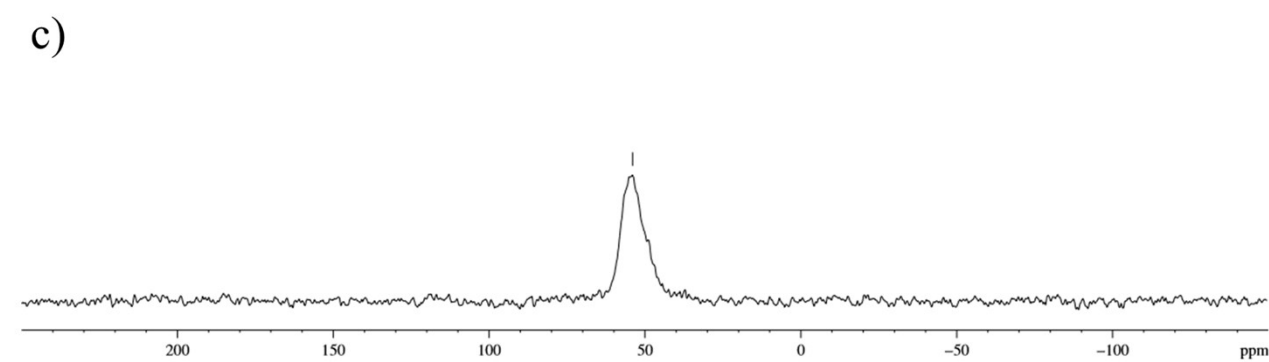
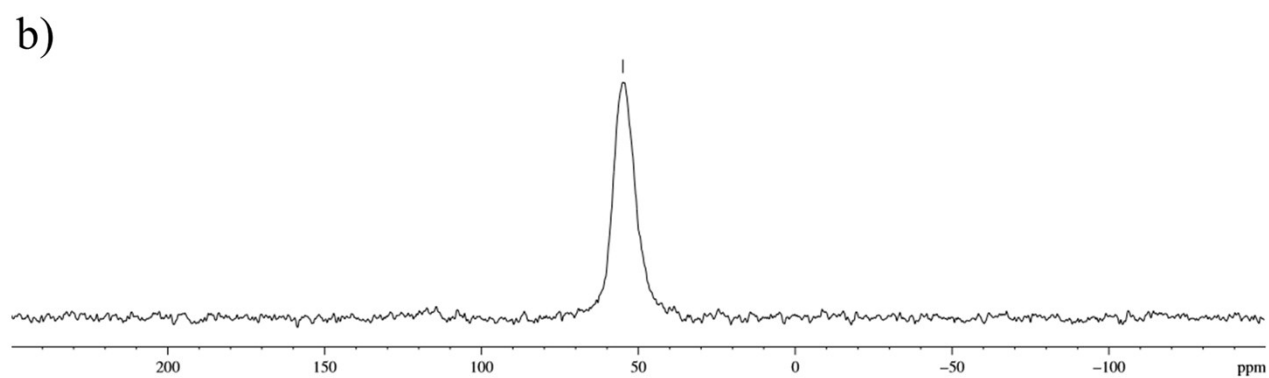
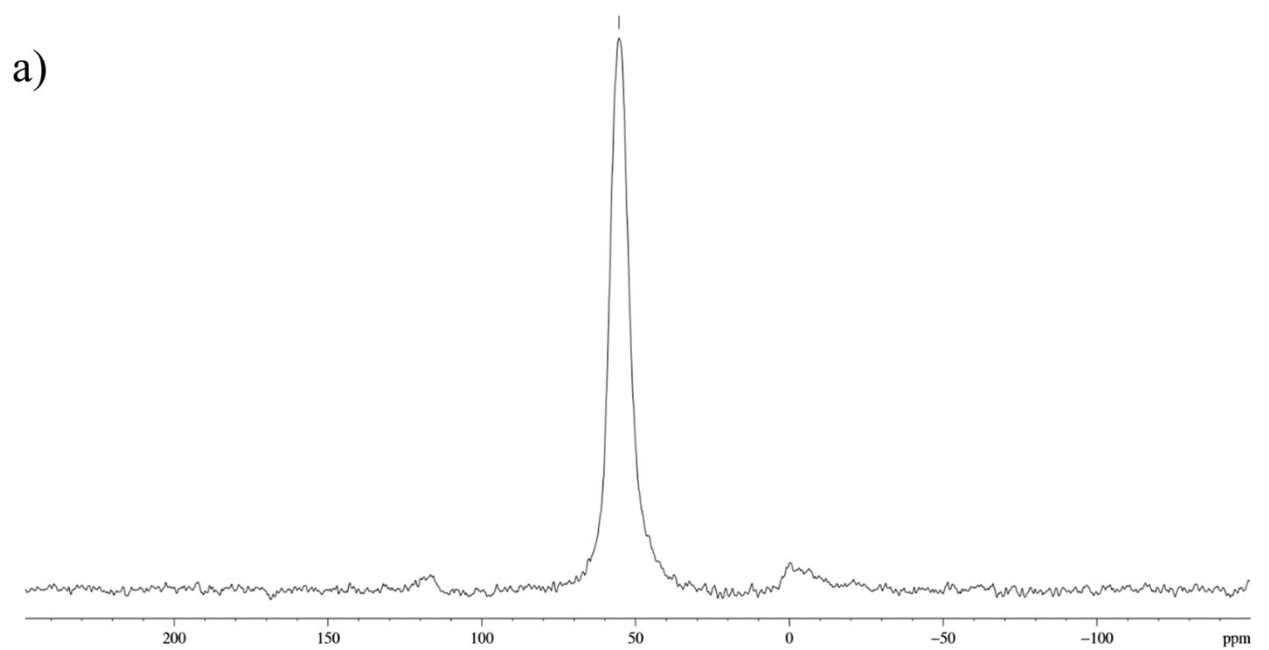


