Electronic Supplementary Information

Synthesis of Nanostructured Catalysts by Surfactant-Templating of Large-Pore Zeolites

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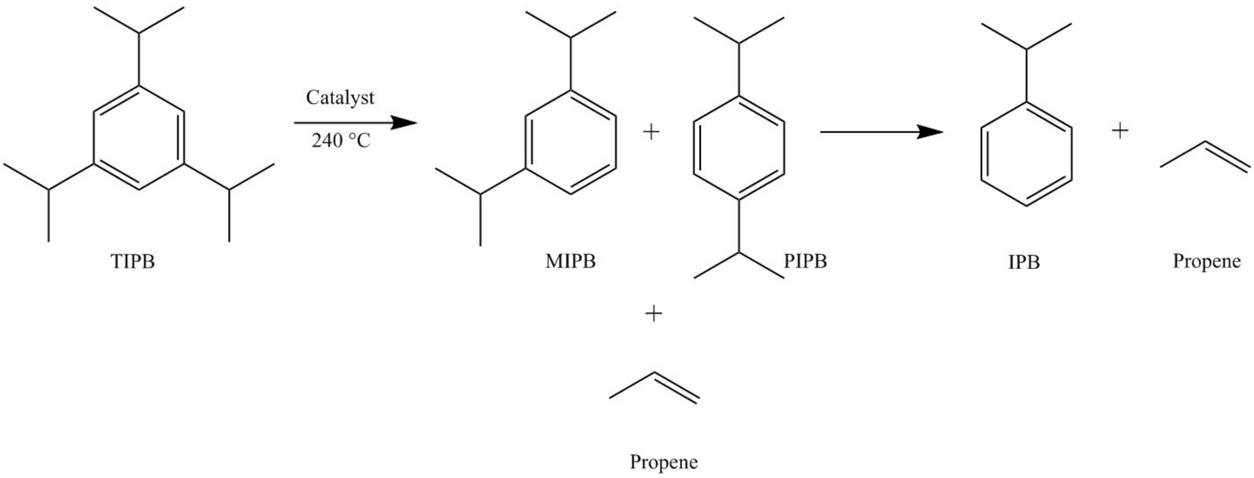
Experimental section

The catalytic studies, utilising 1,3,5-tri-isopropylbenzene (TIPB) dealkylation as a reaction test (Ref. S1), were carried out in a conventionally heated high-pressure reaction system, Monowave-50 supplied by Anton Paar, using specially designed 10-ml glass vials as batch reactors operating at elevated temperature and pressures (up to 250°C and 20 bar).



0.2 g of the zeolite catalyst was activated in an open reactor at 400°C for 5 h, cooled down to ~100°C and then mixed with 2 mL of TIPB. The reactor was purged with nitrogen and sealed, the temperature was raised to 240°C (the temperature ramp was ~ 40 °C/min) and kept for 1 h. Next, the reaction mixture was cooled down to ~0°C and the liquid products were isolated and identified using an Agilent 7890A GC with the 5975C mass detection system equipped with a capillary column BPX90 SGE, 15m×0.25mm×0.25µm (1 % solution of the products in MTBE with 0.1 v% of nonane as the internal standard).

Table S1. GC-MS analysis conditions.

Split ratio	100
Carrier gas	Helium at 1 ml/min
Column temperature	50°C for 3 min
	25°C/min to 300°C
	Hold at 300°C for 2 min
Injector and detector temperature	250°C
Injection volume	0.2 µL

(S) Qin, Z.; Cychosz, K.A.; Melinte, G.; El Siblani, H.; Gilson, J-P.; Thommes, M.; Fernandez, C.; Mintova, S.; Ersen, O.; Valtchev, V. Opening the Cages of Faujasite-Type Zeolite. *J Am Chem Soc*, **2017**,139,17273-17276.

