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- Supporting Information-

Promoting the production of 5-hydroxymethylfurfual from high-concentration fructose by creating micro-reactors in a mixed solvent

Yexin Hu, Hui Li, Ping Hu, Linzhen Li, Di Wu, Zhidan Xue, Changwei Hu, and Liangfang Zhu*

Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, P. R. China.

**E-mail: zhulf@scu.edu.cn; Fax: +86 28 85411105; Tel: +86 28 85411105.*

Table S1. Product distributions with time for the fructose dehydration in the absence or presence of CTAB. [a]

Entry	CTAB/ mM	t /min	Conv. /%	Yield/%				TCB[b] /%	ACB[c] /%	(100-TCB) /%	(TCB-ACB) %
				HMF	FA	LA	FF				
1	-	1	50.8	1.6	-	-	-	50.8	50.8	49.2	-
2	-	2	78.9	6.6	-	-	0.1	27.8	27.8	72.2	-
3	-	3	82.3	12.4	0.4	-	0.2	30.7	30.3	69.3	0.3
4	-	5	85.9	23.0	2.0	0.8	0.5	39.5	38.5	60.5	1.0
5	-	10	86.9	28.5	3.5	1.2	0.5	45.5	43.6	54.5	1.9
6	-	15	94.2	47.3	6.0	3.6	1.3	60.1	58.1	39.9	2.0
7	70	1	53.2	4.2	-	-	-	51.0	51.0	49.0	-
8	70	2	80.8	18.2	-	-	0.1	37.5	37.5	62.5	-
9	70	3	88.1	39.2	-	-	0.1	51.2	51.2	48.8	-
10	70	5	91.0	50.3	0.5	-	0.2	60.0	59.6	40.0	0.4
11	70	10	92.1	60.5	1.5	0.6	0.3	70.2	69.4	29.9	0.8
12	70	15	97.8	70.3	1.7	0.8	0.3	74.5	73.7	25.5	0.8

[a] Reaction conditions: 500 mg/mL of fructose, 21 mM of H_2SO_4, 5 mL of solvent (V_{DIO}/V_{H2O}=95/5), 140 °C, under a N_2 atmosphere. [b] TCB [mol%] = (output of carbon + carbon in degraded fructose) / (input of carbon) × 100%. [c] ACB [mol%] = (output of carbon) / (input of carbon) × 100%.

Table S2. The possible ionic species deconvoluted from the ESI-MS spectra of the reaction mixture in absence of CTAB. [a]

