Electronic supplementary information

Si-doped γ-Al_2O_3 from solid-phase grinding for highly efficient one-step production of *L*, *L*-lactide

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Experiments

Reagents

All chemicals and reagents in the experiments were analytically pure and used as received. Aluminum chloride, aluminum nitrate hydrate, ammonia, ammonium bicarbonate, *o*-xylene, *p*-xylene, ethylbenzene, toluene, and cyclohexane were purchased from Aladdin Biochemical Technology (Shanghai, China). Acetonitrile, anhydrous ethanol and hydrochloric acid were purchased from Tianjin Bohua Chemicals (Tianjin, China). Tetraethoxysilane (TEOS) was purchased from Merck Chemical Technology (Shanghai, China). Polyethylene glycol 400 (PEG-400) was purchased from Jindong Tianzheng Fine Chemical Reagent Factory (Tianjin, China); Pure water from Hangzhou Wahaha was used in all experiments. *L*-lactic acid (*L*-LA, 90 wt.%) and *L, L*-lactide (*L, L*-LD, 98%) was from Macklin Biochemical Technology (Shanghai, China).

Instruments

X-ray diffraction (XRD) patterns were recorded on a D/max-2500a X-ray diffraction spectrometer (Rigaku, Japan). Nitrogen adsorption-desorption isotherms, pore size distributions, and pore volumes were measured on an ASAP 2460 surface area and porosimetry analyzer (Micromeritics, America). Transmission electron microscopy (TEM) images were recorded on a Talos F200X G2 (FEI, Czech) field emission transmission electron microscope. High performance liquid chromatography (HPLC) data were acquired on a Waters 2996 HPLC with a C18 reversed-phase column of 4.6 × 250 mm. HPLC-MS analysis was by Agilent 6545 Q-TOF LC/MS (with DAD detector, ESI negative mode). ^{1}H-NMR was measured on Bruker AV Ⅲ (400 MHz).

The optical purity of *L*-lactide was measured by Agilent 5973 gas chromatography-mass spectrometry (GC-MS), with a chiral capillary column of Agilent WCOT fused silica CP-Chirasil-DEX CB (0.32 mm × 30 m, film thickness of 0.25 μm). Pyridine-adsorption IR spectroscopy (Py-IR) was performed on a Bruker Tensor 27 spectrometer to characterize Brønsted and Lewis acid sites of the catalysts.

Preparation of γ-Al_2O_3 and Si-doped γ-Al_2O_3 catalysts

Si-doped γ-Al_2O_3 marked as NH_4HCO_3/Al/Si=400/100/0.36: 0.08 mL PEG-400 was added into an onyx mortar, the NH_4HCO_3, $Al(NO_3)_3·9H_2O$ and TEOS at molar ratio of NH_4HCO_3/Al/Si=400/100/0.36 were added and mixed thoroughly. After grinding at room temperature for 20 min, the mixture was transferred to Teflon-lined stainless-steel autoclave and placed in an oven at 80 °C for 7 h. Then the solid was filtered out, washed twice with deionized water and once with anhydrous ethanol respectively and dried in an oven at 80 °C for 2 h. That solid was the AACH precursor, which was ground into powder and then calcined at 500 °C for 4 h using a muffle furnace.

Synthesis of γ-Al_2O_3 and Si-doped γ-Al_2O_3 with different feeding ratios: the operation was the same as the above description, except the following mentioned:

(1) Pure γ-Al_2O_3 without Si doping was synthesized at NH_4HCO_3/Al = 400/100 without adding TEOS.

(2) Fixed NH_4HCO_3/Al ratio with varying Si doping content: NH_4HCO_3/Al/Si = 400/100/0.18、NH_4HCO_3/Al/Si = 400/100/0.36、NH_4HCO_3/Al/Si = 400/100/0.54.

(3) Fixed Si doping content with varying NH_4HCO_3/Al ratio: NH_4HCO_3/Al/Si = 300/100/0.36、NH_4HCO_3/Al/Si = 400/100/0.36、NH_4HCO_3/Al/Si = 500/100/0.36.

HT-AACH-Al_2O_3: the synthetic procedure in the literature was adopted with some changes.[1] $AlCl_3$ (0.14 g) and NH_4HCO_3 (0.32 g) were fully dissolved in 30 mL deionized water and stirred at room temperature, then $NH_3·H_2O$ was added dropwise until pH 9. Thirty minutes later, the mixture was placed into an oven at 37 °C for 24 h. Then the mixture was poured out and centrifuged to collect the precipitate. Subsequently, the precipitate was washed twice with deionized water and once with anhydrous ethanol respectively and dried in an oven at 80 °C for 2 h. The obtained AACH precursor was ground finely and further calcination at 500 °C for 4 h was conducted with a muffle furnace to give HT-AACH-Al_2O_3.

HT-AlOOH-Al_2O_3: The operation was nearly the same as the reported procedure.[1] 0.14 g $AlCl_3$ and 0.12 g urea were fully dissolved in 30 mL deionized water and stirred at room temperature for 30 min. The resultant solution was then transferred into Teflon-lined stainless-steel autoclave placed in an oven of 125 °C. After 15 h of reaction, the mixture was poured out and centrifuged to collect the precipitate. Subsequently, the precipitate was washed three times with deionized water and dried in an oven at 80 °C for 2 h. The obtained AlOOH precursor was ground finely, and further calcination at 500 °C for 4 h was conducted with a muffle furnace to give HT-AlOOH-Al_2O_3.

