Electronic Supplementary Information (ESI)

Transformation of cellulose and related carbohydrates into lactic acid with bifunctional Al(III)-Sn(II) catalysts

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1. Catalytic performances of various dual-cation catalysts for the conversion of fructose

Fig. S1 Conversion of fructose into lactic acid catalysed by various dual-cation combinations. Reaction conditions: fructose, 0.56 mmol; dual metal cations (metal/metal ratio = 1/1), 0.10 mmol; H₂O, 20 mL; N₂, 3 MPa; 463 K; 2 h.

2. Effect of counter anions on conversion of cellulose

Catalyst	Conversion	Yield (%)				
	(%)	Glucose	Fructose	Lactic acid	Others	
$Al_2(SO_4)_3 + SnSO_4$	84	0.6	0.5	65	17	
$AlCl_3 + SnSO_4$	82	0.4	0	65	15	
$Al_2(SO_4)_3 + SnBr_2$	83	0.4	0.6	64	16	
$AlCl_3 + SnBr_2$	82	0.4	0.2	64	17	
$AlCl_3 + SnCl_2$	82	0.5	0	64	15	
$Al_2(SO_4)_3 + SnI_2$	85	0.4	0	64	18	
$AlCl_3 + SnI_2$	84	0.5	0.3	66	16	

Table S1 Catalytic performances of Al(III) and Sn(II) salts with different counter anions for the conversion of cellulose

Reaction conditions: cellulose, 0.10 g (glucose unit: 0.62 mmol); metal cations [Al(III)/Sn(II) = 1/1], 0.10 mmol; H₂O, 20 mL; N₂, 3 MPa; 463 K; 2 h. Others include levulinic acid and 5-hydroxymethylfurfural.

3. Conversions of microcrystalline cellulose and other biomasses with the Al(III)-Sn(II) catalyst

Substrate	Reaction	Conversion	Yield (%)				
	time (h)	(%)	Glucose	Fructose	Glyceraldehyde	Lactic acid	
Cellulose ^a	2	83	0.5	0.3	3.9	65	
Cellulose ^b	2	51	0.1	0	0.2	36	
Starch	2	99	0	0	5.2	71	
Inulin	2	99	0.5	1.2	1.2	81	
Cellobiose	2	99	1.2	0.5	3.6	80	
Glucose ^c	0.5	99	-	0.2	4.2	89	

Table S2 Conversions of microcrystalline cellulose and other biomasses catalysed by Al(III)

 Sn(II) catalyst

Reaction conditions: substrate, 0.10 g (hexose unit: 0.62 mmol except for glucose); Al(III)-Sn(II) cations [Al(III)/Sn(II) = 1/1], 0.10 mmol; H₂O, 20 mL; N₂, 3 MPa; 463 K.

^{*a*} Ball-milled cellulose.

^b Microcrystalline cellulose.

^c 0.56 mmol.

4. Conversions of glucose and fructose with high concentrations by the Al(III)-Sn(II) catalyst

Table S3 Conversions of glucose and fructose with different concentrations in the presence of Al(III)-Sn(II) catalyst

Substrate	Conc.	Conv.	Yield (%)					
	(wt%)	(%)	Glucose	Fructose	Lactic acid	Levulinic acid	Others	
Glucose	10	100	/	0.1	13	14	7.4	
	5	100	/	0	29	11	6.4	
	2.5	100	/	1.8	51	7.0	5.5	
Fructose	10	100	0	/	14	14	7.6	
	5	100	0	/	30	12	7.5	
	2.5	100	0	/	52	9.0	7.7	

Reaction conditions: Al(III)-Sn(II) cations [Al(III)/Sn(II) = 1/1], accounting for 18 mol% of substrate; H₂O, 20 mL; N₂, 3 MPa; 453 K; 2 h. Others include 5-hydroxymethylfurfural, glyceric acid, acetic acid and formic acid. The formation of humins was also observed.





