SUPPORTING INFORMATION

Synergistic effects of bimetals and hierarchical structures in Mg-Sn-Beta-H zeolites for lactic acid synthesis from biomass-derived carbohydrates

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Text

1. The formulas of substrate conversion and products yield

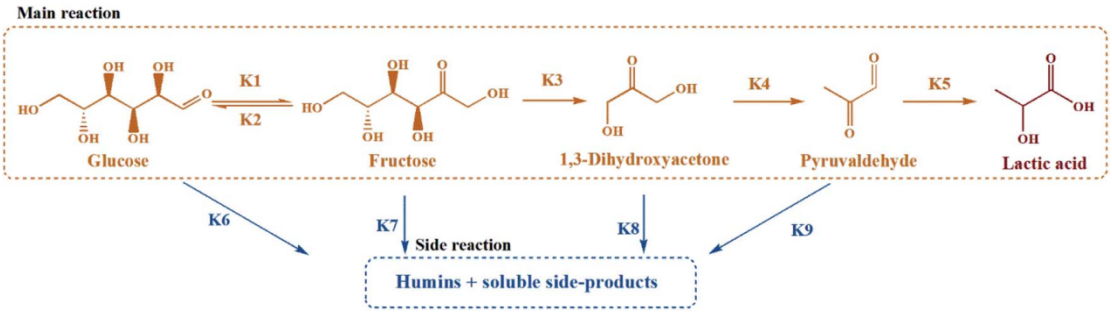
The conversion and yield of the key intermediates (fructose, dihydroxyacetone, glyceraldehyde and pyruvaldehyde) was determined based on carbon as follows:

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

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

2. Modeling of the reaction kinetics

From the point of view of kinetic calculation, considering the main reaction steps and the competing side reaction steps, a simplified kinetic model had been proposed in our previous work, as shown in Scheme S1, and the kinetic model was proposed based on the following assumptions:



Scheme S1 Proposed simplifiied kinetic model for the conversion of glucose.

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

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

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

According to the above hypothesis and proposed reaction scheme of glucose decomposition (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. In order to reduce the accumulated errors in the step-by-step process, the concentration of lactic acid formation was solved using the K_L parameter, which represented the total reaction rate from fructose to lactic acid. 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

Figure S1-S9

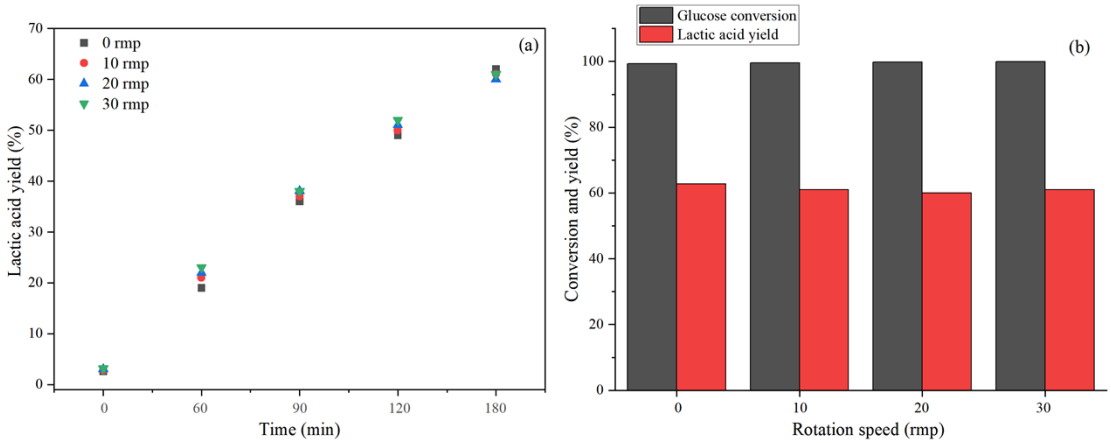


Figure S1. (a) Effect of rotation speed on glucose conversion with time; (b) Effect of rotation speed on glucose conversion and lactic acid yield. (Reaction conditions: 200 mg Mg-Sn-Beta-H-2 , 375 mg substrate, 190℃, 3 h.)

