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Supplementary Materials for

Design of a heterogeneous catalytic process for continuous and direct synthesis of lactide from lactic acid

Pravin P. Upare[1], Ji Woong Yoon[1], Dong Won Hwang[1,2]*, U-Hwang Lee[1,2], Young Kyu Hwang[1,2], Do-Young Hong[1,2], Jin Chul Kim[3], Jeong Hyeon Lee[3], Sang Kyu Kwak[3], Hyeyoung Shin[4], Hyungjun Kim[4], Jong-San Chang[1,5]*

[1]Green Carbon Catalysis Research Group, Korea Research Institute of Chemical Technology (KRICT), 141 Gajeongro, Yuseoung, Daejeon 305–600, Republic of Korea.
[2]Department of Green Chemistry & Biotechnology, University of Science and Technology (UST), 113 Gwahangno, Yuseong, Daejeon 305–333, Republic of Korea.
[3]School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulju-gun, Ulsan 689-798, Republic of Korea
[4] Graduate School of EEWS, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong, Daejeon 305-701, Republic of Korea
[5]Department of Chemistry, Sungkyunkwan University, Suwon 440-476, Republic of Korea.

*Correspondence to: dwhwang@krict.re.kr, jschang@krict.re.kr

Materials and Methods

Materials

SnO (99%, Aldrich), SnO_2 (99%, Aldrich), $SnCl_4.5H_2O$ (99%, Aldrich), and silica sol (Ludox SM-30, Aldrich) were used without further treatment. L-Lactic acid (90%, Aldrich) and L-lactide (99.9%, Purac) were used as feedstocks, without further treatment. Gammabutyrolactone (> 99%, Aldirch) and ethanol (99.9%, Samchum) was used as received. ZSM-5 materials with Si/Al rato of 23, 50, 280 and and H-Beta (Si/Al ratio of 25, CP814E*) were purchased from Zeolyst and then they were calcined before use at 500 °C for 5 h.

Catalyst Preparation

The SnO_2-SiO_2 nanocomposite catalyst was prepared by a precipitation/deposition method. A known amount of $SnCl_4.5H_2O$ dissolved in distilled water and a required amount of silica sol (Ludox SM-30) comprising 7 nm silica nanoparticles were added dropwise simultaneously into water at 5 ^oC. For precipitation, 0.1N NaOH solution was added to the above suspension until pH of the solution reached 8.5. The suspension was then stirred for 12 h at room temperature, and then it was stirred at 80°C for 5 h. The resulting suspension was filtered and washed with distilled water repeatedly until Na was not detected in the filtrate. The solid was then dried at 120 °C in air for 12 h, pressed, crushed and sieved (No. 20–40 mesh) and finally calcined at 450°C in air for 6 h. (1,2)

Catalytic reaction

The catalytic reaction was performed in a conventional stainless steel fixed-bed reactor (internal diameter 5 mm and length 300 mm) after loading 1 g catalyst. 75% aqueous L-LA was introduced into the reactor via a liquid pump, mixed with N_2 and then vaporized in a preheated line. The product was withdrawn from the reactor via heated line into sample receiver maintained at 5 ^oC, at which temperature the crude LT and the unreacted LA was separated as a crystalline phase and liquid phase, respectively.

Catalyst characterization

Operando FTIR spectroscopic measurements

IR measurements for determination of temperature programmed reaction(TPRs) of LA were performed at 423-573 K after dehydration under nitrogen (15 mL/min) at 573 K for 2 h using a

Thermo Nicolet 6700 spectrometer with MCT detectors in a“sandwich” reactor-cell (3). The weigh hourly space velocity conditions for the operando IR experiments were established at a WHSV = 1.0 h^{-1} for 75% aqueous L-LA (90% in water, Aldrich) and aqueous L-L_2A (30% in water) , in which 10 mg/cm^2 (diameter=16mm) of catalyst was packed.

In-situ FTIR spectroscopic measurements

In-situ FTIR spectra were recorded using a Thermo Nicolet iS-50 spectrometer with MCT detector in transmission mode, operated at 4 cm^{-1} optical resolution and four levels zero-filling, on self supporting wafers (10mg/cm^2 and diameter = 16mm) of the sample and placed in a quartz cell specially designed in our laboratory with KBr windows, and outgassed in a dynamic vacuum (residual pressure, < 10^{-6} Torr) and for the introduction of gases into the infrared cell, as CO and pyridine, respectively. Before the adsorption of CO (30 Torr) and pyridine (5 Torr), the samples were activated at 400^{o}C under O_2(100torr) and vacuum for 2 h, respectively. Spectra were recorded at room temperature.

NH_3-TPD

NH_3-TPD experiments were carried out in a quartz fixed-bed tubular reaction system equipped with a thermal conductivity detector. Before TPD experiments, the samples were activated by heating from room temperature to 600 ^{o}C (10 ^{o}C/min) for 1 h under He. After the ammonia adsorption using NH_3 (10%) at 100 ^{o}C, the samples were evacuated to remove the physisorbed ammonia at the same temperature under He(30cc/min). Once the baseline of the integrator was stable, the TPD run was started with flowing hellium as a carrier gas at a heating rate of 10 ^{o}C/min from 100 to 650 ^{o}C.

Analysis of samples

Gas Chromatography (GC)

For analysis of LA conversion and LT selectivity, the whole sample (crystalline and liquid phase) was mixed with an equal amount of GBL and then the mixture of sample and GBL was subjected to gas chromatography. GC analysis was performed on a DS Science (IGC 7200) equipped with a flame ionization detector held at 280 ^{o}C and a chiral Cyclosil-B capillary column (internal diameter of 0.32 mm and 30 m length). The injection temperature was 270 ^{o}C and the initial oven temperature was 100 ^{o}C. After holding this oven temperature for 1.2 min, it was raised to 240 ^{o}C with ramping rate of 15 ^{o}C/min, and then held for 6 min.

