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Supplementary Information

Base free, one-pot synthesis of lactic acid from glycerol using a bifunctional Pt/Sn-MFI catalyst

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Catalyst preparation

Synthesis of Sn-MFI

Sn-MFI was prepared using a method reported previously.[1] In a typical synthesis, 0.07 g of tin (IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, Alfa Aesar) was mixed with 5.5 g of tetrapropylammonium hydroxide (TPAOH, 40% Alfa Aesar) under stirring. 5.20 g of tetraethyl orthosilicate (TEOS, 98%, Alfa Aesar) was added to the solution, followed by stirring for 30 minutes. After adding 6.33 g of deionized water to the mixture, the solution was kept stirring for 24 h. Subsequently, the resulting solution, with a final molar composition of 1 SiO_2 : 0.008 SnO_2 : 0.44 TPAOH : 22.2 H_2O, was transferred into a closed Teflon vessel in a stainless steel autoclave and crystallized in an oven at 170

^{o}C for 2 d. The obtained solid was thoroughly washed with deionized water until pH became neutral, and then dried at 100 ^{o}C overnight. The zeolite was calcined at 550 ^{o}C for 12 h for the removal of the organic structure directing agent.

Synthesis of silicalite-1

Silicalite-1 was synthesized following the protocol reported by Watanabe *et al*.[2] Typically, 2.39 g of tetrapropylammonium hydroxide (TPAOH, 40% Alfa Aesar) was mixed with 11.43 g of deionized water, and then 4 g of TEOS (98%, Alfa Aesar) was added to this solution. The mixture was stirred at 80 ^{o}C for 24 h to obtain the final molar composition of 1 SiO_2 : 0.25 TPAOH : 38 H_2O. The resulting gel was transferred to an autoclave for crystallization at 170 ^{o}C for 24 h. The solid product was washed with deionized water, dried at 100 ^{o}C overnight and calcined at 550 ^{o}C for 12 h.

Synthesis of Sn-BEA

The detailed procedures for the preparation of Sn-BEA were described in previous literature.[3] Tetraethylorthosilicate (TEOS, 98%, Alfa Aesar) was mixed with tetraethylammonium hydroxide (TEAOH, 35 wt%, Alfa Aesar) solution and stirred until a homogeneous solution was formed. Tin (IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, Alfa Aesar) was then added into the solution. The resulting solution was stirred in a fumed hood until ethanol (generated from hydrolysis of TEOS) was completely evaporated. Hereafter a suspension of dealuminated zeolite beta crystal seeds were added into the gel and well mixed. Lastly, hydrofluoric acid (48%, Alfa Aesar) was added into the mixture by mixing with a plastic spatula. The final molar composition of the gel was SiO_2 : 0.008 SnO_2 : 0.54 TEAOH : 0.54 HF : 7.5 H_2O. The solid-like white gel was moved into an autoclave and heated at 140 ^{o}C for 4 d with a rotation rate of 3 rpm. The as-made product was washed thoroughly by filtration with 2 L of deionized water and dried in an oven at 100 ^{o}C overnight. The Sn-BEA was obtained after calcination at 550 ^{o}C for 12 h in a muffle furnace.

Synthesis of bifunctional catalysts

Bifunctional catalysts were prepared by impregnating Sn-MFI, silicalite-1, Sn-BEA and TiO_2 (P25, Degussa) with an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ (99.9%, Alfa Aesar), respectively. After the impregnation, the samples were dried at 100 ^oC overnight. The impregnated samples were placed on a small beaker in the middle of a plastic bottle. Ethanol was used as a reducing agent in the synthesis. It was placed at the bottom of the bottle without directly contacting with the samples. The reduction was performed in an oven at 70 ^oC for 4 h. Obtained products were washed with deionized water by centrifugation and dried at 100 ^oC overnight. The Pt loading was fixed at 1.5 wt% on the basis of the final product.

