

Electronic Supplementary Information (ESI)

Mesoporogen-free synthesis of single-crystalline hierarchical Beta zeolite for efficient catalytic reactions

Yuyao Wang,^a Junyan Li,^{ac} Weiyi Tong,^e Zhenhao Shen,^e Lin Li,^d Qiang Zhang,^{*a} Jihong Yu^{*ab}

^aState Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, P. R. China

^bInternational Center of Future Science, Jilin University, 2699 Qianjin Street, Changchun 130012, P. R. China

^cCenter for High-resolution Electron Microscopy (C_HEM), School of Physical Science and Technology, Shanghai Tech University, 393 Middle Huaxia Road, Pudong, Shanghai 201210, P. R. China

^dElectron Microscopy Center, Jilin University, 2699 Qianjin Street, Changchun 130012, China

^eState Key Laboratory of Green Chemical Engineering and Industrial Catalysis, Shanghai Research Institute of Petrochemical Technology, SINOPEC, Shanghai 201208, P. R. China

Email address: qiangz@jlu.edu.cn

jihong@jlu.edu.cn

Supplementary Figures and Tables

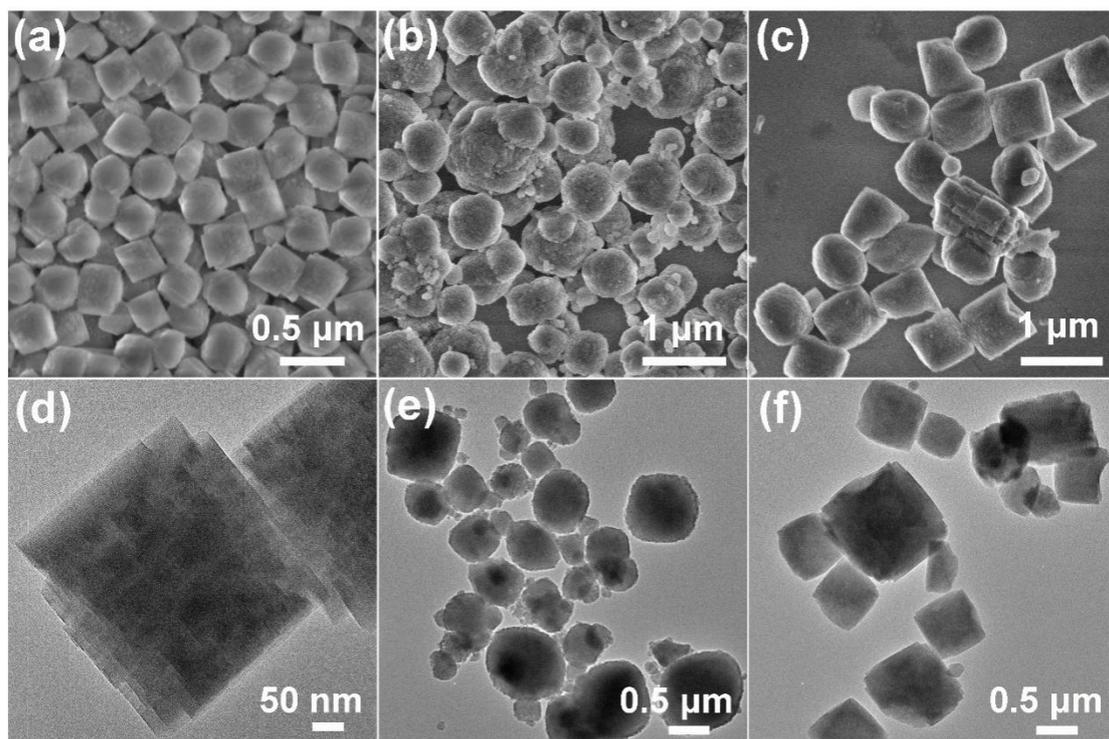


Fig. S1 SEM images of (a) conv-Beta-16, (b) comm-Beta-19, (c) comm-Beta-30; TEM images of (d) conv-Beta-16, (e) comm-Beta-19, (f) comm-Beta-30.