HT-Si-Al_2O_3: 0.08 mL of PEG-400 and NH_4HCO_3, $Al(NO_3)_3·9H_2O$ and TEOS at molar ratio of NH_4HCO_3/Al/Si=400/100/0.36 were dissolved in 50 mL deionized water

and stirred at room temperature for 20 min. The mixture was then transferred to a Teflon-lined stainless-steel autoclave and placed in an 80 °C oven. After 7 h of reaction, washed twice with deionized water and once with anhydrous ethanol respectively and dried in an oven at 80 °C for 2 h. The obtained AACH precursor was ground into powder and then calcined at 500 °C for 4 h using a muffle furnace to get Si-doped γ-Al_2O_3 marked as HT-Si-Al_2O_3.

SPG-$Al_2(SO_4)_3$-Si-Al_2O_3: All the operations were the same as "**Si-doped γ-Al_2O_3 marked as NH_4HCO_3/Al/Si=400/100/0.36**" except using $Al_2(SO_4)_3 \cdot 18H_2O$ instead of $Al(NO_3)_3 \cdot 9H_2O$. The final product was named as SPG-$Al_2(SO_4)_3$-Si-Al_2O_3.

General operation for the catalytic synthesis of L-lactide and relevant analysis

Al_2O_3-based catalyst (0.25 g), *L*-LA (90 wt.%, 0.5 g), and *o*-xylene (10 mL) were mixed in a 25 mL single-neck round-bottomed flask, and a Dean-Stark apparatus with a condenser tube was set on top of the flask to separate the water produced during the condensation reaction. Suitable volume of *o*-xylene was added to prefill the separator ahead of warming the reaction mixture. After that, the reaction mixture was placed in an oil bath at 170 °C and stirred for different duration. After being cooled down, the mixture was poured out and diluted with acetonitrile (12 mL), and the resultant mixture with 22 mL volume was marked as reaction liquid. The solid catalyst was removed by centrifugation, and the supernatant (1 mL) was taken out and purged with a gentle stream of nitrogen to remove the *o*-xylene and acetonitrile. Finally, the residual was re-dissolved in acetonitrile/water (v/v = 50/50, 1 mL) for high-performance liquid HPLC and HPLC-MS measurement, in 0.7 mL DMSO-D_6 (99.8%, containing 0.03% TMS) for ^{1}H-NMR measurement, and in 1 mL acetonitrile for GC-MS analysis.

The solid catalysts after use were harvested and washed ultrasonically for 30 min in 6, 3 and 3 mL of acetonitrile/water (1/1, v/v) respectively, and the resultant supernatants assigned as Extract 1, 2 and 3 were filtered by 0.22 μm membrane and analyzed by HPLC directly.

Analytic Methods

Typically, the yield of LD was determined by HPLC, and the purity of LD in the products was determined by ^{1}H-NMR, while the optical purity of *L*-LD was measured by chiral gas chromatography.

In HPLC chromatograms, *L*-LA, *L*-LD, other oligomers, and *o*-xylene can be well-separated with retention time of 3.3, 8.2, 10-15, and 17 min respectively. The *L*-LA and *L*-LD content in reaction liquid (total volume of 22 mL) and Extract 1-3 was determined by the external standard method calibrated with the standard *L*-LA and *L*-LD. The *L*-LA consumed for producing *L*-LD can be calculated as

$$m_{\text{consumed LA}} = m_{\text{fed LA}} - m_{\text{reaction liquid LA}} - m_{\text{Extract 1 + 2 + 3 LA}} \#\#\#\#\#\#\#$$

The final *L*-LD yield can be calculated using the following expression:

$$L\text{-}LD \text{ yield } (\%) = \frac{m_{LD} \times 90 \times 2}{m_{\text{consumed LA}} \times 144} \times 100\%$$

In ^{1}H-NMR, the quadruple peak at 5.45 ppm is the methine proton [-CH]-CH_3 in *L*-LD, the signal of 5.35-5.40 ppm suggests the existence of *meso*-LD, the peaks at 4.2-5.2 ppm are corresponding to the methine proton of the OH end-groups in LA oligomer, and the quadruple peak at 4.0 ppm is the methine protons in unreacted *L*-LA.[2] The purity of *L*-LD can be calculated using the spectral integral (HI) of ^{1}H-NMR with the following equation:

$$L\text{-}LD \text{ purity } (\%) = \frac{\text{HI}_{L\text{-LD}}/2}{\text{HI}_{L\text{-LA}} + \text{HI}_{\text{oligomers}} + \text{HI}_{L\text{-LD}}/2} \times 100\%$$

In chiral GC-MA analysis, *L*-LD, *D*-LD, and *meso*-LD can be separated, and the stereoselectivity of LD can be estimated from the following formula based on the peak area (AP) of each substance in the TIC:

$$\text{stereoselectivity } (\%) = \frac{\text{AP}_{L\text{-lactide}}}{\text{AP}_{L\text{-lactide}} + \text{AP}_{D\text{-lactide}} + \text{AP}_{meso\text{-lactide}}} \times 100\%$$

