

Supporting information

Controlled Synthesis of L-Lactide using Sn-beta Zeolite Catalysts in a One-step Route

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- Text S1.** Catalyst synthesis
- S1.1** Chemicals
 - S1.2** Synthesis of Sn-beta
 - S1.3** Synthesis of SnO₂-SiO₂ xerogels
 - S1.4** Synthesis of supported SnO₂/Si-beta
 - S1.5** Synthesis of Sn-MCM-41

- Text S2.** Analysis of samples
- S2.1** High Performance Liquid Chromatography (HPLC)
 - S2.2** ¹H Nuclear Magnetic Resonance (¹H NMR)
 - S2.3** Gas Chromatography (GC)

Supporting figures

- Figure S1** Scheme of the experiment setup for catalytic reaction.
- Figure S2** PXRD patterns of Sn-beta with different Si/Sn ratios.
- Figure S3** DR UV-Vis spectra of Sn-Si catalysts
- Figure S4** The N₂ isotherms of Sn-beta zeolites.
- Figure S5** The pore size patterns of Sn-beta zeolites.
- Figure S6** SEM (A) and TEM (B) image of Sn-beta-30.
- Figure S7** Corresponding O, Si, and Sn elemental maps of Sn-Beta-30.
- Figure S8** HPLC profiles of La conversion over Sn-beta-30.
- Figure S9** Typical gas chromatogram of the sample.
- Figure S10** Sn-beta reused study in the production of lactide.
- Figure S11** PXRD patterns of Sn-beta-50 zeolite after recycle test.
- Figure S12** HPLC profiles of L₂a conversion over Sn-beta-30. Reaction conditions:
0.2 g catalyst and 1.2 g 39 wt% aqueous L₂a feedstock in 12 mL mesitylene for 120 min in an oil bath.
- Figure S13** Typical time profile of catalytic reactions with HC-La feed stock.
Reaction conditions: 0.2 g Sn-beta-30 zeolite and 0.5 g HC-La feedstock

in 12 mL mesitylene for 120 min in an oil bath.

Figure S14 Typical time profile of catalytic reactions with L_na feed stock. Reaction conditions: 0.2 g Sn-beta-30 zeolite and 0.5 g L_na feedstock in 12 mL mesitylene for 120 min in an oil bath.

Figure S15 Typical time profile of catalytic reactions with HC-La feed stock. Reaction conditions: 0.2 g Sn-MCM-41-30 zeolite and 0.5 g HC-La feedstock in 12 mL mesitylene for 120 min in an oil bath.

Figure S16 The N₂ isotherms and the pore size patterns of Sn-MCM-41 zeolites.

Supporting Scheme and Table

Scheme S1. Reaction mechanism for L₃a dehydration to L-lactide over Sn-beta zeolite.

Table S1. The optimized reaction conditions of Sn-beta-50 as a catalyst for the synthesis of lactide

Table S2. Actual Si/Sn Ratio, Surface Si/Sn ratio, Porosity, and Particle sizes of As-prepared Sn-Si catalysts

Table S3. The distribution of different feedstocks measured by HPLC

Text S1. Catalyst synthesis

S1.1 Chemicals

H-Beta aluminosilicate (Si/Al=12.5) were obtained from Nankai University Catalyst Company Co., Ltd. concentrated nitric acid (HNO₃, 69%), Tin tetrachloride (SnCl₄·5H₂O), ammonium fluoride (NH₄F), hydrochloric acid (HCl, 37%), ammonia hydroxide solution (NH₃·H₂O, 28%), Ethanol (EtOH, 99.7%) were obtained from Macklin Biochemical Co., Ltd., China. Tetraethylammonium hydroxide aqueous solution (25%), Tetraethyl orthosilicate (TEOS), tetraethylammonium hydroxide aqueous solution (TEAOH, 35%), hexadecyltrimethylammonium hydroxide aqueous solution (CTAOH, 16%), hexadecyltrimethylammonium bromide (CTAB) were supplied by Aladdin Co. Ltd., China.

S1.2 Synthesis of Sn-beta

Sn-beta zeolites with different Si/Sn ratios were synthesized by a post synthetic procedure reported by Zhu ¹. In a typical synthesis, dealumination treatments of H-beta zeolites (Si/Al=12.5) were performed using nitric acid. 150 mL concentrated nitric acid (HNO₃, 69 %) was added to 6 g H-beta zeolites and stirred in a single-necked flask for 16 h at 80 °C. The dealuminated beta zeolites were recovered by filtration and washed with water until the pH of filtrate was 6-7, and dried for 12 h at 100 °C.