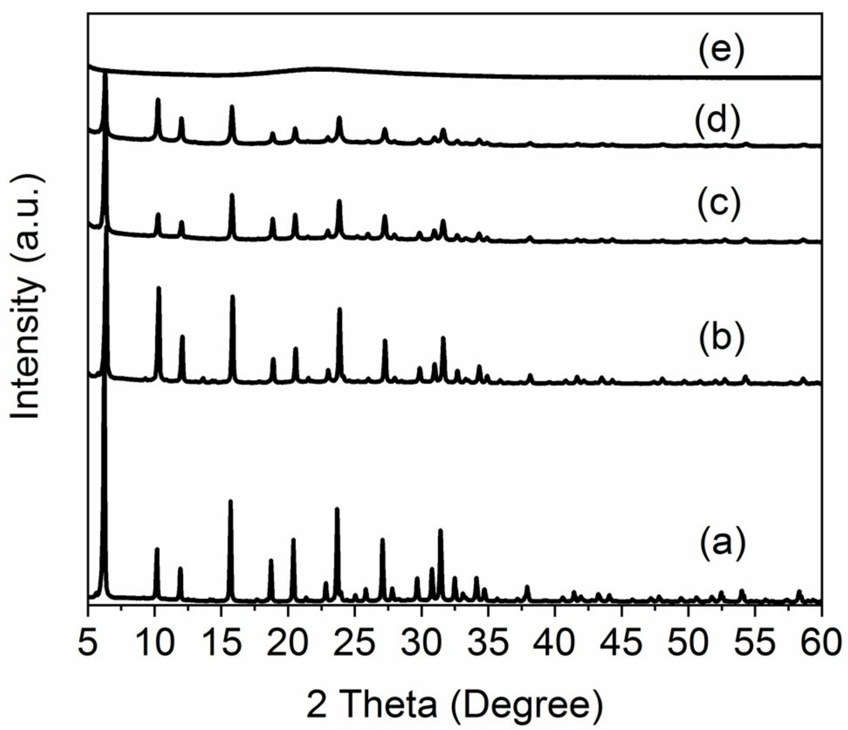
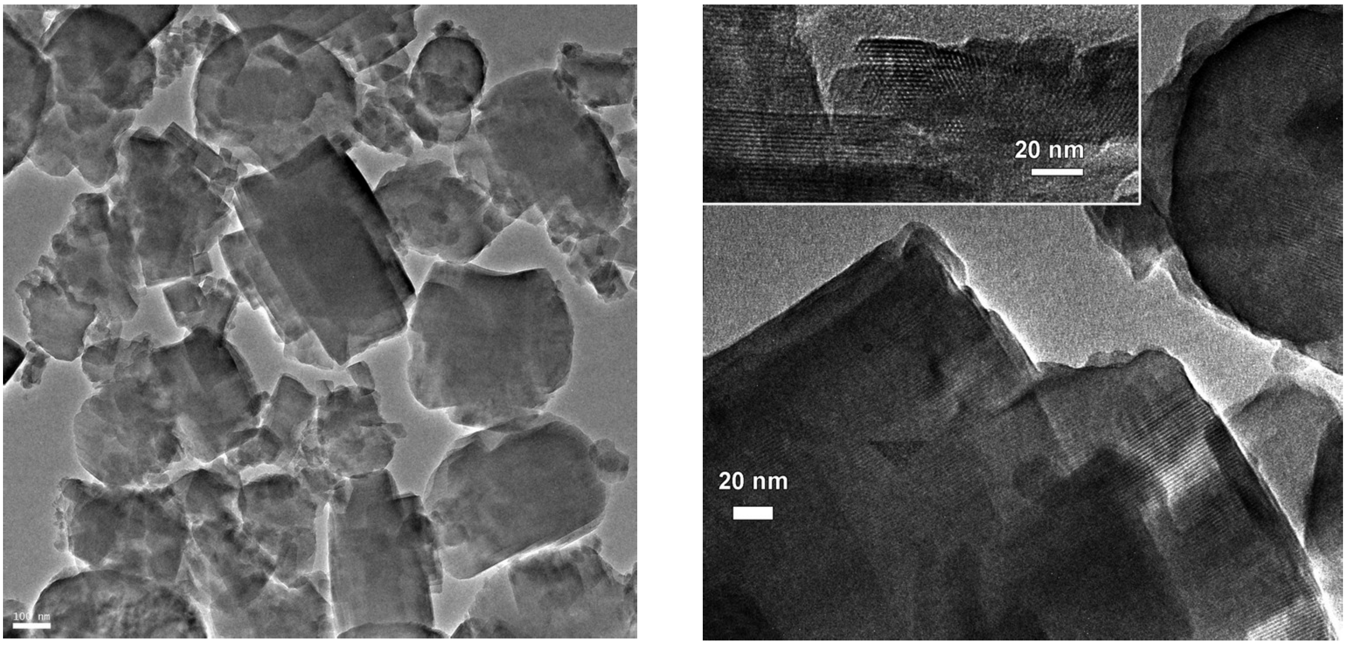
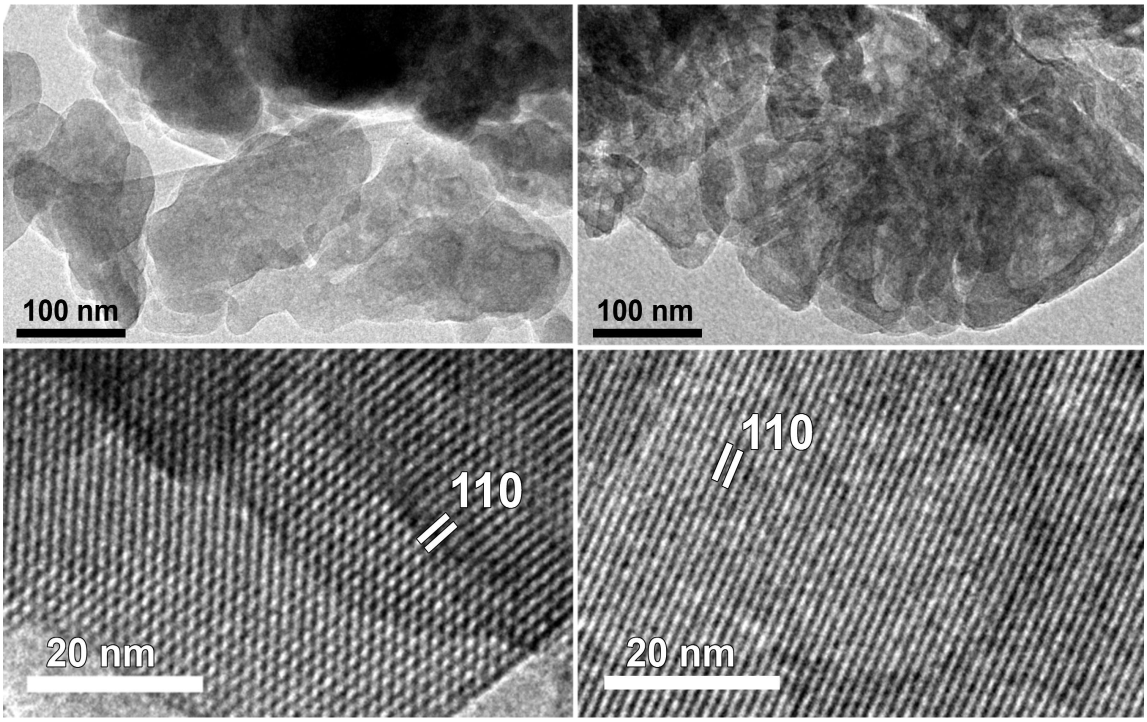


Figure S1. XRD patterns of faujasite-type zeolites treated with different amount of citric acid (a) 0 meq, (b) 4.5 meq, (c) 6 meq, (d) 9 meq and (e) 12 meq.

(a)



(b)



