Supporting information

ln-situ carbonic acid from CO_2: A green acid for highly effective conversion of cellulose in the presence of Lewis acid

Shuangshuang Jing,[a] Xuefei Cao,[b] Linxin Zhong,*[a] Xinwen Peng,*[a] Xiaoting Zhang,[a] Sha Wang [a] and Runcang Sun [a, b]

[a] *State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, 381 Wushan Road, Tianhe District, Guangzhou,Guangdong, P. R. China, 510640.*

[b] *Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, No.35 Tsinghua East Road, Haidian District, Beijing, P. R. China,100083.*

*Corresponding author. E-mail address: lxzhong0611@scut.edu.cn (L. X. Zhong); fexwpeng@scut.edu.cn (X. W. Peng)

Supporting Information, 8 pages, 4 figures, 2 tables.

The Program of Heating and Cooling

Table S1. Differences in yields of products between HTCs with $CrCl_3/CO_2$ and $CrCl_3$ alone.

Table S2. Differences between the yields of FA and LeA from the HTC of HMF.

Figure S1. Time courses of the yields of Glu (a), Fru (b), LaA (c), FA (d), LeA (e), and HMF (f), as well as the corresponding first derivative curves of cellulose HTCs with $CrCl_3$ alone and $CrCl_3/CO_2$.

Figure S2. Time course of the conversion of HMF (a) and the yields of FA (b) and LeA (c), as well as the corresponding first derivative curves of HMF HTCs with $CrCl_3$ alone and $CrCl_3/CO_2$.

Figure S3. Time course of the conversion of fructose (a) and the yields of Glu (b), LaA (c), FA (d), LeA (e), and HMF (f), as well as the corresponding first derivative curves of fructose HTCs with $CrCl_3$ alone and $CrCl_3/CO_2$.

Figure S4. Time course of the conversion of glucose (a) and the yields of Fru (b), LaA (c), FA (d), LeA (e), and HMF (f), as well as the corresponding first derivative curves of glucose HTCs with $CrCl_3$ alone and $CrCl_3/CO_2$.

The Program of Heating and Cooling

The hydrothermal conversion was conducted in a batch reactor made of C276 stainless steel (100 mL capacity, 45 mm i.d.). Heating and temperature controlling were regulated by proportion integration differentiation (PID) control system. Curves of heating up and cooling could not output, and no fixed heating rate could be received. It took about 30 min to achieve 120-160 ^{o}C, and 40 min to 180-200 ^{o}C. After completing the reaction, the reactor was cooled down by cold wind for 10 min and then rinsed with cool water for 20 min.

Table S1. Differences in yields of products between HTCs with $CrCl_3/CO_2$ and $CrCl_3$ alone.

Temperature/^{o}C	Difference/%			
	LaA	**FA**	**LeA**	**HMF**
120	1.45	0	0	0.58
140	2.5	8.4	4.2	1.5
160	6.1	31	22	-1.1
180	2.2	13	11	-2.7
200	2.7	5.8	1.3	0.022

Table S2. Differences between the yields of FA and LeA from the HTC of HMF.

Time/min	Yields/%							
	$CrCl_3$				$CrCl_3/CO_2$			
	FA	**LeA**	**D-value**	**Average**	**FA**	**LeA**	**D-value**	**Average**
70	79	58	21		68	56	12	
90	84	63	21		74	57	17	
120	86	65	21	21	69	54	15	15.4
150	88	67	21		68	50	18	
180	89	68	21		70	55	15	