The dealuminated beta zeolites and SnCl₄·5H₂O were added to TEAOH aqueous solution under stirring at 70 °C for approximately 30 min, resulting in a gel composition of 1.0 SiO₂: x SnCl₄ : 0.5 TEAOH : 7.5 H₂O, where x represents the Sn/Si ratio in the synthetic gel. Subsequently, the gel was transferred to a Teflon-lined autoclave and preheated at 140 °C for 45 min statically. After quenching to ambient temperature with water, the mixture was denoted as Sn-beta-x and then ammonium fluoride (NH₄F) was blended with the mixture. The final molar composition of the mixture was SiO₂ : x SnO₂ : 0.5 TEAOH : 7.5 H₂O : 0.5 NH₄F. The mixture was further treated at 413 K for

a certain time under static conditions. The solids were recovered by filtration and washed with water and dried for 12 h at 100 °C. The recovered solid was calcined at 550 °C for 6 h under static air with a temperature ramp of 3 °C/min. Finally, the calcined Sn-beta zeolite is denoted as Sn-beta-n, where n indicates the Si/Sn ratio in the synthetic gel. Additionally, Sn-free siliceous beta, designated Si-beta, was hydrothermally synthesized via structural reconstruction without adding a Sn source to the synthetic gel.

S1.3 Synthesis of SnO₂-SiO₂ xerogels

SnO₂-SiO₂ xerogels were prepared as follows: first, tetraethyl orthosilicate (TEOS) was diluted in EtOH with aqueous HCl (10 wt%) under stirring conditions according to the molar ratio TEOS : EtOH : HCl = 1:6:0.02. Then the desired SnCl₄·5H₂O solution (molar ratio, SnCl₄·5H₂O:H₂O=1:40) was added dropwise with continuous stirring. After homogenization, aqueous NH₃ (1 M) was dropped into the above solution until the pH of the solution reached 6-7. The resulting gel was covered and aged at 60 °C for 48 h. Then, the gel was dried overnight at 80 °C, ground into a fine powder, and finally calcined at 500 °C for 4 h. A Sn-free SiO₂ xerogel was synthesized with the same process described above, but with no addition of the SnCl₄·5H₂O solution.

S1.4 Synthesis of supported SnO₂/Si-beta

Supported SnO₂/Si-beta was prepared by equal volume impregnation. The prepared Si-beta zeolite was dried for 12 h before impregnation. The impregnation solutions, SnCl₄ aqueous solution with different concentrations, were added dropwise to the support, while occasionally mixing the powder with a spatula. The total volume of the impregnation solution was equal to the pore volume of the support. After impregnation, the powder was dried overnight at 100 °C, and calcined at 500 °C for 4 h (heating rate 5 °C min⁻¹) in static air.

S1.5 Synthesis of Sn-MCM-41

Sn-MCM-41 (Si/Sn=30) was synthesized according to literature ². The homogeneous gel (with composition 1 SiO₂: 0.13 C₁₆TAOH: 0.03 C₁₆TABr: 0.26 TMAOH: 0.33 SnCl₄: 24.3 H₂O) was transferred to a Teflon-lined stainless steel autoclave and heated at 135 °C under static conditions for 24 h. The resulting solid product was filtered, washed thoroughly with H₂O, dried at 80 °C overnight, and finally calcined at 550 °C for 5 h (heating rate 5 °C min⁻¹).

Text S2. Analysis of samples

S2.1 High Performance Liquid Chromatography (HPLC)

The quantitative determination of synthesized lactide was conducted by high performance liquid chromatography (HPLC, U3000, Dionex), The HPLC was equipped with C18 column and UV detector at 210 nm. Acetonitrile (HPLC grade, with addition of 2 mL of 85% H₃PO₄ per L) and water (with addition of 2 mL of 85% H₃PO₄ per L) were used as mobile phases. The LC column and oven temperature was maintained at 40 °C and the mobile phase flow rate was maintained at 0.7 mL/min. The elution program (water/acetonitrile, V/V) was as follows: (98/2) from 0 to 2 min; linear ramp to (0/100) from 2 to 30 min; (0/100) from 30 to 60 min; (98/2) from 30 to 60 min ³.