High Performance Liquid Chromatography (HPLC)

Lactide, lactic acid monomer and lactic acid oligomer analyses were carried out by high performance liquid chromatography (HPLC) (YL9100, Youngin HPLC), the HPLC was equipped with water symmetry C_{18} 5μm column reverse phase column (4.6 x 250 mm) (Waters) and UV detector at 210 nm. The mobile phase was a water/acetonitrile (HPLC grade, Samchun chemicals) mixture in gradient concentration; both acetonitrile and water were acidified with phosphoric acid 0.1 vol. % (85% H_3PO_4, Alfa aser). The LC column and oven temperature was maintained at 40 ^{o}C and the mobile phase flow rate was maintained at 0.7mL/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. (4)

Codari et al. developed an efficient techniques for the formation of low molecular weight PLA oligomers as well as HPLC analysis procedure for their separation and identification. We also followed the almost similar procedure for the confirmation of low MW (>Ln2) on HPLC (4).

Karl-Fischer Titration

The moisture in the lactide samples was measured by Metrohm Karl Fischer Titrator (831 KF Coulometer). 1.0 g of lactide sample was dissolved in 1.0 g solvent (GBL), and then 50 mg of the prepared samples were titrated with anolyte (HYDRANAL @ Coulomat AG, Fluka Chemicals).

Acid Titration

For quantification of acid concentration, 2.0 g of lactide sample was dissolved in 20 ml of absolute methanol. Then the solution was titrated with the solution of 0.01 N KOH in methanol and phenolphthalein indicator.

^{1}H Nuclear Magnetic Resonance

Latide samples were dissolved in $CDCl_3$ from Aldrich containing TMS at 0.05%. ^{1}H NMR spectra were obtained at 500 MHz at room temperature a Bruker ULTRASHIELD TM 300 spectrometer. TMS was used as internal reference. (5)

Grand Canonical Monte Carlo (GCMC) simulation (6)

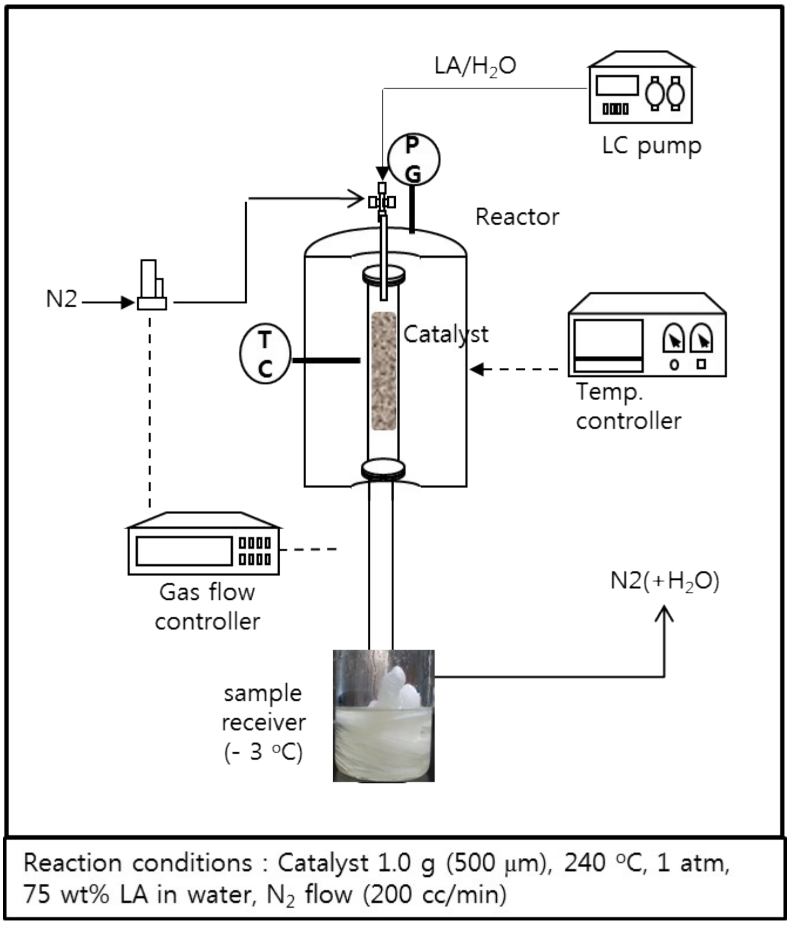
First, we have modeled the three slab models of SnO_2, TiO_2, and Al_2O_3, and one periodic model of H-ZSM-5 (Si/Al=23) as shown in Fig. S4. SnO_2 and TiO_2 models were made by 10×5 supercell of (1 1 0) surface with 4 metal atom layers, and the other was modeled by 6×4 supercell of (1 0 0) surface with the height of the two Al_2O_3 unit cells. In order to avoid the self interactions of adsorbed molecules, the vacuum regions above and below the slab models were introduced. For the case of H-ZSM-5, four protons were randomly attached inside and corresponding four Al atoms were substituted to Si atoms in the unit cell. The unit cell was extended to be the 2×2×3 supercell. Next, we applied GCMC method using Materials Studio 2016 to estimate the amounts and binding energies of adsorbed molecules (i.e. L-lactic acid (LA) and lactide (LT)). The temperature was set to be 544K. To trace the average adsorption isotherms, the GCMC simulations have been independently performed 3 times with over 1×10^6 equilibrium steps by varying the fugacity from 0.01 kPa to 100 kPa. In order to estimate the non-bonding energies (i.e. binding energies) between adsorbates and substrates, we have employed the COMPASS forcefield. (7, 8) The energies were decoupled to van der Waals and Columbic energies to elucidate each effect.

Density Functional Theory (DFT) calculations

For the investigation of the reaction mechanism, we performed spin-polarized density functional theory (DFT) calculations using the Vienna Ab-initio Simulation Package (VASP) program (9). We chose exchange-correlation functional of Perdew-Burke-Emzerhof (10), and a plane-wave basis set with a cutoff energy of 450 eV. Monkhorst k-point grids of (13×13×19) and (13×13×20) were employed for the optimization of bulk SnO_2 structure. The calculated bulk lattice parameters of a=4.81 Å and c=3.24 Å for SnO_2 were comparable to the experimental values of a=4.74 Å and c=3.19 Å for SnO_2 (11). To model the catalyst surface, we used rutile (3×1) slab model in (110) direction, which is known as the most stable surface of SnO_2 with an additional ~20 Å of vacuum regime (12). We used two bilayers in our slab calculations, where one bottom bilayer was fixed at the lattice point to approximate the bulk, whereas the upper layers were allowed to relax. Gamma centered k-point grid of (5×5×1) was employed for the slab models and the dipole correction was applied in the surface normal direction. For the calculation of the entropy of the adsorbed species ($S_{ad.}^0$) on the catalyst surface, we first computed the gas-phase entropies (S_{gas}^0) of the non-adsorbed molecules by calculating the translational, rotational, and vibrational entropies using ideal gas, rigid rotor, and harmonic oscillator partition functions, respectively. We then estimated entropies of the molecules when they are adsorbed on the catalyst surface species ($S_{ad.}{}^{0}$) using the previously reported empirical formula (13);

$S_{ad.}{}^{0}$ (T) = 0.70 × $S_{gas}{}^{0}$ (T) − 3.3R

where R is the gas constant and T is the temperature.