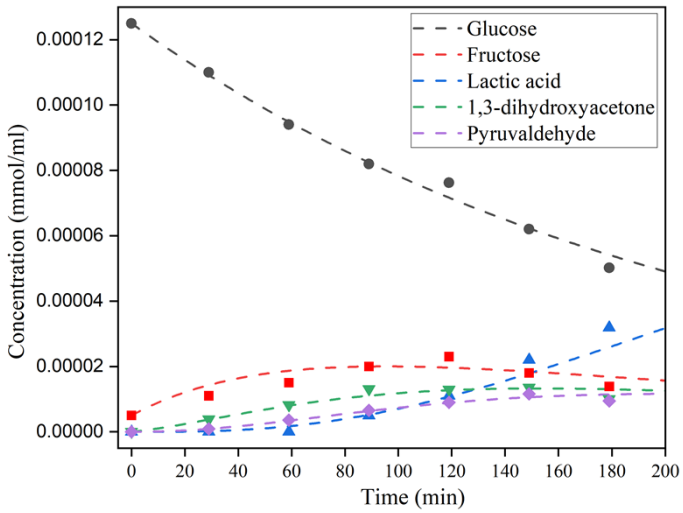


Figure S2. Comparison of experimental data (points) and kinetic models (dashed lines) for the glucose conversion. (Reaction conditions: 200 mg Mg-Sn-Beta-H-2 , 225 mg substrate, 170℃, 3

h.)

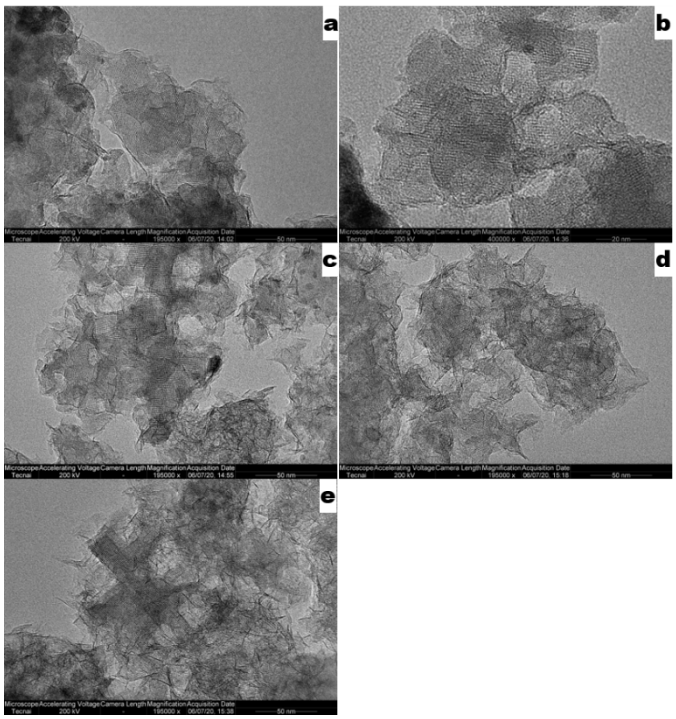


Figure S3. TEM images of Mg-Sn-Beta-H with different Mg loading. (a) Mg-Sn-Beta-H-1, (b) Mg-Sn-Beta-H-2, (c) Mg-Sn-Beta-H-3, (d) Mg-Sn-Beta-H-4, (e) Mg-Sn-Beta-H-5.