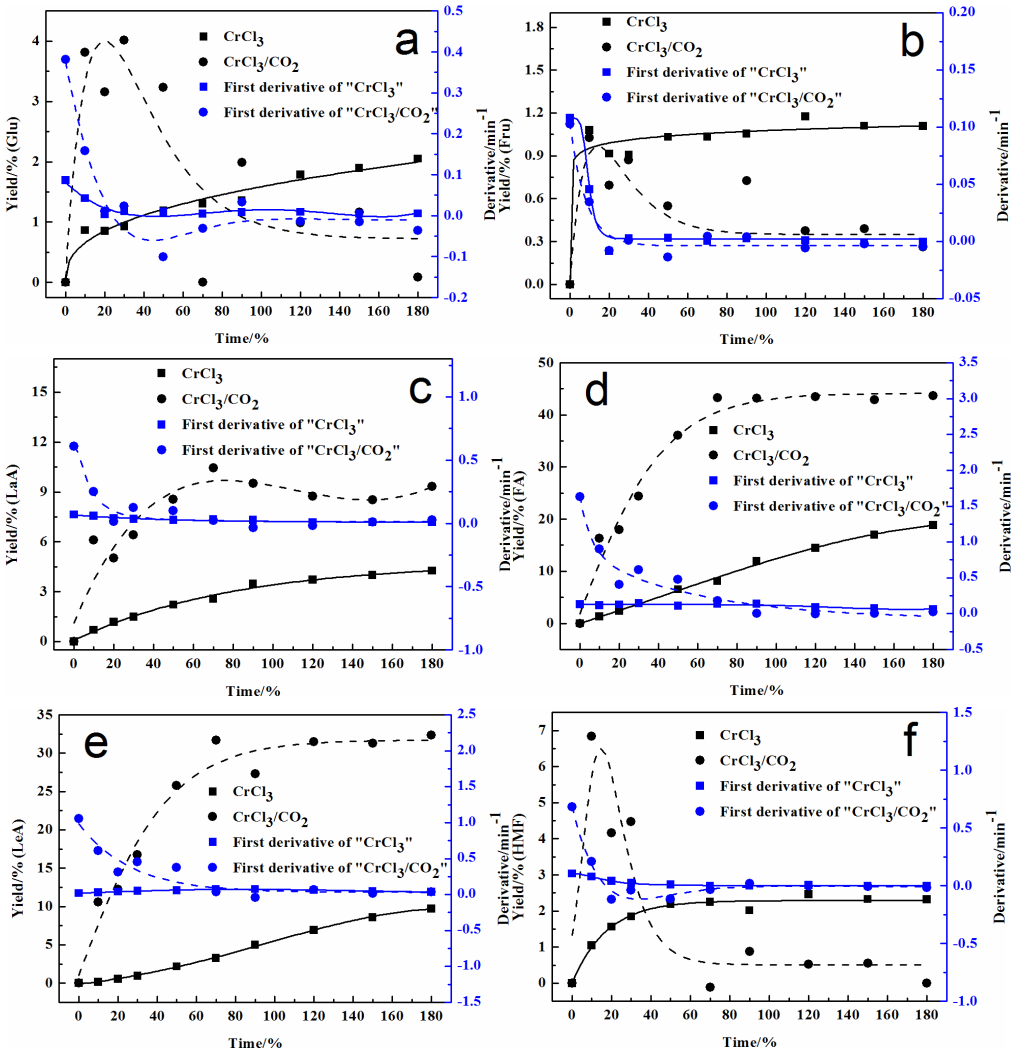

Figure S1. Time courses of the yields of Glu (a), Fru (b), LaA (c), FA (d), LeA (e), and HMF (f), as well as the corresponding first derivative curves of cellulose HTCs with $CrCl_3$ alone and $CrCl_3/CO_2$. Reaction condition: initial CO_2 pressure of 4 MPa, Cr^{3+} to cellulose molar ratio of 2.7:100, 160 ^{o}C.