Fig. S2 Time course for conversion of glucose catalysed by Al(III)-Sn(II) catalyst. Reaction conditions: glucose, 0.10 g (0.56 mmol); Al(III)-Sn(II) cations (molar ratio = 1/1), 0.10 mmol; H₂O, 20 mL; N₂, 3 MPa; 423 K.

6. Analysis of residue in the Sn(II)-catalysed conversion of fructose by the MALDI-TOF technique



Fig. S3 MALDI-TOF spectrum for the residue in the conversion of fructose catalysed by Sn(II). Reaction conditions: fructose, 0.10 g (0.56 mmol); Sn(II), 0.10 mmol; H₂O, 20 mL; N₂, 3 MPa; 383 K; 2 h.

7. Time courses for the conversions of glyceraldehyde and pyruvaldehyde catalysed by Sn(II)

Time	Conversion	Yield (%)						
(h)	(%)	Glucose	Fructose	Pyruvaldehyde	Lactic acid	Dihydroxyacetone	Others	
0.5	8.5	0.3	0.6	7.5	0	0	0.1	
1.0	17	0	0.9	14	0	0	2.0	
1.5	29	0.6	0.8	21	1.7	1.3	4.1	
2.0	48	0.7	1.0	33	3.6	1.7	8.0	
3.0	58	0.8	0.9	39	5.0	2.3	9.9	

Table S4 Time course for the Sn(II)-catalysed conversion of glyceraldehyde

Reaction conditions: glyceraldehyde, 0.10 g (1.1 mmol); Sn(II), 0.050 mmol; H₂O, 30 mL; N₂, 3 MPa; 383 K. Others include humins and unknown polymeric products.

Table S5 Time course for the Sn(II)-catalysed conversion of pyruvaldehyde

Time	Conv.	Yield (%)							
(h)	(%)	Glucose	Fructose	Lactic acid	Glyceraldehyde	Dihydroxyacetone	Others		
0.5	16	0.9	0	2.9	10	2.1	0.1		
1.0	29	0	0	4.2	12	2.2	11		
1.5	42	0.6	0	4.8	8.7	2.6	26		
2.0	52	0.6	0	7.0	9.8	2.8	31		
3.0	58	0.3	0	10	9.6	2.5	35		

Reaction conditions: pyruvaldehyde, 0.10 g (1.1 mmol); Sn(II) cation, 0.05 mmol; H₂O, 30 mL; N₂, 3 MPa; 383 K. Others include humins and unknown polymeric products.

8. DFT studies on the key steps in the conversion of glucose to lactic acid



(1) Al(III)-catalysed isomerization of glucose to fructose

Fig. S4 Optimized geometries of Al(III)-(glucose)₂in different deprotonated forms.

 $(Glu-Al-Glu)^{3+} + H_8O_4 \rightarrow (Glu-Al-Glu)^{2+}_2 + H_9O_4^{+} \Delta G = -10.1 \text{ kcal/mol}$ (1) $(Glu-Al-Glu)^{2+}_2 + H_8O_4 \rightarrow (Glu-Al-Glu)^{1+}_{2-2} + H_9O_4^{+} \Delta G = -4.7 \text{ kcal/mol}$ (2) $(Glu-Al-Glu)^{1+}_{2-2} + H_8O_4 \rightarrow (Glu-Al-Glu)^{0}_{2,3-2} + H_9O_4^{+} \Delta G = 7.4 \text{ kcal/mol}$ (3)

Equations (1), (2) and (3) are employed to predict the Gibbs energy of proton transfer from the substrate to the outer water phase. Clearly, the three positively charged form of $(Glu-Al-Glu)^{3+}$ is quite unstable, and it can beeasily converted to the two positively charged form of $(Glu-Al-Glu)^{2+}$, with a Gibbs energy change of -10.1 kcal/mol. $(Glu-Al-Glu)^{2+}$ can be further converted to the most stable form of $(Glu-Al-Glu)^{1+}$. Therefore, Al(III)-(glucose)₂ is dominantly in the form of (Glu-Al-Glu)¹⁺, with two protons dissociated.



