Supporting Information

Green Chemistry

Lactic acid production from glucose over polymer catalysts in aqueous alkaline solution under mild conditions

Xincheng Wang,[a] Yanlei Song,[a] Chongpin Huang,*[a] Fengbing Liang[b] and Biaohua Chen[a]

[a] *State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China. Fax: 86 10 6441 9619; Tel: 86 10 6441 2054;*
E-mail: huangcp@mail.buct.edu.cn

[b] *CAS Key Laboratory of Biobased Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China.*

1. The exchange rate of the counter-anions for different types of IMEP-based catalysts

Potentiometric titration with silver nitrate was used to determine the concentration of chloride ion in the final catalysts and the rate of anion exchange. The results are shown in Table S1. The exchange rates, which were calculated according to the concentration of chloride ion, were a little higher than the actual values because the yields of modified catalysts were hardly as complete as 100%.

Table S1 Potentiometric titration results of different kinds of IMEP-based catalysts.

Entry	Catalyst	Cl^- (g/mL)	Exchange rate (%)
1	[IMEP]Cl	0.446	0
2	[IMEP]BF_4	0.013	97.1
3	[IMEP]ClO_4	0.016	96.4
4	[IMEP]Ac	0.019	95.7
5	[IMEP]PF_6	0.014	96.9
6	[IMEP]PhCOO	0.012	97.3

2. Thermogravimetric analysis (TGA) of [IMEP]Cl

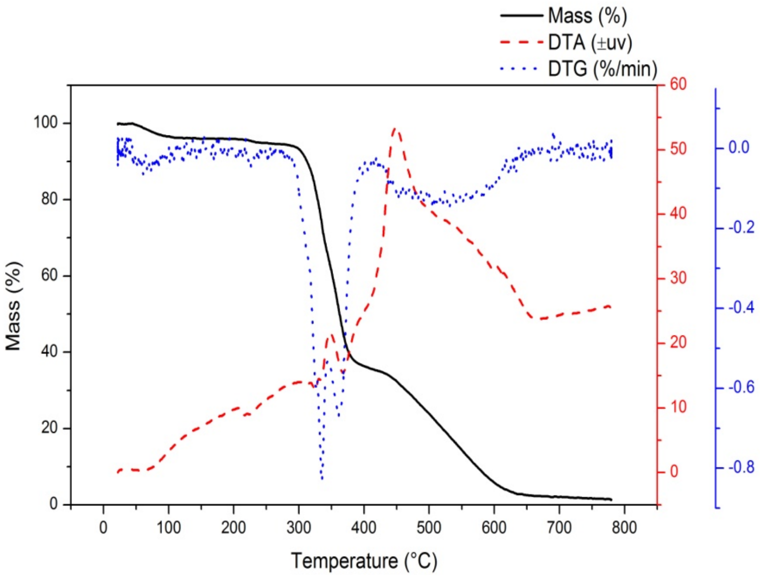


Figure S1 TGA of [IMEP]Cl from 25 °C to 800 °C.

3. The GC/MS analysis of the aqueous phase products

After the reaction, the resultant aqueous phase product samples were prepared for gas chromatography coupling with mass spectrometer (GC/MS) analysis. Derivatization of the polar components was performed according to the literature. The resultant aqueous phase were dried overnight in vacuum. After that, acetonitrile was added and ultrasonicated to allow the solids to dissolve. Then, pyridine and BSFTA with TMCS (99:1) were added and the vial was capped. The capped vial was put in a oil bath maintained at 65 °C for 2 hours to allow complete silylation. After silylation, the sample was cooled down to room temperature and injected in an Agilent 6890 series GC/MS equipped with an Agilent HP-5MS column. The column temperature was maintained at 50 °C for 1 minute then ramped at 10 °C /min to 220 °C and held at 220 °C for 2 minutes.