Table S1 Specific surface area and pore volume of Al_2O_3 synthesized by different methods and SPG with various NH_4HCO_3/Al/Si ratios

	BET Surface Area ($m^2\ g^{-1}$)	V_p（$mL\ g^{-1}$）
HT-AACH-Al_2O_3	307.8	1.27
HT-AlOOH-Al_2O_3	199.9	0.44
HT-Si-Al_2O_3	231.5	0.72
SPG-$Al_2(SO_4)_3$-Si-Al_2O_3	49.4	0.07
NH_4HCO_3/Al=400/100	340.8	1.64
NH_4HCO_3/Al/Si=300/100/0.36	275.2	0.91
NH_4HCO_3/Al/Si=400/100/0.18	387.8	1.47
NH_4HCO_3/Al/Si=400/100/0.36	387.2	1.55
NH_4HCO_3/Al/Si=400/100/0.54	362.6	1.64

NH_4HCO_3/Al/Si=500/100/0.36	332.5	1.25

Table S2 B/L acidic sites of SPG-Al_2O_3 and SPG-Si-Al_2O_3 with Si/Al ratio of 0.36%

Catalysts	Temperature (^oC)	Brønsted acidity ($\mu mol\ g^{-1}$)	Lewis acidity ($\mu mol\ g^{-1}$)
SPG-Al_2O_3 (NH_4HCO_3/Al=400/100)	40	0	289.9
	200	0	149.5
	350	0	41.0
SPG-Si-Al_2O_3 (NH_4HCO_3/Al/Si=400/100/0.36)	40	0	283.4
	200	0	149.3
	350	0	38.5

Table S3 Comparison of the catalysts for liquid-phase one-step synthesis of lactide

Catalyst	Synthesis condition of catalysts	Catalytic Condition	Yield (%)	Sel. (%)	Ref.
OH-COOH-COF	Pyrex tube, quick-frozen, vacuumed and sealed heating, 120 °C, 4 days	140 °C, 3.5 h	81	99	[3]
ZIF-8[a]	Precipitation method, 1.5 days (2-methylimidazole)	140 °C, 4 h	89	89	[4]
Al-UTL[b]	Hydrothermal synthesis (175 °C), 23 days	145 °C, 3 h	58	100	[5]
Al-IPC-7[c]	Hydrothermal synthesis (60 °C), 2 days	145 °C, 3 h	65	99	[5]
Sn-beta zeolite	Hydrothermal synthesis (70-140 °C), 4 days (NH_4F)	180 °C, 2 h	88	99	[6]
Beta-15-10 zeolite	Hydrothermal synthesis (80-140 °C), 5-7 days	140 °C, 5 h	74	-	[7]
ZSM-5-ball milling[d]	Ball-milling of commercial ZSM-5-III[e]	144 °C, 4 h	76	100	[8]
H-beta zeolite	Hydrothermal synthesis (140 °C), 12 days (HF)	170 °C, 3 h	79	99	[9]
SnO_2/Si-beta-30	Hydrothermal synthesis + impregnation (70-140 °C), 5.5 days (NH_4F)	180 °C, 2 h	48	99	[6]
Si-doped γ-Al_2O_3	Solid-phase grinding, 0.6 days	170 °C, 3 h	82	100	This work

[a] ZIF-8 refers to Zeolitic Imidazolate Framework-8.
[b] Al-UTL refers to Aluminosilicate University of Toledo-1 Zeolite.
[c] Al-IPC-7 refers to Aluminosilicate Institute of Physical Chemistry-7 Zeolite.
[d] ZSM-5 refers to Zeolite Socony Mobil-5.
[e] ZSM-5-III refers to Zeolite Socony Mobil-5 Type III.