Figure S4. ^{27}Al MAS NMR spectra of (a) Commercial ZSM-5, (b) Hierarchical ZSM-5(34), and (c) Hierarchical ZSM-5(90).

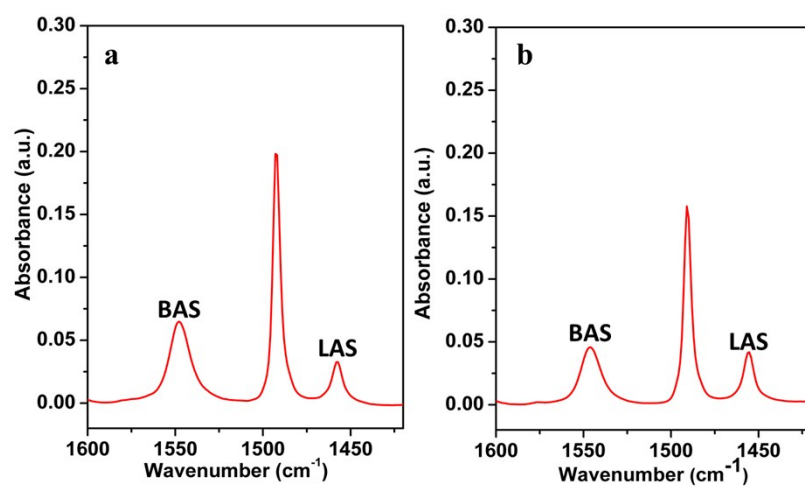


Figure S5. FTIR spectra of pyridine adsorbed on a) Commercial ZSM-5 and b) Hierarchical ZSM-5(34), after evacuation at 573 K.

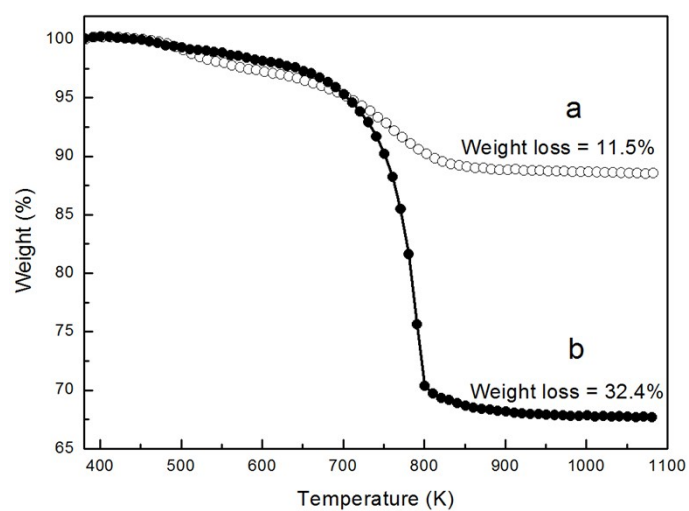


Figure S6. Weight loss profiles of a) Hierarchical ZSM-5(34), and b) Commercial ZSM-5 catalysts.