Reaction conditions : Catalyst 1.0 g (500 μm), 240 °C, 1 atm, 75 wt% LA in water, N_2 flow (200 cc/min)

Fig. S1 one-step continuous catalytic system for lactide production from aqueous lactic acid.

After the catalytic reaction, a vapor mixture of lactide, lactic acid and water was condensed at sample receiver maintained at -3 ^{o}C so that lactide degradation to lactic acid dimer could be prevented. Typically, the sample was collected after 24 h after feeding lactic acid. The mass balance was higher than 99.5% and the main loss was due to evaporation of water with N_2 carrier gas.

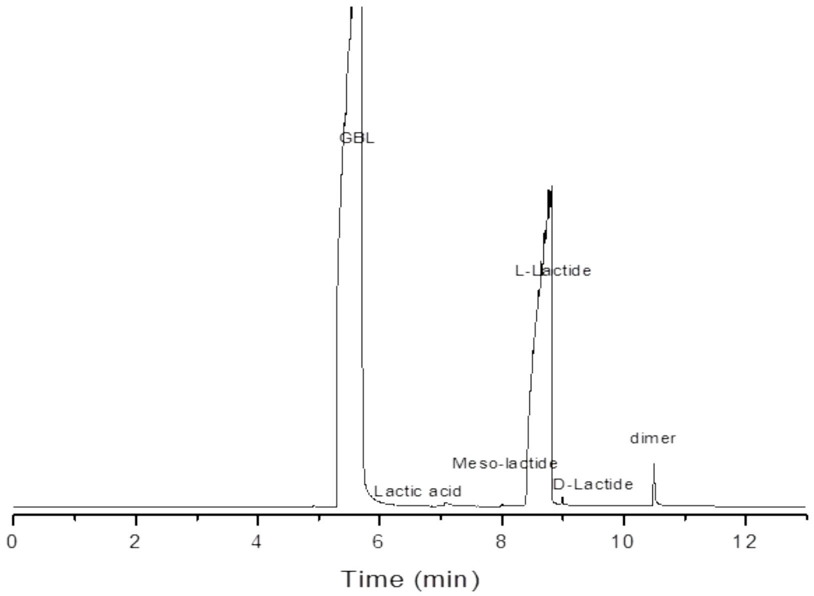


Fig.S2 Typical gas chromatogram of a sample mixed with GBL solvent.

The typical chromatogram for the product below shows that our GC analysis method allowed to separate GBL, lactic acid (LA), meso-lactide (M-LT), L-lactide (L-LT), D-lactide (D-LT), and L_2A. But, oligomer (L_nA, n > 3) was not detected by this analysis method.

For quantification of LA conversion, we prepared the standard sample of 0% LA conversion (0.375 g LA, 0.125 g H_2O and GBL 0.5 g). LA conversion was calculated using the equation (1), since the feed contained mostly L_1A and L_2A.

LA conversion (%) = [1 –[(L_1A area% + L_2A area%) of the sample]/[(L_1A area% + L_2A area%) at 0% LA conversion]] ×100 --------- (1)

For quantification of LT yield, we prepared the standard sample of 100% LA conversion (LT 0.3 g, H_2O 0.2 g, and GBL 0.5 g). LT yield was calculated using the equation (2).

LT (L-LT or M-LT) yield (%) = [LT area% of the sample/LT area% at 100% LA conversion]×100 ------------ (2)

Oligomer (L_nA, n > 3) yield (%) = LA conversion – LT yield -------------------- (3)

When we injected the feed (75% LA) to GC, about 2.3% L-LT was produced due to thermal reaction in oven condition, the actual L-LT yield was calibrated by subtracting this value from the as-calculated one. The raw data and the calculation result was summarized in the below table.

Table S1. The GC analysis results

sample	GC area percentage (%)						LA Conv. (%)	L-LT YLD (%)		M-LT YLD (%)	LT YLD (%)	Oligomer YLD (%)
	GVL	L1A	L2A	L-LT	M-LT	LA (L1A + L2A)		before calibration	after calibration			
Feed 75%LA	79.25	14.59	5.58	0.58	0.00	20.17	0	2	0	0	0	0
no catalyst	78.84	12.03	4.93	4.13	0.07	16.96	16	16	14	0	14	2
SiO2	81.3	10.85	3.82	3.87	0.16	14.67	27	15	13	1	14	13
ZSM-5 (23)	85.91	4.19	2.41	6.79	0.7	6.60	67	27	25	3	28	39
ZSM-5 (50)	78.43	3.58	1.92	15.39	0.68	5.50	73	61	59	3	62	11
ZSM-5 (280)	78.55	10.47	2.3	7.98	0.7	12.77	37	32	29	3	32	5
Beta (25)	79.57	7.4	4.36	8.36	0.31	11.76	42	33	31	1	32	10
SSO(40)	79.06	2.49	1.78	16.39	0.28	4.27	79	65	63	1	64	15
SSO(60)	76.61	1.28	1.48	20.52	0.11	2.76	86	82	79	1	80	6
SSO(80)	74.68	0.37	0.82	24.05	0.08	1.19	94	96	94	0	94	0
SSO(90)	75.11	0.42	0.86	23.52	0.09	1.28	93	93	91	0	91	2
SnO2	76.81	2.31	1.81	17.86	1.21	4.12	80	71	69	5	74	6
TiO2	76.83	5.4	2.63	14.85	0.29	8.03	60	59	57	1	58	2
pure lactide	74.84	0.00	0.00	25.16	0.00	0.00	100	100	100	0	100	0

