

Electronic Supplementary Information (ESI)

for

Reducing *meso*-lactide formation from racemic lactic acid using shape-selective H-Beta zeolite

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1. Catalysts characterization.

Scanning electron micrographs (SEM) were acquired on a GeminiSEM500 at resolution: ≤ 0.5 nm@15KV (secondary electron). Powder X-ray diffraction (PXRD) experiments were conducted on a Bruker D2 diffractometer (Cu-K α , 10 kV, 30 mA) to determine the phase of catalysts. The adsorption-desorption isotherms were acquired on a Quantachrome iQ-2 instrument by Ar-sorption experiments at 87 K after outgassing at 573 K for 7 h, and textural parameters were calculated by Brunauer-Emmett-Teller (BET) method and t-plot method. The FT-IR studies of pyridine adsorption were conducted via the Nicolet 6700 spectrometer equipped with an analysis platform. Self-supported wafer of sample was placed in the IR cell and evacuated at 723 K for 75 min with a vacuum system. Reference spectra at 573 K were recorded (64 scans at a 4 cm⁻¹ resolution). After cooling to room temperature, the sample was subjected to pyridine vapor for enough time and IR spectra were recorded repeatedly until the evolution of adsorbed species indicated that pyridine saturation of the surface was reached. Afterwards, the sample was evacuated under vacuum at 573 K for 30 min and spectra were collected. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed on a PE-8000 atomic emission spectrometry for evaluating the element content of product.

2. Analysis method.

Measurement of the static adsorption process. 10 mL 0.67 wt% pretreated *rac*-L₂A_{com.} mesitylene solution (including 3.4 wt% cyclohexanone), 6 mg H-Beta zeolite catalyst was then added and the time was recorded. 0.1 mL of sample was taken out at different times and the catalyst was filtered out in time, the ratio of DL-L₂A/DD/LL-L₂A was then measured by HPLC.

Measurement of the liquid phase breakthrough curve (dynamic adsorption process). The liquid phase breakthrough curve was recorded at room temperature by a handmade instrument as the Figure S3 scheme shown. For a typical run, 10 mg H-Beta zeolite was loaded into the stainless steels tube with cotton wool loaded in advance and another piece of cotton wool was loaded to encapsulate the sample. The H-Beta zeolite was first flushed by pure mesitylene solution at 0.1 mL/min. The adsorption solution consisted of racemic lactic acid solution as adsorbate, mesitylene as solvent, and cyclohexanone was added to achieve miscibility. The H-Beta zeolite was flushed by 0.67 wt% pretreated *rac*-L₂A_{com.} mesitylene solution (including 3.4 wt% cyclohexanone) at 0.1 mL/min. The effluent was collected over time and the ratio of DL-L₂A/DD/LL-L₂A was then measured by HPLC. The background curve was recorded with empty tube.

High Performance Liquid Chromatography (HPLC). Determination of L₂A and the ratio of DD/LL-L₂A/DL-L₂A in the reactants and products were performed by HPLC (Agilent Corporation). The sample was dissolved in water: acetonitrile mixture 50: 50 (V: V) and analyzed with ZORBAX-C₁₈ column (4.6 mm × 250 mm) and UV detector at 210 nm. Acetonitrile (HPLC grade, with addition of 0.8 mL of 85% H₃PO₄ per L) and water (with addition of 0.8 mL of 85% H₃PO₄ per L) were used as mobile phases. The elution program (water/acetonitrile, V/V) was as follows: (98/2) from 0 to 1 min; linear ramp to (20/80) from 1 to 15 min; (20/80) from 15 to 20 min; return to (98/2) from 20 to 25 min.

The determination of L₂A and the ratio of DD/LL-L₂A/DL-L₂A in the adsorption reaction were performed by HPLC (Agilent Corporation). The sample is analyzed without dilution with ZORBAX-C₁₈ column (4.6 mm × 150 mm) 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 elution program (water/acetonitrile, V/V) was as follows: (98/2) from 0 to 1 min; linear ramp to (40/60) from 1 to 15 min; (40/60) from 15 to 20 min; return to (98/2) from 20 to 25 min.