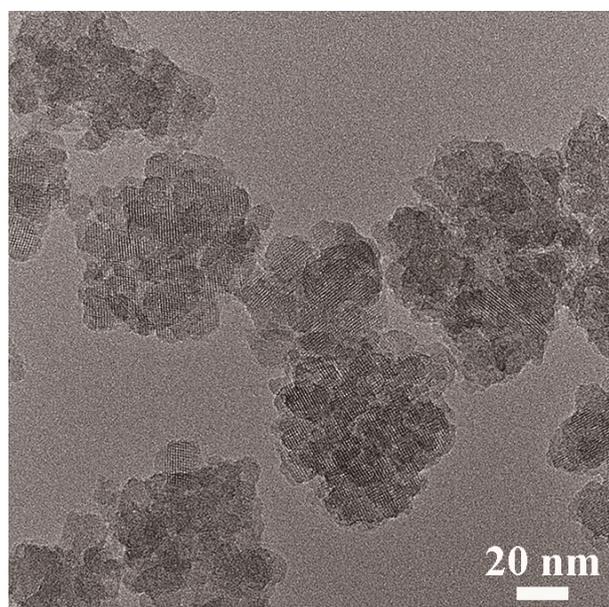


Fig. S2 TEM image of sample meso-Beta-23.

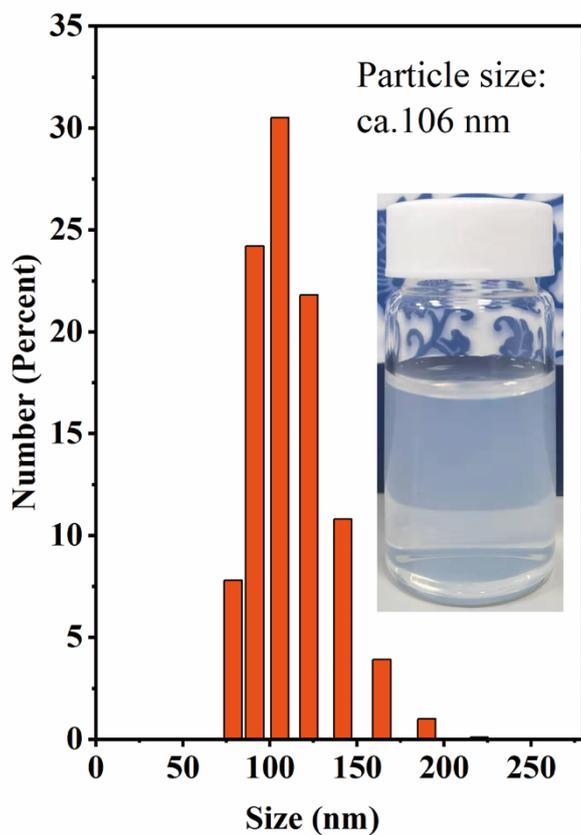


Fig. S3 Dynamic light scattering characterization of sample meso-Beta-23.

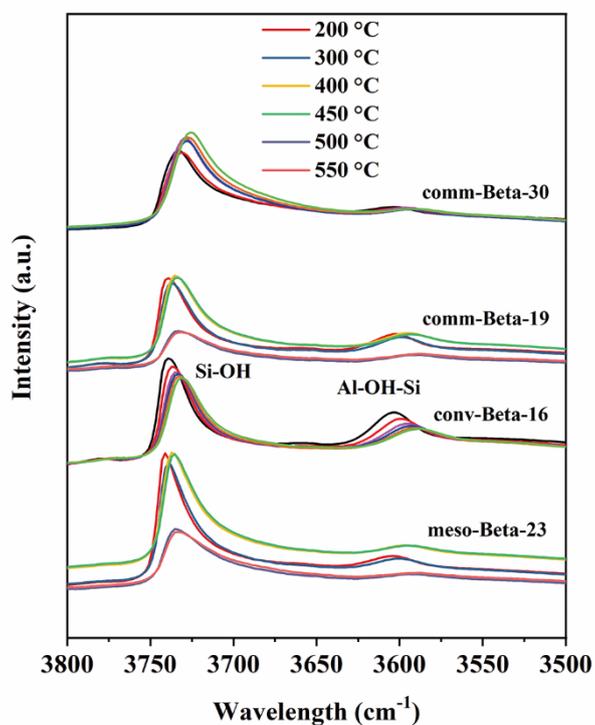


Fig. S4 FT-IR spectra in the OH region of selected Beta samples under different temperature.