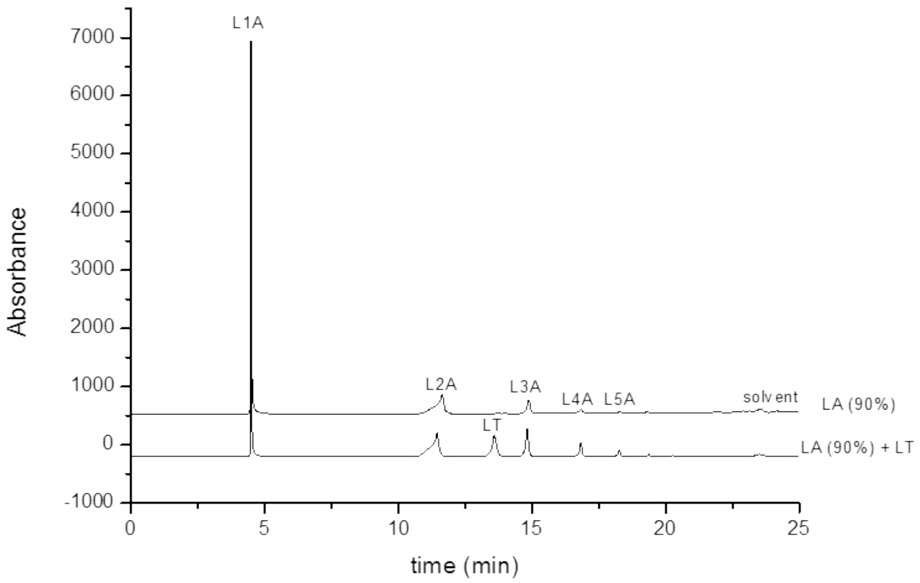


Fig. S3 HPLC analysis results of LA(90%) and a mixure of LA and LT

It clearly shows that all lactic acid species (L1A, L2A, L3A, ..) and lactide (LT) is separable, but L-LT and meso-LT is not seprarble. The lactide yield was also calculated from its area percentage using equation (4).

LT yield (%) = [LT area% after reaction/LT area% at 100% LA conversion] ×100 ----------------- (4)

The LT yield by HPLC analysis was about 1% lower than tha value by GC analysis. This difference might reslut from LT hydrolysis during HPLC analysis, since pure LT sample also showed some L_2A peak. But, the trend of LT yield with diffrent catalyst by HPLC analysis was the same by GC analysis. From both analysis methods, it is evident that only SSO(80) catalyst produced L-LT much more selectively from aqueous LA than the conventional ZSM-5 catalyst.

Table S2. HPLC analysis results

sample	HPLC Area percentage (%)					LT yield (%)
	LA	LT	L2A	L3A	> L4A	
Feed (75% LA)	52.88	0.00	35.01	9.82	2.29	0
no catalyst	46.00	13.50	33.00	7.50	1.4	14
SSO(80)	3.04	92.10	4.12	0.49	0.25	93
H-ZSM-5(Si/Al=280)	35.22	29.31	27.04	7.90	0.53	30
H-ZSM-5(Si/Al=50)	17.51	59.85	10.08	9.80	2.76	60
H-ZSM-5(Si/Al=23)	16.49	26.51	22.96	7.50	26.54	27
pure lactide	0.00	99.31	0.69	0.00	0.00	100

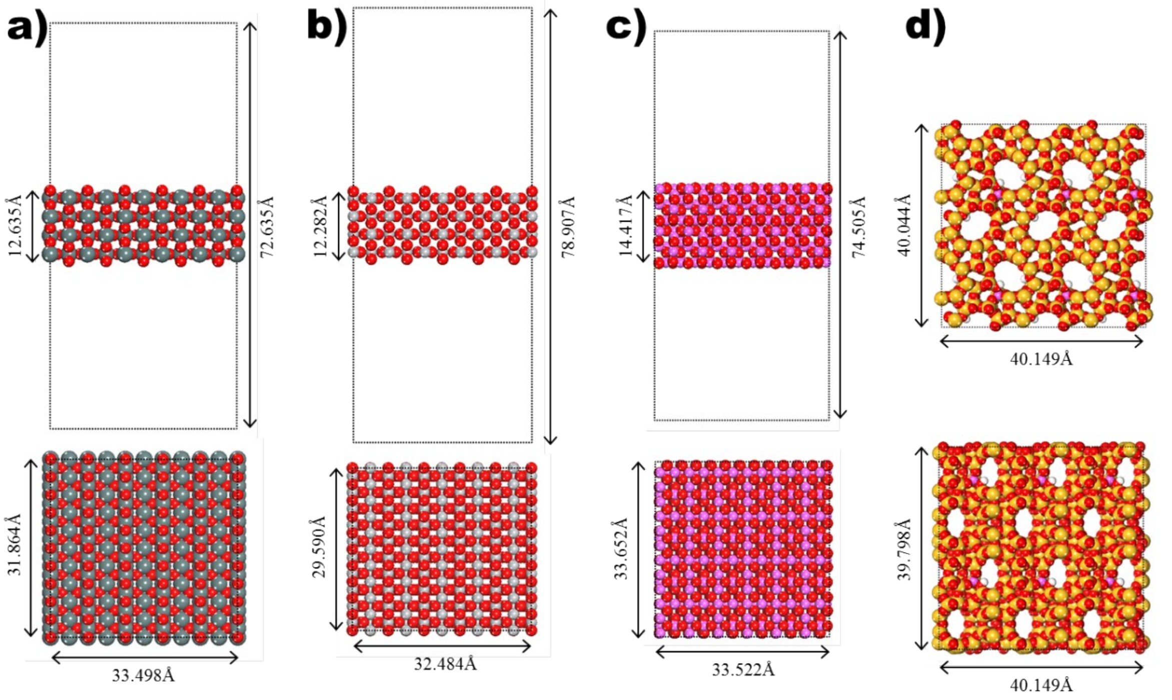


Fig. S4 Model systems for the GCMC calculation, where top pictures represent the side view and bottom pictures represents the top view. a) Slab model of (1 1 0) surface of SnO_2 b) (1 1 0) surface of TiO_2 c) (1 0 0) surface of γ-Al_2O_3 d) Periodic model of H-ZSM-5 (Si/Al=23). Sn atoms are dark gray, Ti atoms are light gray, Al atoms are pink, Si atoms are yellow, O atoms are red, and H atoms are white.