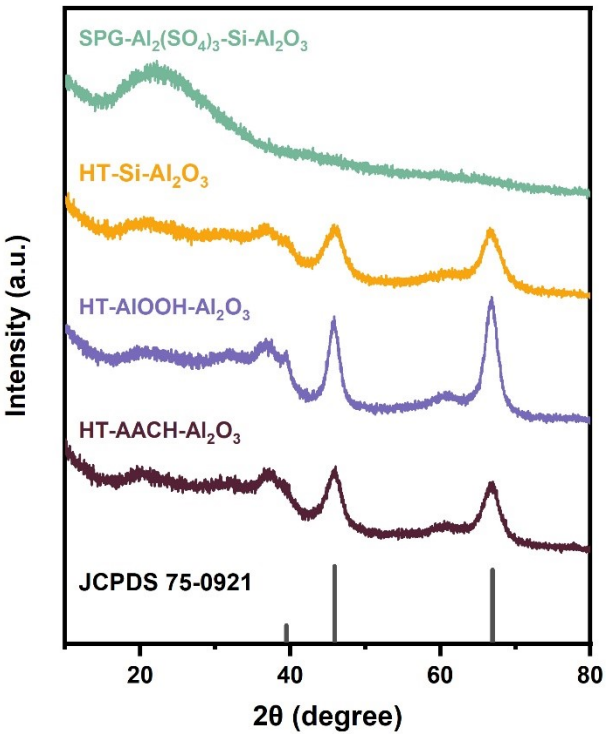

Fig. S1 XRD patterns of Al_2O_3 synthesized by different methods

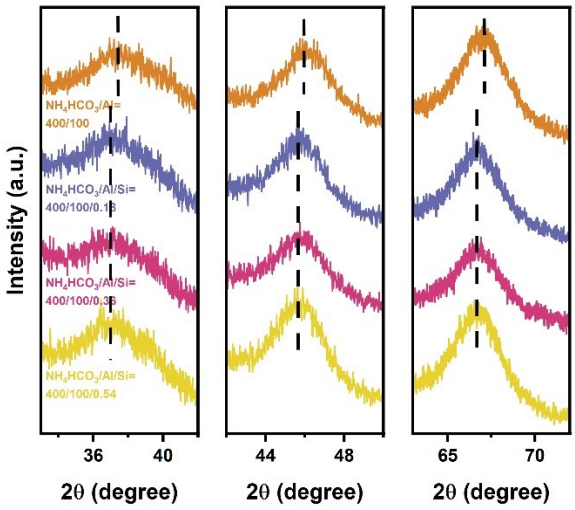

Fig. S2 The locally magnified XRD patterns of undoped SPG-Al_2O_3 and Si-doped SPG-Si-Al_2O_3 with different Si amount.

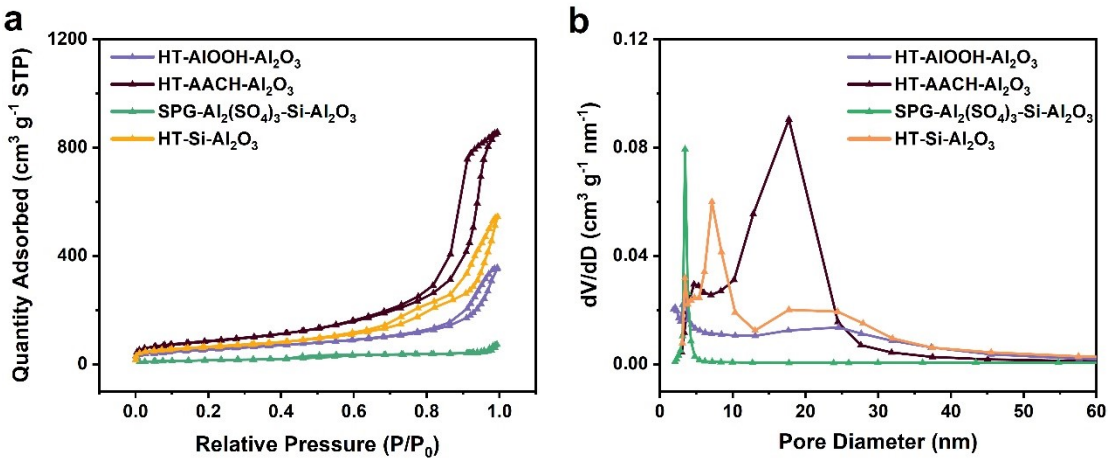

Fig. S3 (a) N_2 adsorption-desorption isotherms and (b) pore size distribution profiles of Al_2O_3 synthesized by different methods

