Supporting Information

Highly Efficient Production of Lactic Acid from Xylose Using Sn-Beta Catalysts

Yanfei Zhang [a,b,&], Hu Luo [a,b,&], Lingzhao Kong [a,b,*], Gai Miao [a], Xinpeng Zhao [a,b], Lijun Zhu [a,b], Shenggang Li [a,b,c], Yuhan Sun [a,b,c,*]

a. CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210 (P.R. China). E-mail: konglz@sari.ac.cn, sunyh@sari.ac.cn

b. University of Chinese Academy of Sciences, Beijing 100049 (P.R. China)

c. School of Physical Science and Technology, ShanghaiTech University, Shanghai 201203（P.R. China）

&： These two authors contribute equally.

General Information

All chemicals were used as received from the commercial suppliers:, xylose (≥98%), lactic acid (LA) (≥95 %), $SnCl_4$ $5H_2O$··(AR, ≥99.0 %), hydrofluoric acid (HF) (GR, ≥40 %), tetraethyl orthosilicate (TEOS) (99.9 %), tetraethylammonium hydroxide (TEAOH) (99.99 %), glucose (AR, 99.0 %), glycolaldehyde dimer(AR，≥94 %), 1,3-dihydroxyacetone (DHA) (GC, ≥95 %), pyruvaldehyde (PAL) (40.0 %), glyceraldehyde (GLY) (≥99.0 %). All reactions were performed in a 100.0 mL Parr pressure reactor. Centrifugation of the reaction mixture was performed on Thermo LYNX6000 (3000 rpm, 10 min).

Carbon-13 Nuclear Magnetic Resonance Spectrometry (^{13}C NMR): Agilent 500 MHz (125MHz), The product was dissolved in D_2O and scanned 1024 times.

X-Ray powder diffraction (XRD) patterns of the catalysts were performed on Rigaku Ultima IVX-Ray diffractometer using Cu Kα radiation in the 2θ range from 5 ° to 80 ° at a scan rate of 2°/min.

Scanning electron microscope (SEM) analysis: The Supra 55 Sapphire field emission scanning electron microscope of Carl Zeiss (shanghai) Co was used to analyze the morphology of the catalyst. The test voltage was 15 KV, catalyst powder needed to be taken for gold spraying before the test.

Pyridine adsorption Fourier-transform infrared (Py-IR): The catalyst was detected by the FT-IR Nicolet 670. Weigh out 0.05 g of catalyst, press it into a translucent sheet in a tablet press, and place it in the sample tank (the material of the sample tank and the window is quartz). The sample tank was evacuated and treated at 200 °C for 2 h, after which the temperature was lowered to room temperature and the sample background spectrum was measured. Firstly, the pyridine gas is introduced into the sample tank to absorb the saturation of the sample. Raise the sample temperature to 200 °C and hold it for 1 h to measure the spectrum at 200 °C. After that, the temperature was increased to 350 °C for 1 h, and infrared spectra of pyridine adsorption at 200 °C and 350 °C were obtained.

Analysis of specific surface area of nitrogen adsorption (BET): Micromeritics, TriStar Ⅱ3020, The sample to be tested is first degassed at 300 °C for more than 3 h, and then tested with N_2 as the medium at -196 °C.

Inductively coupled plasma-atomic emission spectrometry (ICP): Perkin Elmer Optima 8000, digest and filter a certain amount of catalyst to measure the content of Sn.

UV Vis absorption spectrum: Agilent Spectrophotometer technologies Cary 5000 UV vis-NIR, measuring wavelength range: 200-500 nm.

Total Organic Carbon (TOC): Shimadzu TOC-LCSH/CPH, Liquid products need to be diluted, range : 4 μg/L~30000 mg/L. According to the TOC results, the carbon balance was 93 % when Sn-Beta as the catalyst.

The data were recorded on the HPLC (Shimadzu LC-20A, Aminex HPX-87H Ion Exclusion Column: 300 mm × 7.8 mm. RID-10A). Analysis condition: column temperature 50 °C, injection volume 10 μL, the mobile phase 12.5 mmol/L H_2SO_4, 0.65 ml/min. After reaction, the solids were separated by filtration and the composition of the liquid phase was analyzed by HPLC. Besides the main product LA, a variety of other compounds were detected, which were comprehensively analyzed. By drawing a standard working curve with the standard product of the specific component to be tested, and then measuring the content of the component in the sample under the exact same chromatographic conditions, the concentration can be found from the working curve. Conversion and yield values were calculated based on the equations shown in the quantification part.

