Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Synthesis of hierarchical ZSM-12 nanolayers for levulinic acid esterification with ethanol to ethyl levulinate

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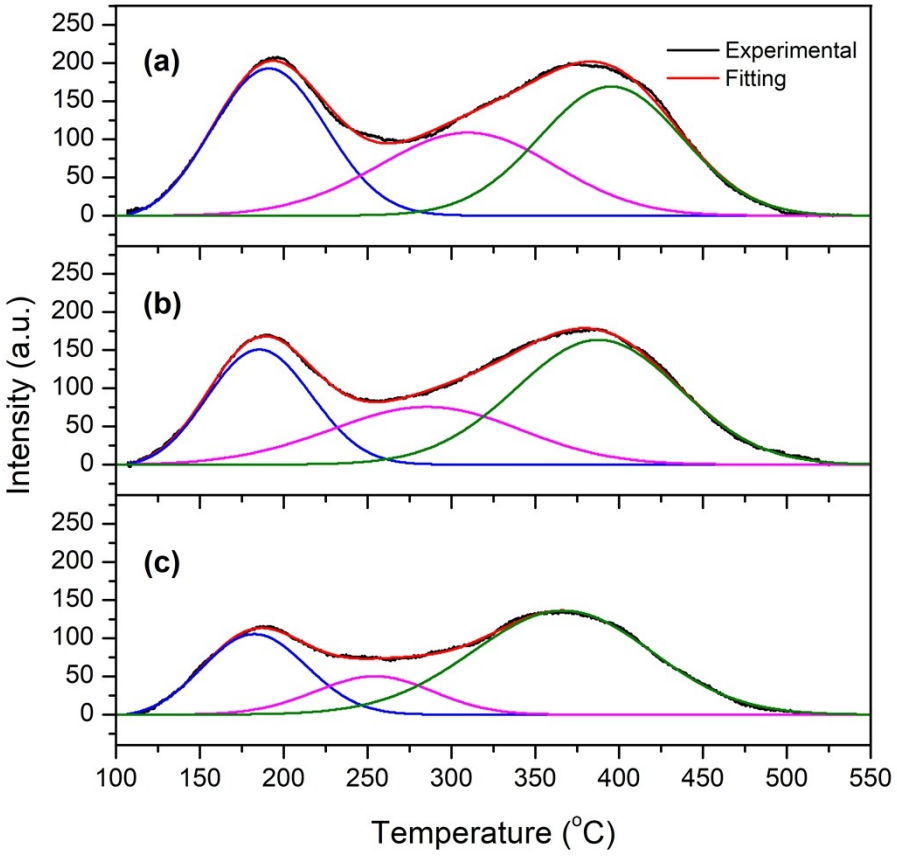

Figure S1. NH_3-TPD profiles and their deconvolution of ZSM-12 zeolites synthesized with different TPOAC/SiO_2 molar ratios: (a) ZSM-12-0, (b) ZSM-12-0.03, and (c) ZSM-12-0.09.