S2.2 ¹H Nuclear Magnetic Resonance (¹H NMR)

¹H NMR spectra of lactide samples were recorded on a Bruker DRX-500 spectrometer operating at 100 MHz with DMSO-d₆ as a solvent and tetramethylsilane as an internal reference. As shown in Figure 2B, Methylene protons of the lactide exhibit peaks at 5.5 ppm (1), while the signals at 5.2 ppm (2), 5.0 ppm (4), 4.2 ppm (3) were assigned to the carboxylic end groups of oligomers, centers of oligomers, and hydroxyl end groups of oligomers, respectively. The methylene protons derives from lactic acid were detected at 4.0 ppm (5).

S2.3 Gas Chromatography (GC)

For analysis the chiral purity of the synthesized lactide, the dry sample was dissolved in 1 mL acetonitrile and analyzed on an Agilent 7890B gas chromatography. The GC measurement was equipped with a flame ionization detector (FID), and an Agilent CP-cyclodextrinb-236M-19 capillary. The injector and FID temperatures were maintained at 250 and 270 °C, respectively. The initial column temperature was set at 70 °C. This temperature is held for 3 minutes, and then ramped to 250 °C at 10 °C·Min⁻¹ and held there for 3 minutes.

S3. Supporting figures

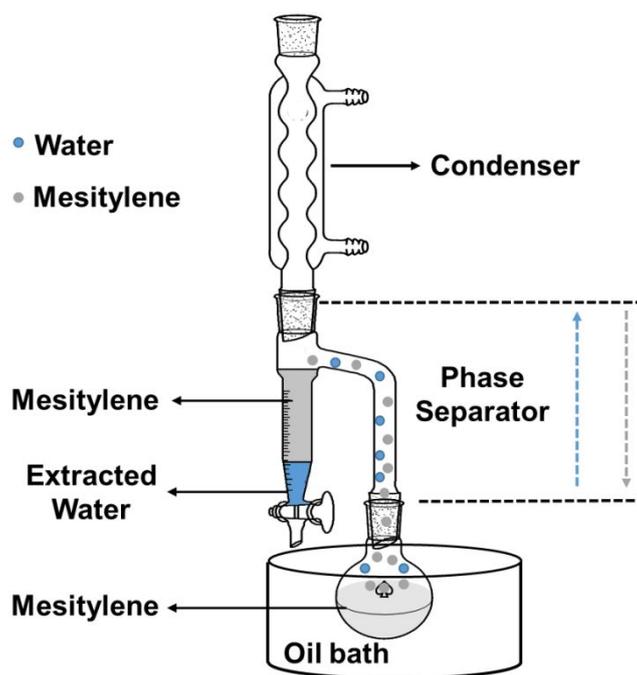


Figure S1 Scheme of the experiment setup for catalytic reaction.