Recycling Test

After a typical catalytic run (0.3 g Sn-Beta catalyst, 30 ml water, 200 °C, 1 h, 4 MPa N_2), the catalyst was separated from the reaction solution by centrifugation and subsequent decantation. The solid was additionally washed with water (5*30 ml) and dried overnight at room temperature under vacuum prior to the next run.

Preparation of Sn-Beta Catalyst

Accurately weigh 30.6 g TEOS and 33.1 g TEAOH (35 %) and mix well. Stir while reacting at room temperature for 2 h. After the reaction, add 0.257 g $SnCl_4$ and continue stirring for 1 h. During the stirring process, add 0.3 wt% of dealuminated molecular sieve seed crystals, and then evaporate the ethanol and part of the water to make the material reach the following ratio: 1 SiO_2: 0.005 $SnCl_4$: 0.55 TEAOH: 0.55 HF: 7.5 H_2O. Add 3.97 g HF, the material liquid changes from sol state to solid gel, transfer it to the crystallizing kettle, and put it into the oven at 140 °C for 7 days. After taking it out, it was washed by suction filtration, dried and baked at 550 °C for 6 h.

Quantification

The yield of products was calculated based on the number of carbons in the product as follows: where represents the number of carbons and C_i is the molar concentration of the compound i, C_{xylose} indicates molar concentration of xylose before the reaction.

$$\text{Yield /\%} = (C_i / C_{xylose}) \times 100\ \%$$

Conversion was based on the molar carbon concentration of the compounds according to the equations below, where C_{xylose} indicates molar carbon concentration of xylose before the reaction and C_{xylose}' indicates molar carbon concentration of xylose after the reaction.

$$\text{Conversion /\%} = (C_{xylose\ -}\ C_{xylose}') / C_{xylose} \times 100\ \%$$

Conversion of Xylose to Lactic Acid

In a typical experiment, the catalyst (0.3 g unless otherwise stated) was placed in an intermittent high-pressure reactor (100 mL), and deionized water (30 mL) were added. The reactor was sealed and placed in a heating sleeve at the desired temperature. After the indicated reaction time, the reactor was cooled down with an ice-water bath and subsequently carefully opened.

Table S1: Examples of different catalysts for the conversion of various biomass to lactic acid.

Feedstocks	Temperature	Catalysts	Reaction	Yield of LA	References

	/°C		time	/ %	
Glucose	200	Sn-Beta	0.5 h	67.1	1
Glucose	200	Sn-BEA	1.0 h	24.0	2
Xylose	200	Sn-BEA	1.0 h	9.0	
Xylose	120	Ortho-Nb_2O_5	2.0 h	56.0	3
Xylose	120	$Sc(OTf)_3$	2.0 h	27.0	
Xylose	190	Sn-Beta-NH_2	4.0 h	58.0	4
Cellulose	240	$Er(OTf)_3$	0.5 h	※89.6	5
1,2-propanediol	90	AuCu/TiO_2	1.0 h	94.0	6
Cellulose	210	Sn-KIT-6-SO_3H	1.0 h	16.0	7
Dihydroxyacetone	160	Nb_2O_5	1.0 h	98.0	8
Glucose	140	Nb_2O_5	5.0 h	3.2	9
Glucose	140	$YNbO_4$	5.0 h	19.6	
Glucose	140	MgO	5.0 h	17.5	
Glucose	140	ZrO_2	5.0 h	9.6	
Glucose	140	ZrO_2	5.0 h	9.6	
Glucose	180	Al-Zr	2.0 h	34.0	10
Glucose	300	ZnO	60.0s	28.0	11
Fructose	300	ZnO	40.0s	30.0	11
Glycerin	100	Pt/Sn-MFI	1.0 h	70.0	12
Glyceraldehyde	60	H-USY	6.0 h	61.0	13
Sucrose	190	Zn-Sn-Beta	2.0 h	54.0	14

*: The yield of products was calculated based on the molar yield.

Table S2: Catalyst recycling experiments.

Cycles	Conversion/%	Yield/ %
		LA
1	99.9	69.1
2	99.8	65.3
3	99.5	63.0
4	99.5	62.8
5	99.6	64.1
Regeneration	99.7	67.9

Reaction conditions: 200 °C, 1 h, 30.0 mL deionized water, 4 MPa N_2, 300.0 mg Sn-Beta catalyst, 300.0 mg xylose.