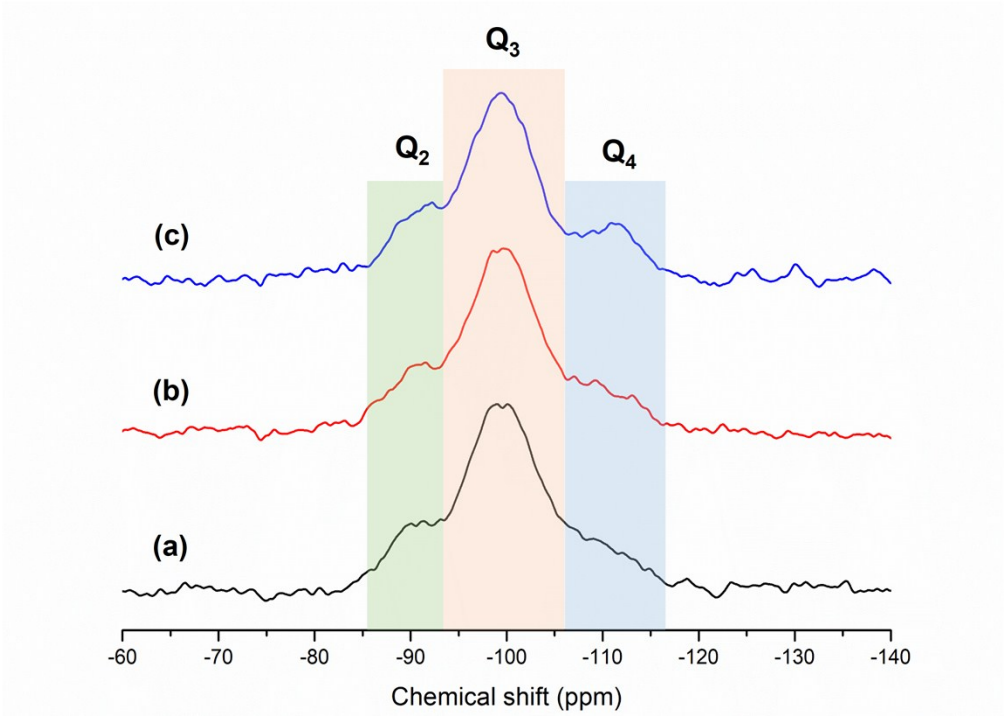

Figure S2. ^{29}Si-NMR spectra of synthesized ZSM-12 zeolites obtained at different crystallization times: (a) 2 h, (b) 12 h, and (c) 24 h.

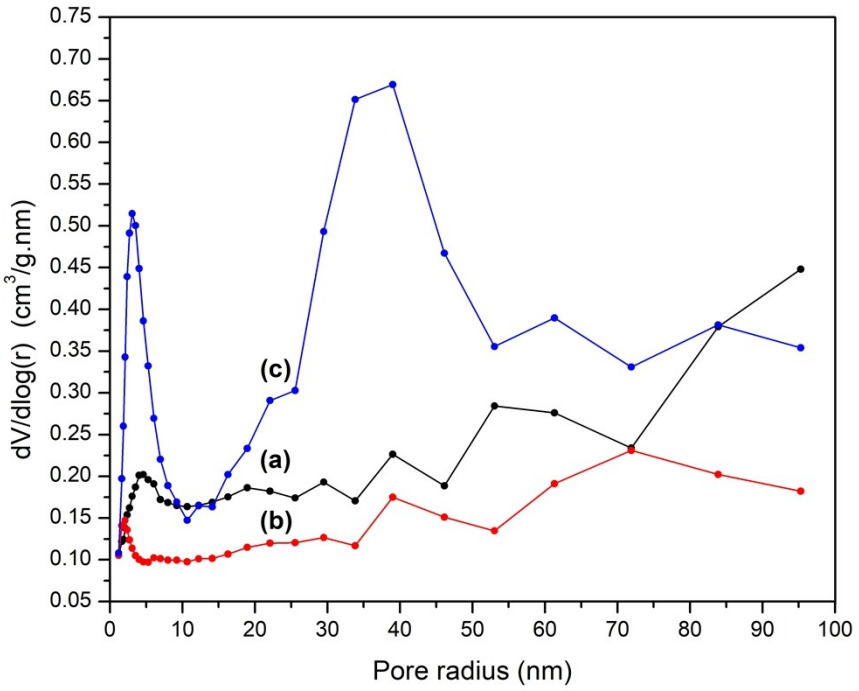

Figure S3. BJH pore size distribution (PSD) derived from the adsorption branch of isotherm of ZSM-12 zeolites synthesized with different TPOAC/SiO_2 molar ratios: (a) ZSM-12-0, (b) ZSM-12-0.03, and (c) ZSM-12-0.09.