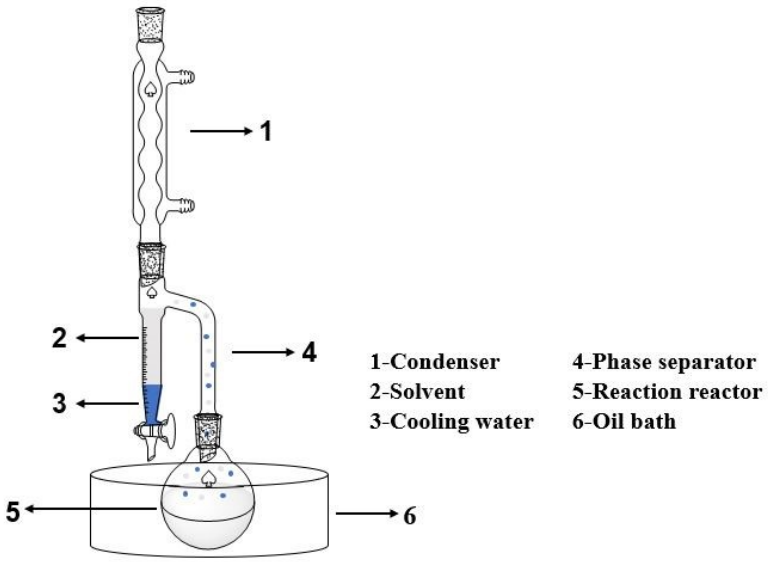

Fig. S4 The setup of azeotropic distillation for the catalytic reactions

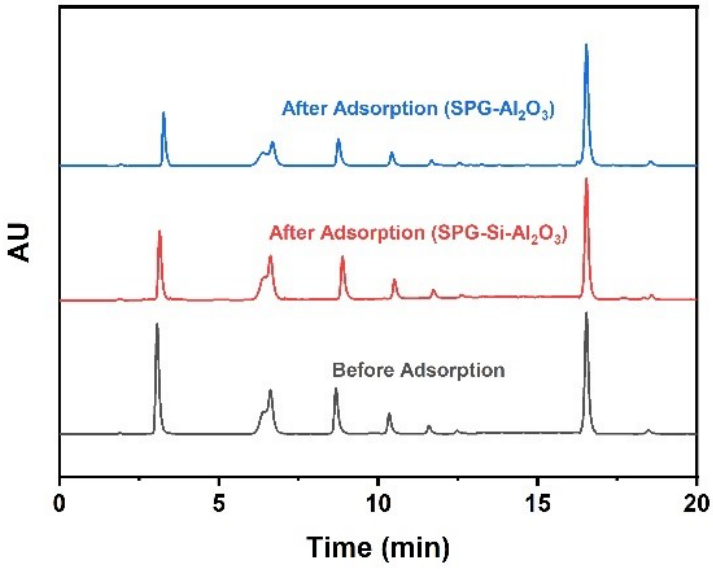

Fig. S5 The HPLC chromatograms of 90 wt.% *L*-LA before and after adsorption: 0.25 g SPG-Si-Al_2O_3 (NH_4HCO_3/Al/Si=400/100/0.36) or SPG-Al_2O_3 (NH_4HCO_3/Al =400/100) and 0.5 g 90 wt.% *L*-LA were stirred in 10 mL *o*-xylene at room-temperature for 3 h, and then 1 mL supernatant was dried by N_2-flow, and the residue was dissolved in 1 mL acetonitrile/water (v/v = 50/50) for HPLC analysis; For "Before adsorption", without 0.25 g SPG-Si-Al_2O_3 or SPG-Al_2O_3 , other operations were the same as "After adsorption".