Fig. S5 Optimized geometries of $[glucose-Al(III)-glucose]^{2+}$ complex and their relative Gibbs energies. The energies are relative to the most stable form of $(Glu-Al-Glu)^{2+}_{2-}$. Since the two glucose molecules are equally coordinated to Al(III) centre, there are mainly three singly deprotonated forms.



Fig. S6 Optimized geometries of $[glucose-Al(III)-glucose]^{1+}$ complex and their relative Gibbs energies. The energies are relative to the most stable form of $(Glu-Al-Glu)^{1+}_{2-2}$. Since the two glucose molecules are equally coordinated to Al(III) centre, there are mainly nine doubly deprotonated forms.



Fig. S7 Optimized structures (in Å) of the most stable reactant complex and all the transition state complexes for the glucose-fructose transformation with explicit $6H_2O$ molecules in the cluster-continuum model in the (Glu-Al-Glu)²⁺model. The relative Gibbs energies are shown below the structures, the Gibbs energy in normal fonts are relative to the reactant complex RC1- Al^{2+}_{1} , while the Gibbs energies in parentheses are overall free energy barriers relative to the most stable species of (Glu-Al-Glu)¹⁺₂₋₂.



Fig. S8 Optimized structures (in Å) of the most stable reactant complex and all the transition state complexes for the glucose-fructose transformation with explicit $6H_2O$ molecules in the cluster-continuum model in the (Glu-Al-Glu)¹⁺model. The relative Gibbs energies are shown below the structures, and the Gibbs energies are relative to the reactant complex RC2-Al¹⁺₂₋₂.

(2) Al(III)-OH catalysed isomerization of glucose to fructose



Fig. S9 Optimized geometries of AlOH-(glucose)₂ in different deprotonated forms and corresponding free energy changes.



Fig. S10 Calculated relative Gibbs energy profiles (in kcalmol⁻¹) and optimized structures (in Å) of species for the glucose-fructose isomerization via 1,2-hydride shift mechanism in the (Glu-AlOH-Glu)²⁺ model.



Fig. S11 Calculated relative Gibbs energy profiles (in kcalmol⁻¹) and optimized structures (in Å) of species for the glucose-fructose isomerization via 1,2-hydride shift mechanism in the (Glu-AlOH-Glu)²⁺ model with inclusion of $2H_2Oexplicit$ waters.



Fig. S12 Calculated relative Gibbs energy profiles (in kcal mol⁻¹) and optimized structures (in Å) of species for the glucose-fructose isomerization via 1,2-hydride shift mechanism in the (Glu-AlOH-Glu)¹⁺ model.



Fig. S13 Calculated relative Gibbs energy profiles (in kcal mol⁻¹) and optimized structures (in Å) of species for the glucose-fructose isomerization via 1,2-hydride shift mechanism in the (Glu-AlOH-Glu)¹⁺ model with inclusion of two explicit waters.



(3) Al(III) catalysed C-C bond cleavage

Fig. S14 Optimized different configurations of $[fructose-Al(III)-fructose]^{3+}$ complex and their relative Gibbs energies. It can be seen that $(Fru-Al-Fru)^{3+}$ -a is the most stable, and we will focus on this configuration in the following studies. In $(Fru-Al-Fru)^{3+}$ -a complex, two fructose molecules are equally coordinated to Al(III) centre.



Fig. S15 Optimized different deprotonated forms of [fructose-Al(III)-fructose]²⁺complex and their relative Gibbs energies.



Fig. S16 Optimized different deprotonated forms of [fructose-Al(III)-fructose]¹⁺complex and their relative Gibbs energies.



Fig. S17 Optimized geometries of [fructose-Al(III)-fructose]complex in different deprotonated forms and corresponding free energy changes.



Fig. S18 Calculated relative Gibbs energy profiles (in kcal mol⁻¹) and optimized structures (in Å) of species for the C-C bond cleavage in (Fru-Al-Fru)³⁺-a complex.