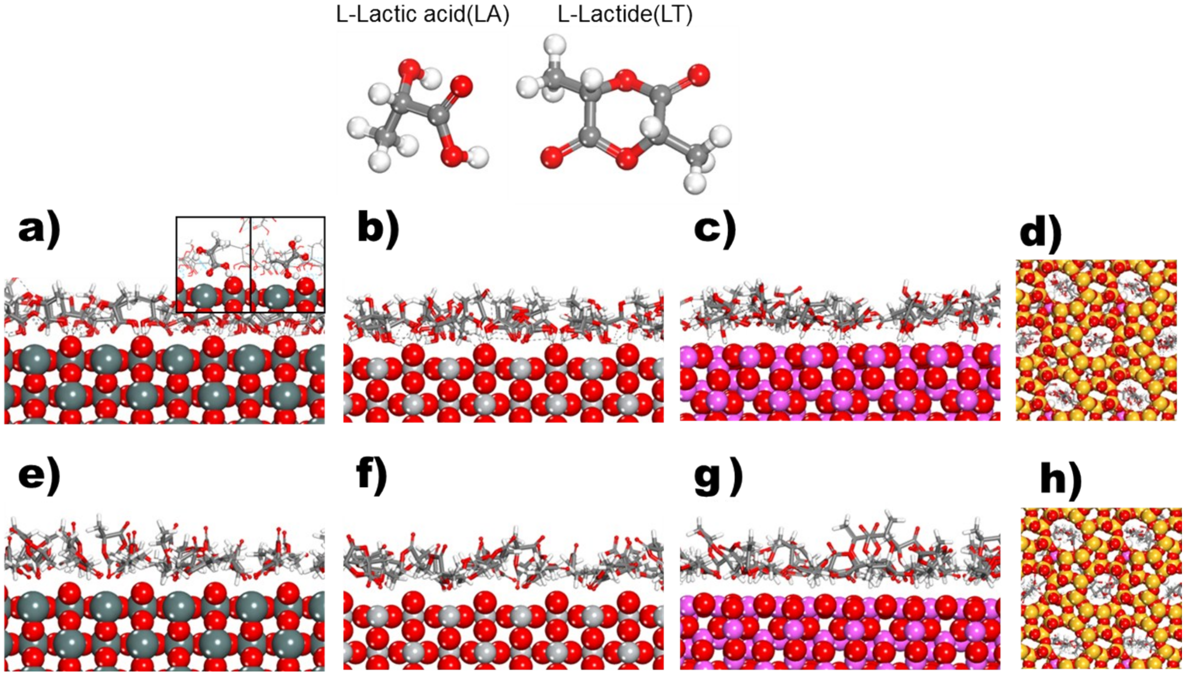


Fig. S5. Adsorbed configurations of lactic acid on a) SnO_2, b) TiO_2, c) γ-Al_2O_3, and d) H-ZSM-5, respectively. Adsorbed configurations of lactide on e) SnO_2, f) TiO_2, g) γ-Al_2O_3, and h) H-ZSM-5, respectively. Black dashed line represents hydrogen bondings. The inset pictures show typical adsorbed states of LA.

Table S3. Binding energies (kcal/mol) of Lactic acid and Lactide on substrates. Note that adsorbed molecules only within first layer region were included for the calculation

Catalyst	**L-Lactic acid**[a]			**L-Lactide**[b]		
	Total	van der Waals	Coulombic	Total	van der Waals	Coulombic
SnO_2	-27.426	-0.297	-27.129	-24.403	-16.334	-8.069
TiO_2	-21.373	-7.149	-14.223	-24.736	-14.241	-10.495
γ-Al_2O_3	-16.784	-11.126	-5.659	-22.330	-18.095	-4.235
H-ZSM-5 (Si/Al=23)	-16.442	-15.612	-0.830	-22.875	-22.531	-0.345

[a] Adsorbed lactic acid molecules at 100 kPa

[b] Adsorbed lactide molecules at 10 kPa

Table S4. ICP-OES analysis results of SnO_2-SiO_2 catalysts

Catalysts	weight %	
	SnO_2	SiO_2
SnO_2(40)-SiO_2	39.04	60.64
SnO_2(60)-SiO_2	59.99	39.08
SnO_2(80)-SiO_2	79.89	20.03
SnO_2(90)-SiO_2	87.36	12.51