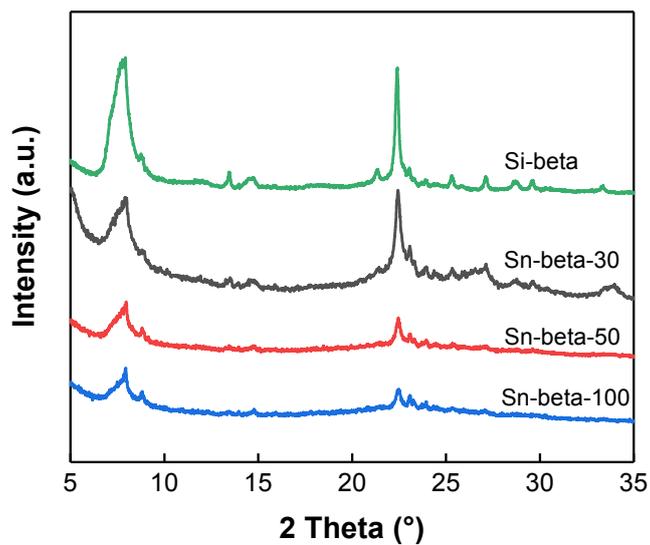


Figure S2 PXRD patterns of Sn-beta with different Si/Sn ratios

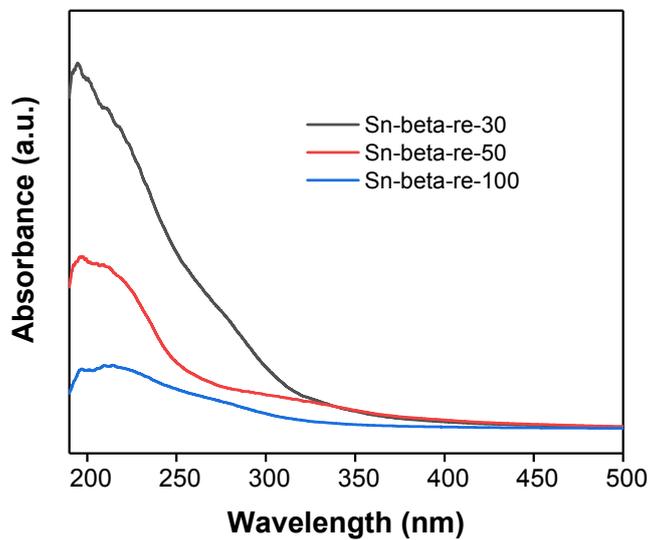


Figure S3 DR UV-Vis spectra of Sn-Si catalysts

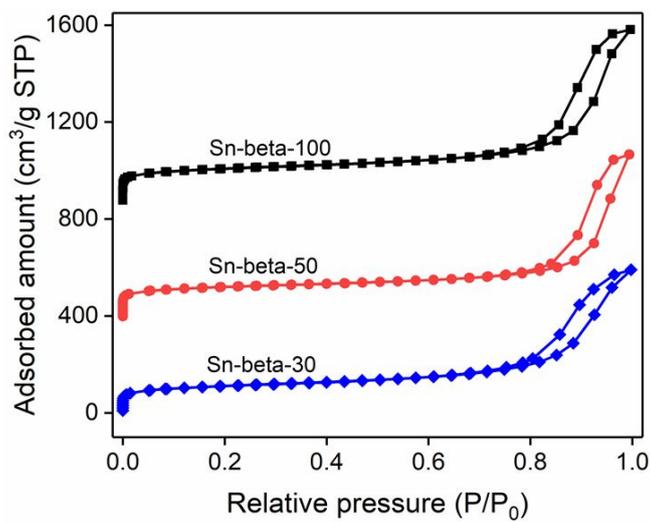


Figure S4. The N₂ isotherms of Sn-beta zeolites.

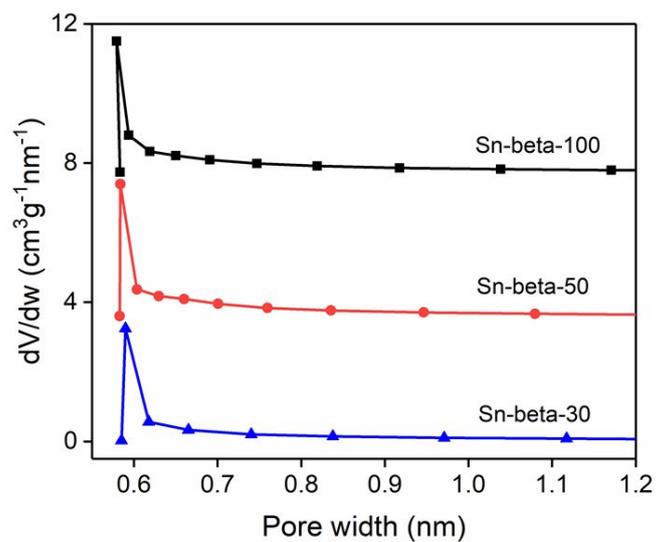


Figure S5. The pore size patterns of Sn-beta zeolites.

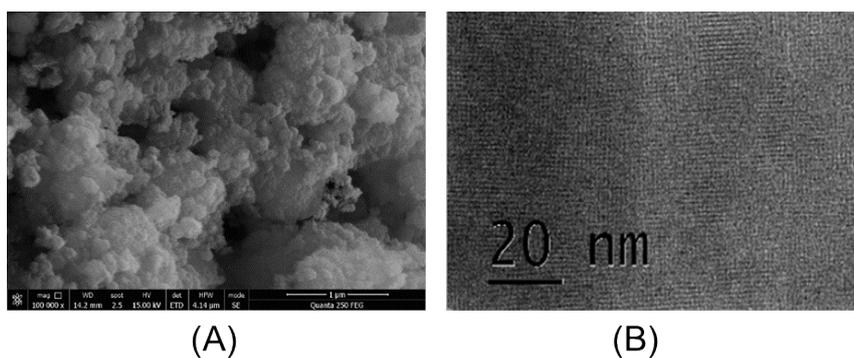


Figure S6 SEM (A) and TEM (B) image of Sn-beta-30.