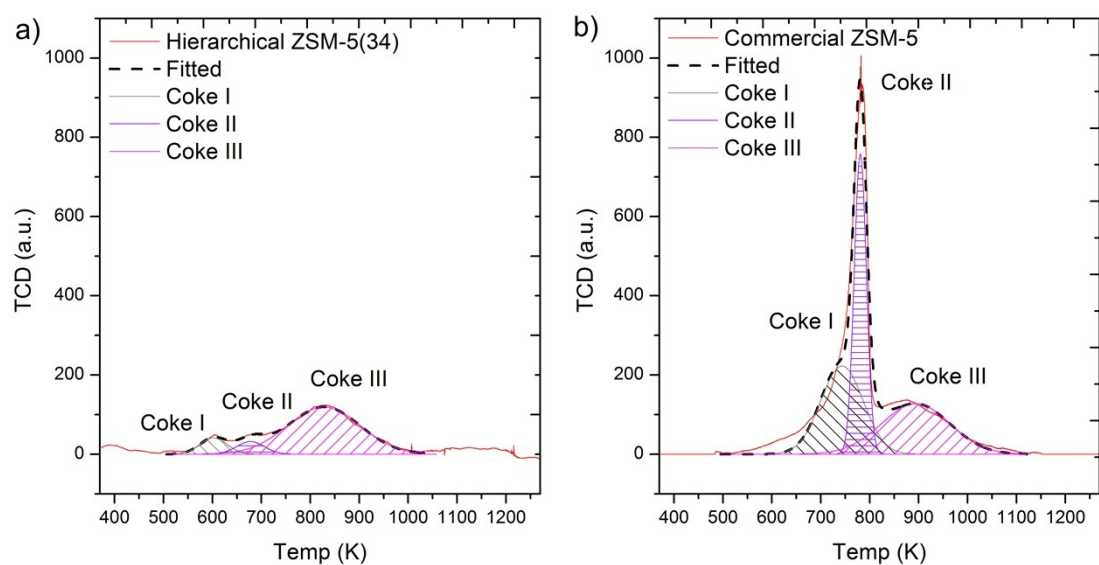


Figure S7. O₂ TPO profiles of a) Hierarchical ZSM-5(34), and b) Commercial ZSM-5 catalysts.

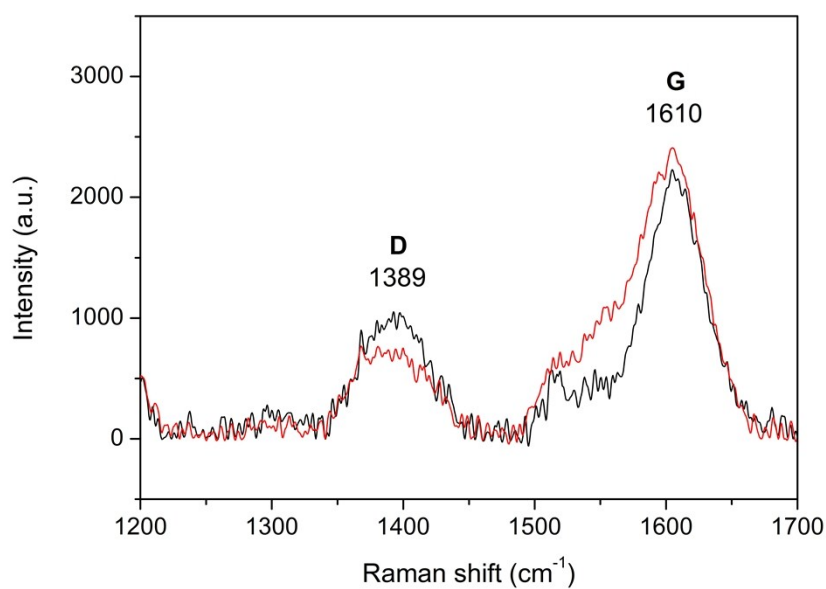


Figure S8. Raman spectra at 532 nm of spent catalysts: Commercial ZSM-5 (black) and Hierarchical ZSM-5(34) (red).