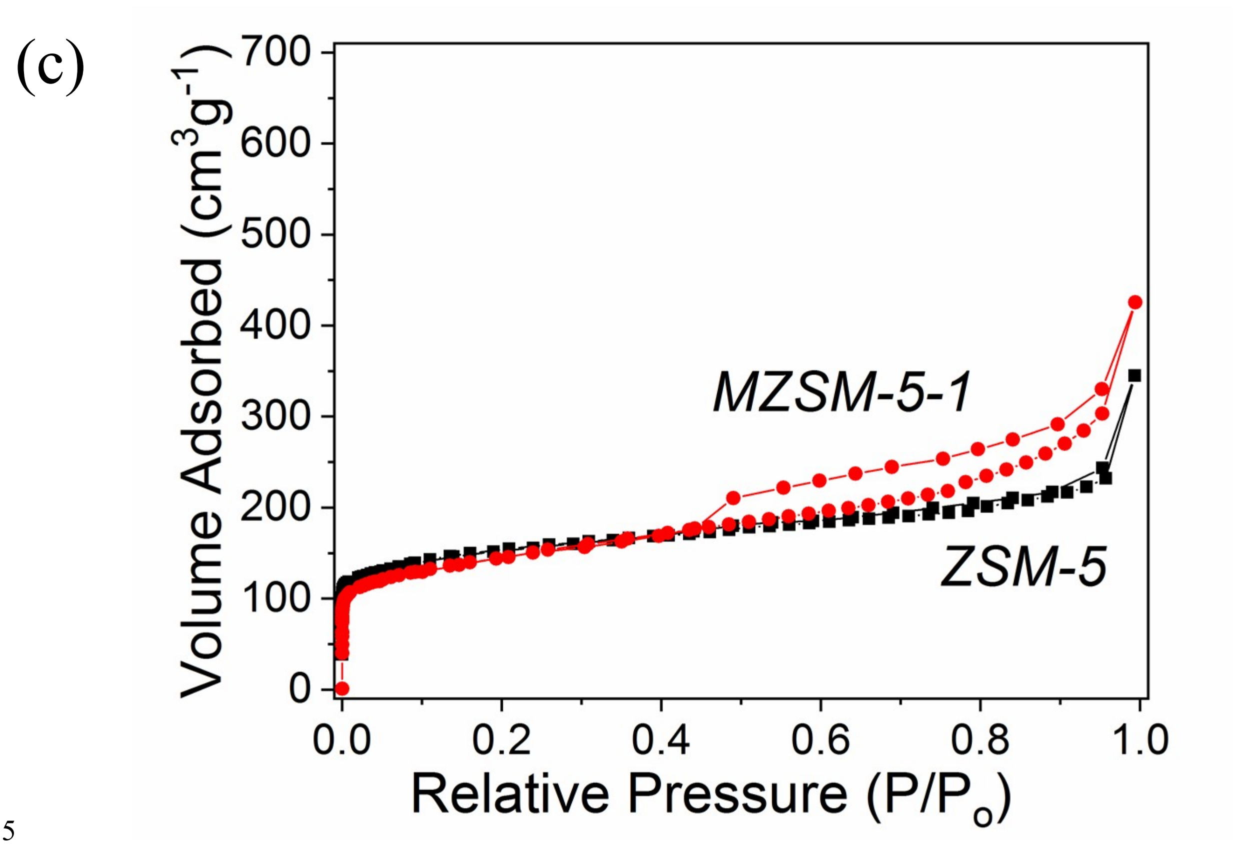


Figure S2. (a) Bright field TEM images for the parent LTL zeolite; (b) TEM images of the parent ZSM-5 (left) and mesostructured MZSM-5-1 (right); (c) N_2 adsorption and desorption isotherms for parent and modified ZSM-5 zeolites.

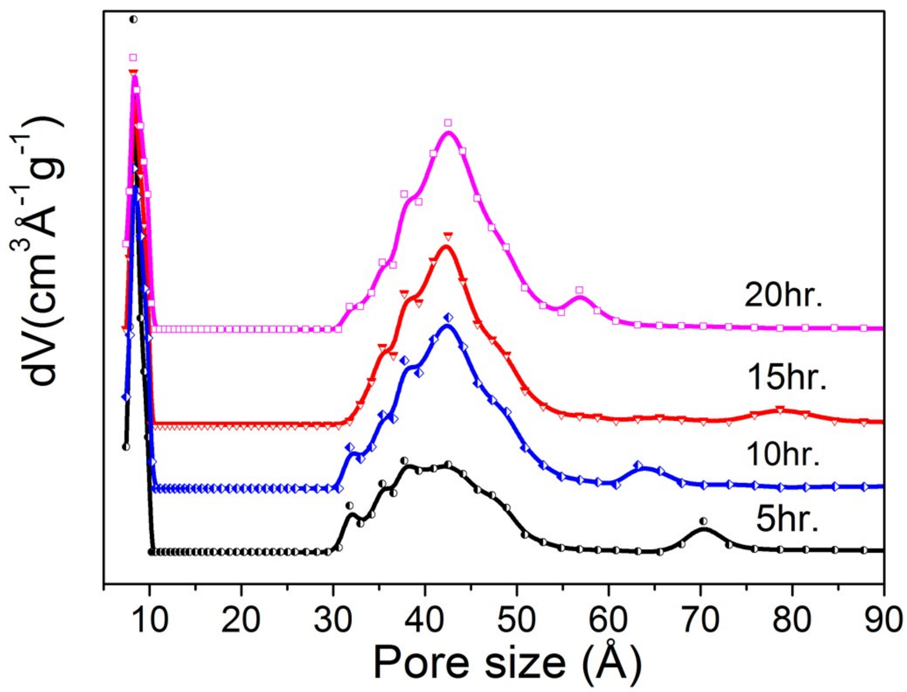


Figure S3. Pore size distribution of treated MOR at different times.

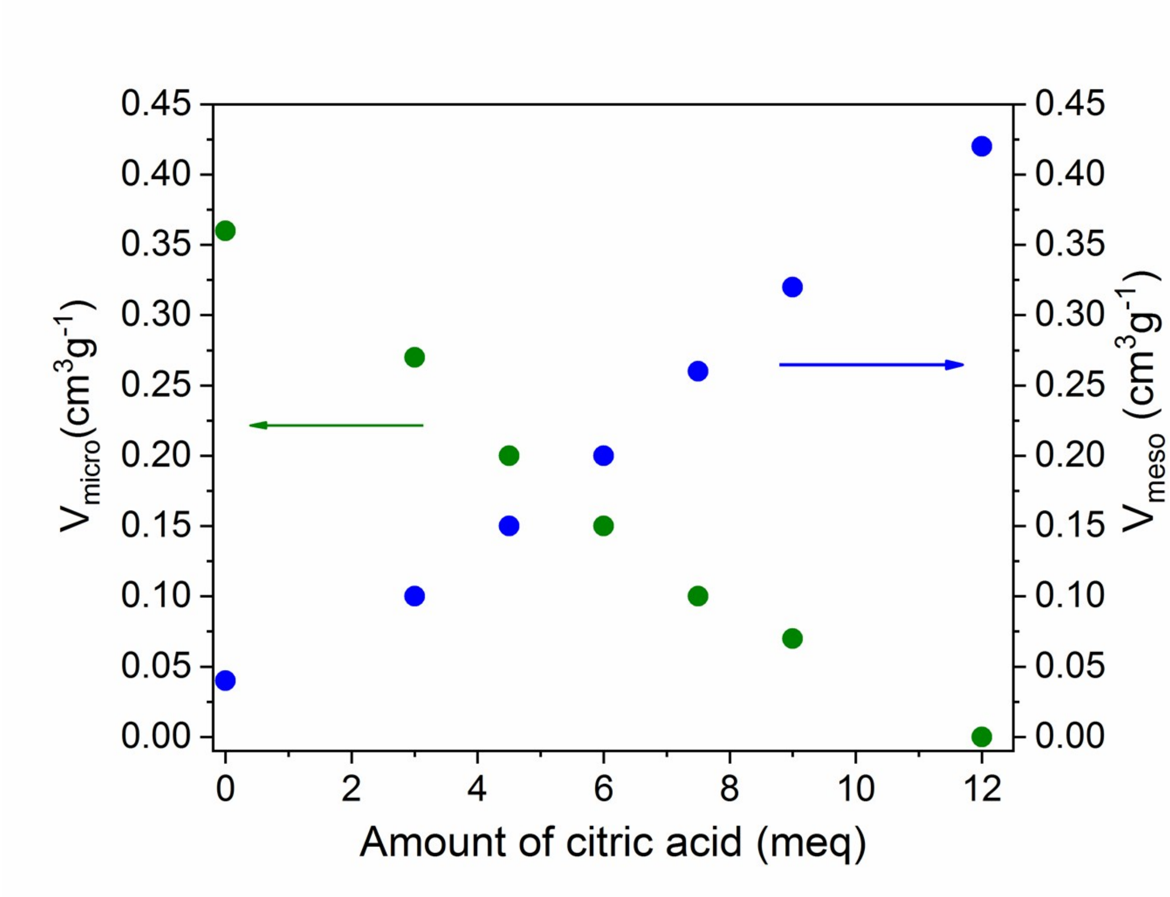


Figure S4. The relationship between the amount of citric acid added and the pore volume of modified faujasite-type zeolite.