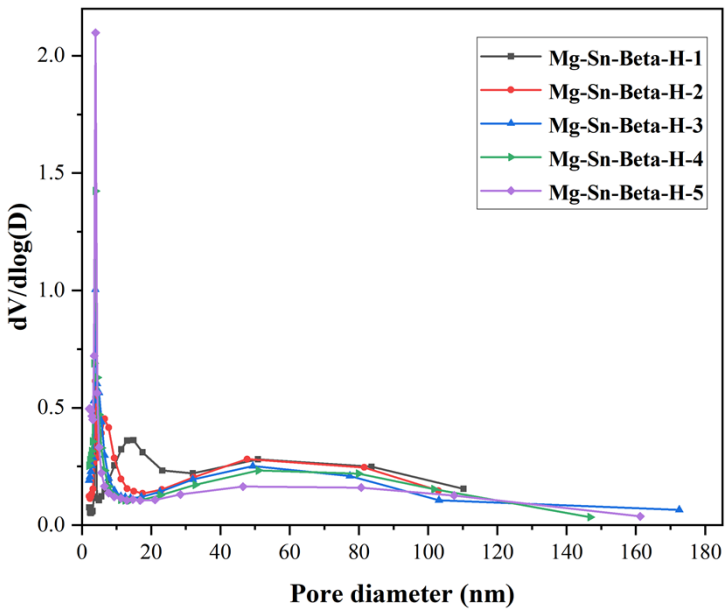


Figure S4. The pore size distribution of different Mg-Sn-Beta-H catalysts

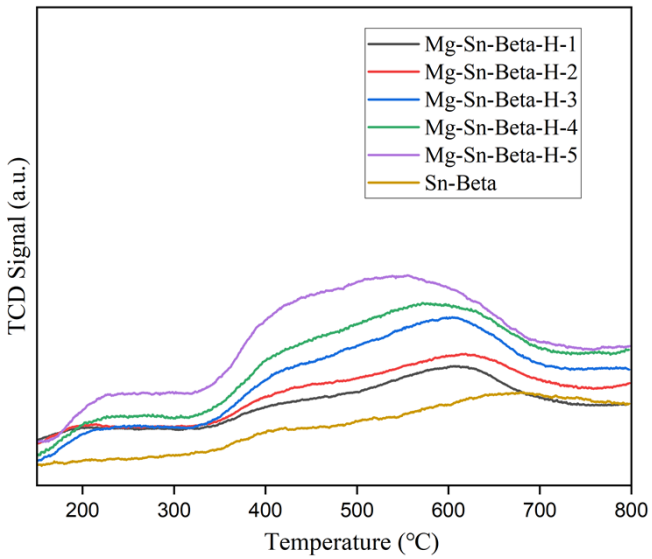


Figure S5. CO_2-TPD results for different catalysts.

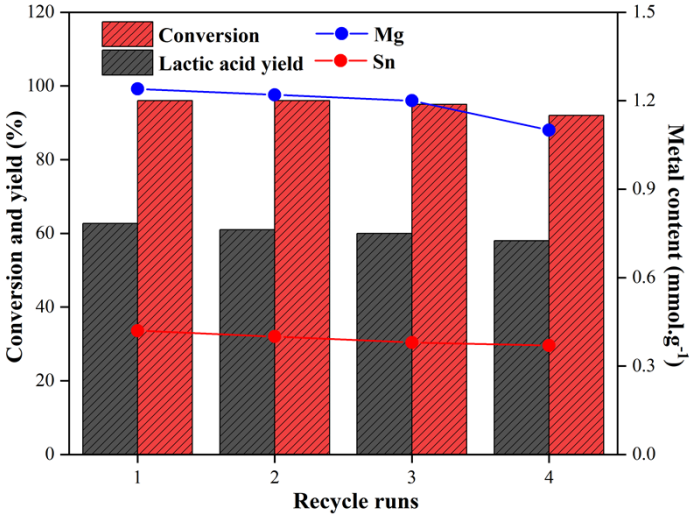


Figure S6. Reusability and metal leaching of catalysts (Reaction condition: 200 mg Mg-Sn-Beta-H-2 , 375 mg substrate, 190 °C, 3 h)