¹H Nuclear Magnetic Resonance (¹H NMR). After reaction, added 10 mL acetonitrile and leaved overnight to get a homogeneous solution. Then, 4 mL reaction mixture was dried in flowing Ar-atmosphere to remove organic solvent and acetonitrile. The dry sample was separately dissolved in 0.6 mL of CDCl₃/DMSO-d₆ and ¹H NMR characterization was measured on BRUKER AVANCE III HD 400MHz.

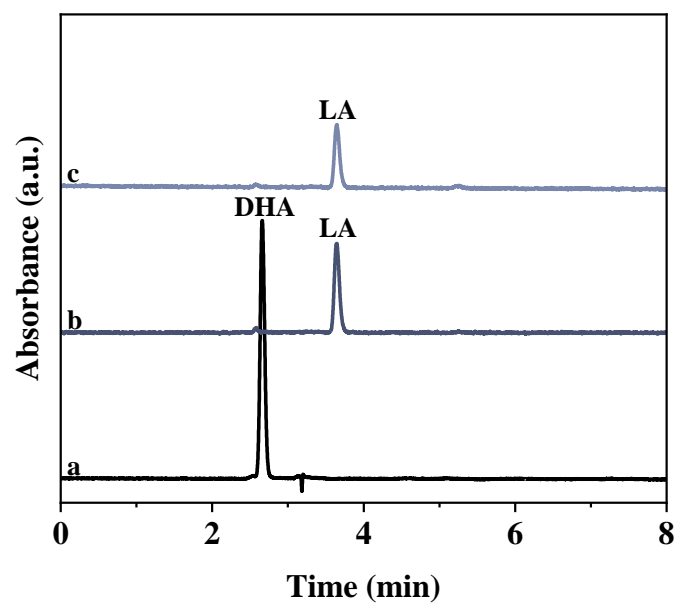


Figure S1. HPLC analyses of DHA solution (a), 2 wt% *rac*-LA_{chem.} solution obtained from DHA (b), 7.5 wt% *rac*-LA_{chem.} solution (c).

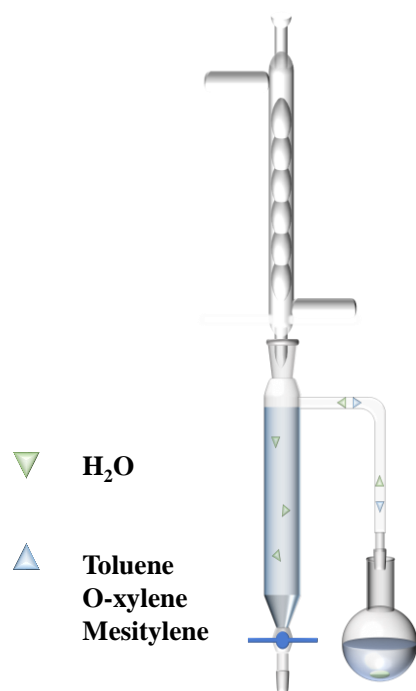


Figure S2. The experimental setup for LD production.