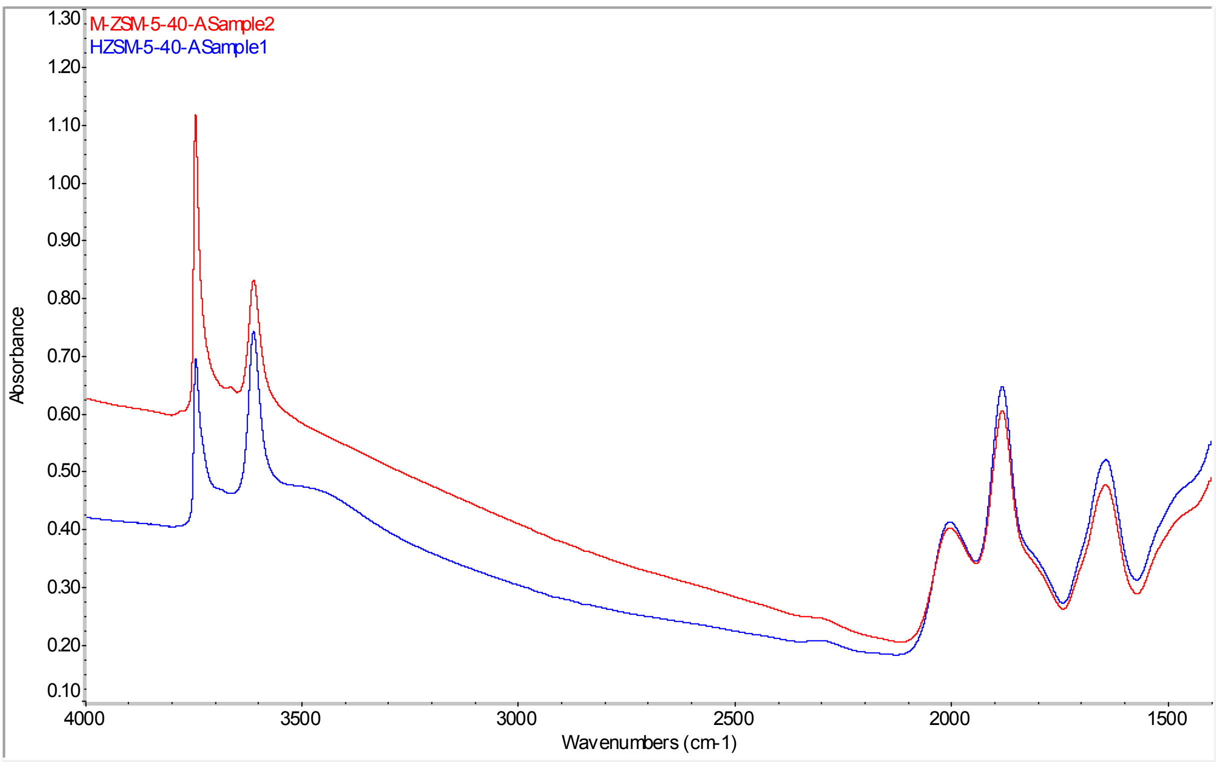


Figure S5a. FTIR spectra of the O-H region of the parent (blue) and mesostructured (red) ZSM-5.

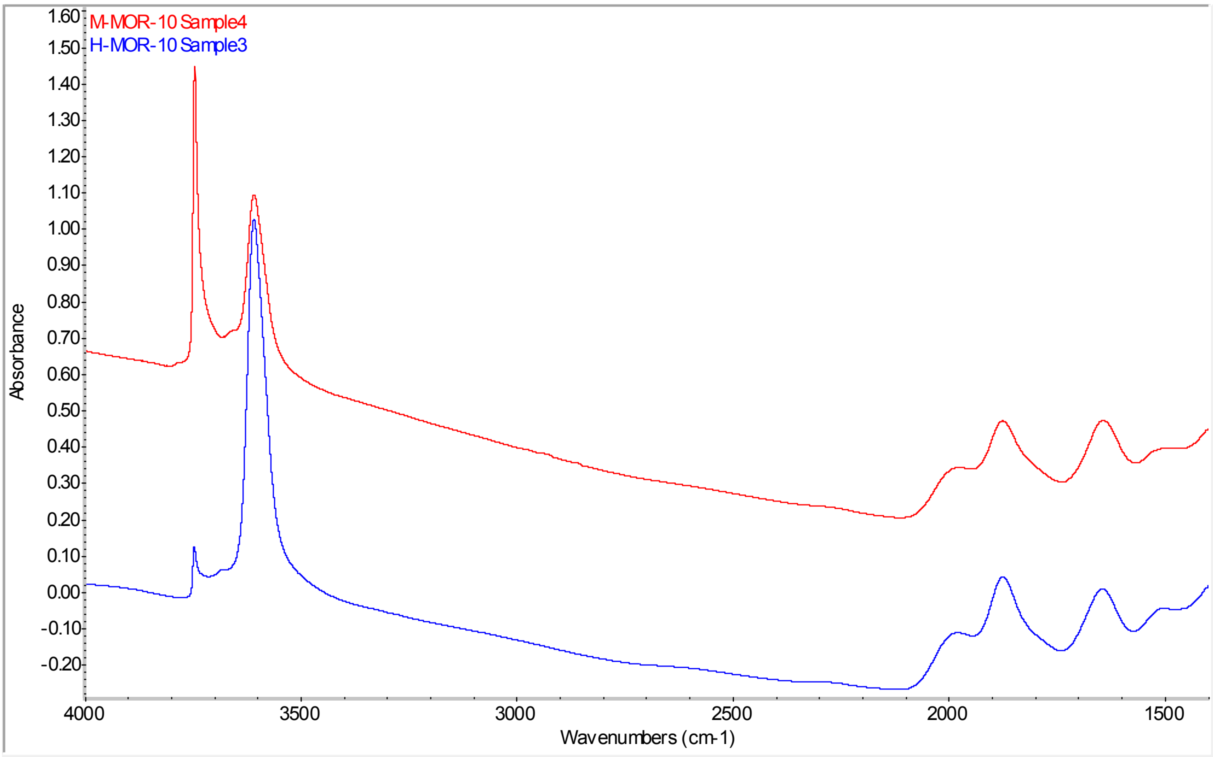


Figure S5b. FTIR spectra of the O-H region of the parent (blue) and mesostructured (red) MOR.

