Supplementary Information

Understanding the mechanism of the enhanced alcoholysis of biomass carbohydrate to alkyl levulinate over bifunctional catalysts: Does it resemble that in water?

Yuxuan Zhang[a], Zhaoyang Ju[b], Xueli Chen[a], Qian Lyu[a], Jiaqi Mei[a], Lujia Han[a], Dong Liu[cd], Weihua Xiao[a*]

[a] College of Engineering, China Agricultural University, 17 Qinghua Donglu, Haidian District, Beijing, P.R. China 100083

[b] College of Chemical & Material Engineering, Quzhou University, Quzhou, P.R. China 324000

[c] School of Agricultural Equipment Engineering, Jiangsu University, Zhenjiang, Jiangsu, P.R. China 212013

[d] Jiangsu Province and Education Ministry Co-Sponsored Synergistic Innovation Center of Modern Agricultural Equipment, Jiangsu, P.R. China 212013

* Corresponding author, e-mail address: xwhddd@163.com (W. Xiao).

Experimental methods

Kinetic Study

A kinetic study on the alcoholysis of glucose over AlPW and HPW was conducted to investigate the reaction process. Some assumptions on the basis of experimental results were are expressed as follows (1) glucose does not selectively convert to MDGP, and all the other decomposition products are regarded to be humin and byproducts, generated in a parallel first-order reaction model [1]; (2) ML is defined as the main subsequent degradation product of MDGP, because the intermediate product 5-MMF is rapidly converted into ML, which keeps a low level in the whole reaction process, and at the same time produces undesirable products; (3) ML will be decomposed to a certain extent under some extreme reaction conditions, such as excessive reaction temperature [2]. Based on the assumptions, a pseudo-first-order reaction model on the formation of ML from glucose is proposed as given in Scheme 2.

This reaction model results in the following first-order differential rate equations:

$$\frac{d(100-[Glucose])}{dt} = -\left(k_1+k_3\right)(100-[Glucose]) \qquad (1)$$

$$\frac{d[MDGP]}{dt} = k_1(100-[Glucose]) - \left(k_2+k_4\right)[MDGP] \qquad (2)$$

$$\frac{d[ML]}{dt} = k_2[MDGP] - k_5[ML] \qquad (3)$$

Solving the linear differential rate equations above, the time-dependent expressions are obtained below.

$$[Glucose] = 100[1-\exp\left(-\left(k_1+k_3\right)t\right)] \qquad (4)$$

$$[MDGP] = \frac{100k_1}{k_2+k_4-k_1-k_3}[\exp\left(-\left(k_1+k_3\right)t\right) - \exp\left(-\left(k_2+k_4\right)t\right)] \qquad (5)$$

$$[ML] = \frac{100k_1k_2}{k_2+k_4-k_1-k_3}\left[\frac{\exp\left(-\left(k_1+k_3\right)t\right)}{k_5-k_1-k_3} - \frac{\exp\left(-\left(k_2+k_4\right)t\right)}{k_5-k_2-k_4}\right] + \quad (6)$$

where [Glucose] is the conversion of glucose, whereas [MG] and [ML] represent the yield of MDGP, and ML at time t (min), in mol%. k_1 (min^{-1}), k_2 (min^{-1}), k_3 (min^{-1}), k_4 (min^{-1}) and k_5 (min^{-1}) are reaction rate constants (min^{-1}).

The kinetic parameters in the equations were fitted to simulate the conversion of glucose and yields of MDGP and ML obtained under applied conditions, respectively,

using the method of non-linear least squares regression analyses by MATLAB.

Results and discussion

Fig. S6 demonstrates the comparison between the experimental data and the kinetic models under different conditions. It can be found that the model results are in good agreement with the experimental results. Table S1 shows the kinetic parameters for the kinetic models. It is notable that the coefficients of determination (R^2) for all the models except that over AlPW at 140 ℃ are larger than 0.9, indicating a good fitting between the models and experimental results.