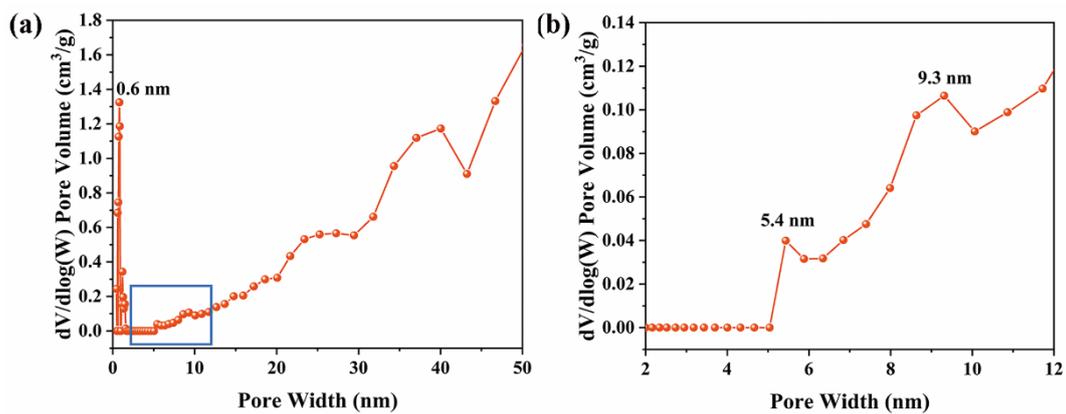


Fig. S5 (a) Pore size distributions of sample meso-Beta-23, (b) magnification of the region marked by blue rectangle in (a).

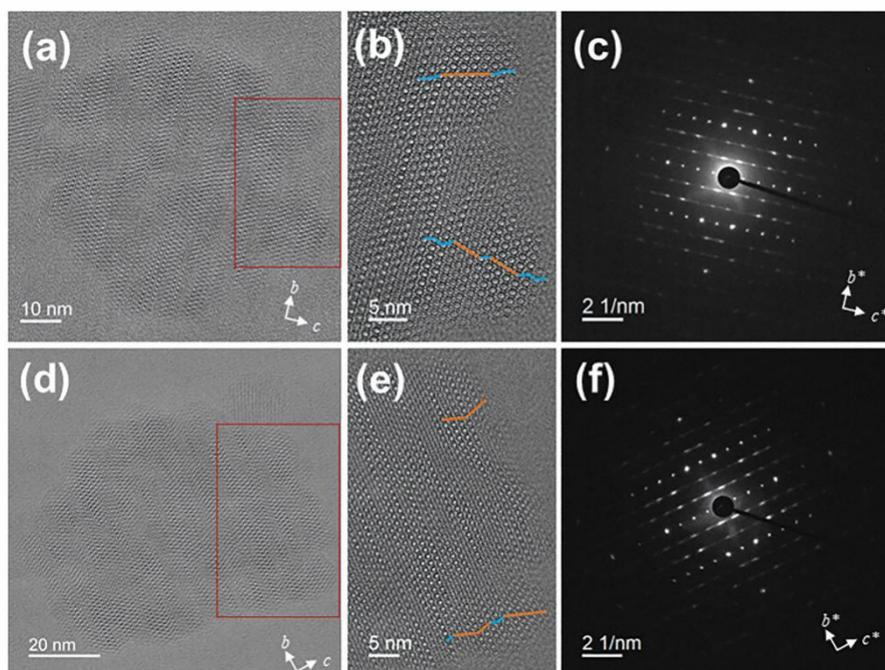


Fig. S6 (a, d) HRTEM images of two representative nanoparticles of sample meso-Beta-23. (b, e) enlarged images corresponding to the red rectangles in (a) and (d), respectively. Intergrowth of polymorph A (blue) and B (orange) can be observed. (c, f) ED patterns taken from the entire particle in (a) and (d), respectively.