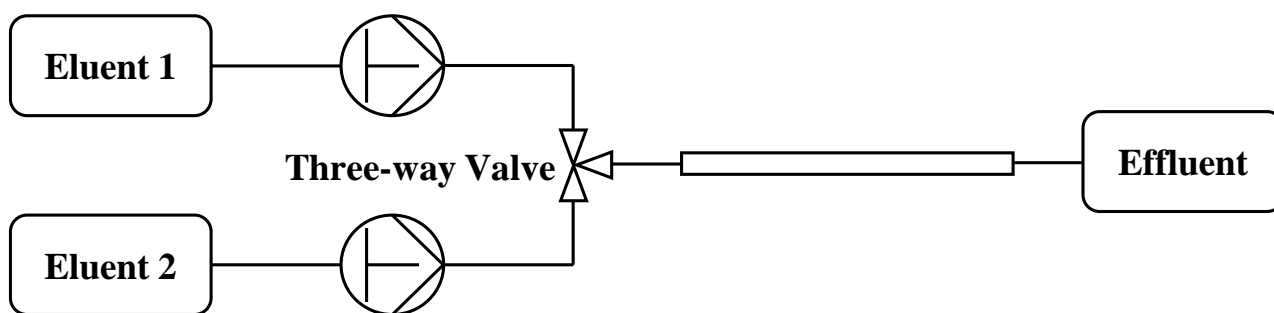


Figure S3. The instrument measuring liquid phase breakthrough curve. Eluent 1 is mesitylene solution, Eluent 2 is 0.67 wt% *rac*-LA_{com}. mesitylene solution.

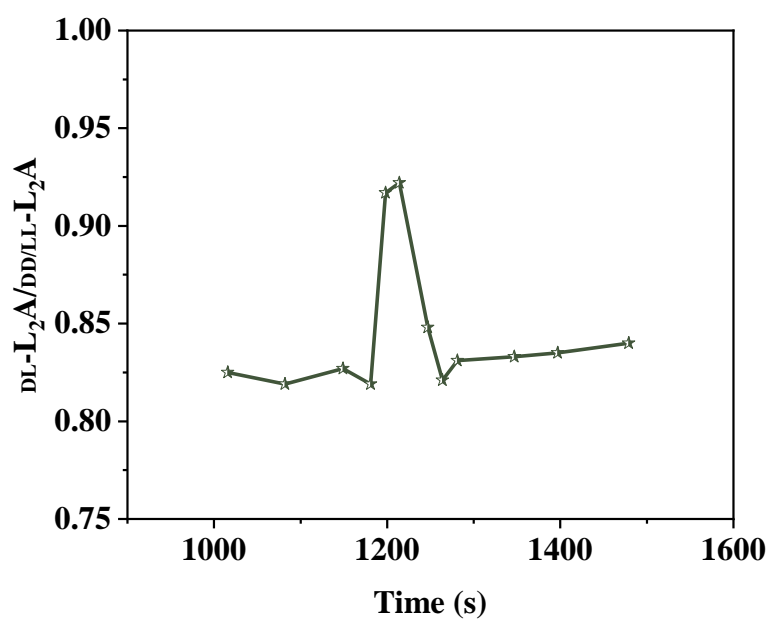


Figure S4. The liquid phase adsorption breakthrough curve of *rac*-LA_{com.} solution in the presence of H-Beta zeolite.

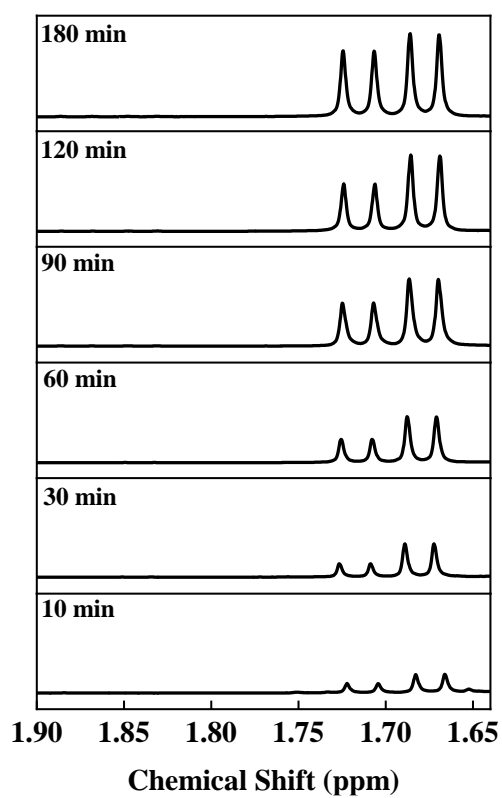


Figure S5. Typical ¹H NMR spectra (in CDCl₃) of LD obtained from 90 wt% *rac*-LA_{com}. with the increasing reaction time in the presence of H-Beta zeolite at 413 K.