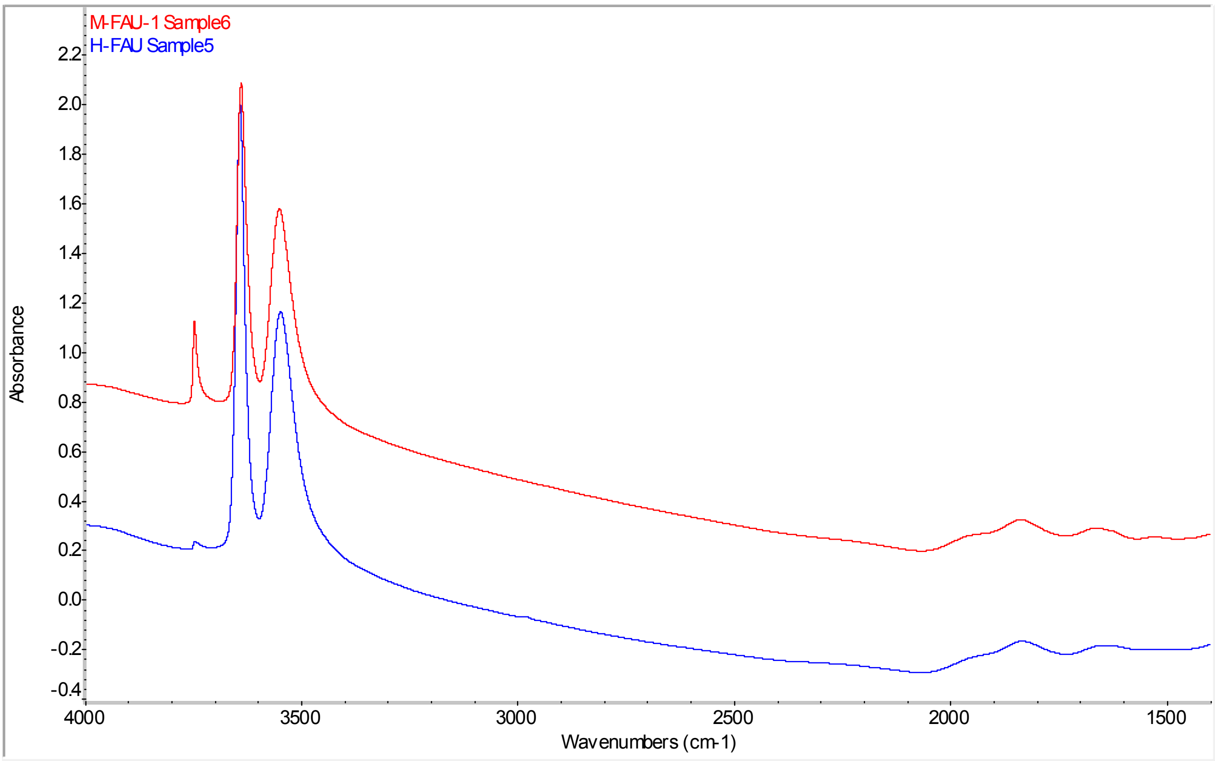


Figure S5c. FTIR spectra of the O-H region of the parent (blue) and mesostructured (red) FAU.

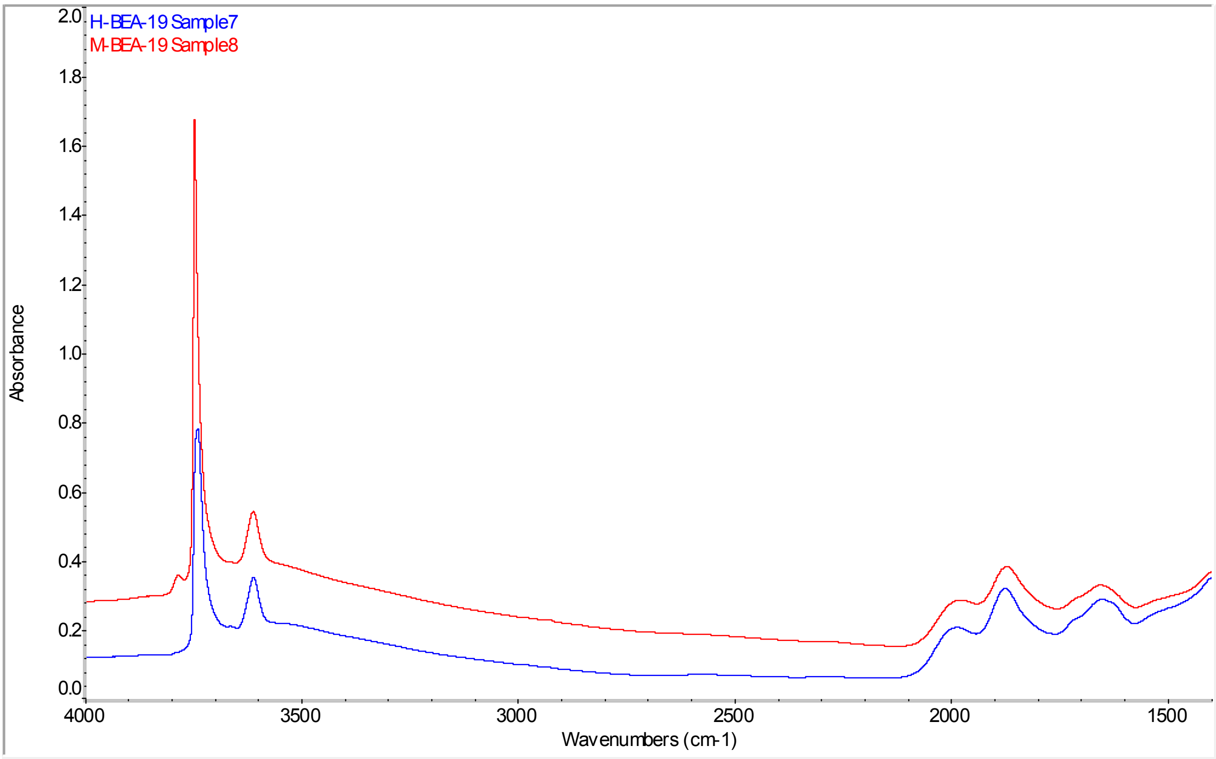


Figure S5d. FTIR spectra of the O-H region of the parent (blue) and mesostructured (red) BEA.