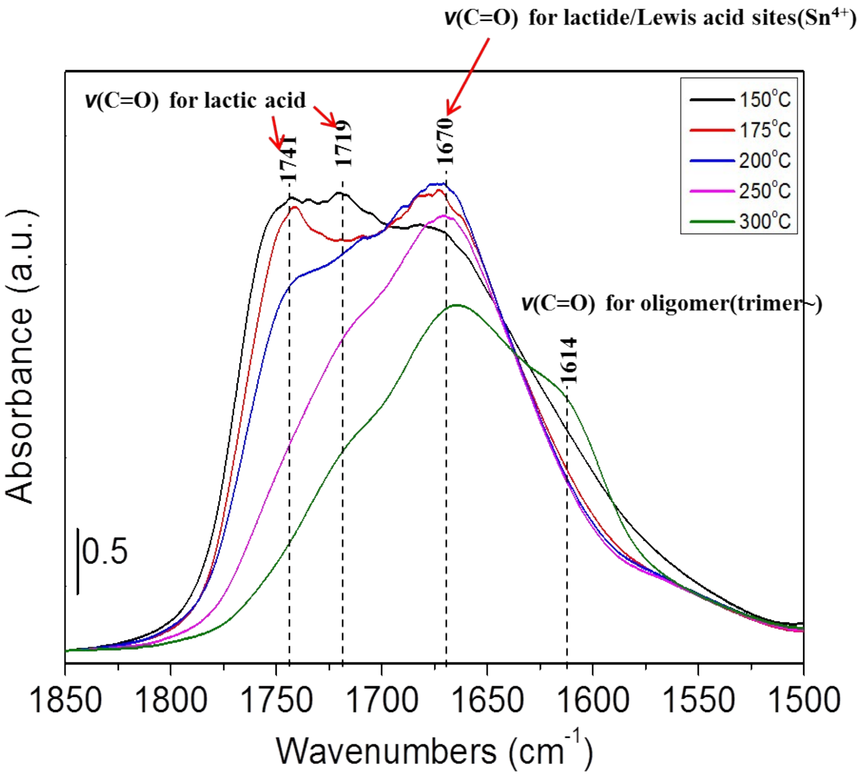


Fig. S6 Operando-IR spectroscopy of SSO-80 with different temperature

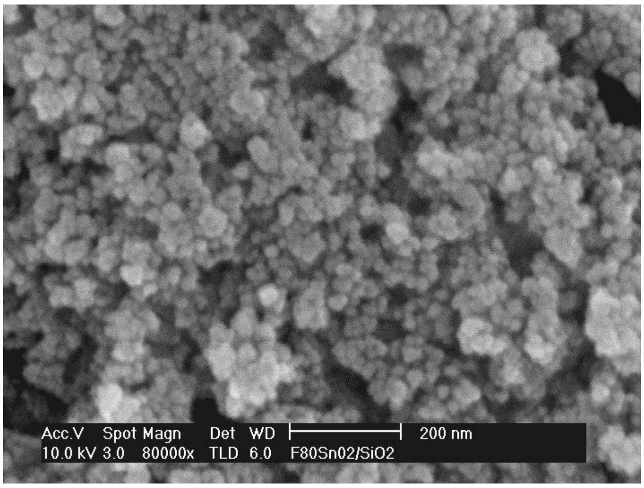
Pretreatment : 240°C for 2h under He

Cat. wt. : 20mg (10mg/cm^2)

Reaction condition : WHSV = 1.0/h under N_2, Temperature =150 ~ 300 °C

Reactant : 75% lactic acid

(A)



(B)

Fig. S7. (A) Picture and (B) SEM image of SSO-80.

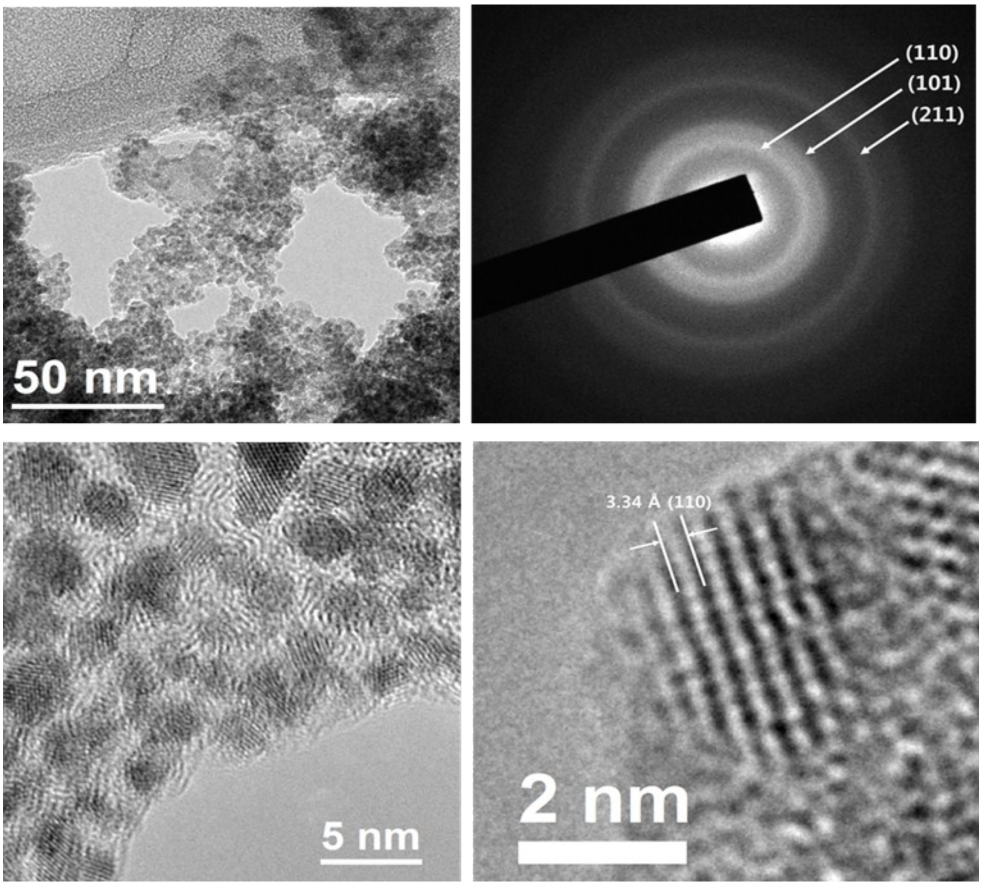


Fig. S8.TEM image of SSO-80.

Table S5. The catalytic results and BET surface areas of the various materials

catalyst	BET surface area (m2/g)	LA Conversion (%)	L-LT Yield (%)	M-LT Yield (%)	Oligomer Yield (%)
no catalyst	-	15.9	14.1	0.3	1.5
SiO_2	261	27.3	13.1	0.6	13.6
ZSM-5 (23)	387	67.3	24.7	2.8	39.8
ZSM-5 (50)	396	72.7	58.9	2.7	11.2
ZSM-5 (280)	403	36.7	29.4	2.8	4.5
H-Beta (25)	680	41.7	30.9	1.2	9.5
SSO-40	240	78.8	62.8	1.1	14.9
SSO-60	197	86.3	79.3	0.4	6.6
SSO-80	180	94.1	93.3	0.3	0.5
SSO-90	134	93.7	91.2	0.4	2.1
crystalline SnO_2	27	79.6	68.7	4.8	6.1
TiO_2	49	60.2	56.7	1.2	2.3

Reaction conditions: 101.3 kPa, 513K, WHSV 1.0 h^{-1}, N_2 flow rate 250 mL min^{-1}, time on stream 50h