Fig. S19 Optimized structures (in Å) of the transition state complexes for the C-C bond cleavage in the $(Fru-Al-Fru)^{2+}$ model. The relative Gibbs energies are shown below the structures, the Gibbs energies in normal fonts are relative to the $(Fru-Al-Fru)^{2+}$, while the Gibbs energies in parentheses are overall free energy barrier relative to the most stable species of $(Fru-Al-Fru)^{1+}$.



Fig. S20 Optimized structures (in Å) of the transition state complexes for the C-C bond cleavage in the (Fru-Al-Fru)¹⁺model. The Gibbs energies are relative to the (Fru-Al-Fru)¹⁺₁₋₁.



Fig. S21 Optimized structures (in Å) of the transition state complexes with different configurations for the C-C bond cleavage in the $(Fru-Al-Fru)^{1+}$ model. The Gibbs energies are overall Gibbs barrier relative to the $(Fru-Al-Fru)^{1+}_{1-1}$.

(4) Al(III)-OH catalyzed C-C bond cleavage



Fig. S22 Optimized geometries of [fructose-AlOH-fructose] complex in different deprotonated forms and corresponding free energy changes.



Fig. S23 Calculated relative Gibbs energy profiles (in kcal mol⁻¹) and optimized structures (in Å) of species for the C-C bond cleavage in the (Fru-AlOH-Fru)²⁺ model. It should be noted we did not rigorously locate the TS10b-Al due to the flat energy surface, and structure of TS10b-Al is taken from the relaxed potential energy scan in Fig. S24. Herein, the energy of TS10b-Al is just electronic energy relative to IN10-Al without ZPE and thermal corrections.



Fig. S24 Scanned potential energy profiles for C-C bond cleavage starting from IN10-Al.



Fig. S25 Optimized different deprotonated forms of [fructose-AlOH-fructose]¹⁺complex and their relative Gibbs energies.



Fig. S26 Calculated relative Gibbs energy profiles (in kcal mol⁻¹) and optimized structures (in Å) of species for the C-C bond cleavage in the (Fru-AlOH-Fru)¹⁺¹ model.



Fig. S27 Optimized structures (in Å) of the transition state complexes for the C-C bond cleavage in the different deprotonated forms of (Fru-AlOH-Fru)¹⁺ model. The Gibbs energies are overall Gibbs barrier relative to the most stable species of IN11-Al.

(5) Al(III)-OH-catalysed triose-lactic acid isomerization



Fig. S28 Calculated relative Gibbs energy profiles (in kcal mol⁻¹) and optimized structures (in Å) of species for the rate-determining step of triose-lactic acid transformation via the 1,2-hydride shift mechanism in Al-OH model.

(6) Sn(II)-catalysed glucose-fructose isomerization



Fig. S29 Optimized geometries of Sn(II)-(glucose)₂ in different deprotonated forms and calculated relative free energy changes.

 $(Glu-Sn-Glu)^{2+} + H_8O_4 \rightarrow (Glu-Sn-Glu)^{1+}_2 + H_9O_4^+ \varDelta G = -0.6 \text{ kcal/mol}$ (1) (Glu-Sn-Glu)^{1+}_2 + H_8O_4 \rightarrow (Glu-Sn-Glu)^{0}_{2,3'} + H_9O_4^+ \varDelta G = 11.9 \text{ kcal/mol} (2)



Fig. S30 Optimized geometries of [glucose-Sn-glucose]¹⁺ complex and their relative Gibbs energies.



Fig. S31 Optimized structures (in Å) of the reactant complexes and the transition states complexes involved in the rate-determining step of the glucose-fructose transformation in the [glucose-Sn-glucose]complex with explicit $6H_2O$ molecules in the cluster-continuum model. The corresponding Gibbs energy barriers are shown below the structures of transition states. The Gibbs energy barriers are first given as the barriers relative to the corresponding reactant complex, while the Gibbs energies in parentheses are barriers relative to the most stable species of (Glu-Sn-Glu)¹⁺₂.



