SUPPORTING INFORMATION

Efficient production of lactic acid from biomass-derived carbohydrates under synergistic effects of indium and tin in In-Sn-Beta zeolites

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1. The formulas of substrate conversion and products yield

The conversion and yield of the key intermediates (fructose, dihydroxyacetone, glyceraldehyde and pyruvaldehyde) was calculated based on carbon as follows:

$$\text{Carbohydrate conversion (C\%)} = \left(1 - \frac{moles\ of\ unconverted\ carbohydrates}{moles\ of\ initial\ carbohydrates}\right) \times 100\%$$

$$\text{Product yield (C\%)} = \frac{moles\ of\ carbon\ in\ the\ produt}{moles\ of\ carbon\ in\ initial\ carbohydrate} \times 100\%$$

[#] These authors contributed to the work equally.

2. Modeling of the reaction kinetics

The data-fitting was solved by using the genetic algorithm to optimize the parameters, which is built in MatlaR2019a. The kinetic model was proposed based on the following assumptions:

(1) All the reaction rate equations are proposed based on the pseudo homogeneous first-order approach.

(2) Lactic acid is the target product from glucose conversion and side products include insoluble solid (humins), identified soluble side products and unidentified soluble products.

(3) All reactions are considered irreversible except the isomerization reaction of glucose into fructose.

According to the above hypothesis and constructed reaction scheme of glucose transformation (Scheme 1), the following set of differential Eqs. (1–5) were obtained:

$$\frac{dC_G}{dt} = -K_1C_G + K_2C_F - K_6C_G \quad \text{eq.1}$$

$$\frac{dC_F}{dt} = K_1C_G - K_2C_F - K_3C_F - K_7C_F \quad \text{eq.2}$$

$$\frac{dC_D}{dt} = K_3C_F - K_4C_D - K_8C_D \quad \text{eq.3}$$

$$\frac{dC_p}{dt} = K_4C_d - K_5C_p - K_9C_p \quad \text{eq.4}$$

$$\frac{dC_{LA}}{dt} = K_5C_p \quad \text{eq.5}$$

Here, C is the molar concentration and K is the reaction rate constants. The

nomenclature of the above Eqs (1-5) are as follows. C_G, C_F, C_D, C_P and C_{LA} refer to the concentration of glucose, concentration of fructose, concentration of 1,3-diohydroxyacetone, concentration of pyruvaldehyde and concentration of lactic acid, respectively. Meanwhile, K_1, K_2, K_3, K_4, K_5, K_6, K_7, K_8 and K_9 are the kinetic constants of reaction 1, reaction 2, reaction 3, reaction 4, reaction 5, reaction 6, reaction 7, reaction 8, reaction 9 respectively. The all reaction rate constants for kinetic studies of glucose transformation were computed as follows:

The initializing genetic parameters include evolutionary algebra, population size, crossover probability and mutation probability, and their values are 2000, 100, 0.5 and 0.2, respectively. The fitness calculation formula is according to eq.6.

error=mean(abs(glu-GLU(obt))/length(glu)+abs(fru-FRU(obt))/length(fru)+abs(la-LA(obt))/length(la),'omitnan')*1000 eq.6

3. Supporting Figures

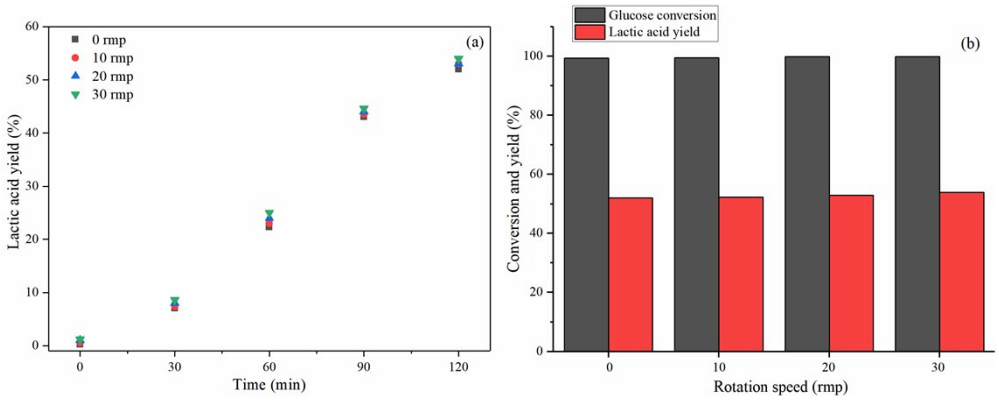


Fig. S1 (a) Effect of rotation speed on lactic acid yield with time; Reaction conditions: glucose, 7.5 mmol C; catalyst, 200 mg; H_2O, 10 mL; reaction temperature, 190 °C. **(b) Effect of**

rotation speed on glucose conversion and lactic acid yield; Reaction conditions: glucose, 7.5 mmol C; catalyst, 200 mg; H_2O, 10 mL; reaction temperature, 190 °C; reaction time, 2 h.