Catalyst characterization

FT-IR study was carried out on an EQUINOX 55 (Bruker) FT-IR spectrometer equipped with an MCT detector. The sample was loaded in a high-temperature reaction cell (Harrick) located within a DRIFT accessory (Praying Mantis^{TM}, Harrick). The sample was degassed at 550 °C for 1 h under He in order to remove adsorbed water. After that, FT-IR spectra (with a resolution of 2 cm^{-1}) were collected from the sample at 120 °C. For pyridine adsorption, small aliquots of pyridine were subsequently exposed to the sample at 120 °C for 15 min. Prior to the measurement the weakly adsorbed pyridine was removed by flowing He at 250 °C for 1 h, and the spectra were then collected at 120 ^oC. Powder X-ray diffraction (XRD) patterns of the catalysts were collected on a XRD diffractometer (X'pert Pro, PANalytical) operated at an acceleration voltage of 45 kV and a current of 40 mA using CuK_α radiation. The XRD data for the prepared samples were recorded in a 2θ range of 4-60^o. The nitrogen adsorption-desorption isotherms were measured using an automated gas sorption analyzer (Autosorb iQ_2, Quantachrome) after the samples were degassed at 300 ^oC for 12 h under vacuum. Elemental analysis for the samples was carried out using inductively coupled plasma-optical emission spectroscopy (ICP-OES, iCap 6500 Dual view, Thermo Scientific). The morphology of each catalyst was examined by transmission electron microscopy (TEM, JEOL 2000FX) with an accelerating voltage of 200 kV. The particle size distribution was calculated by counting over 60 particles. The average Pt particle size in this distribution was determined using the equation

$\sum d^3 / \sum d^2$ where d (nm) is particle size. Pt metal surface area was measured by H_2 chemisorption using a chemisorption analyzer (ChemBET pulsar TPR/TPD, Quantachrome). In this experiment, the catalysts were reduced at 300 °C for 10 h under the flow of 5% H_2/95%N_2 gas and H_2 chemisorption was then carried out at room temperature with a gas flow rate of 12 mL min^{-1}. From this result, average Pt crystallite diameter for each catalyst was estimated with the assumption of spherical geometry.

Catalytic test

Glycerol oxidation into lactic acid (LA)

In a typical experiment for converting glycerol (99.5%, Alfa Aesar), Pt/Sn-MFI or Pt/AC catalyst and 80 mL of 0.2 M aqueous solution of glycerol (glycerol/Pt molar ratio = 350, glycerol/Sn molar ratio = 226) were put into a 160 mL Parr reactor. Initially, the reactor was pressurized with nitrogen at 0.62 MPa. After heating the reactor from room temperature to 100 °C, the oxidation was allowed to proceed under stirring at 1000 rpm by switching from inert gas to oxygen (0.62 MPa). Time course of glycerol oxidation was monitored by taking samples (0.5 mL) for analysis at specified time intervals. Under the same reaction conditions, the Pt/Sn-BEA catalyst was tested with the glycerol to Sn molar ratio of 211. Te same reaction conditions were also applied for Pt/silicalite-1 and Pt/TiO_2 samples.

Conversions of pyruvaldehyde (PA) into LA

A conversion of PA into LA has been performed over Pt/Sn-MFI, Sn-MFI, Pt/Sn-BEA and Sn-BEA catalysts. The catalysts, corresponding to 226 of PA to Sn molar ratio, were added into a 1.3 g of 0.2 M PA solution. The reaction was carried out in a 4 mL glass vial reactor which was placed in a temperature-controlled aluminum heating block set at 100 °C under 1000 rpm stirring. After the specified times of the reaction, the glass reactors were quenched in ice for 20 min, dried and weighed before opening to ensure no leaking occurred during the reaction.

Sample analysis

After the reaction, glycerol, glyceric acid (20 wt% in water, TCI), PA (40 wt% in water, Aldrich), pyruvic acid (98%, Aldrich), LA (98%, Sigma Aldrich), glyceraldehyde (90%, Sigma Aldrich), acetic acid (99.9%, Fisher Scientific), DHA (dimer, 97%, Sigma Aldrich), oxalic acid (97%, Fluka), tartronic acid (98%, Alfa Aesar) and glycolic acid (99%, Sigma Aldrich) were quantified in the reaction vials. The quantitative analysis of these samples was conducted by Agilent 6890 gas chromatography equipped with an FID-detector and a Restek RTX-VMS capillary column (30.0 m length, 0.25 mm id, 1.4 μm film thickness). Besides, the products were also cross-checked on HPLC (Shimadzu, LC-20AT) using an HPX-87H column operated at 30 ^{o}C. In HPLC experiments, ultraviolet (UV) and refractive index (RI) detectors were utilized to determine the chemicals with 0.6 mL min^{-1} of a flow rate of 0.005 M H_2SO_4 aqueous solution as a mobile phase.