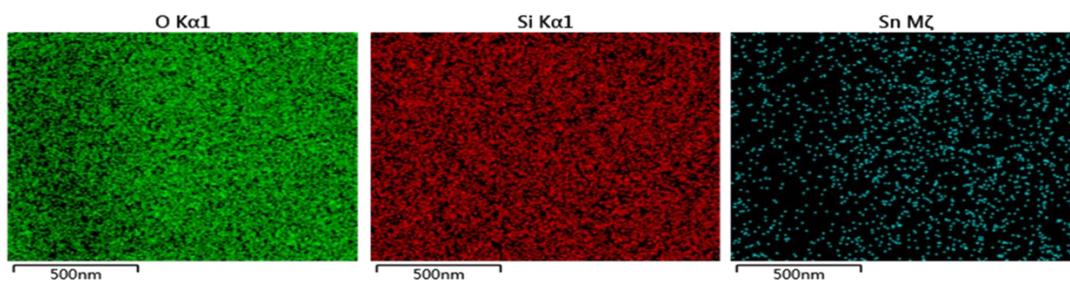


Figure S7 Corresponding O, Si, and Sn elemental maps of Sn-Beta-30

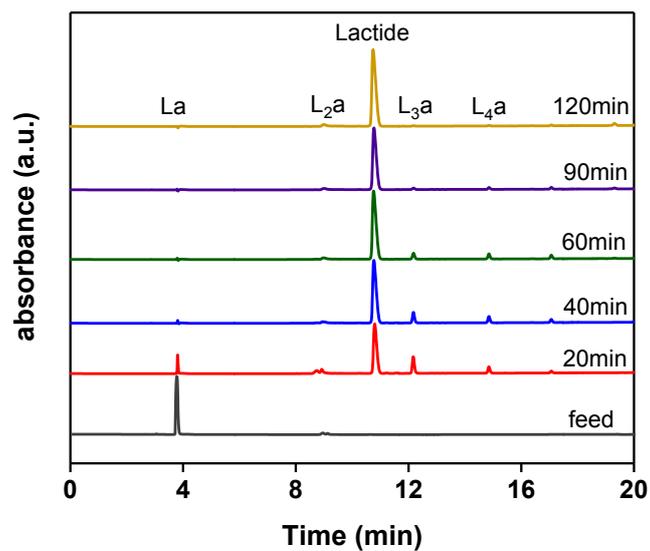


Figure S8 HPLC profiles of LA conversion over Sn-beta-30

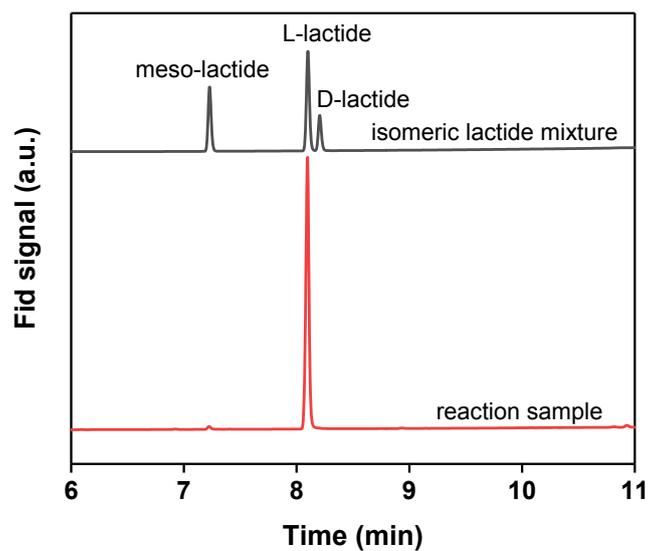


Figure S9 Typical gas chromatogram of the sample.

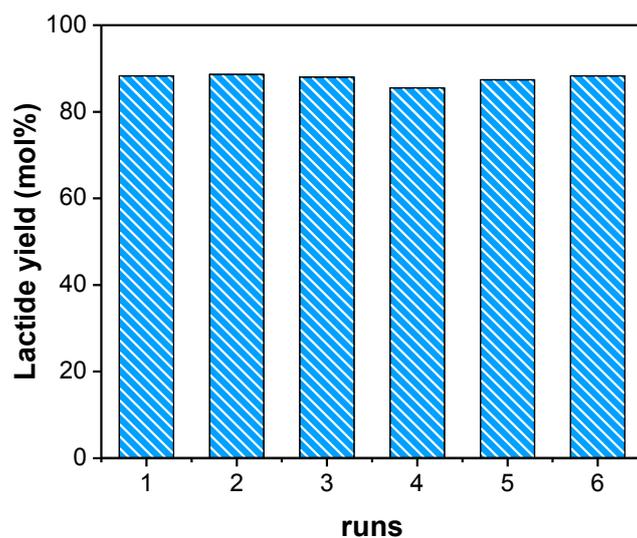


Figure S10 Sn-beta-50 reused study in the production of lactide.