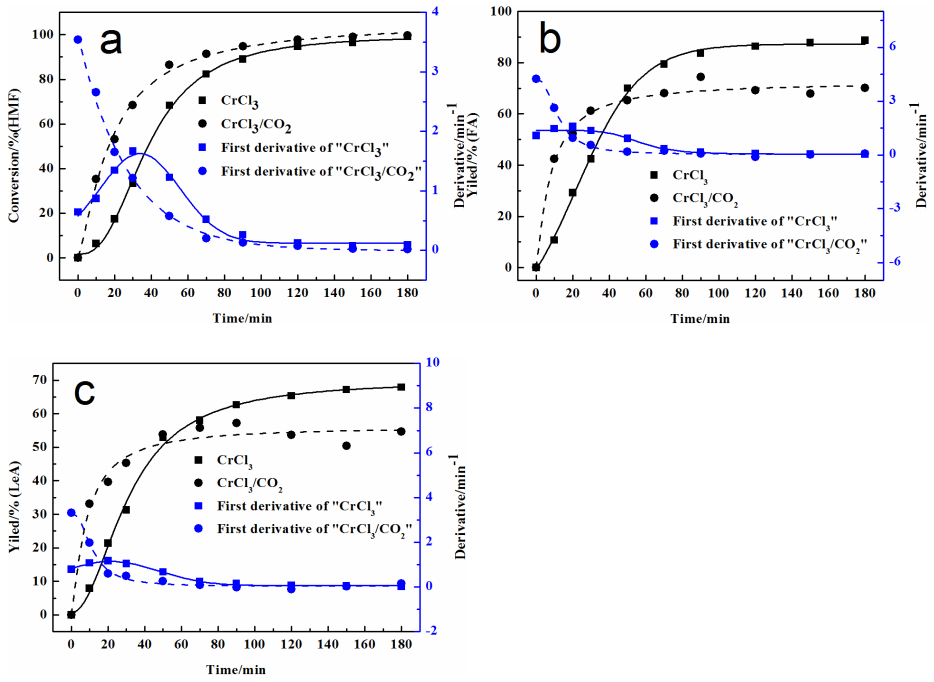

Figure S2. Time course of the conversion of HMF (a) and the yields of FA (b) and LeA (c), as well as the corresponding first derivative curves of HMF HTCs with $CrCl_3$ alone and $CrCl_3/CO_2$. Reaction condition: initial CO_2 pressure of 4 MPa, Cr^{3+} to HMF molar ratio of 3:100, 160 ^oC.