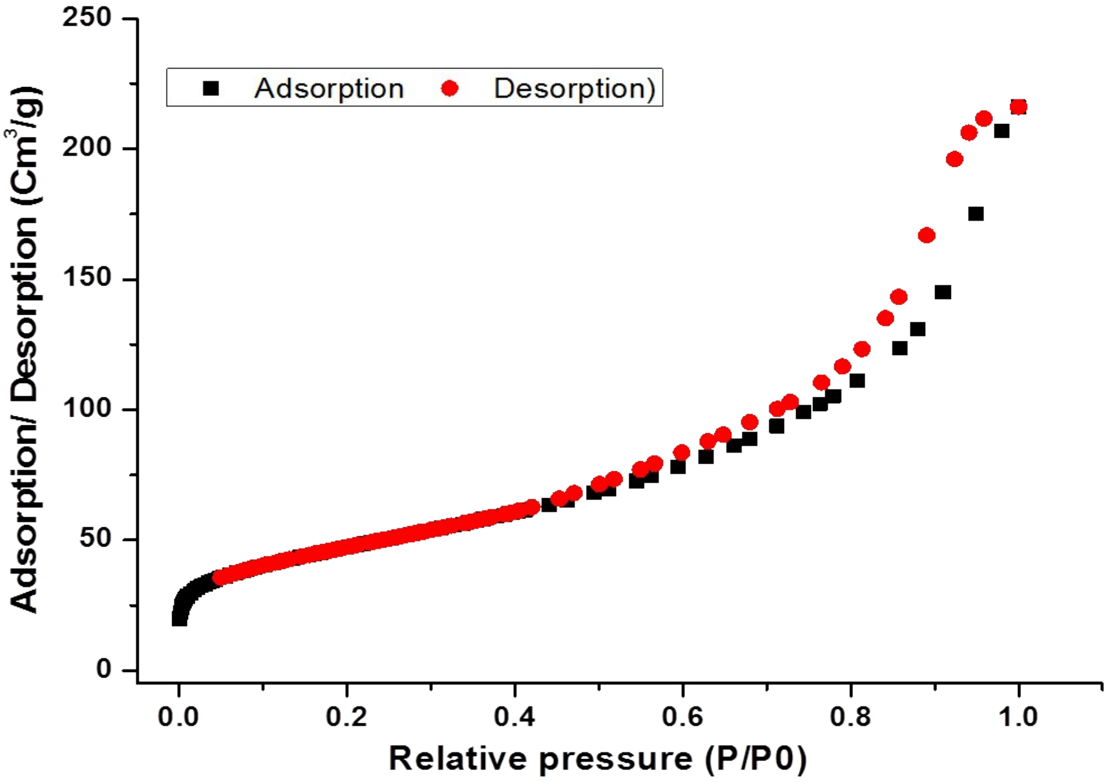


Fig. S9. Nitrogen adsorption/desorption isotherms of SSO-80.

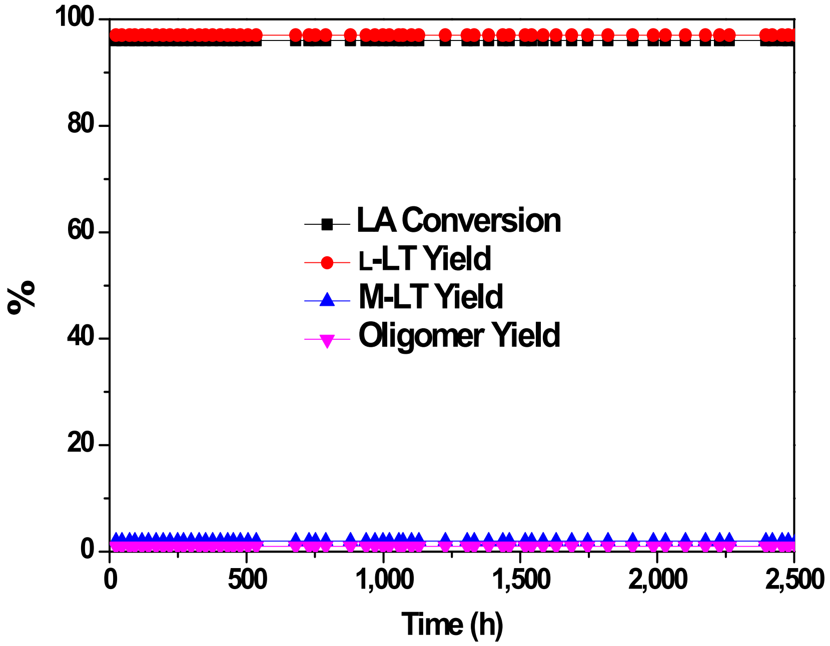
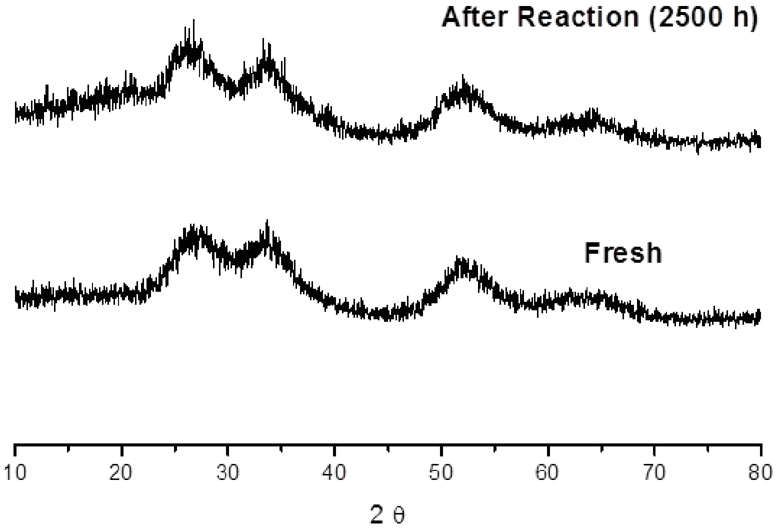
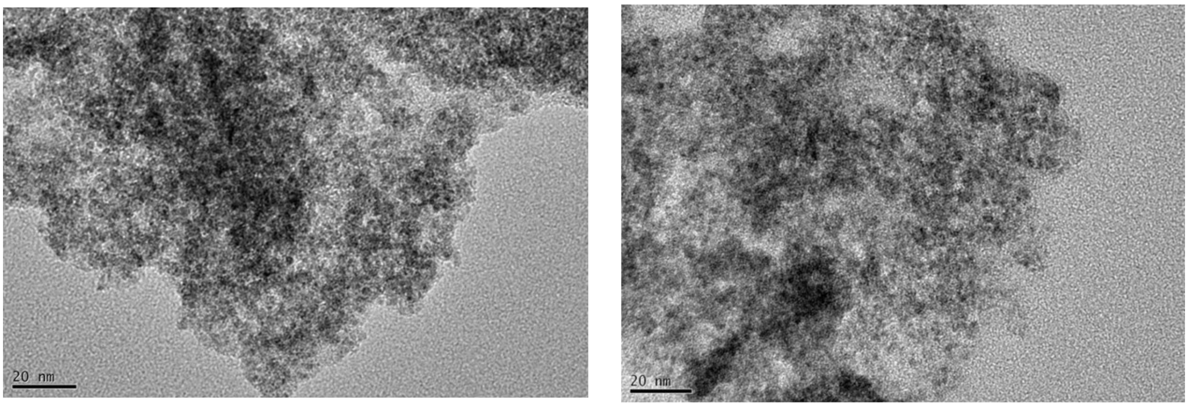