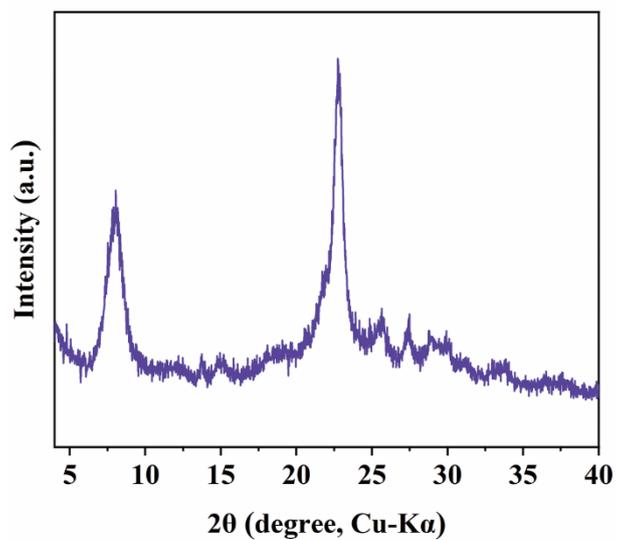


Fig. S7 PXR D pattern of sample meso-Beta-23 after exposing to boiling water for 48 h.

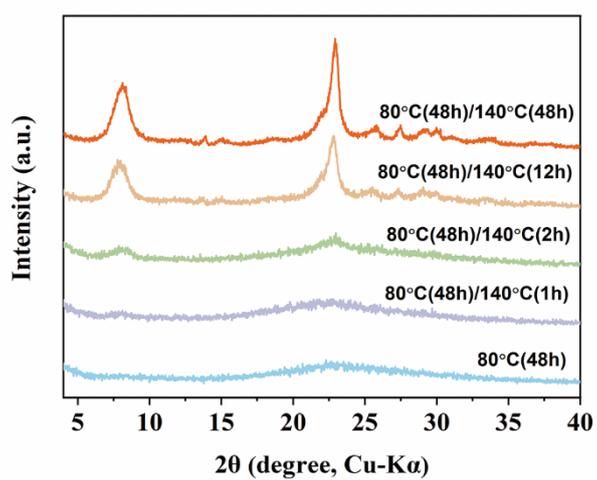


Fig. S8 PXR D patterns of meso-Beta-23 sample under different crystallization time.

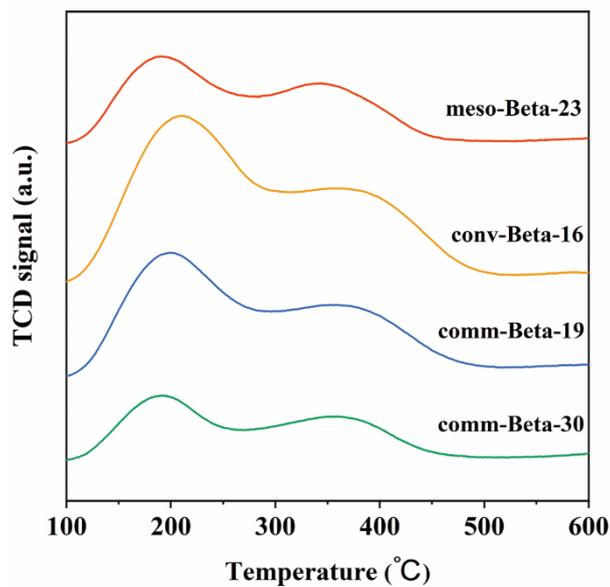


Fig. S9 NH₃-TPD profiles of Beta zeolites.