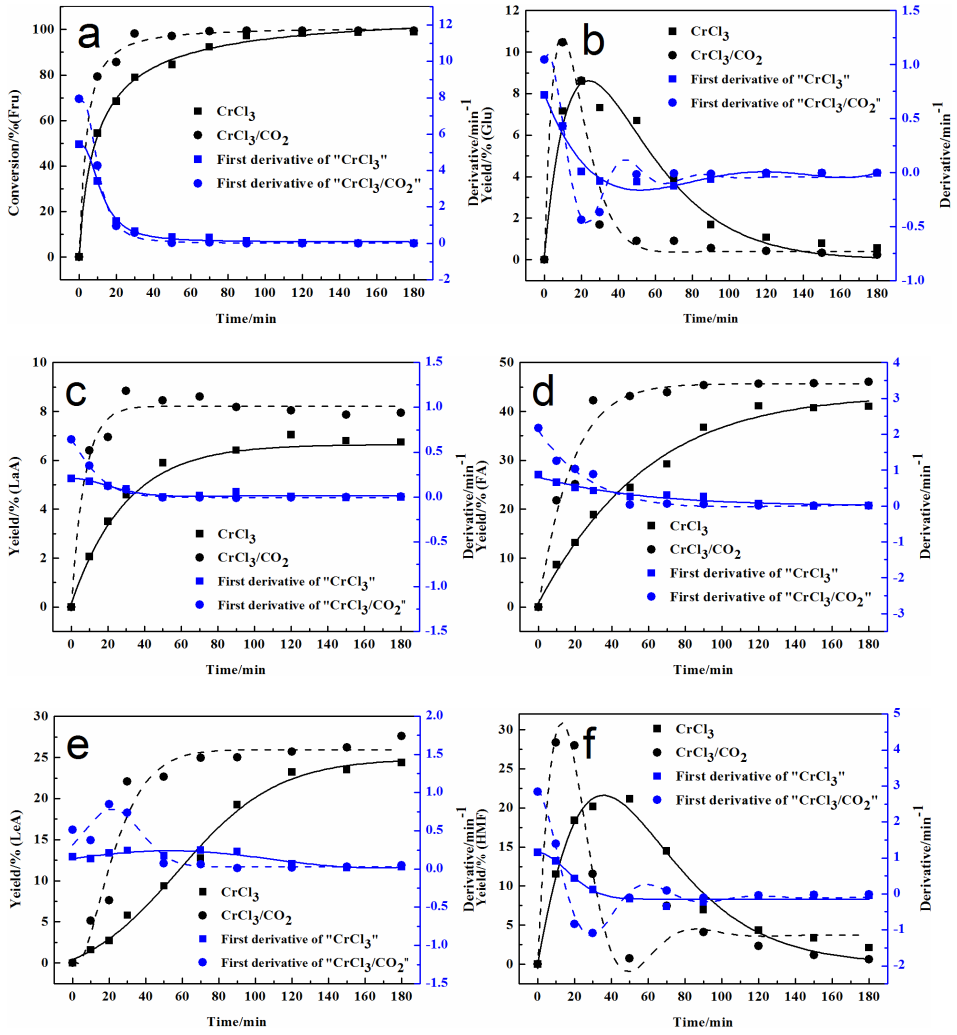

Figure S3. Time course of the conversion of fructose (a) and the yields of Glu (b), LaA (c), FA (d), LeA (e), and HMF (f), as well as the corresponding first derivative curves of fructose HTCs with $CrCl_3$ alone and $CrCl_3/CO_2$. Reaction condition: initial CO_2 pressure of 4 MPa, Cr^{3+} to glucose molar ratio of 3:100, 160 ^{o}C.

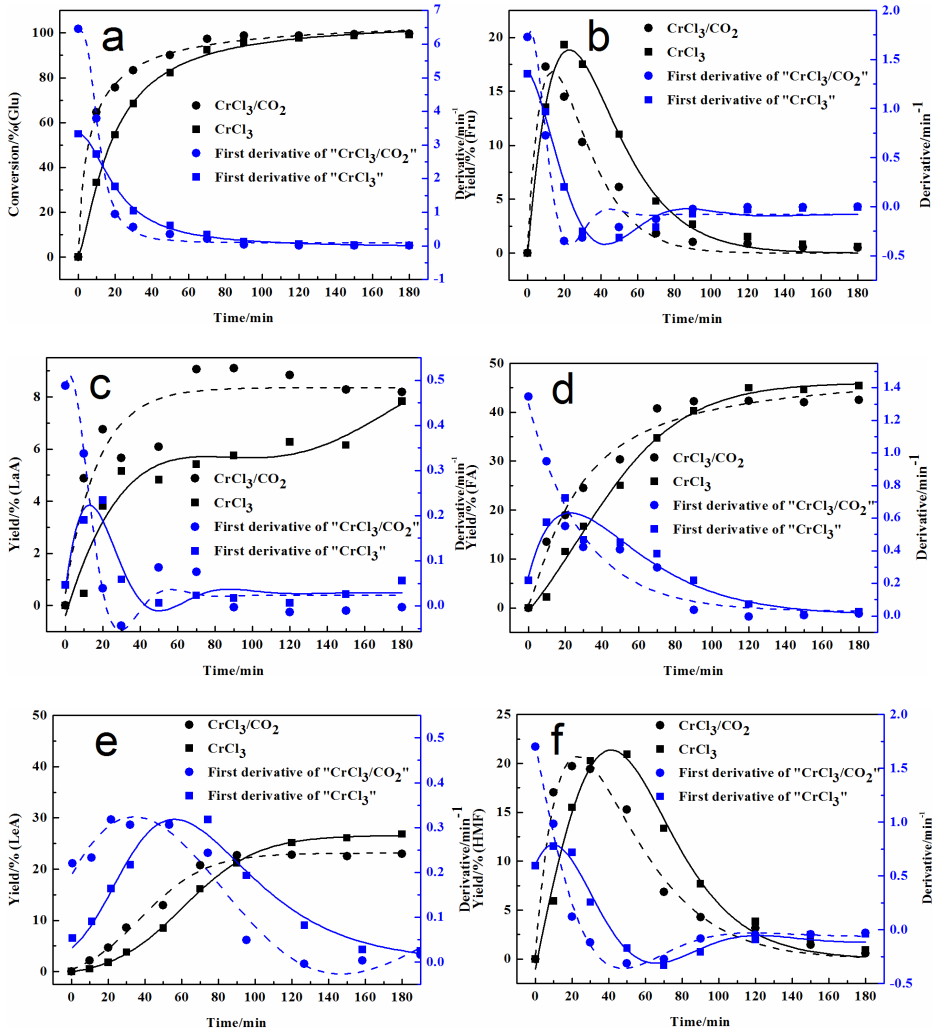

Figure S4. Time course of the conversion of glucose (a) and the yields of Fru (b), LaA (c), FA (d), LeA (e), and HMF (f), as well as the corresponding first derivative curves of glucose HTCs with $CrCl_3$ alone and $CrCl_3/CO_2$. Reaction condition: initial CO_2 pressure of 4MPa, Cr^{3+} to fructose molar ratio of 3:100, 160 ^{o}C.