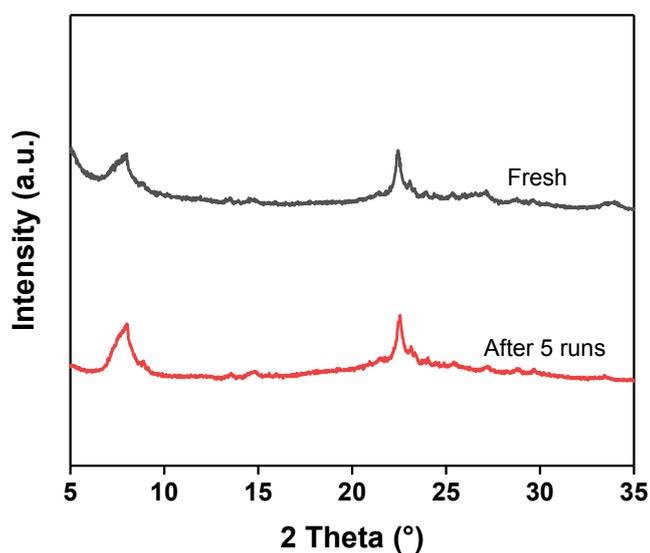


Figure S11 PXRD patterns of Sn-beta-50 zeolite after recycle test.

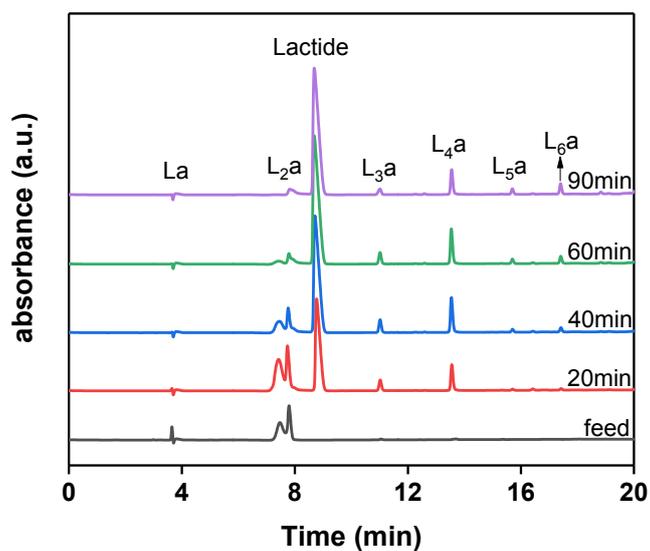


Figure S12 HPLC profiles of L_2A conversion over Sn-beta-30. Reaction conditions: 0.2 g catalyst and 1.2 g 39 wt% aqueous L_2a feedstock in 12 mL mesitylene for 120 min in an oil bath.

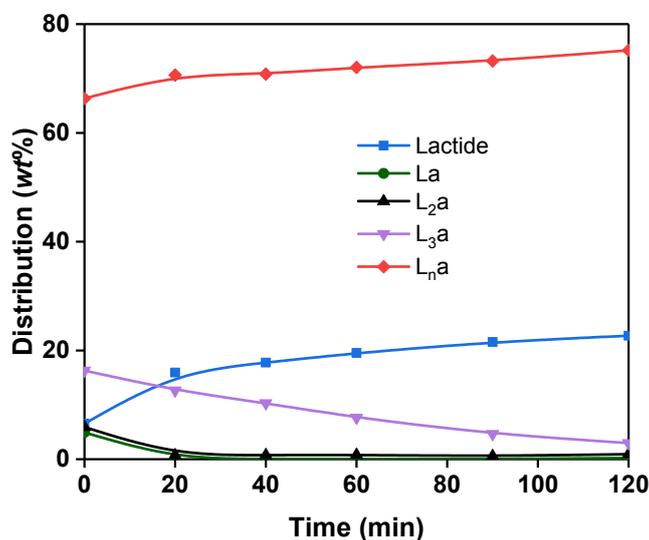


Figure S13 Typical time profile of catalytic reactions with HC-La feed stock. Reaction conditions: 0.2 g Sn-beta-30 zeolite and 0.5 g HC-La feedstock in 12 mL mesitylene for 120 min in an oil bath.