Fig. S32 Calculated relative Gibbs energy profiles (in kcal mol⁻¹) and optimized structures (in Å) of species for the rate-determining step of the glucose-fructose isomerization with explicit $9H_2O$ molecules in the cluster-continuum model in the presence of Sn(II). The model is based on one glucose coordinated to Sn(II).



(7) Sn(II)-OH-catalysed glucose-fructose isomerization

Fig. S33 Calculated relative Gibbs energy profiles (in kcalmol⁻¹) and optimized structures (in Å) of species for the glucose-fructose isomerization via 1,2-hydride shift mechanism in the Sn(II)-OH model.



Fig. S34 Calculated relative Gibbs energy profiles (in kcalmol⁻¹) and optimized structures (in Å) of species for the glucose-fructose isomerization via 1,2-hydride shift mechanism in the Sn(II)-OH model (2H₂O coordinated to Sn(II)). The model is based on one glucose coordinated to Sn(II)-OH

(8) Sn(II) catalyzed C-C bond cleavage of fructose



Fig. S35 Optimized geometries of Sn(II)-(fructose)₂ in different deprotonated forms and calculated relative free energy changes.

 $(Fru-Sn-Fru)^{2+} + H_8O_4 \rightarrow (Fru-Sn-Fru)^{1+}_{2^{\prime}} + H_9O_4^{+} \varDelta G = -0.4 \text{ kcal/mol}$ (1) (Fru-Sn-Fru)^{1+}_{2^{\prime}} + H_8O_4 \rightarrow (Fru-Sn-Fru)^{0}_{3,2^{\prime}} + H_9O_4^{+} \varDelta G = 8.9 \text{ kcal/mol} (2)



Fig. S36 Optimized structures (in Å) of various transition state complexes for the ratedetermining step of C-C bond cleavage in the presence of Sn(II). The relative Gibbs energy barriers are shown below the structures, the Gibbs energy barriers are relative to the most stable species of (Fru-Sn-Fru)¹⁺₂.



Fig. S37 Calculated relative Gibbs energy profiles (in kcal mol⁻¹) and optimized structures (in Å) of species for the rate-determining step of C-C bond cleavage in the presence of Sn(II). (a) 1H₂O coordinated to Sn(II). (b) 2H₂O coordinated to Sn(II). This calculation adopted the same cluster model of Pb(II), and it should be noted that we did not located the water assisted pathways as $TS[1H_2O-[Pb^{2+}(1H_2O)]$ or $TS[1H_2O-[Pb^{2+}(4H_2O)]$ (*Nat. Commun.***2013**, *4*, 2141). The model is based on one glucose coordinated to Sn(II).



(9) Sn(II)-OH-catalysed C-C bond cleavage of fructose

Fig. S38 Calculated relative Gibbs energy profiles (in kcal mol⁻¹) and optimized structures (in Å) of species for the rate-determining step of C-C bond cleavage by Sn(II)-OH model.



Fig. S39 Calculated relative Gibbs energy profiles (in kcal mol⁻¹) and optimized structures (in Å) of species for the rate-determining step of C-C bond cleavage in the Sn(II)-OH model (1H₂O coordinated to Sn(II)). The model is based on one glucose coordinated to Sn(II)-OH.

(10) Sn(II)-OH-catalysed triose-lactic acid transformation



Fig. S40 Calculated relative Gibbs energy profiles (in kcal mol⁻¹) and optimized structures (in Å) of species for the rate-determining step of triose-lactic acid transformation via the1,2-hydride shift mechanism with explicit $4H_2O$ molecules in the cluster-continuum model.

9. ESI-Mass spectra for glucose-Al(III) and glucose-Sn(II) species



Fig. S41 ESI-Mass spectra of (a) Al(III)-glucose species, (b) Sn(II)-glucose species, (c) the enlargement of the marked rectangular zone in (b).

Spectra (a) and (b) reveal that Al(III) tends to coordinate with two glucose molecules, whereas Sn(II) tends to coordinate with either one or two glucose molecules with the latter being majority species. In spectra (b) and (c), an unknown species at 470.6 was observed. Since there is no Sn related isotope near the peak, this can be excluded from the Sn-containing species.