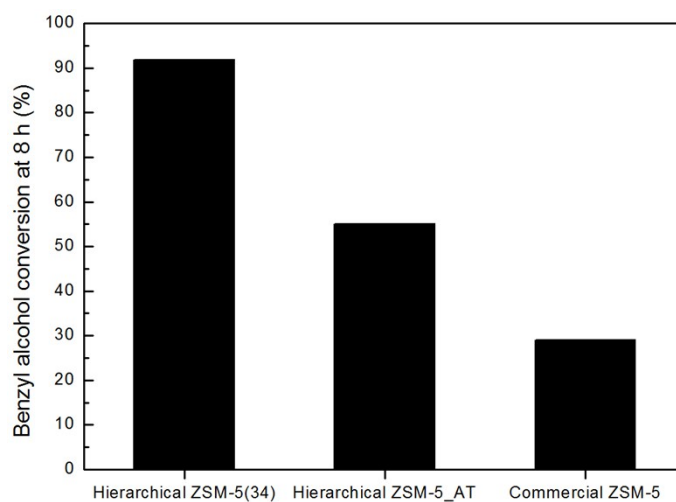


Figure S9. Benzyl alcohol conversion (%) on different samples obtained by different methods: Hierarchical ZSM-5(34), Commercial ZSM-5, and Hierarchical ZSM-5_AT.

Table S1. Relative crystallinity (%) of all synthesized ZSM-5 samples

Samples	% Crystallinity
C_ZSM-5	95.0
ZSM-5_(4.8)TPOAC	58.4
ZSM-5_(9.6)TPOAC	66.0
ZSM-5_(38.4)TPOAC	40.0

Table S2. Brønsted and Lewis acidity of Commercial HZSM-5 and Hierarchical ZSM-5(34), after evacuation at 573 K.

Sample	[BAS] ($\mu\text{mol/g}$)	[LAS] ($\mu\text{mol/g}$)
	573 K	573 K
Commercial HZSM-5	109	18
Hierarchical ZSM-5(34)	82	31

Table S3. Textural properties of hierarchical zeolites obtained from direct- and post synthesis approaches.

Samples	S_{BET}^a	S_{micro}^b	S_{ext}^c	V_{total}^d	V_{micro}^e	$V_{\text{ext/meso}}^f$	$V_{\text{Meso}}/V_{\text{total}}^g$
Hierarchical ZSM-5(34)	434	287	147	0.3378	0.1151	0.2227	0.66
Hierarchical ZSM-5_AT	349	186	164	0.4562	0.0755	0.3807	0.83

^a S_{BET} : BET specific surface area; ^b S_{micro} : micropore surface area; ^c S_{ext} : external surface area; ^d V_{total} : total pore volume; ^e V_{micro} : micropore volume; ^f $V_{\text{micro}} = V_{\text{total}} - V_{\text{ext/meso}}$; All surface areas and pore volumes are in the units of m^2/g and cm^3/g , respectively. ^gFraction of mesopore volume.

Table S4. Catalytic activity of commercial ZSM-5 and hierarchical ZSM-5(34) for the esterification of levulinic acid with ethanol.

Catalyst	Time (h)	Conversion of Levulinic acid (%)	Selectivity of Ethyl levulinate (%)
Commercial ZSM-5	3	7.43	89.13
	6	18.72	100.00
	24	25.20	100.00
	48	28.66	100.00
Hierarchical ZSM-5(34)	3	31.09	88.59
	6	48.49	97.78
	24	64.51	100.00
	48	73.37	100.00

*Reaction condition: Catalyst 0.45 g, Levulinic acid 3 ml, Ethanol 1.75 ml, decane (internal standard) 0.1 ml, Toluene (Solvent) 15 ml, 373 K under an atmospheric pressure.