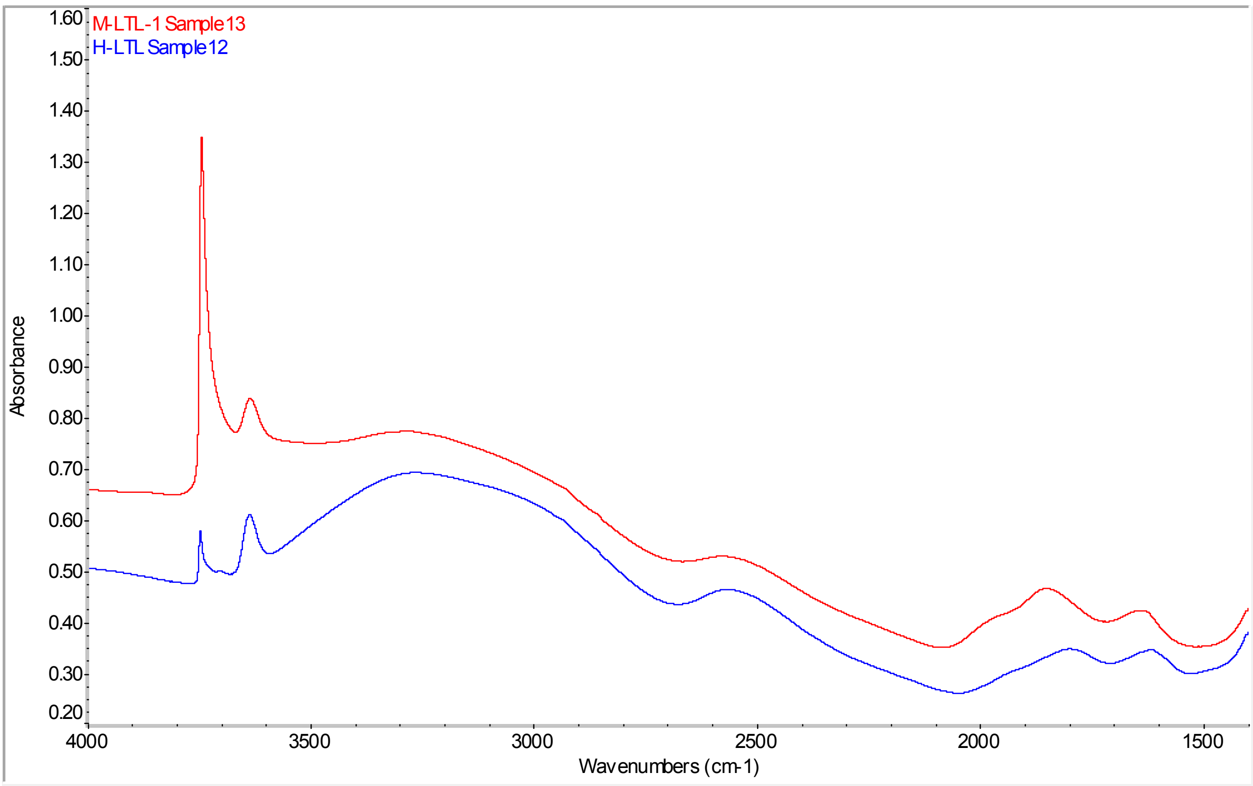


Figure S5e. FTIR spectra of the O-H region of the parent (blue) and mesostructured (red) LTL. All sets of FTIR spectra are offset for clarity.

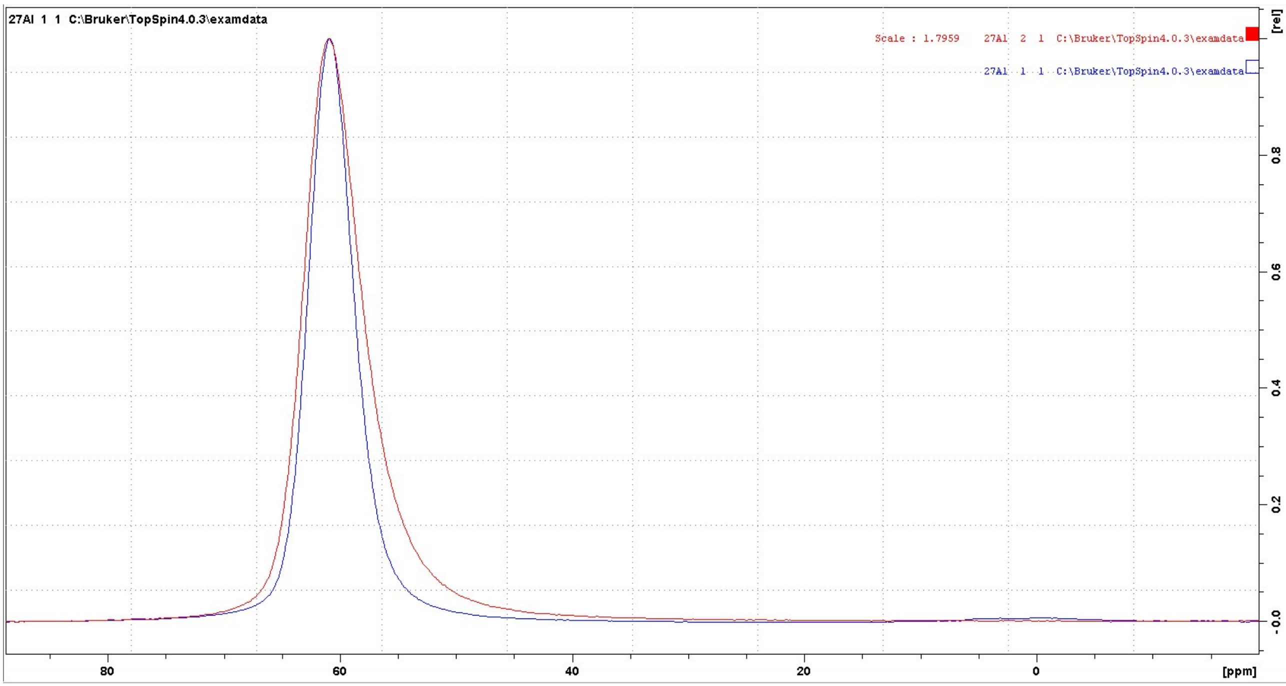


Figure S6a. ^{27}Al MAS NMR spectra (normalised to the same peak intensity) of the parent (blue) and hierarchical (red) FAU.

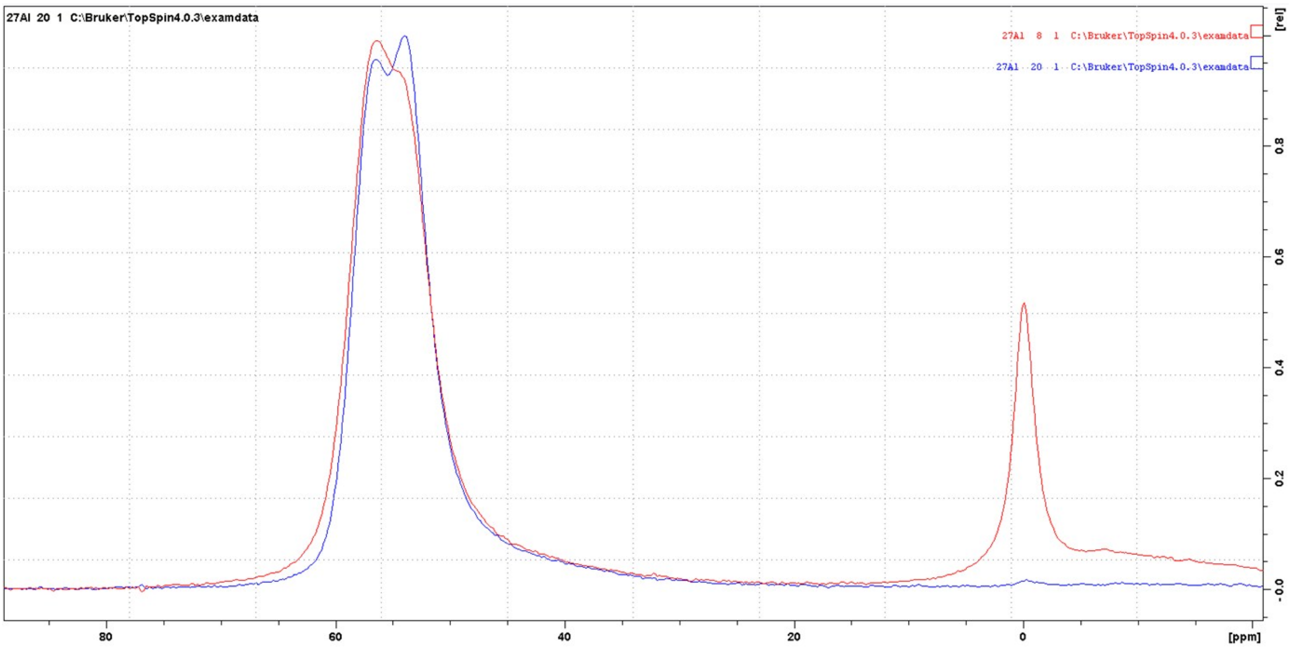


Figure S6b. ^{27}Al MAS NMR spectra (normalised to the same peak intensity) of the parent (blue) and hierarchical (red) BEA.