Fig. S10 Dependence of lactic acid conversion and product selectivity over SSO-80 catalyst on reaction time (reaction conditions: 101.3 kPa, 240 °C, WHSV: 1.0 h^{-1}, N_2 flow rate: 250 mL)



(A) XRD



fresh

after reaction (2500 h)

(B) TEM

Fig. S11. Physical property of SSO-80 catalyst before and after reaction

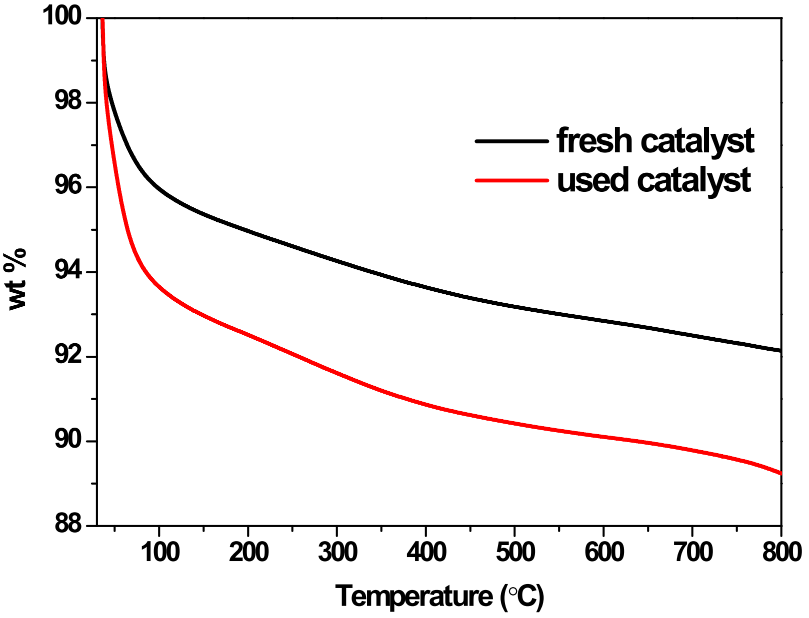


Fig. S12 TGA pattern of SSO-80 catalyst before and after reaction for 2,500 h

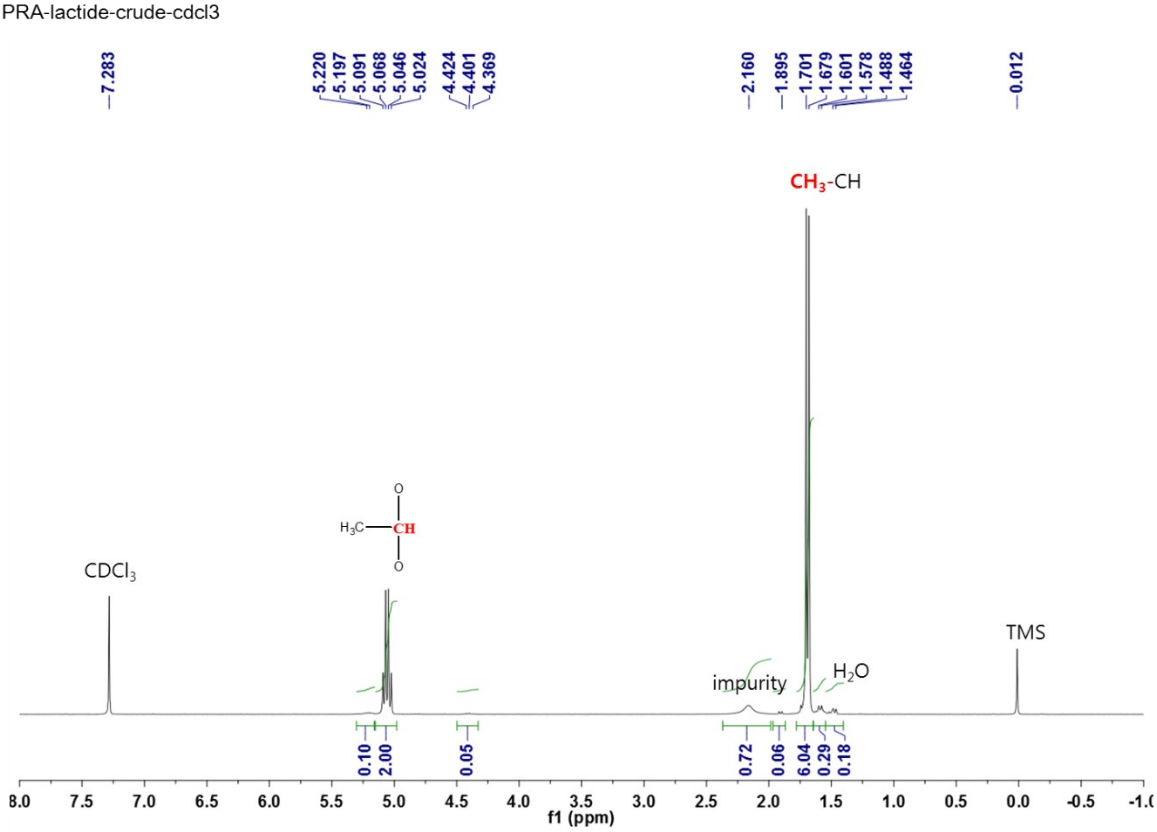


Fig. S13 The ^{1}H NMR spectrum of the crude lactide

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