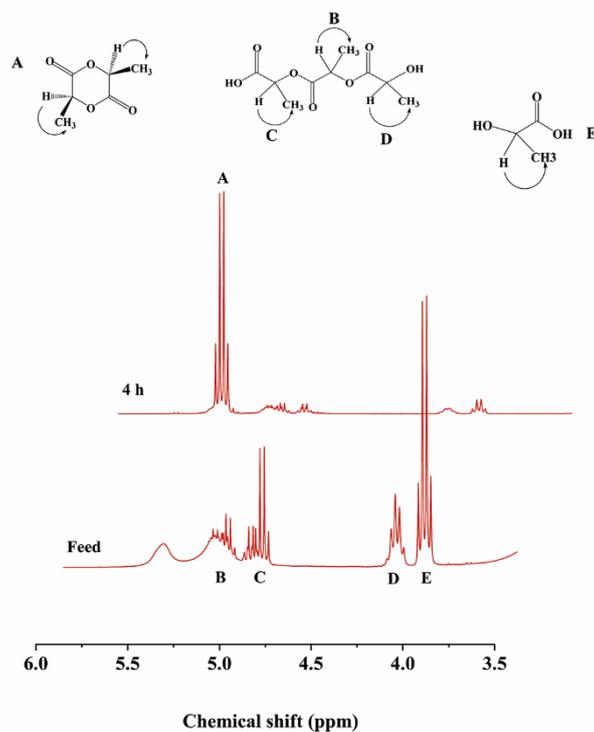


Fig. S10 Typical ¹H-NMR analysis in DMSO-d₆. The methine [-CH-CH₃] quartet region of a series of reaction mixtures. Methine proton signals of A: lactide, B: centers of oligomers, C: carboxylic end groups of oligomers, D: hydroxyl end groups of oligomers, and E: lactic acid are assigned; product distribution after reaction with sample meso-Beta-23 (0.25 g) on 1.0 g of aqueous lactic acid solution (105 wt %) in 20 ml of toluene refluxed for 4 h with water removal.

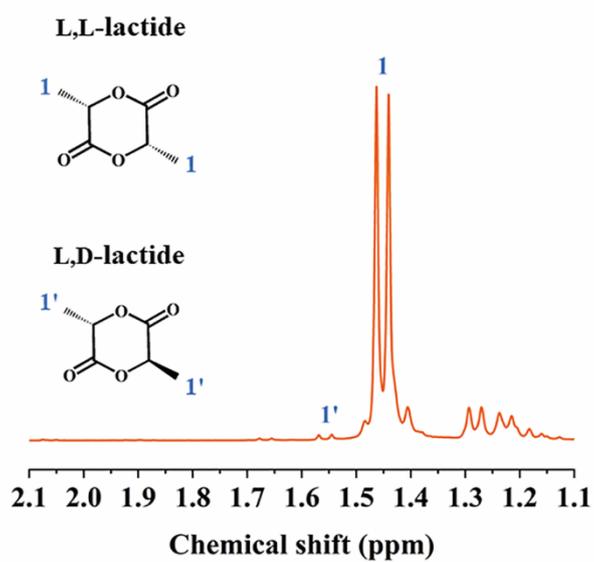


Fig. S11 Typical $^1\text{H-NMR}$ analysis in the methyl $[-\text{CH}-\text{CH}_3]$ doublet region.

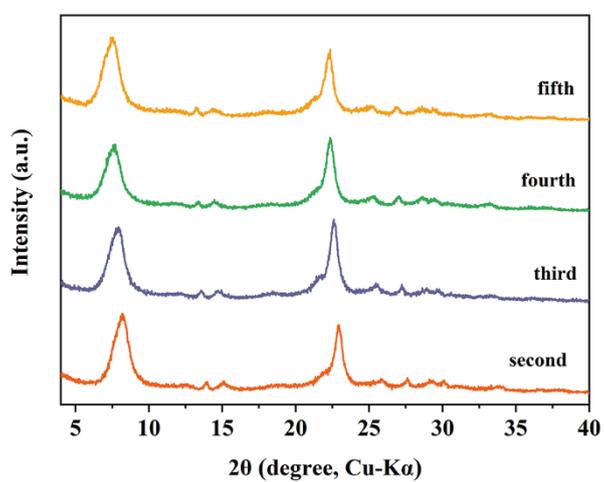


Fig. S12 PXRD patterns of meso-Beta-23 after recycling tests.