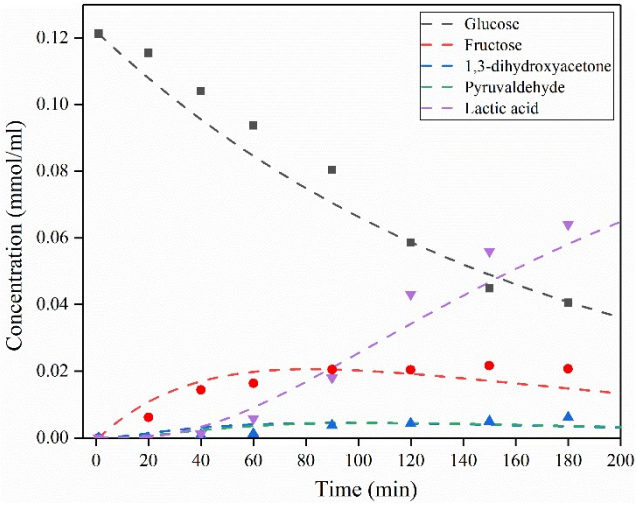


Fig. S2. Comparison of experimental data (points) and kinetic models (dashed lines) for the glucose conversion. Reaction conditions: glucose, 225 mg; water, 10 ml; In-Sn-Beta catalyst, 200 mg; reaction temperature, 170°C.

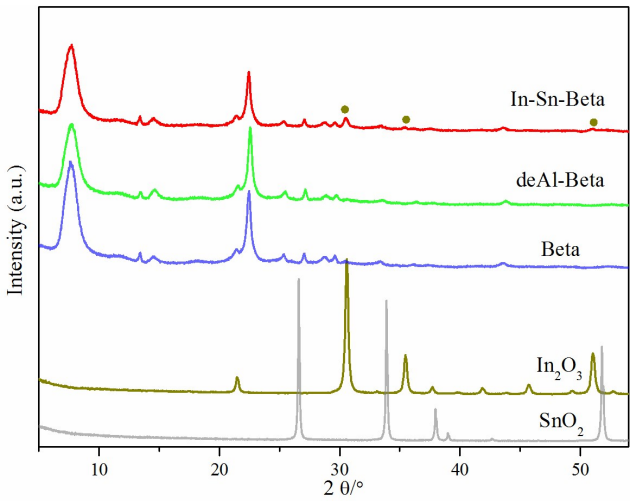


Fig. S3. XRD of SnO_2, In_2O_3, Beta, deAl-Beta and In-Sn-Beta zeolites.

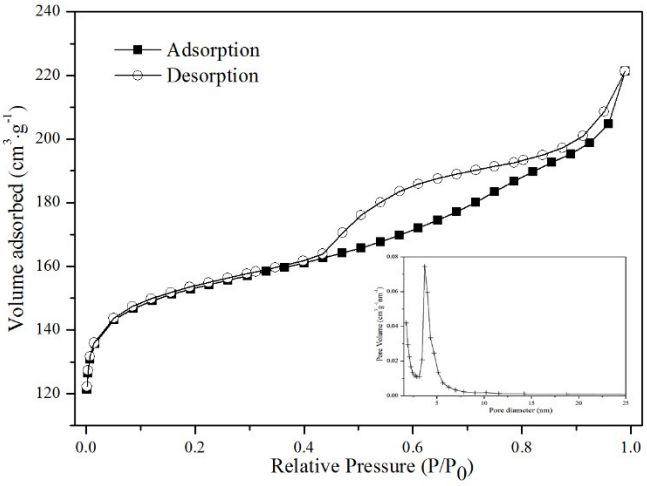


Fig. S4. Nitrogen adsorption/desorption isotherm and pore size distributions of In-Sn-Beta zeolite.

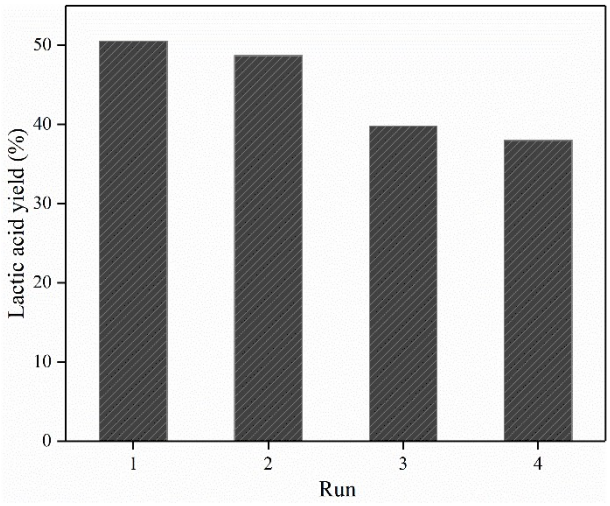


Fig. S5. Recycling of In-Sn-Beta zeolite for the conversion of glucose to lactic acid. Reaction conditions: glucose, 225 mg; water, 10 ml; In-Sn-Beta catalyst, 200 mg; reaction temperature, 190°C, reaction time, 2h.