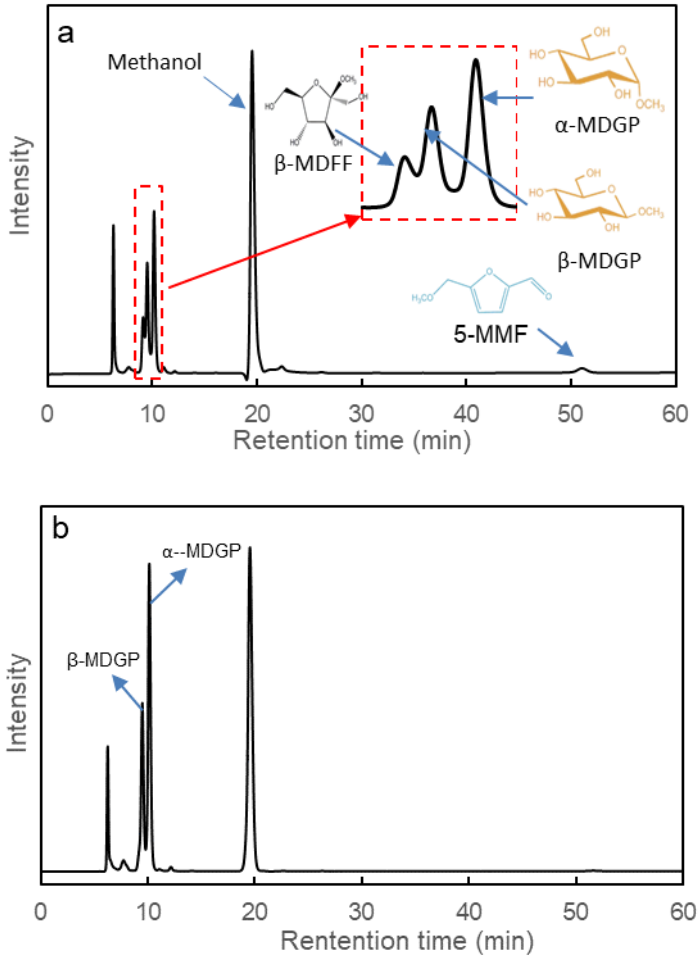

Fig. S1 HPLC chromatograms of the reaction mixture obtained from the methanolysis of (a) glucose and (b) MDGP. Reaction conditions: substrate (1 g), methanol (15 g), AlPW (0.4 mmol), 140 ºC, cooled down right after reaching the target temperature,

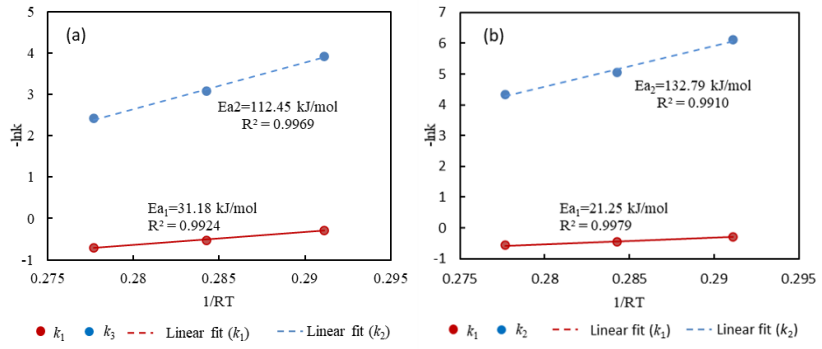

Fig. S2 Arrhenius plot for the conversion of glucose over (a) AlPW (b) HPW in the range from 140 ℃ to 160 ℃.