Table S3: Leaching tests during catalyst recycling for Sn-Beta catalyst.

Cycles	※Sn (mg/L)	#Sn (wt%)
Before reaction	-	0.78
1	0	0.78
5	0	0.69

Reaction conditions: 200 °C, 1 h, 30.0 mL deionized water, 4 MPa N_2, 300.0 mg Sn-Beta catalyst, 300.0 mg xylose.

※Sn (mg/L): The Sn concentration in solution after reaction by ICP.

#Sn (wt%): The percentage mass content of Sn in Sn-Beta catalyst.

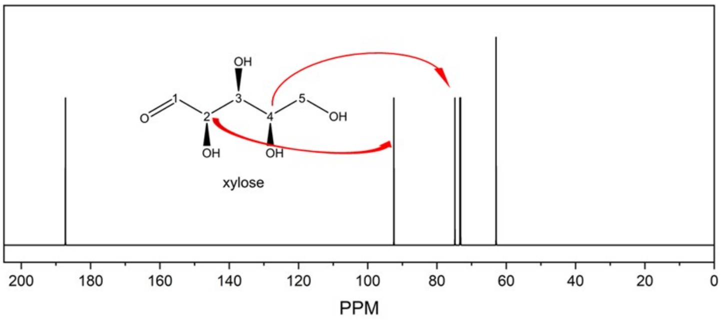

Fig. S1: Standard ^{13}C NMR of xylose

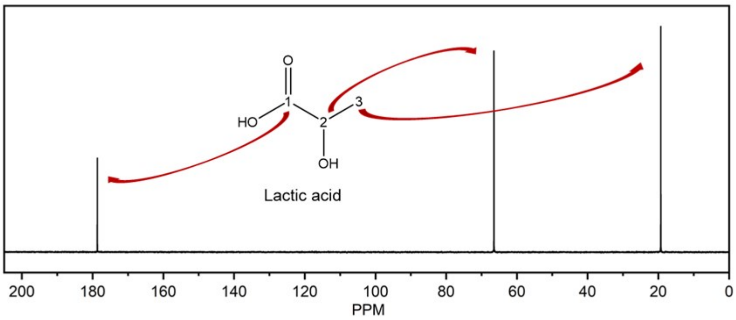

Fig. S2: Standard ^{13}C NMR of lactic acid