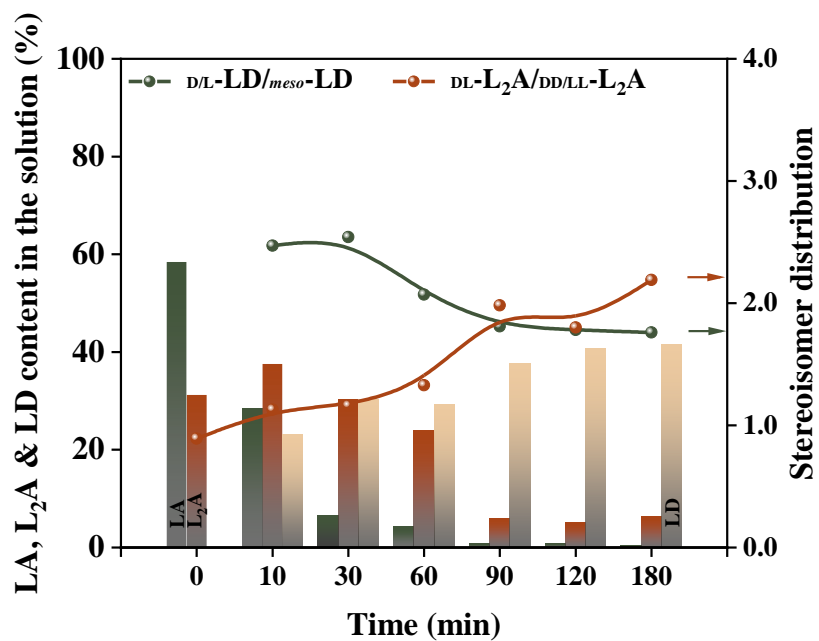


Figure S6. The composition changes of the 90 wt% *rac*-LA_{com.} solution with the increasing reaction time in the presence of H-Beta zeolite at 433 K as well as the corresponding DL-L₂A/DD/LL-L₂A ratio and D/L-LD/*meso*-LD ratio.

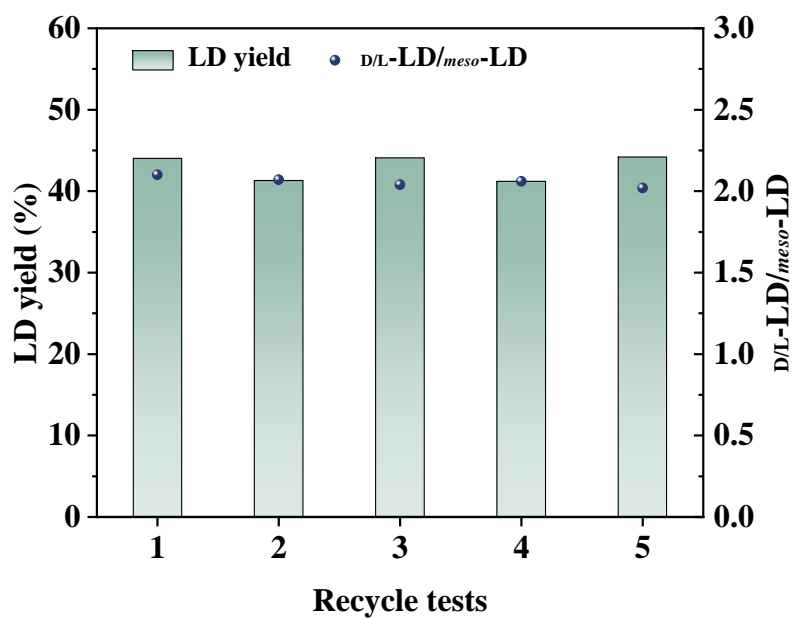


Figure S7. Recycle test results over H-Beta zeolite catalyst. Reaction conditions: 0.25 g catalyst, 0.5 g 90 wt% *rac*-LA_{com}, 5 mL *o*-xylene, 433 K, 3 h.