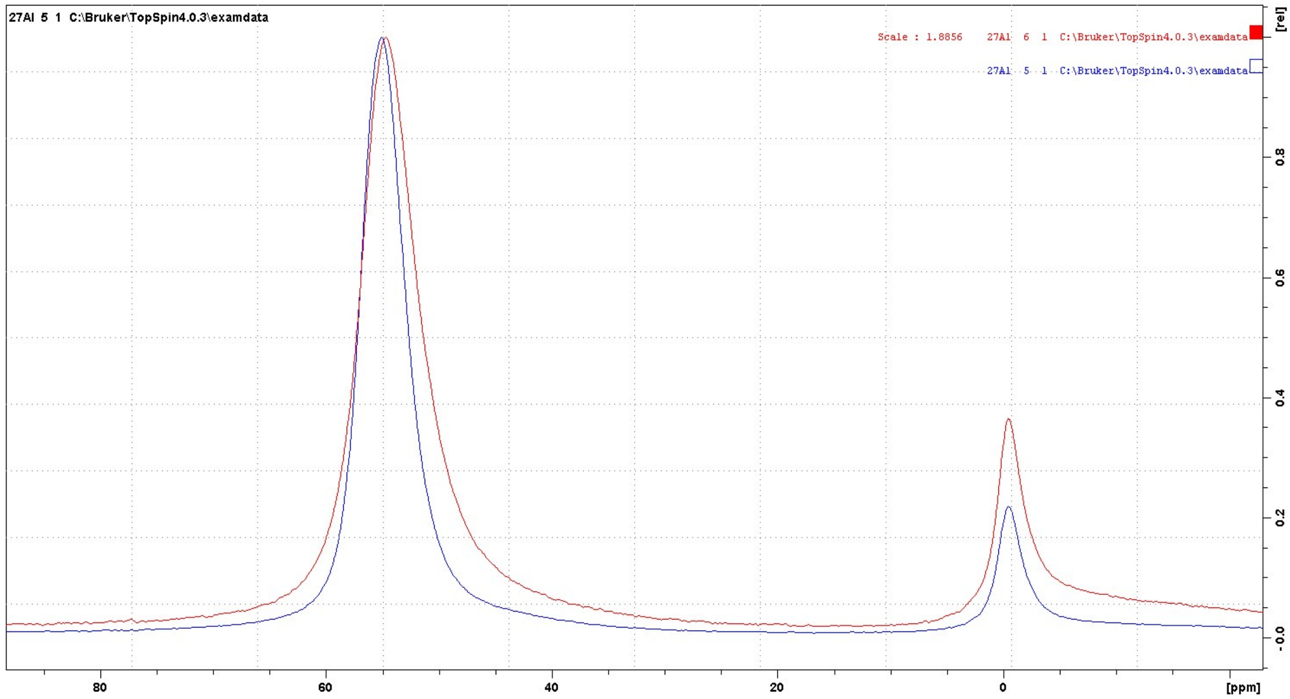


Figure S6c. ^{27}Al MAS NMR spectra (normalised to the same peak intensity) of the parent (blue) and hierarchical (red) MOR.

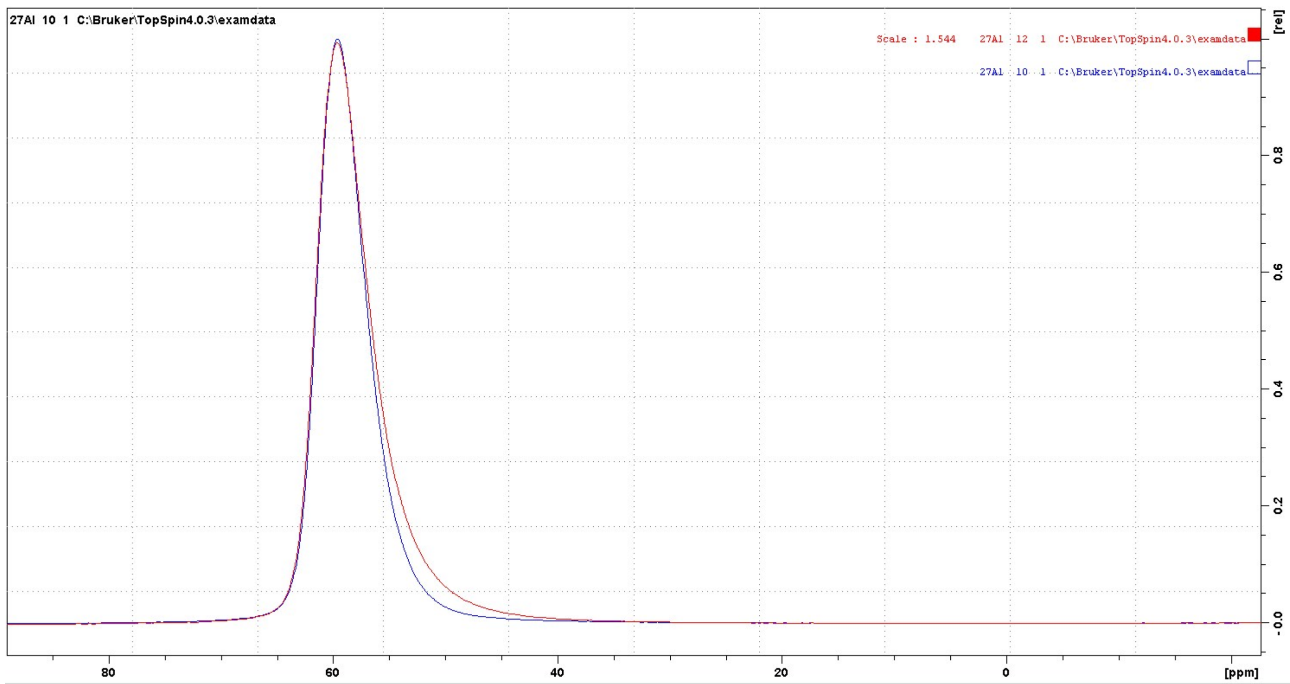


Figure S6d. ^{27}Al MAS NMR spectra (normalised to the same peak intensity) of the parent (blue) and hierarchical (red) LTL.