Table S1 Molar compositions of the initial gel mixtures, crystallization conditions, and Si/Al ratios of Beta zeolites.

Sample	TEAOH	SiO ₂	Al ₂ O ₃	L-Lysine	H ₂ O	Si/Al ^a	Temperature (time)
meso-Beta-23	0.55	1	0.025	0.3	7.5	23	80°C(2d)/140°C(2d)
meso-Beta-23-0h	0.55	1	0.025	0.3	7.5	-	80°C(2d)/140°C(0h)
meso-Beta-23-1h	0.55	1	0.025	0.3	7.5	-	80°C(2d)/140°C(1h)
meso-Beta-23-2h	0.55	1	0.025	0.3	7.5	-	80°C(2d)/140°C(2h)
meso-Beta-23-12h	0.55	1	0.025	0.3	7.5	-	80°C(2d)/140°C(12h)
conv-Beta-16	0.55	1	0.025	0	7.5	16	80°C(2d)/140°C(2d)
comm-Beta-19 ^b	-	-	-	-	-	19	-
comm-Beta-30 ^c	-	-	-	-	-	30	-

^aTested by ICP-OES; ^bPurchased from Alfa Aesar Company; ^cPurchased from Hubei Shentan Environmental Protection New Material Company.

Table S2 The catalytic performance of Beta zeolite catalysts for 1,3,5-trimethylbenzene cracking reaction.

Sample	1,3,5-trimethylbenzene conversion (wt%)	benzene selectivity (wt%)	toluene selectivity (wt%)	xylene selectivity (wt%)	BTX selectivity (wt%)	C ₉ selectivity (wt%)	C ₁₀ selectivity (wt%)
meso-Beta-23	88.3	0.25	3.86	22	26.11	32.18	25.6
conv-Beta-16	87.8	0.17	2.97	18.62	21.76	31.66	33.65
comm-Beta-19	89.4	0.13	2.74	17.74	20.61	29.87	37.86
comm-Beta-30	87.6	0.17	3.28	20.58	24.03	34.37	28.83

Reaction conditions: 385 °C, 3.0 Mpa, H₂/1,3,5-trimethylbenzene = 4:1, WHSV = 2 h⁻¹, 2.0 g catalyst.

Note: The xylene product is a mixture of xylene isomers including p-xylene (PX), o-xylene (OX), and m-xylene (MX); BTX means the total amount of benzene, toluene, and xylene.

Table S3 The catalytic performance of Beta zeolite catalysts for alkylation of benzene with ethylene.

Sample	ethylene conversion (%)	ethylbenzene selectivity (%)	diethylbenzene selectivity (%)	triethylbenzene selectivity (%)	by-products selectivity (%)
meso-Beta-23	75.8	73.05	22.96	3.56	26.52
comm-Beta-19	74.9	71.66	23.80	4.07	27.87
comm-Beta-30	68.8	71.72	23.46	4.28	27.74

Reaction conditions: 160 °C, 3.5 Mpa, benzene/ethylene= 3:1, WHSV = 6 h⁻¹, TOS = 12 h, 0.5 g catalyst.

Table S4 The catalytic performance of Beta zeolite catalysts for conversion of highly concentrated lactic acid to produce lactide.

Sample	Lactic acid (mol%)	Oligomers (mol%)	Lactide (mol%)
meso-Beta-23	7.3	19.7	73
conv-Beta-16	7.5	24.5	68
comm-Beta-19	1.6	45.4	53

Reaction conditions: 140 °C, 0.25 g H-Beta zeolites, 1.0 g of aqueous lactic acid solution (105 wt %), 20 ml of toluene, 4 h.