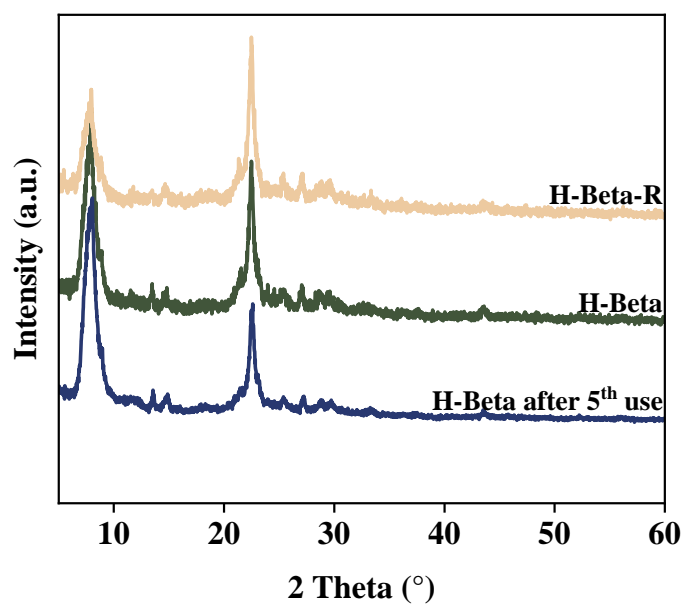


Figure S8. PXRD of the H-Beta zeolite catalysts used in the conversion of LA.

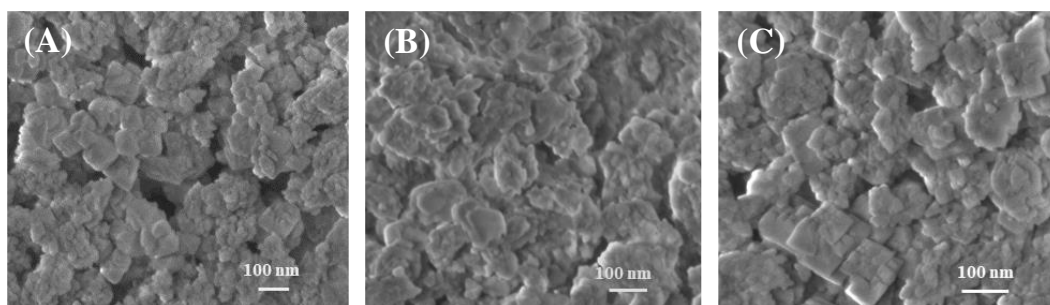


Figure S9. SEM images of the H-Beta zeolite catalysts used in the conversion of LA: H-Beta (A), H-Beta after 5th use (B), H-Beta-R (C).