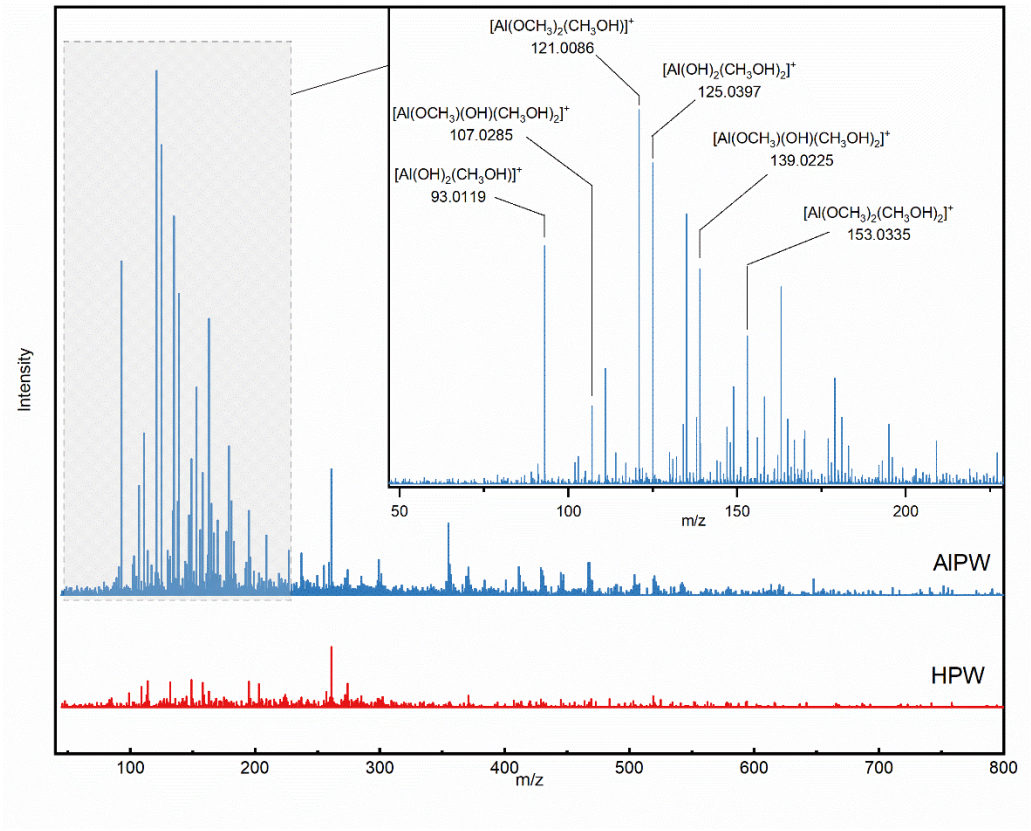

Fig. S3 ESI-MS spectra of HPW and AlPW solution at positive ion mode.

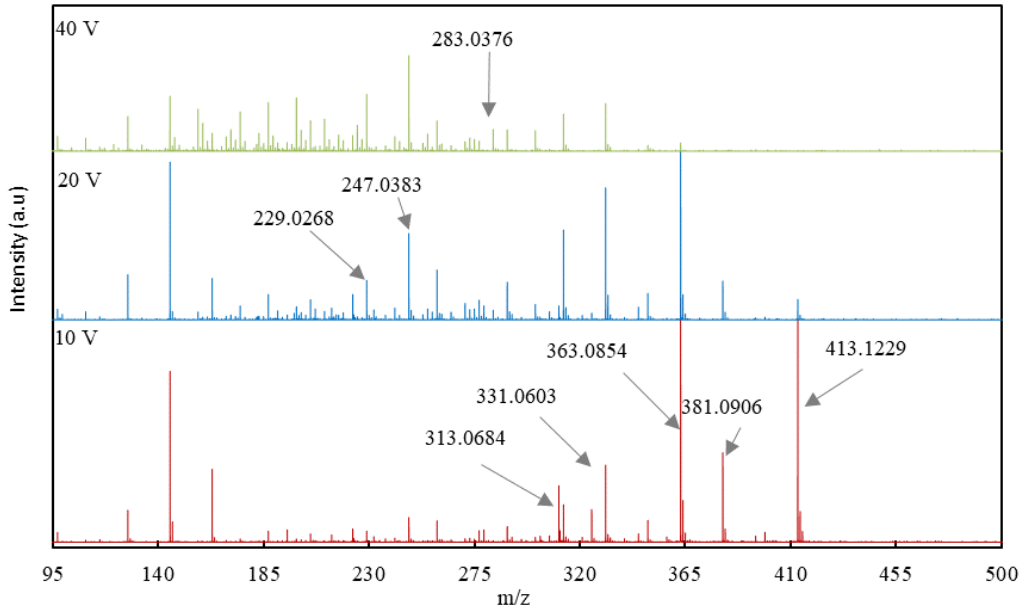

Fig. S4 ESI-MS/MS spectra of selected species at m/z of 498 in the MDGP solution containing AlPW.

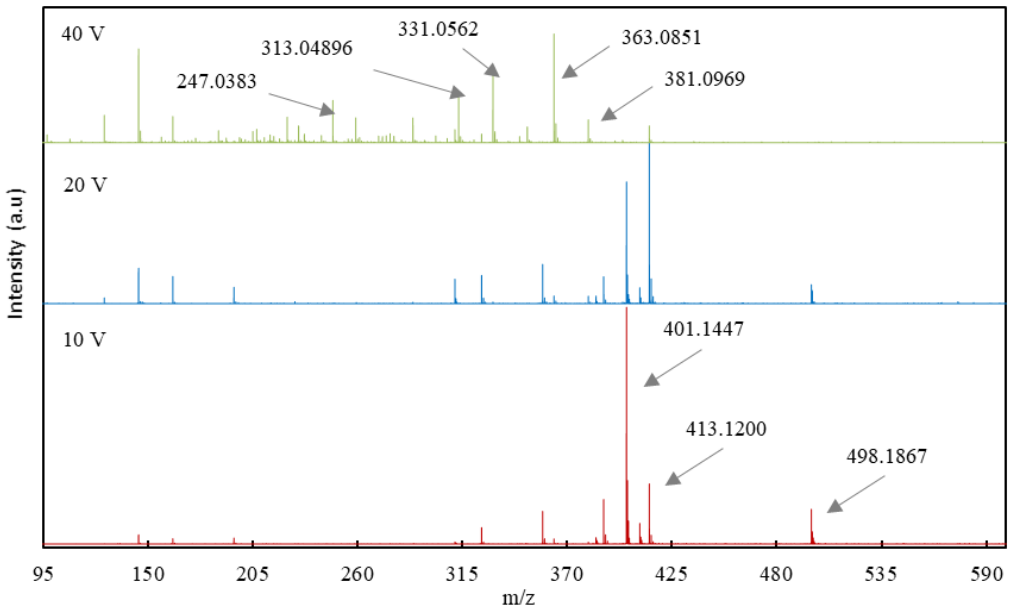

Fig. S5 ESI-MS/MS spectra of selected species at m/z of 595 in the MDGP solution containing AlPW.