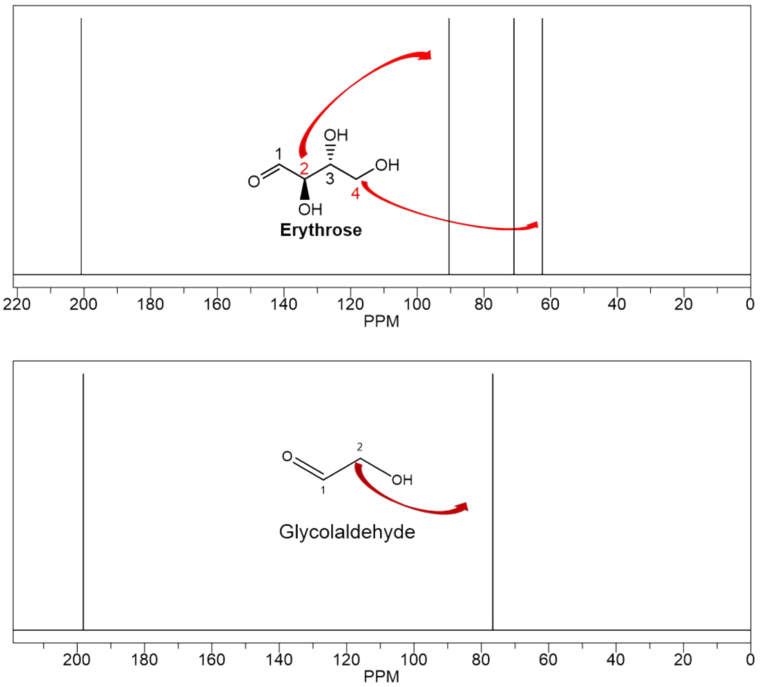

Fig. S3: Standard ^{13}C NMR of erythrose and glycolaldehyde

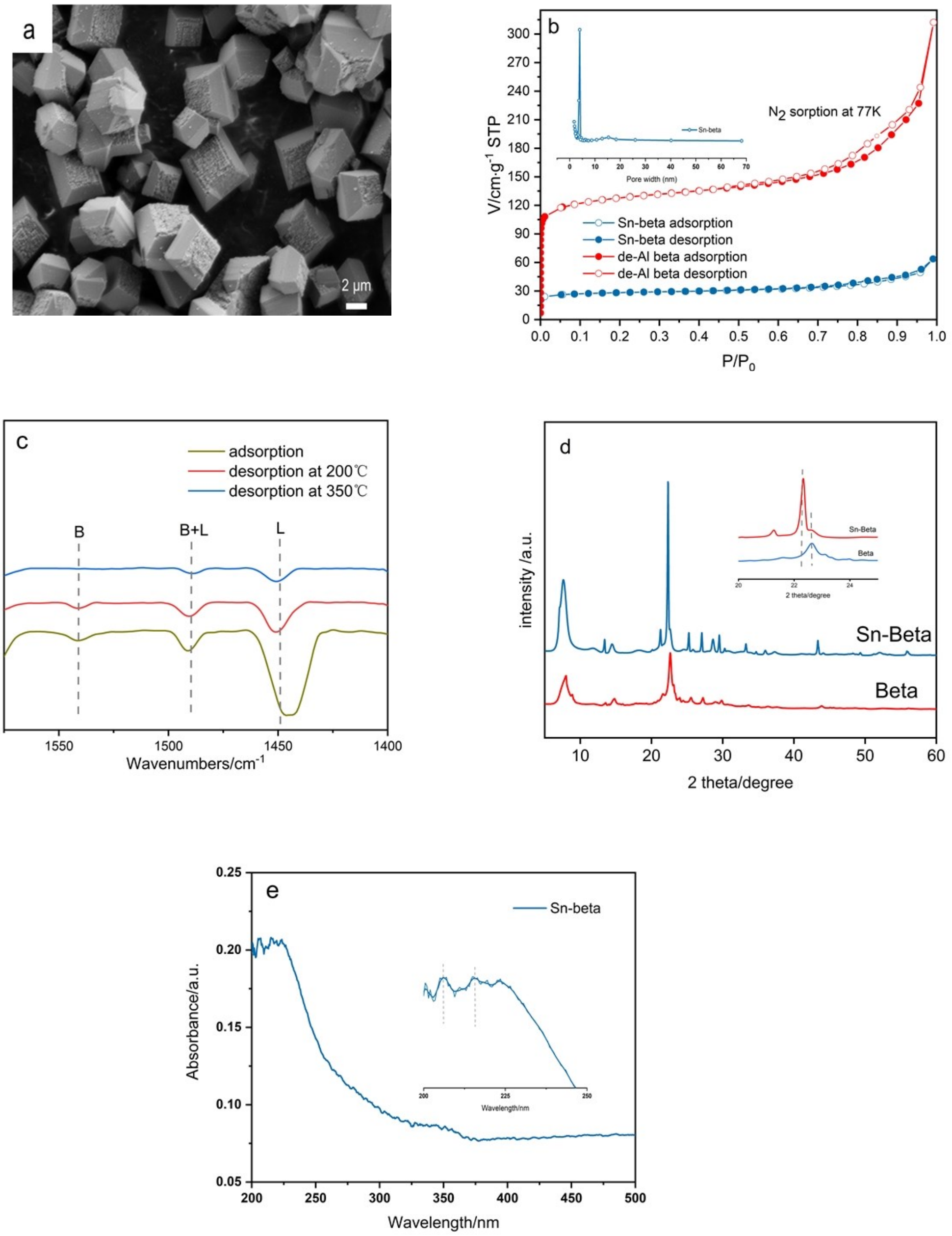

Fig. S4: Illustration: (a) SEM micrograph of Sn-Beta. (b) Hysteresis loop and pore size distribution of Sn-Beta and Beta. (c) Py-IR of Sn-Beta. (d) XRD patterns of Sn-Beta and Beta. (e) UV-Vis of Sn-Beta.

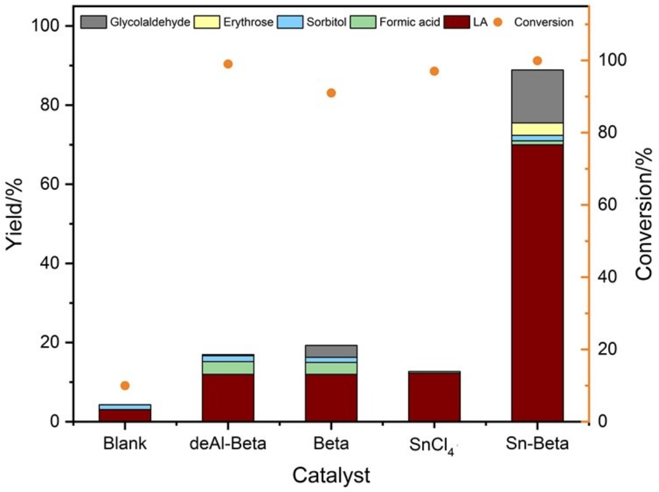

Fig. S5: Product distributions of xylose from different catalysts. Reaction conditions: 300.0 mg xylose, 300.0 mg catalyst, 200 °C, 30 mL deionized water, 4 MPa N_2, 1 h.