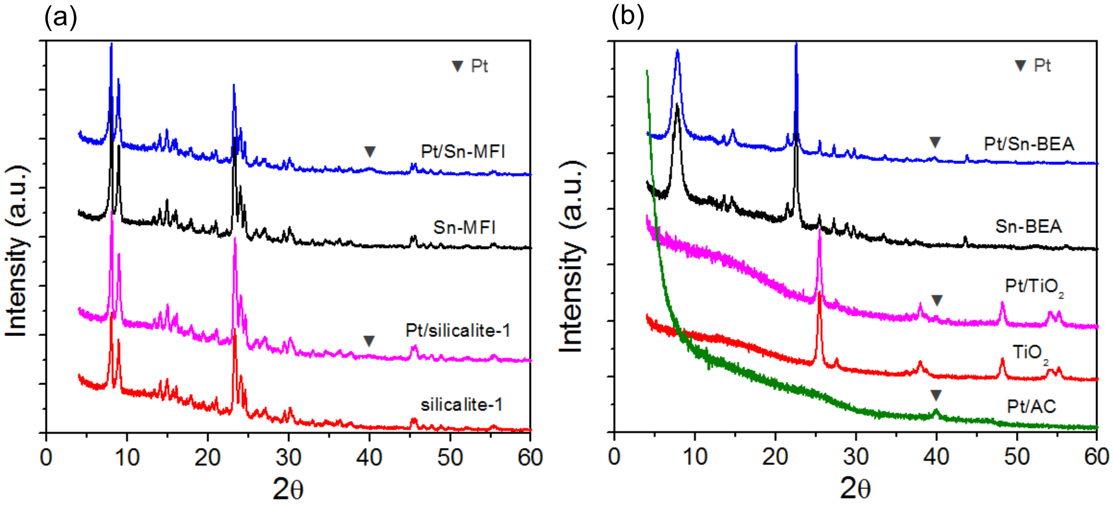

Fig. S1 XRD patterns of the prepared catalysts: (a) Pt/Sn-MFI, Sn-MFI, Pt/silicalite-1 and silicalite-1, and (b) Pt/Sn-BEA, Sn-BEA, Pt/TiO_2, TiO_2 and Pt/AC.

Table S1. Pt metal surface area and crystallite diameter for each catalyst determined by H_2 chemisorption

	Pt metal surface area (m^2 g^{-1})	Crystallite diameter [a] (nm)
Pt/Sn-MFI	0.18	7.9
Pt/silicalite-1	0.15	9.5
Pt/Sn-BEA	0.21	6.6
Pt/TiO_2	0.22	6.4
Pt/AC [b]	6.01	0.8

[a] Assumption of the spherical crystallite.

[b] Supplied from Sigma Aldrich.

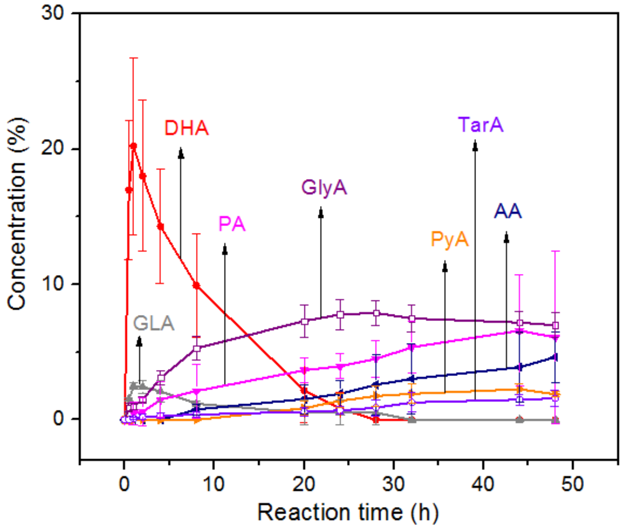

Fig. S2 Detailed concentration profile of glycerol reaction over Pt/Sn-MFI from Figure 1. Reaction conditions: 0.2 M glycerol in H_2O, glycerol/Pt (mol/mol) = 350, glycerol/Sn (mol/mol) = 226, pO_2 = 0.62 MPa and 100 °C. The error bars in the figures are from three repeated reactions.

Table S2. Textural Information from N_2 adsorption-desorption isotherms

	BET surface area [a] (m^2 g^{-1})	Micropore volume [b] (cm^3 g^{-1})	Total pore volume [c] (cm^3 g^{-1})
Sn-MFI	386	0.12	0.29
Pt/Sn-MFI	347	0.12	0.23
Sn-BEA	511	0.19	0.38
Pt/Sn-BEA	454	0.19	0.27
Pt/silicalite-1	353	0.11	0.34
Pt/TiO_2	38	0	0.31
Pt/AC	1375	0.10	1.20

[a] Calculated from a P/P_0 range of 0.05-0.25 using BET equation.

[b] Calculated by the *t*-plot method.

[c] Calculated from the amount adsorbed at $P/P_0 = 0.975$.