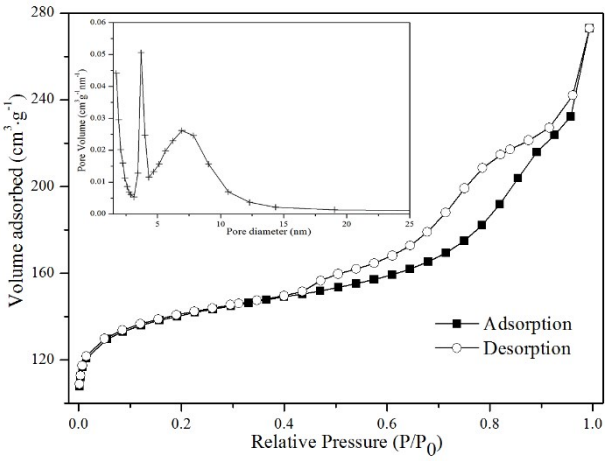


Fig. S6. Nitrogen adsorption/desorption isotherm and pore size distributions of the 2nd used In-Sn-Beta zeolite

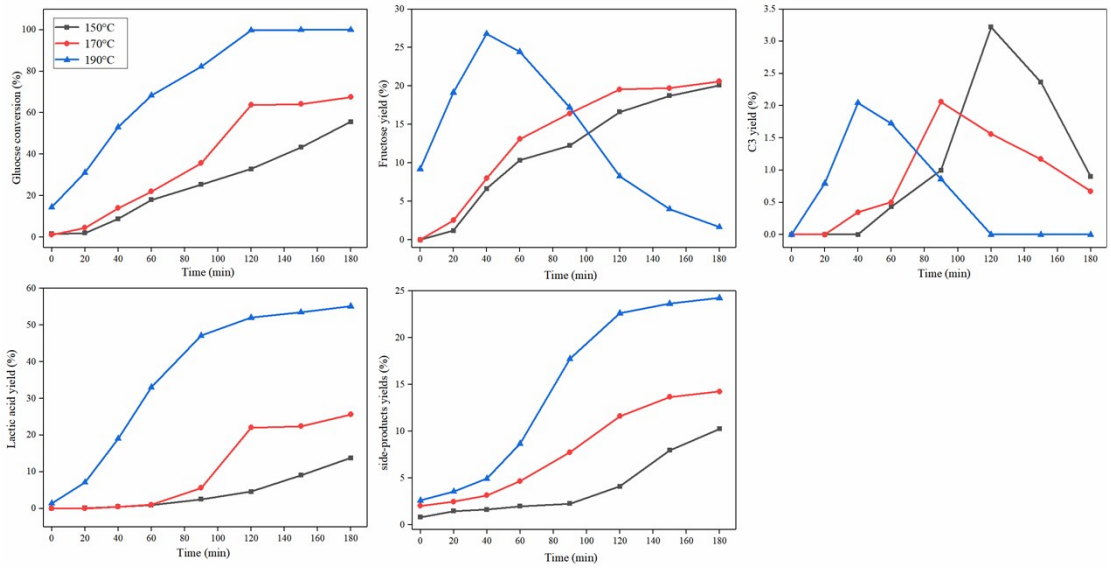


Fig. S7. Glucose conversion at different temperatures with time. Reaction conditions: glucose, 225 mg; In-Sn-Beta catalyst, 200 mg; water, 10 ml.

4. Supporting Tables

Table S1. Comparison with previous kinetic studies

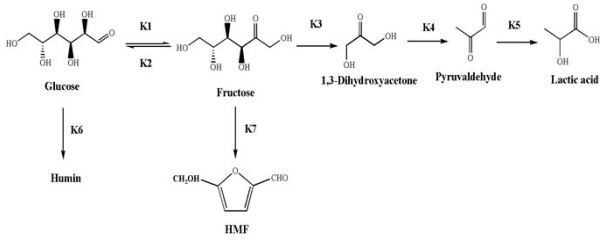
Reaction	Reaction conditions	Ea ($KJ.mol^{-1}$)	Ref
Glucose ⟶ Fructose (isomerization)	100°C triethylamine	61	[1]
	75°C -90°C Sn-Beta	95.28	[2]
	130°C $CrCl_3$	100 ± 5	[3]
	Ti-BEA	155	[4]
Glucose ⟶ Humins	130°C $CrCl_3$	71 ± 19	[3]
	130°C HCl	51 ± 2	
Fructose ⟶ Humins	130°C $CrCl_3$	114 ± 6	[3]
	130°C HCl	133 ± 7	
	190°C Cr-Sn-Beta	Ea_1=56.6 Ea_2=52.0 Ea_3=80.1 Ea_4=68.0 Ea_5=67.3 Ea_6=18.8 Ea_7=48.2	[5]

Table S2. Conversion of glucose using different catalysts.