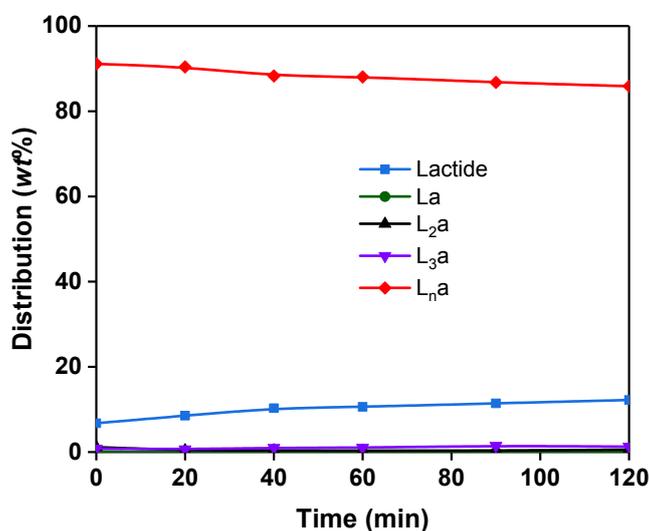


Figure S14 Typical time profile of catalytic reactions with $L_n a$ feed stock. Reaction conditions: 0.2 g Sn-beta-30 zeolite and 0.5 g $L_n a$ feedstock in 12 mL mesitylene for 120 min in an oil bath.

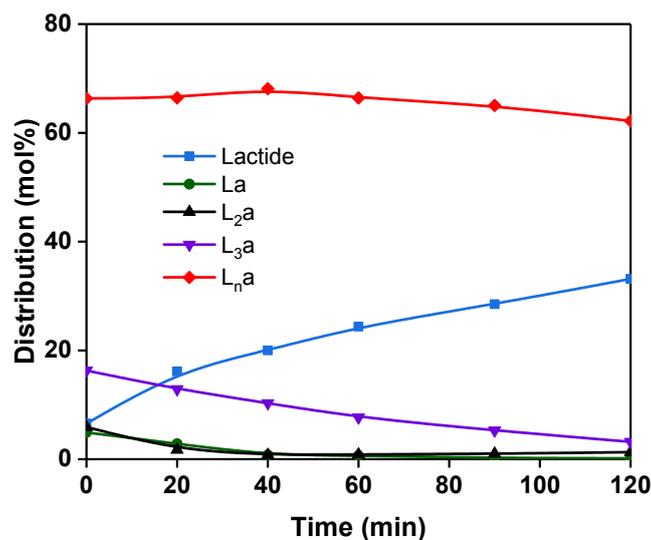


Figure S15 Typical time profile of catalytic reactions with HC-La feed stock. Reaction conditions: 0.2 g Sn-MCM-41-30 zeolite and 0.5 g HC-La feedstock in 12 mL mesitylene for 120 min in an oil bath.

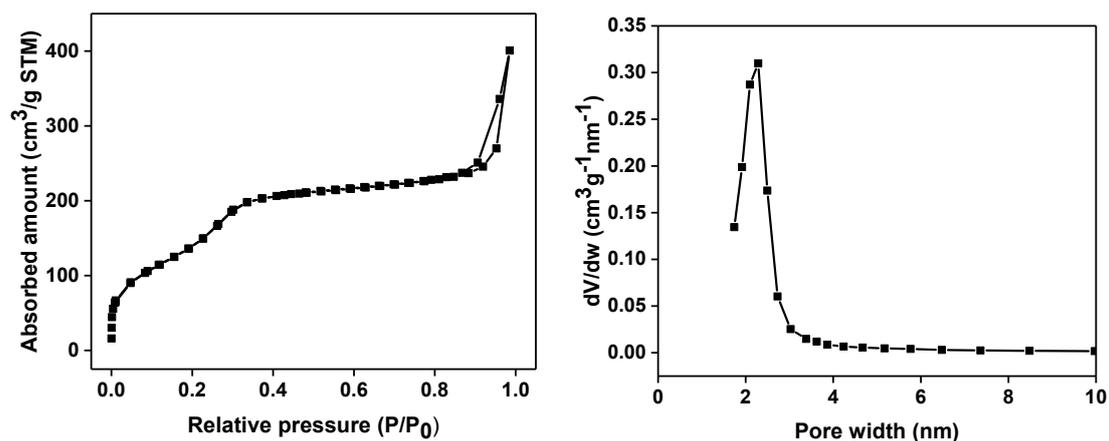


Figure S16: The N₂ isotherms and the pore size patterns of Sn-MCM-41 zeolites.