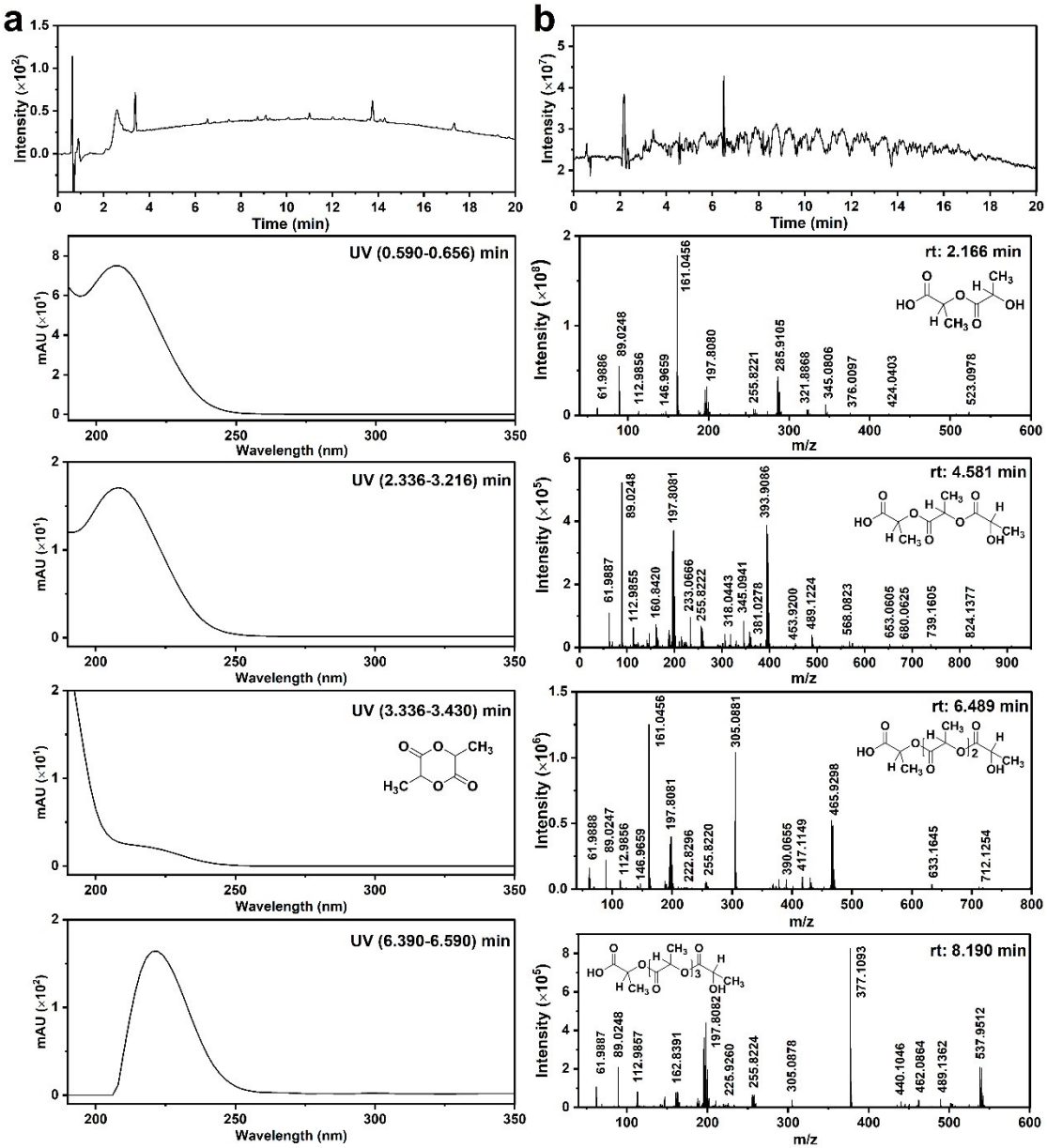

Fig. S6 LC-MS analysis of the reaction liquid: (a) HPLC chromatogram detected by DAD and UV spectra of representative components; (b) TIC and negative ESI mass spectra of some components (reaction conditions: 0.5 g 90 wt.% *L*-LA, 0.25 g SPG-Si-Al_2O_3 catalyst synthesized with NH_4HCO_3/Al/Si=400/100/0.36, 10 mL *o*-xylene, 170 ^oC oil bath, 3 h).

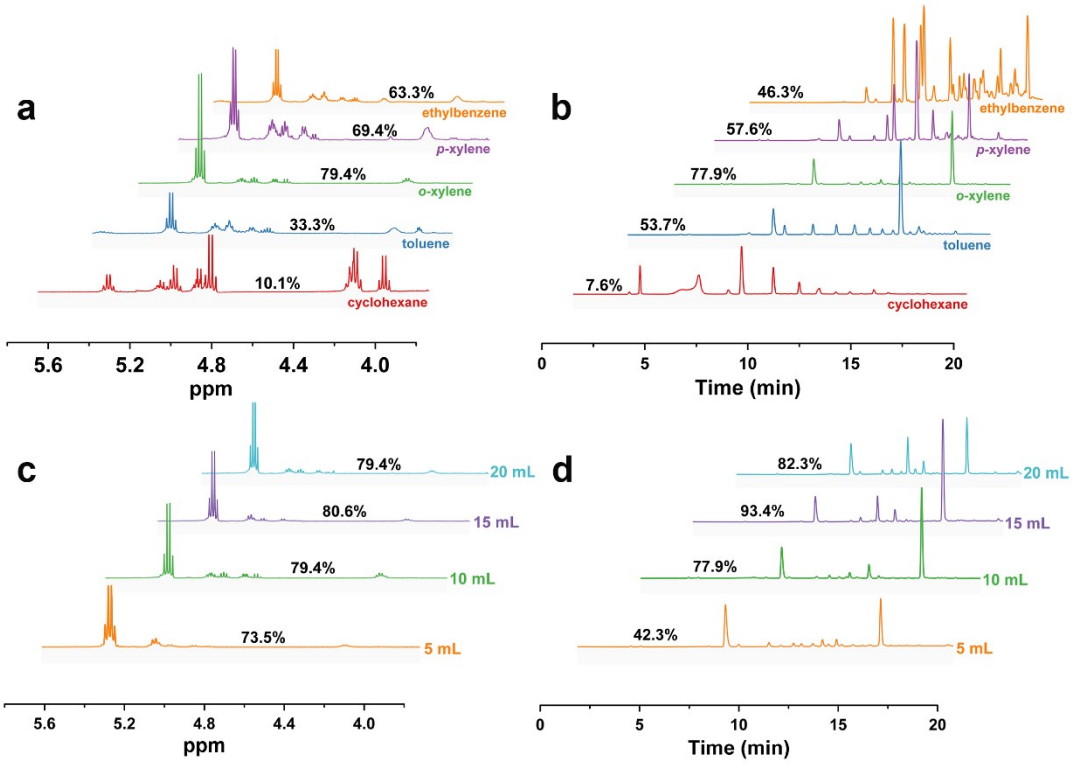

Fig. S7 The products analysis of the catalytic conversion of *L*-LA to *L*, *L*-LD by SPG-Si-Al_2O_3 (NH_4HCO_3/Al/Si=400/100/0.36) in (a, b) 10 mL of different solvents and (c, d) different volume of *o*-xylene: (a, c) ^{1}H-NMR spectra and (b, d) HPLC chromatograms (reaction conditions: 0.5 g 90 wt.% *L*-LA, 0.25 g catalyst, for different solvent, the temperature set as boiling point plus 20 °C, and *o*-xylene at 170 °C oil bath, 3 h).

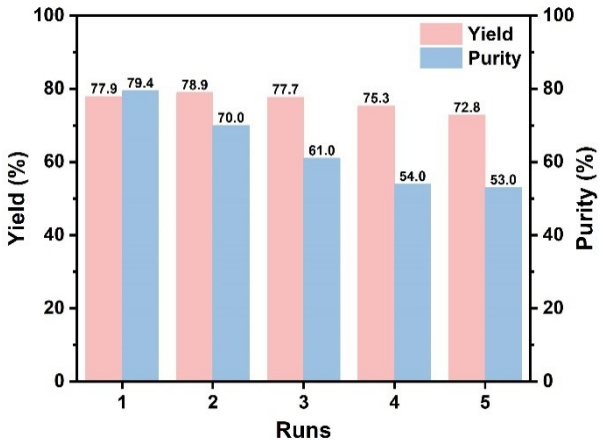

Fig. S8 *L*, *L*-LD yield and purity of five repeated use of SPG-Si-Al_2O_3 catalyst (reaction conditions as Fig. 3).