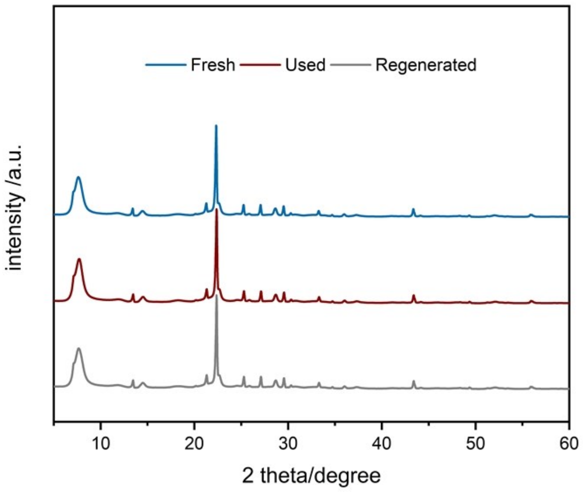

Fig. S6: XRD patterns of the fresh, used and regenerated Sn-Beta catalyst by calcination at 550 °C for 3 h.

Reference:

1. Y. Y. Sun, L. Shi, H. Wang, G. Miao, L. Z. Kong, S. G. Li, Y. H. Sun, Sustain. Energ. Fuels 2019, **3**, 1163-1171.
2. H. S. Chen, A. Wang, H. Sorek, J. D. Lewis, Y. Roman-Leshkov, A. T. Bell, Chemistryselect 2016, **1**, 4167-4172.
3. K. Nakajima, J. Hirata, M. Kim, N. K. Gupta, T. Murayama, A. Yoshida, N. Hiyoshi, A. Fukuoka, W. Ueda, ACS. Catal 2018, **8**, 283-290.
4. L. Kong, Z. Shen, W. Zhang, M. Xia, M. Gu, X. Zhou, Y. Zhang, ACS. Omega 2018, **3**, 17430-17438.
5. F. F. Wang, C. L. Liu, W. S. Dong, Green. Chem. 2013, **15**, 2091-2095.
6. F. Du, H. Wang, X. Jin, W. Deng, C. Li, Z. Ren, H. Yan, B. Yin, Catal. Lett 2019, **149**, 1037-1045.
7. W. Cai, Q. Chen, H. Xuan, C. Li, H. Yu, L. Cui, Z. Yu, S. Zhang, F. Qu, Korean. J. Chem. Eng. 2019, **36**, 513-521.
8. X. Wang, Y. Song, L. Huang, H. Wang, C. Huang, C. Li, Catal. Sci. Technol. 2019, **9**, 1669-1679.
9. M. Kim, S. Ronchetti, B. Onida, N. Ichikuni, A. Fukuoka, H. Kato, K. Nakajima, ChemCatChem 2020, **12**, 350-359.
10. W. Zeng, D.-g. Cheng, F. Chen, X. Zhan, Catal. Lett. 2009, **133,** 221-226.
11. Z. Wei, F. Jin, G. Zhang, S. Zhang, G. Yao, in 2nd International Symposium on Aqua Science, Water Resource and Low Carbon Energy, Vol. **1251** (Eds.: F. M. Jin, Q. Zhou, B. Wu, L. Xie), 2010, pp. 264-267.
12. H. J. Cho, C.-C. Chang, W. Fan, Green. Chem 2014, **16**, 3428-3433.
13. P. P. Pescarmona, K. P. F. Janssen, C. Delaet, C. Stroobants, K. Houthoofd, A. Philippaerts, C. De Jonghe, J. S. Paul, P. A. Jacobs, B. F. Sels, Green. Chem 2010, **12**, 1083-1088.
14. W. Dong, Z. Shen, B. Peng, M. Gu, X. Zhou, B. Xiang, Y. Zhang, Sci. Rep. 2016, 6-10.