Entry	Catalyst	Con.	Yield (%)					
		(%)	Lactic acid	Formic acid	Acetic acid	Glycollic acid	Acetol	HMF
1	No catalyst	21	1.1	3.6	0.2	3.0	0	3.3
2	Beta	78	5.2	2.1	0.6	3.1	0.1	14.6
3	deAl-Beta	37	1.3	1.8	0.1	2.4	1.0	7.1
4	In-Sn-Beta	100	53.0	4.0	3.0	2.0	1.7	4.9
5[a]	SnO_2[a]	92	2.8	2.1	1.6	1.7	0.3	5.8
6[a]	In_2O_3[a]	94	4.7	3.2	1.4	2.4	0.6	7.3
7[a]	SnO_2+ In_2O_3[a]	95	3.6	2.5	2.6	2.0	0.7	6.0

[a] Equivalent molar amount of Sn or In as for 160 mg of In-Sn-Beta. Reaction conditions: glucose, 225 mg; water, 10 ml; catalyst, 160 mg; reaction temperature, 190°C, reaction time, 2 h. The yield is calculated on a carbon basis.

Table S3. Physicochemical properties of regenerated catalyst

Run	S_{BET}	V_{total}	$V_{micropore}$	In	Sn	Brønsted acid	Lewis acid
number	$m^2 \cdot g^{-1}$	$ml \cdot g^{-1}$		$mmol \cdot g^{-1}$		$mmol \cdot g^{-1}$	
1	576	0.358	0.181	0.29	0.12	0	0.08
2	518	0.434	0.143	0.26	0.12	0	0.04
3	514	0.447	0.140	0.25	0.12	0	0.03
4	513	0.453	0.143	0.25	0.12	0	0.03

Table S4. Catalytic performances of In-Sn-Beta zeolites for the different substrates

Entry	Substrates	Conversion	Yield (%)			
		(%)	HMF	Formic acid	Acetic acid	HSP[a]
1	Fructose	81.5	2.8	1.6	0.9	24.7
2	Dihydroxyacetone	92	-	2.7	2.1	10.3
3	Pyruvaldehyde	100	-	2.2	2.7	8.7
4	HMF	43	-	5.6	-	25.7

[a] Humins and undefined solubility byproducts. Reaction conditions: substrates, 7.5 mmol C; water,

10 ml; catalyst, 200 mg; reaction temperature, 170°C, reaction time, 2h.

Table S5. Rate constants in different reaction temperature

Temperature	Reaction rate constant (min^{-1}) [a]								
(°C)	K_1	K_2	K_3	K_4	K_5	K_6	K_7	K_8	K_9
150	0.00311	6.31E-05	0.00613	0.05341	0.06796	3.51E-06	1.89E-05	1.79E-05	6.27E-06
170	0.00608	7.07E-05	0.02170	0.07872	0.07805	2.04E-05	4.29E-05	4.20E-05	4.28E-05
190	0.02019	8.49E-05	0.04228	0.08157	0.09675	7.84E-05	7.89E-05	0.000842	0.000746

[a] Reaction rate constants correspond to the pathway in scheme 1.

Table S6. Catalytic performances of In-Beta, Sn-Beta and In-Sn-Beta zeolites for the conversion of C3 intermediates

Entry	Substrate	Catalyst	Conversion (%)	Yield (%)			
				LA	GLY	PHY	DHA
1	Pyruvaldehyde	In-Beta	42.9	19.7	7.3	-	-
2	Pyruvaldehyde	Sn-Beta	95.5	36.6	1.9	-	-
3	Pyruvaldehyde	In-Sn-Beta	83.2	28.7	0.9	-	-
4	Glyceraldehyd	In-Beta	89.3	3.1	-	16.7	67.8
5	Glyceraldehyd	Sn-Beta	92.1	28.3	-	1.1	2.3
6	Glyceraldehyd	In-Sn-Beta	93.6	11.2	-	11.4	69.7

Reaction conditions: substrates, 7.5 mmol C; water, 10 ml; catalyst, 200 mg; reaction temperature, 170°C, reaction time, 0.5 h.

References:

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