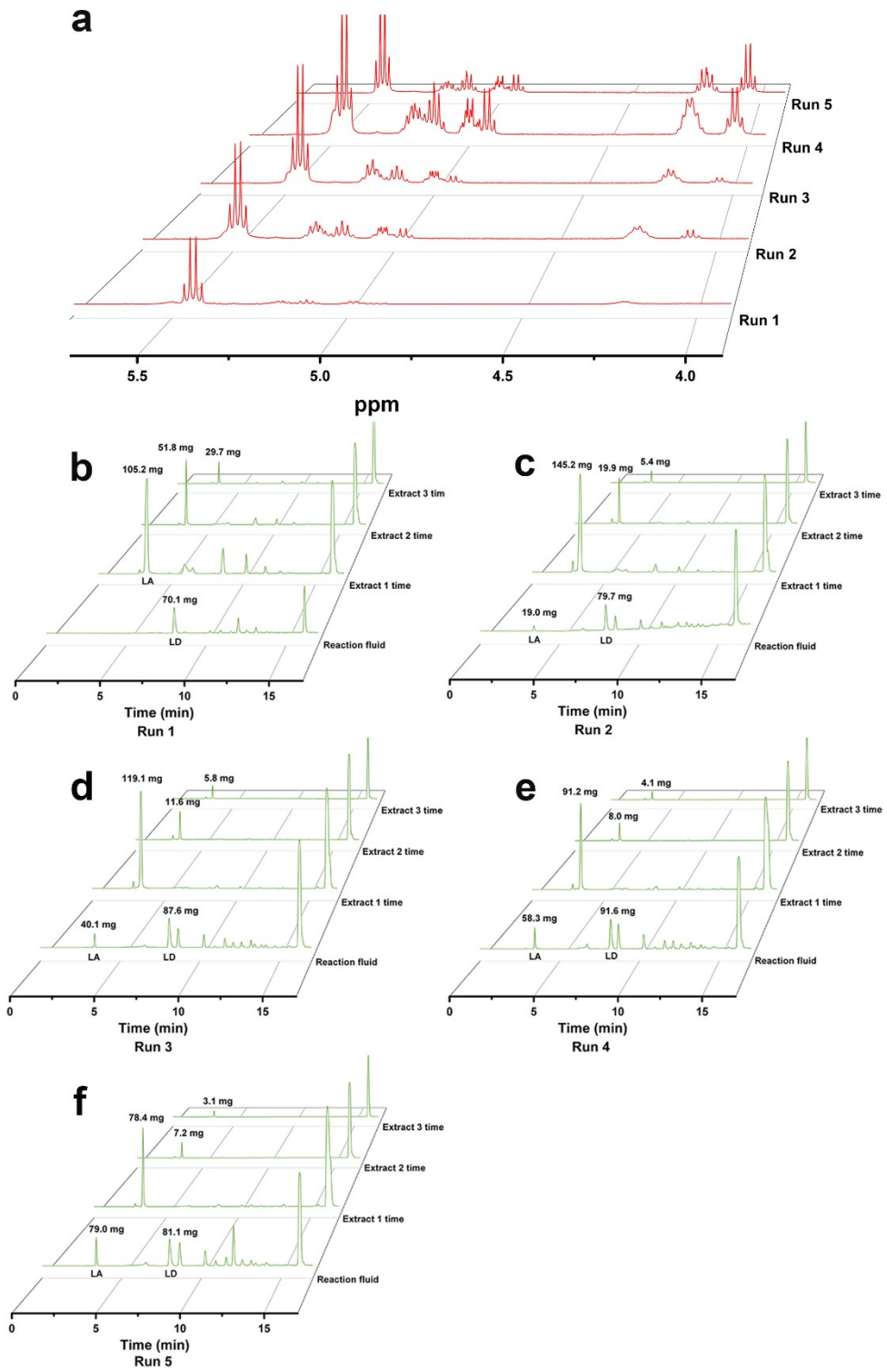

Fig. S9 (a) ^{1}H-NMR, (b-f) HPLC analysis of the products reused for 5 cycles (reaction conditions: 0.5 g 90 wt.% *L*-LA, 0.25 g catalyst synthesized with NH_4HCO_3/Al/Si=400/100/0.36 ratios, 10 mL *o*-xylene, 170 ^{o}C oil bath, 3 h)