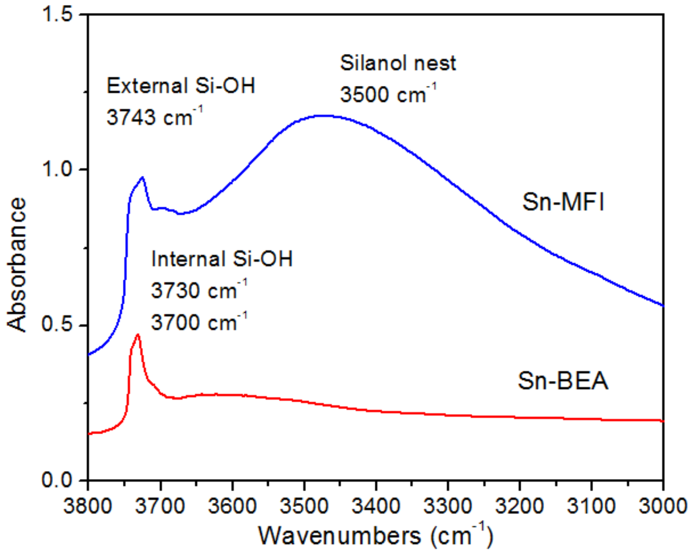

Fig. S3 FT-IR spectra in the OH-stretch region (3800-3000 cm^{-1}) of Sn-MFI and Sn-BEA zeolites. The peak at 3743 cm^{-1} arises from the silanol groups on the external surface of the zeolite whereas the bands at 3730 and 3700 cm^{-1} correspond to the silanol groups located inside the micropores of the zeolites.[4,5] The feature at around 3500 cm^{-1} is ascribed to silanol nests.[4]

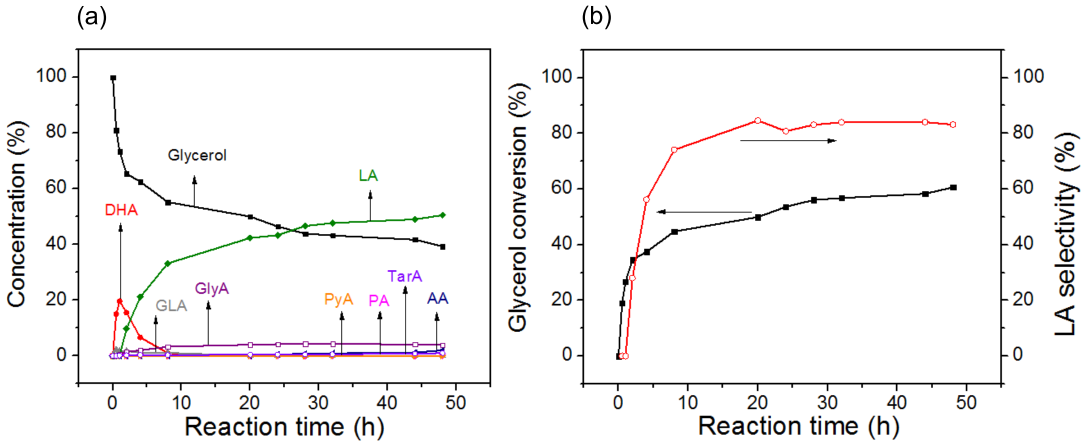

Fig. S4 (a) Concentration profile and (b) glycerol conversion and LA selectivity over a physical mixture of Pt/AC and Sn-MFI. Reaction conditions: 0.2 M glycerol in H_2O, glycerol/Pt (mol/mol) = 350, glycerol/Sn (mol/mol) = 226, pO_2 = 0.62 MPa and 100 °C.

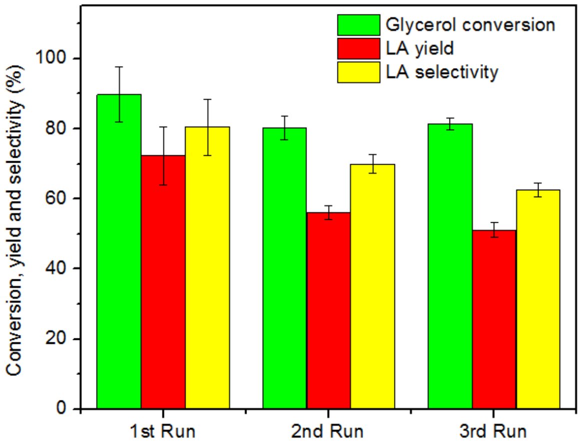

Fig. S5 Recycling of Pt/Sn-MFI catalyst after 24 h of reaction.

Table S3 Elemental analysis by ICP

	Si/Sn (initial gel)	Si/Sn (final product)
Sn-MFI	125	135
Sn-BEA	125	126

Notes and references

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