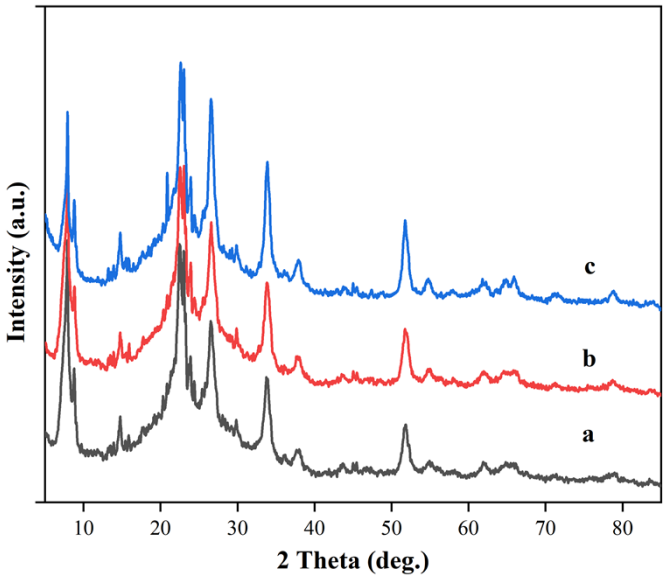


Figure S7. X-ray diffraction patterns of fresh and regenerated catalysts (a) use once, (b) use three times, (c) fresh catalyst