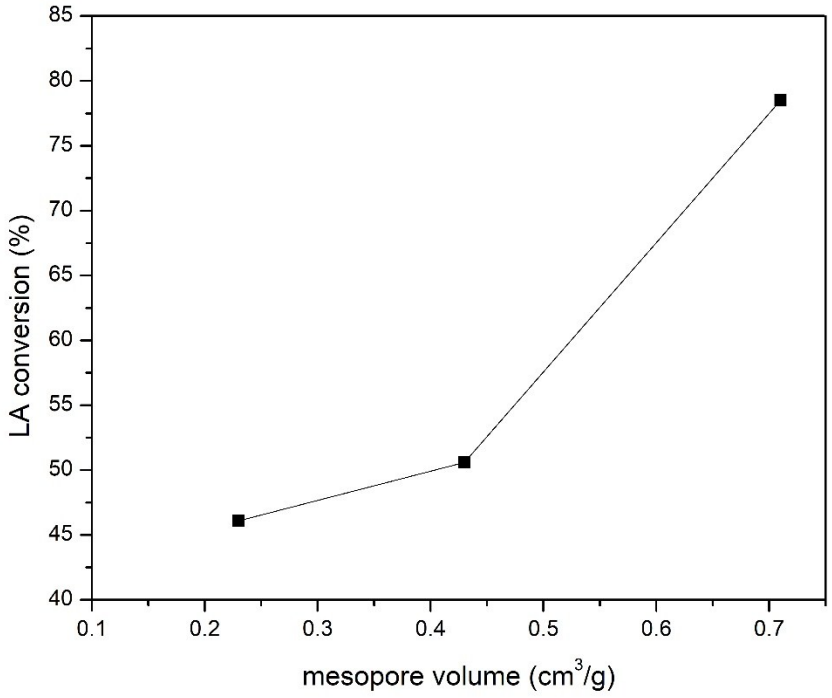

Figure S4. Levulinic acid conversion (%) as a function of mesopore volume of ZSM-12 zeolite.

Table S1. Acetic acid conversion and ethyl acetate selectivity obtained on different catalysts after 24 h of reaction (reaction conditions: T = 100 ºC, acetic acid:ethanol molar ratio of 1:1, catalyst loading of 0.3 g)

Sample	Time (h)	Acetic acid conversion (%)	Ethyl acetate selectivity (%)
ZSM-12-0	24	79.9	99.8
ZSM-12-0.09	24	85.5	97.6

Table S2. NH_3-TPD data and the acid amount of different zeolites.

Sample	T_{peak} (ºC)			Acid amount (mmol/g)			
	LT peak	MT peak	HT peak	Weak acidity	Medium acidity	Strong acidity	Total acidity
ZSM-12-0.09	182.7	254.2	366.6	0.041	0.022	0.098	0.161
ZSM-5 nanosheet	189.6	297.8	385.0	0.064	0.030	0.072	0.166
FAU nanosheet	201.5	-	412	0.159	-	0.553	0.712

Table S3. Textural properties different hierarchical zeolites.

Sample	S_{BET}[a]	S_{micro}[b]	S_{ext}[c]	V_{total}[d]	V_{micro}[e]	V_{ext}[f]	V_{ext}/V_{total}[g]
ZSM-12-0.09	421	143	278	0.75	0.04	0.71	0.95
ZSM-5 nanosheet[1]	542	296	246	0.86	0.12	0.74	0.86
FAU nanosheet[2]	699	540	159	0.46	0.21	0.25	0.54

[a] S_{BET}: BET specific surface area.

[b] S_{micro}: microporous surface area.

[c] S_{ext}: external surface area.

[d] V_{total}: total pore volume.

[e] V_{micro}: micropore volume.

[f] $V_{ext} = V_{total} – V_{micro}$; All surface areas and pore volumes are in the units of m^2/g and cm^3/g, respectively.

[g] fraction of mesopore volume.

References

1. W. Wannapakdee, C. Wattanakit, V. Paluka, T. Yutthalekha and J. Limtrakul, *RSC Adv.*, 2016, **6**, 2875–2881.

2. T. Yutthalekha, C. Wattanakit, C. Warakulwit, W. Wannapakdee, K. Rodponthukwaji, T. Witoon and J. Limtrakul, *J. Clean. Prod.*, 2017, **142**, 1244–1251.