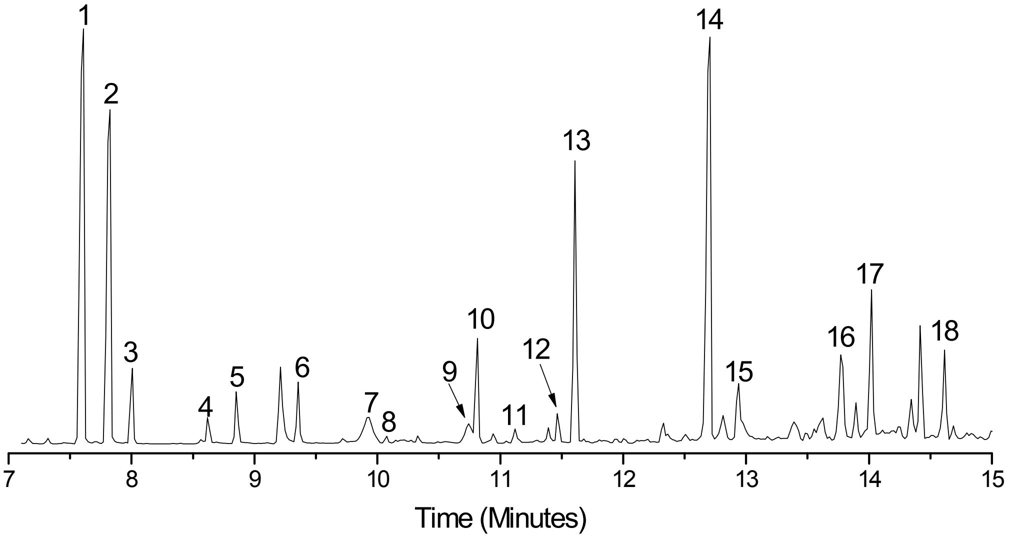


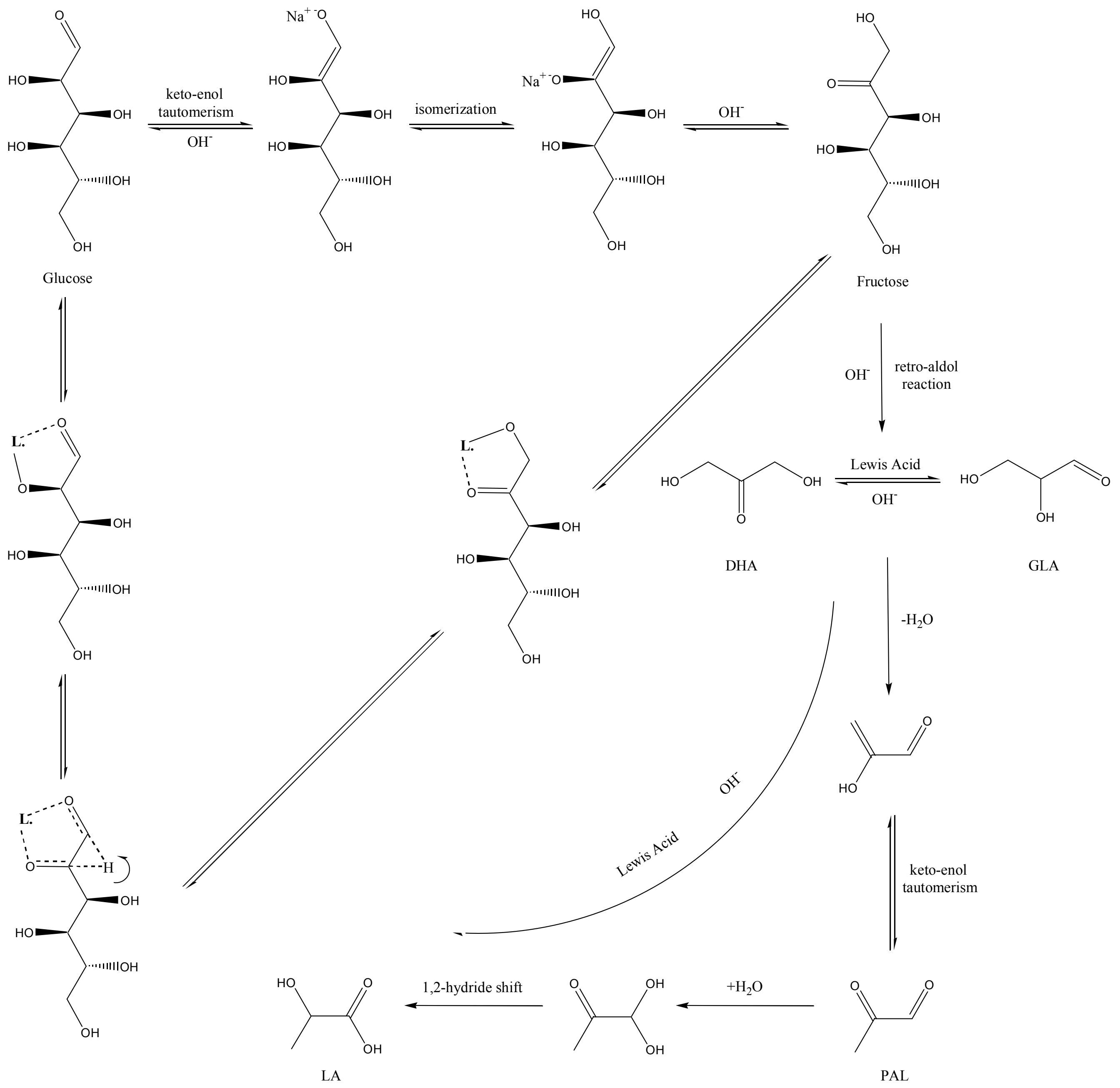
Figure S2 The GC/MS spectra of the aqueous phase products by the conversion of glucose. Reaction conditions: 25 mM glucose, 50 mM NaOH, 100 mM [IMEP]Cl, 100 °C, 0.1 MPa N_2, 30 min). Qualitative information indicating the potential byproducts is given:

Peak Number	Retention Time (min)	Formula	Compound Name
1	7.591	$C_3H_6O_3$	Lactic acid
2	7.808	$C_2H_4O_3$	Glycolic acid
3	7.988	$C_3H_4O_3$	2-Hydroxy-2-propenoic acid
4	8.618	$C_4H_8O_3$	2-Hydroxy-butanoic acid
5	8.852	$C_6H_6O_3$	3-Hydroxy-propanoic acid
6	9.356	$C_4H_6O_3$	2-Hydroxy-2-butenoic acid
7	9.915	$C_4H_8O_5$	2, 3, 4-Trihydroxy-butyric acid
8	10.077	$C_2H_4O_4$	Dihydroxy acetic acid
9	10.743	$C_4H_8O_5$	2, 3, 4-Trihydroxy-butyric acid
10	10.797	$C_3H_8O_3$	Glycerol
11	11.121	$C_5H_8O_3$	4-Hydroxy-pentenoic acid
12	11.464	$C_4H_8O_4$	2-Methyl-2, 3-dihydroxy-propanoic acid
13	11.608	$C_3H_6O_4$	2, 3-Dihydroxy-propanoic acid

14	12.688	$C_4H_8O_4$	2, 4-Dihydroxy-butanoic acid
15	12.940	$C_4H_8O_4$	3, 4-Dihydroxy-butanoic acid
16	13.769	$C_5H_{10}O_5$	3-Deoxy-2, 4, 5-trihydroxy-pentonic acid
17	14.021	$C_4H_8O_3$	4-Hydroxy-butanoic acid
18	14.615	$C_4H_8O_5$	L-Threonic acid

4. The reaction mechanism for converting glucose to LA

Previous studies and the results of this study led to the proposal of a possible mechanism for glucose conversion to form LA in the presence of [IMEP]Cl in alkaline solution, as depicted in Scheme S1. First, glucose was isomerized to form fructose via base-catalyzed isomerizations, which proceed through a proton transfer mechanism generated after the deprotonation of the α-carbonyl carbon,[1, 2] and Lewis acid-catalyzed isomerizations that involve an intramolecular hydride shift;[2, 3] these steps were confirmed both theoretically and experimentally by Wang et al.[4] Subsequently, the C6 backbone of fructose was split into two C3 fragments, specifically dihydroxyacetone (DHA) and glyceraldehyde (GLA), through a retro-aldol reaction that occurs through OH^- addition.[5] In this pathway, the Lewis acidity was too weak to catalyze the conversion of fructose into C3 fragments. Consequently, OH^- addition was thought to be the sole pathway because the [IMEP]Cl showed no activity alone during the conversion of fructose. Subsequently, the DHA in equilibrium with GLA was converted via dehydration and ketol-enol tautomerization to form pyruvic aldehyde (PAL); this process could be catalyzed by both Lewis acids[6-8] and bases[9] under the given conditions. This step was thought to be rate-determining because PAL was only present in trace amounts in the catalytic system, according to de Clippel et al.[6] Finally, the reaction of PAL to form LA likely involved hydration followed by a 1,2-hydride shift; specifically the aldehyde H (of the terminal C=O of PAL) shifted to the adjacent carbon atom.[6-8]



Scheme S1 The reaction mechanism for producing LA (L., Lewis acid sites.)

References

S1 P. Gao, G. Li, F. Yang, X. N. Lv, H. Fan, L. Meng and X. Q. Yu, *Ind. Crops Prod.,* 2013, **48**, 61.

S2 Y. Roman-Leshkov, M. Moliner, J. A. Labinger and M. E. Davis, *Angew. Chem. Int. Ed.,* 2010**, 49**, 8954.

S3 E. A. Pidko, V. Degirmenci, R. A. van Santen and E. J. Hensen, *Angew.Chem.,* 2010**, 122**, 2584.

S4 Y. Wang, W. Deng, B. Wang, Q. Zhang, X. Wan, Z. Tang, Y. Wang, C. Zhu, Z. Cao, G. Wang and H. Wan, *Nat. Commun.,* 2013**, 4**, 2141.

S5 D. Esposito and M. Antonietti, *Chemsuschem*, 2013, **6**, 989.

S6 M. F. de Clippel, M. Dusselier, R. Van Rompaey, P. Vanelderen, J. Dijkmans, E. Makshina, L. Giebeler, S. Oswald, G. V. Baron, J. F. M. Denayer, P. P. Pescarmona, P. A. Jacobs and B. F. Sels, *J. Am. Chem. Soc.*, 2012, **134**, 10089.

S7 Y. Hayashi and Y. Sasaki, *Chem. Commun.*, 2005, 2716.

S8 C. B. Rasrendra, B. A. Fachri, I. G. B. N. Makertihartha, S. Adisasmito and H. J. Heeres, *Chemsuschem*, 2011, **4**, 768.

S9 M. Dusselier, P. Van Wouwe, A. Dewaele, E. Makshina and B. F. Sels, *Energy Environ. Sci.*, 2013, **6**, 1415.