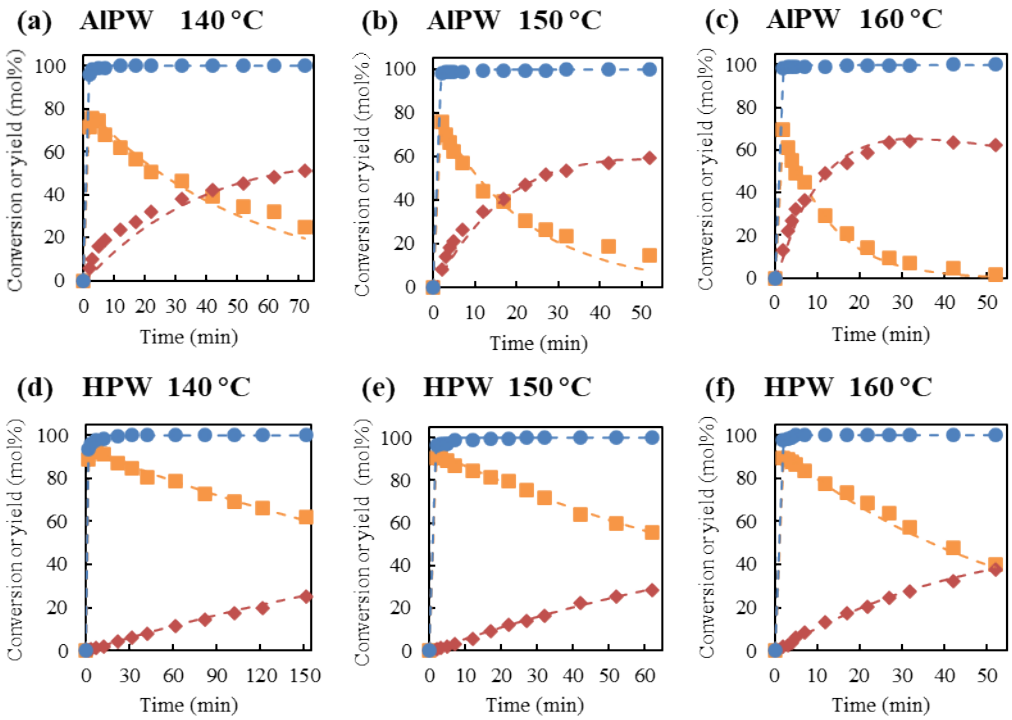

Fig. S6 Comparison of experimental data (♦: ML, ●: Glucose conversion, ■: MDGP) and kinetic model (solid lines). Reaction conditions: 2 g of substrate, 0.4 mmol catalyst, 15 g methanol.

Table S1 Kinetic rate constants and coefficients of determination for kinetic models

Catalyst	Temperature (°C)	k_1 (min^{-1})	k_2 (min^{-1})	k_3 (min^{-1})	k_4 (min^{-1})	k_5 (min^{-1})	R_1^2	R_2^2	R_3^2
HPW	140	1.3259	0.0022	0.0906	0.0010	0.0000	0.9617	0.9857	0.9739
	150	1.5519	0.0064	0.0969	0.0022	0.0000	0.9606	0.9854	0.9600
	160	1.7641	0.0133	0.1215	0.0041	0.0032	0.9646	0.9514	0.9688
AlPW	140	1.2480	0.0198	0.2877	0.0000	0.0038	0.9836	0.9290	0.8390
	150	1.6993	0.0461	0.4006	0.0000	0.0063	0.9751	0.9222	0.9089
	160	2.0110	0.0896	0.5387	0.0000	0.0058	0.9995	0.9445	0.9335

R_1^2, R_2^2, R_3^2 are the coefficients of determination for the simulation model of glucose conversion, MDGP yield, and ML yield, respectively.

References

1. Y. Zhang, X. Chen, X. Lyu, G. Zhao, T. Zhao, L. Han and W. Xiao, *J. Clean. Prod.*, 2019, **215**, 712-720.
2. L. Peng, L. Lin and H. Li, *Ind. Crops Prod.*, 2012, **40**, 136-144.