Table S1: The optimized reaction conditions of Sn-beta-50 as a catalyst for the synthesis of lactide^a

Entry	Time	Catalyst	Solvent	Conversion ^b	Yield ^b
	min	g	mL	%	%
1	180	0.2	4	99.74	61.78
2	180	0.2	8	99.65	73.14
3	180	0.2	12	99.90	88.37
4	180	0.2	16	98.96	87.06
5	120	0.2	12	99.59	88.04
6	60	0.2	12	99.29	78.21
7	20	0.2	12	84.08	38.84
8	120	0.1	12	99.66	79.63
9	120	0.3	12	99.72	91.09
10	120	0.4	12	99.75	93.63
11	120	0	12	98.73	47.06

^aReaction conditions: Sn-beta-50 zeolites and 1.0 g 50 wt% L-La feedstock in mesitylene refluxed with water removal at 180 °C. ^bDetermined by HPLC using the equation shown in section 2.4.

Table S2. Actual Si/Sn Ratio, Surface Si/Sn ratio, Porosity, and Particle sizes of As-prepared Sn-Si catalysts

Entry	Catalyst	Si/Sn ^a	Surface Si/Sn ^b	S _{BET} ^c m ² /g	Pore volume ^c cm ³ /g	Pore size ^c nm	Particle size ^d nm
1	Si-beta	-	-	465	0.19	0.6575	153.7
2	SnO ₂	-	-	1.49	0.0026	-	272.2
3	SnO ₂ /Si-beta	30.2	25.41	313	0.17	0.6574	185.2
4	SnO ₂ -SiO ₂ -30	29.8	58.85	389.7	0.66	4.152	278.4
5	Sn-beta-30	31.44	16.57	485.9	0.19	0.6679	231.7
6	Sn-beta-50	50.53	25.82	421.7	0.19	0.6624	198.7
7	Sn-beta-100	99.63	55.86	456.3	0.19	0.6701	301.2

^aDetermined by ICP-MS. ^bMeasured based on XPS. ^cS_{BET} (total surface area) calculated by applying the BET equation using the linear part of the adsorption isotherm, pore volume and pore size calculated using the H-K method. ^dDetermined by dynamic light scattering (DLS).

Table S3. The distribution of different feedstocks measured by HPLC.

Entry	Feedstock	Lactide %	La %	L ₂ a %	L ₃ a %	L _n a %
1	50% La ^a	0	95.2	4.8	0	0
2	L ₂ a ^b	0	3.66	94.76	0.74	0.84
3	HC-La ^c	6.54	4.92	5.91	16.31	63.32
4	L _n a ^d	6.76	0.13	1.17	0.83	91.11

^a 50 wt% La was produced by adding water to 92 wt% lactic acid (supplied by Henan Jindan Lactic Acid Technology Co., Ltd). After mixing, the solutions were heated at 80°C for 1 week to increase the rate of formation of various oligomers of lactic acid. ^b L₂a was produced by hydrolysis of 5 g of pure L-lactide in 5 g of H₂O 0.8 g with D001 macroporous cation exchange resin for 10 min at 75 °C. The L₂a was isolated from the water phase in a liquid-liquid extraction of the hydrolysis mixture with toluene for several times⁴. The concentration of L₂a was 39% determined by sodium hydroxide titration. ^c HC-La (highly concentrated La) was prepared by removing water from 92 wt% lactic acid at 140 °C and 750 mmHg for 1 h, and then the pressure was gradually reduced to 30torr for 1.5 h. ^d L_na dichloromethane solution was prepared by a liquid-liquid extraction of the HC-La dichloromethane solution with distilled water to remove La, L₂a and L₃a. Then dichloromethane was removed under vacuum to obtain the L_na.

References

1. Zhu, Z.; Xu, H.; Jiang, J.; Wu, H.; Wu, P., Structural reconstruction: a milestone in the hydrothermal synthesis of highly active Sn-Beta zeolites. *Chem Commun* **2017**, *53*, 12516-12519.
2. Corma, A.; Navarro, M. T.; Nemeth, L.; Renz, M., Sn-MCM-41--a heterogeneous selective catalyst for the Baeyer-Villiger oxidation with hydrogen peroxide. *Chem. Commun.* **2001**, *33*, 2190-2191.

3. Codari, F.; Moscatelli, D.; Storti, G.; Morbidelli, M., Characterization of Low-Molecular-Weight PLA using HPLC. *Macromol Mater Eng* **2010**, *295*, 58-66.
4. Dusselier, M.; Van Wouwe, P.; Dewaele, A.; Jacobs, P. A.; Sels, B. F., GREEN CHEMISTRY. Shape-selective zeolite catalysis for bioplastics production. *Science* **2015**, *349*, 78-80.