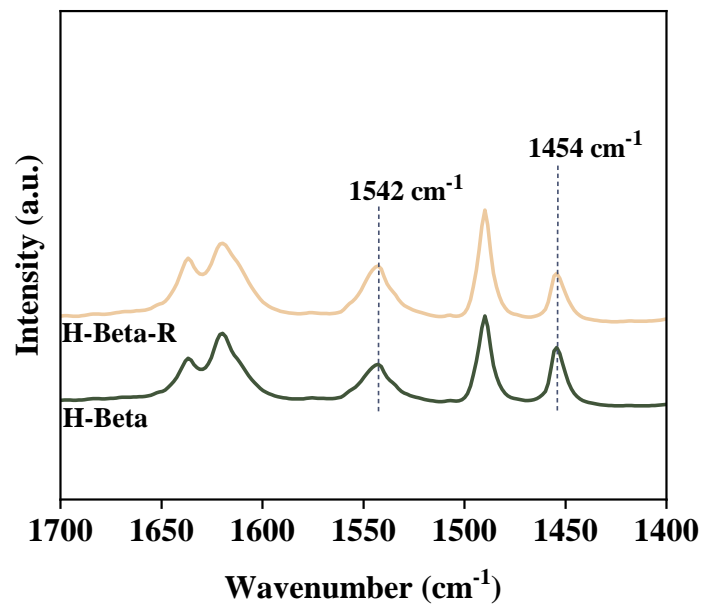


Figure S10. Pyridine FT-IR spectra desorption at 573 K for H-Beta and H-Beta-R.

Table S1. The specific rotation of different LA solutions ^a.

Sample	$[\alpha]^{20}_{\text{D}}$
7.5 wt% <i>rac</i> -LA _{chem.}	0.26
90 wt% <i>rac</i> -LA _{com.}	-0.38
90 wt% DL-LA _{com.}	-0.88
90 wt% D-LA _{com.}	15.77
90 wt% L-LA _{com.}	-15.53

^a The specific rotation was measured in water at concentrations of 1.0% (w/v) using a wavelength of 589 mm cell with Anton Paar MCP5500.

Table S2. The composition of different LA solutions.

Sample	LA	DD/LL-L₂A	DL-L₂A
90 wt% <i>rac</i> -LA _{com.}	58.4%	16.5%	14.7%
90 wt% D-LA _{com.}	57.6%	31.0%	0.0%
90 wt% L-LA _{com.}	57.7%	31.1%	0.0%

Table S3. The composition of the samples with different DD/LL-L₂A/(DD/LL-L₂A+DL-L₂A) ratios.

Sample	90 wt% <i>rac</i>-LA_{com.}	90 wt% DL-LA_{com.}	DD/LL-L₂A/(DD/LL-L₂A+DL-L₂A)
1	0.0 wt%	100.0 wt%	1.00
2	25.0 wt%	75.0 wt%	0.87
3	50.0 wt%	50.0 wt%	0.74
4	75.0 wt%	25.0 wt%	0.62
5	100.0 wt%	0.0 wt%	0.50

Table S4. The composition of the *rac*-LA samples with different content of L₂A.

Sample	1	2	3	4	5
LA	72.7%	64.8%	58.4%	47.9%	13.2%
L ₂ A	19.7%	26.1%	31.2%	36.1%	29.2%
L _n A	7.6%	9.1%	10.4%	16.0%	57.6%

Table S5. Three-dimensional size of the different LA and L₂A.¹

L₂A	Three-dimensional size (Å)
L-LA	7.071×5.955×5.197
D-LA	7.071×5.955×5.197
DD-L ₂ A	10.725×6.856×5.331
LL-L ₂ A	10.725×6.857×5.332
DL-L ₂ A	10.752×6.357×5.403

Table S6. Physicochemical properties parameters of H-Beta and H-Beta-R zeolite.

Catalyst	$V_{\text{micro}}^{\text{a}}$ ($\text{cm}^3 \text{g}^{-1}$)	$S_{\text{ext}}^{\text{a}}$ ($\text{m}^2 \text{g}^{-1}$)	$S_{\text{micro}}^{\text{b}}$ ($\text{m}^2 \text{g}^{-1}$)	Si/Al ^c	B/L acid ^d
H-Beta	0.14	181	364	9.2	1.74
H-Beta-R	0.16	172	411	9.3	2.78

^a V_{micro} (micropore volume) and S_{ext} (external surface area) calculated using the t-plot method.

^b S_{micro} (micropore area) calculated using the BET method.

^c Given by ICP-AES.

^d B/L acid (Brønsted acidity/Lewis acidity) calculated via pyridine-adsorbed FT-IR spectroscopy.²

References

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2. C. A. Emeis, *J. Catal.* 1993, **141**, 347.