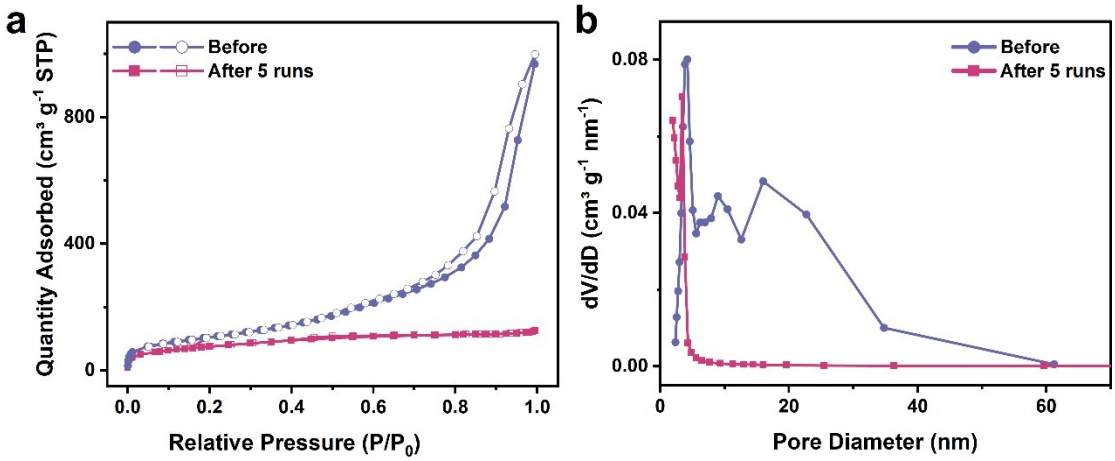

Fig. S10 (a) N_2 adsorption-desorption isotherms and (b) pore size distribution of the catalyst synthesized with NH_4HCO_3/Al/Si=400/100/0.36 ratios after use for 5 cycles (the BET surface area and pore volume are 270.8 m^2 g^{-1} and 0.15 mL g^{-1} respectively).

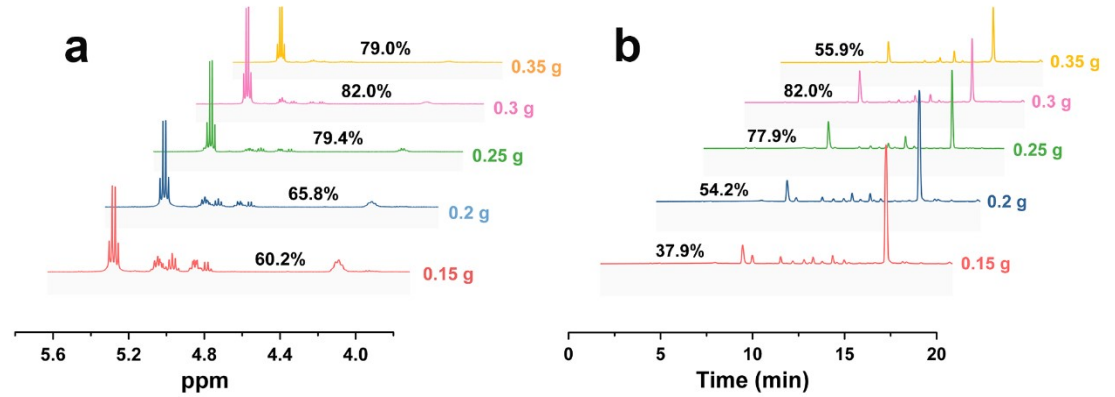

Fig. S11 The products analysis of the catalytic conversion of *L*-LA to *L*, *L*-LD by different dosage of SPG-Si-Al_2O_3 (NH_4HCO_3/Al/Si=400/100/0.36): (a) ^{1}H-NMR spectra and (b) HPLC chromatograms (reaction conditions: 0.5 g 90 wt.% *L*-LA, 0.15-0.35 g catalyst, 10 mL *o*-xylene, 170 °C oil bath, 3 h).

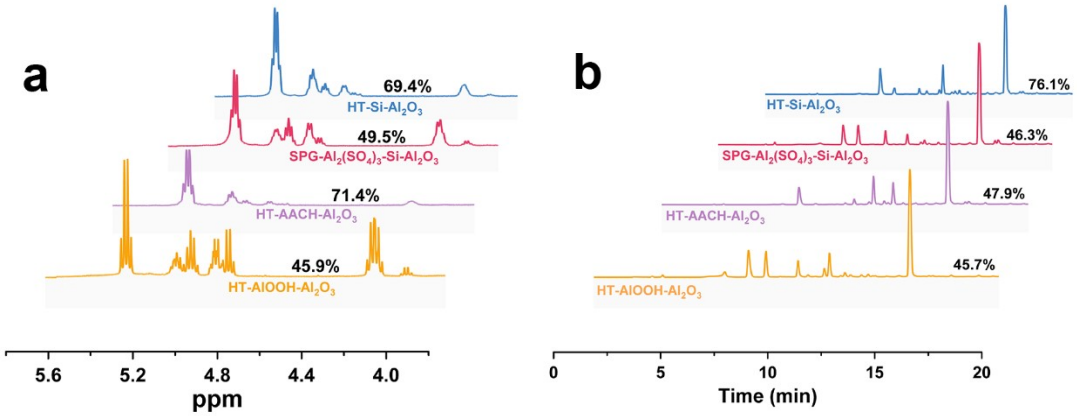

Fig. S12 (a) ^{1}H-NMR spectra and (b) HPLC chromatograms of the reaction liquids catalyzed by Al_2O_3 synthesized from other precursors or methods as indicated (catalytic reaction conditions: 0.5 g 90 wt.% *L*-LA, 0.25 g catalyst, 10 mL *o*-xylene, 170 °C oil bath, 3 h).

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