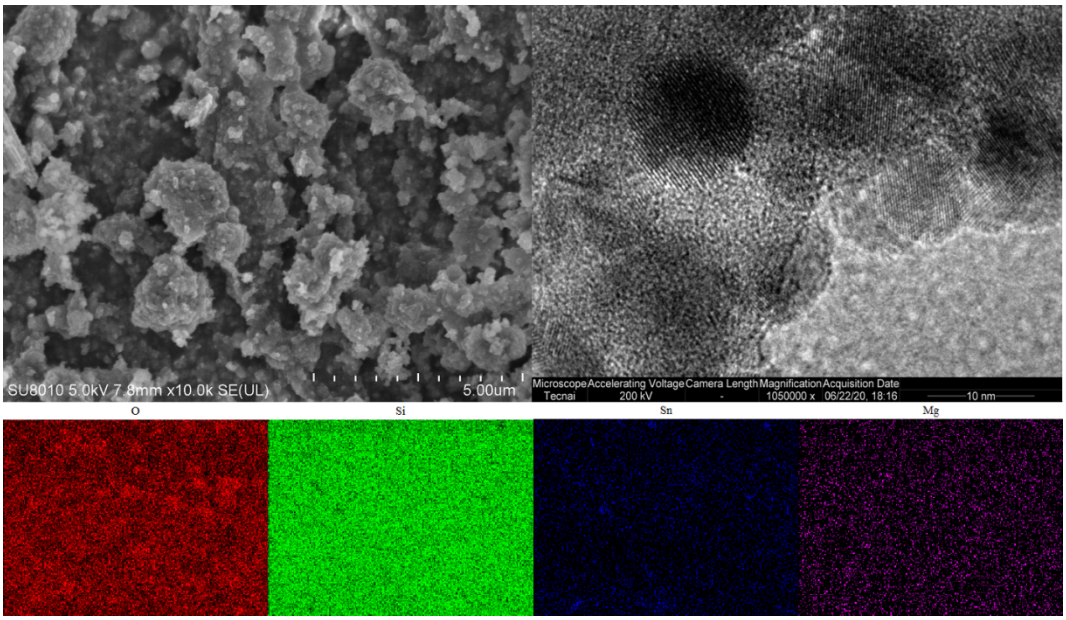


Figure S8. TEM and SEM of reuse catalyst

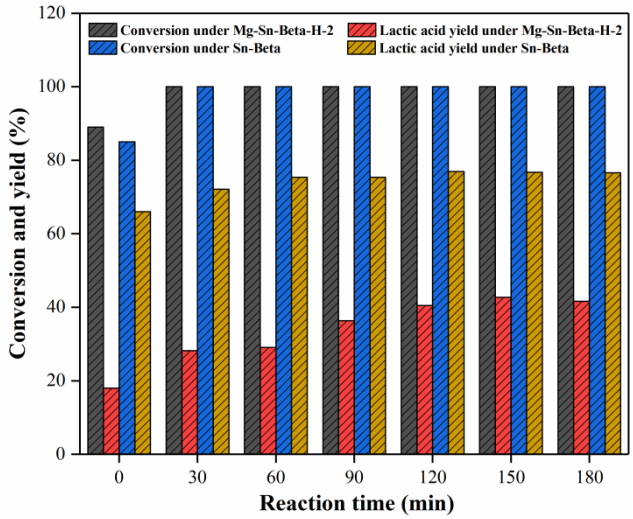


Figure S9. Mg-Sn-Beta-H-2 catalyses the time series of glucose to produce lactic acid. (Reaction conditions: 225 mg dihydroxypropanone, 200 mg catalyst, reaction temperature 190℃.)

Table S1-S3

Table S1 Kinetic parameters determined for reactions shown in Scheme 1

Catalyst	Parameter	Reaction									
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**G**
Sn-Beta	K (min^{-1})	0.0333	0.0060	0.0190	0.0987	0.0953	0.0018	0.0010	0.0004	0.0004	0.0351
Mg-Sn-Beta-H-2		0.0169	0.00006	0.0517	0.0679	0.0719	0.00008	0.00007	0.0009	0.0008	0.0170
Mg-Sn-Beta-H-2	E_A ($KJ \cdot mol^{-1}$)	57.8	113.2	56.8	50.1	47.2	140.2	175.2	91.5	102.2	57.9
	R^2	0.9030	0.9361	0.9805	0.9773	0.9875	0.9443	0.9561	0.9552	0.9576	0.9047

Table S2 The yield of lactic acid obtained from various biomass over Mg-Sn-Beta-H-2 zeolite[a]

Entry	Catalyst	Substrate	Conversion (%)	Lactic acid yield (%)
1	Mg-Sn-Beta-H-2	Sucrose	68.9	43.8
2	Sn-Beta	Sucrose	44.7	33.1
3	Mg-Sn-Beta-H-2	Starch	67.6	25.8
4	Sn-Beta	Starch	36.9	12.6
5	Mg-Sn-Beta-H-2	Cellulose	23.9	18.8
6	Sn-Beta	Cellulose	10.2	7.1
7	Mg-Sn-Beta-H-2	Miscanthus	26.8	34.6
8	Sn-Beta	Miscanthus	17.1	18

[a] Reaction conditions: 213 mg sucrose, 250 mg Starch, 250 mg Cellulose, 200 mg Miscanthus, 200 mg catalyst, reaction time 2 h, reaction temperature 210℃.

Table S3 Comparison of the yields for lactic acid or its esters from large molecular biomass conversion under heterogeneous catalysis

Catalytic system	Substrate	Ratio of substrate to catalyst	Catalyst	Solvent	T (°C)	P_{N2} (MPa)	Time (h)	Conversion %	Yield % (Product name)	Reference
Heterogeneous catalysis	Cellulose	2/1	Zr-SBA-15	95%MeOH	240	4	10	-	28.1 (ML)	Yang et al., 2016[1]
	Starch	2/1	Zr-SBA-15	95%MeOH	240	4	10	-	26.8 (ML)	Yang et al., 2016[1]
	Xylan	0.8/1	ZrO_2	H_2O	190	2.4	1.5	-	30.0 (LA)	Yang et al., 2015[2]
	Oakwood sawdust	4/1	Ga-doped Zn/H-nanozeolite Y	MeOH	300	1	1	63	11.24 (ML)	Vema et al.,2017[3]
	Pine wood	2.35/1	ZrW	H_2O	190	-	10	-	5.0 (LA)	Swesi et al., 2017[4]
	Miscanthus	0.67/1	Cr-Sn-Beta	H_2O	240	-	1	19.6	33.4 (LA)	Xia et al.,2019[5]
	Microalgae residue	0.75/1	Fe-Sn-Beta	H_2O	210	-	2	56.1	33.9 (LA)	Xia et al.,2020[6]
	Miscanthus	1/1	Mg-Sn-Beta-H-2	H_2O	210		2	26.8	34.6 (LA)	This work

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