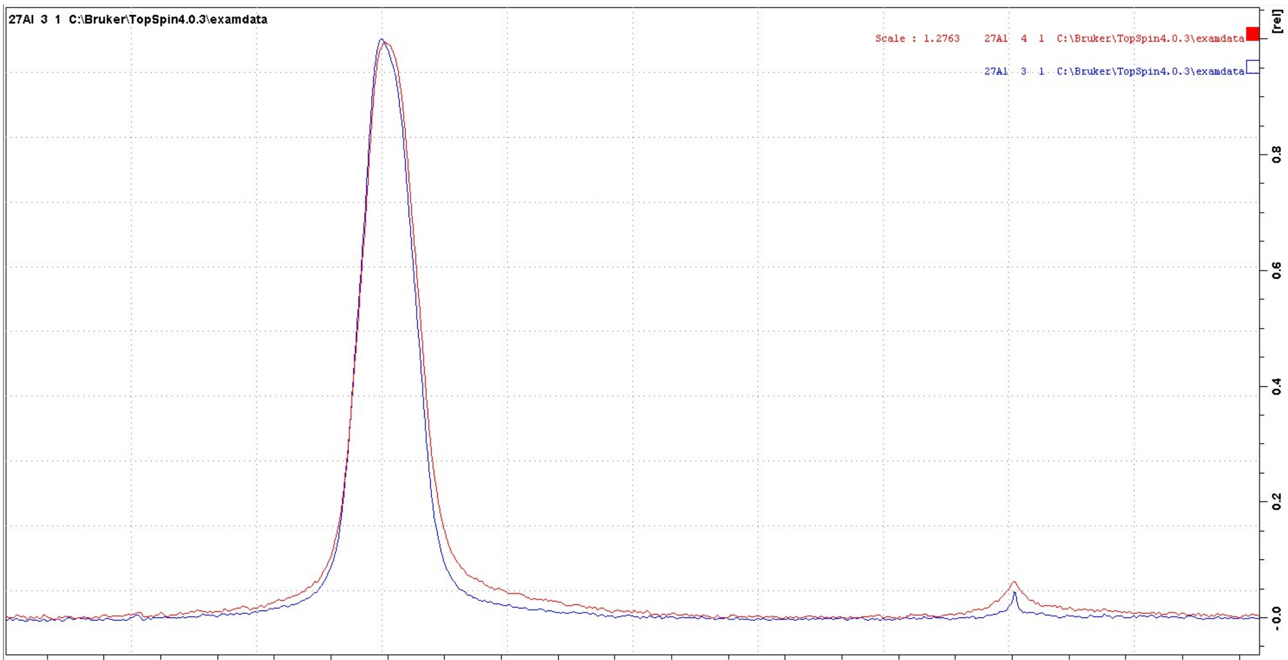


Figure S6e. ^{27}Al MAS NMR spectra (normalised to the same peak intensity) of the parent (blue) and hierarchical (red) ZSM-5.

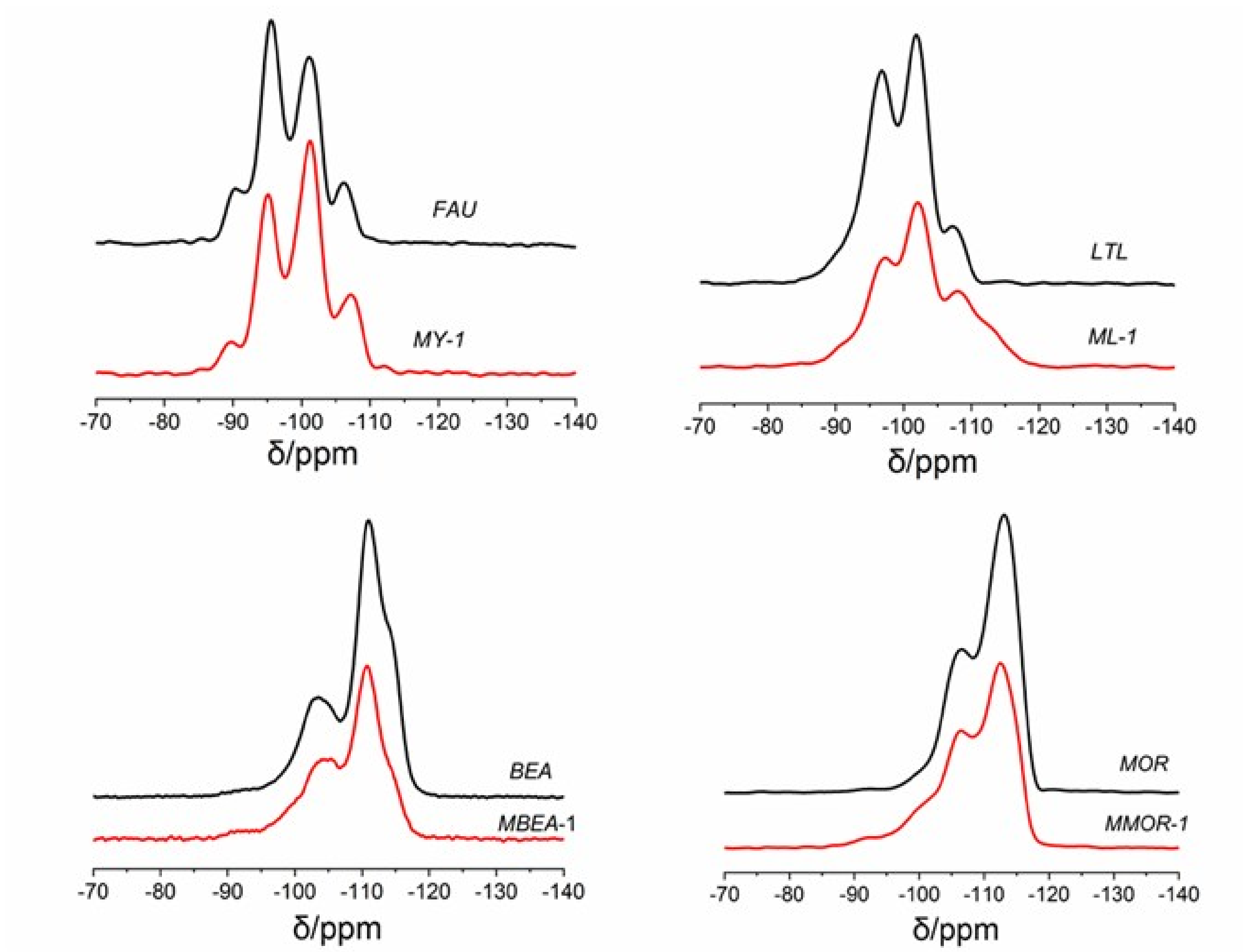


Figure S7. ^{29}Si MAS NMR spectra of the parent and hierarchical zeolites.

Table S2. Reaction test data: product selectivities (mol%) and conversion.

	IPB	MIPB	PIPB	TIPB	Conversion, %
NH4-Y	3%	21%	11%	65%	35%
MY-1	6%	28%	19%	46%	54%
NH4-BEA		8%	4%	88%	12%
MBEA-1		11%	6%	83%	17%
NH4-ZSM-5		2%	0%	98%	2%
MZSM-5-1		6%	0%	94%	6%
NH4-MOR		2%	0%	98%	2%
MMOR-1		7%	3%	91%	9%
NH4-L		1%	0%	99%	1%
ML-1		10%	3%	87%	13%

TIPB - 1,3,5-tri-isopropylbenzene

IPB - mono-isopropylbenzene

MIPB - 1,3- and for all the studied catalysts, and a small amount of

PIPB - 1,4-di-isopropylbenzenes