m/z	Possible structural formula	m/z	Possible structural formula
203	$[Fru+Na]^{+}$	545	$[4Fru\text{-}11H_2O+Na]^{+}$
173	$[Fru\text{-}FA+K]^{+}$	527	$[4Fru\text{-}12H_2O+Na]^{+}$
249	$[3Fru\text{-}FA\text{-}2H_2O+H+K]^{2+}$	491	$[4Fru\text{-}14H_2O+Na]^{+}$
252	$[3Fru\text{-}FA\text{-}2H_2O+2Na]^{2+}$	344	$[4Fru\text{-}4H_2O+H+K]^{2+}$
445	$[3Fru\text{-}FA\text{-}4H_2O+Na]^{+}$	335	$[4Fru\text{-}5H_2O+H+K]^{2+}$
365	$[2Fru\text{-}H_2O+Na]^{+}$	326	$[4Fru\text{-}6H_2O+H+K]^{2+}$
347	$[2Fru\text{-}2H_2O+Na]^{+}$	317	$[4Fru\text{-}7H_2O+H+K]^{2+}$
311	$[2Fru\text{-}4H_2O+Na]^{+}$	308	$[4Fru\text{-}8H_2O+H+K]^{2+}$
273	$[2Fru\text{-}7H_2O+K]^{+}$	299	$[4Fru\text{-}9H_2O+H+K]^{2+}$
257	$[2Fru\text{-}7H_2O+Na]^{+}$	290	$[4Fru\text{-}10H_2O+H+K]^{2+}$
146	$[2Fru\text{-}6H_2O+H+K]^{2+}$	281	$[4Fru\text{-}11H_2O+H+K]^{2+}$
527	$[3Fru\text{-}2H_2O+Na]^{+}$	263	$[4Fru\text{-}13H_2O+H+K]^{2+}$
525	$[3Fru\text{-}3H_2O+K]^{+}$	254	$[4Fru\text{-}14H_2O+H+K]^{2+}$
509	$[3Fru\text{-}3H_2O+Na]^{+}$	398	$[5Fru\text{-}8H_2O+H+K]^{2+}$
473	$[3Fru\text{-}5H_2O+Na]^{+}$	389	$[5Fru\text{-}9H_2O+H+K]^{2+}$
455	$[3Fru\text{-}6H_2O+Na]^{+}$	380	$[5Fru\text{-}10H_2O+H+K]^{2+}$
437	$[3Fru\text{-}7H_2O+Na]^{+}$	371	$[5Fru\text{-}11H_2O+H+K]^{2+}$
419	$[3Fru\text{-}8H_2O+Na]^{+}$	362	$[5Fru\text{-}12H_2O+H+K]^{2+}$
401	$[3Fru\text{-}9H_2O+Na]^{+}$	353	$[5Fru\text{-}13H_2O+H+K]^{2+}$
245	$[3Fru\text{-}5H_2O+H+K]^{2+}$	515	$[6Fru\text{-}5H_2O+H+K]^{2+}$
236	$[3Fru\text{-}6H_2O+H+K]^{2+}$	506	$[6Fru\text{-}6H_2O+H+K]^{2+}$
227	$[3Fru\text{-}7H_2O+H+K]^{2+}$	488	$[6Fru\text{-}8H_2O+H+K]^{2+}$
218	$[3Fru\text{-}8H_2O+H+K]^{2+}$	479	$[6Fru\text{-}9H_2O+H+K]^{2+}$
209	$[3Fru\text{-}9H_2O+H+K]^{2+}$	470	$[6Fru\text{-}10H_2O+H+K]^{2+}$
200	$[3Fru\text{-}10H_2O+H+K]^{2+}$	461	$[6Fru\text{-}11H_2O+H+K]^{2+}$
671	$[4Fru\text{-}4H_2O+Na]^{+}$	452	$[6Fru\text{-}12H_2O+H+K]^{2+}$
617	$[4Fru\text{-}7H_2O+Na]^{+}$	443	$[6Fru\text{-}13H_2O+H+K]^{2+}$
599	$[4Fru\text{-}8H_2O+Na]^{+}$	434	$[6Fru\text{-}14H_2O+H+K]^{2+}$
581	$[4Fru\text{-}9H_2O+Na]^{+}$	425	$[6Fru\text{-}15H_2O+H+K]^{2+}$
563	$[4Fru\text{-}10H_2O+Na]^{+}$	416	$[6Fru\text{-}16H_2O+H+K]^{2+}$
545	$[4Fru\text{-}11H_2O+Na]^{+}$		

[a] In the above structural formula, $[Fru\text{-}3H_2O]$ could also be assigned to [HMF].

Note: structural formulas marked by green represented FA-related species, those marked by pink represented dimerized fructose-related species, those marked by blue represented trimerized fructose-related species, those marked by purple represented tetramerized fructose-related species, those marked by yellow represented pentamerized fructose-related species, and those marked by brown represented hexamerized fructose-related species.

Table S3. The possible ionic species deconvoluted from the ESI-MS spectra of the reaction mixture in presence of CTAB. [a]

m/z	Possible structural formula	m/z	Possible structural formula
203	$[Fru+Na]^+$	527	$[4Fru-12H_2O+Na]^+$
173	$[Fru-FA+K]^+$	491	$[4Fru-14H_2O+Na]^+$
381	$[2Fru-H_2O+K]^+$	344	$[4Fru-4H_2O+H+K]^{2+}$
365	$[2Fru-H_2O+Na]^+$	335	$[4Fru-5H_2O+H+K]^{2+}$
347	$[2Fru-2H_2O+Na]^+$	326	$[4Fru-6H_2O+H+K]^{2+}$
311	$[2Fru-4H_2O+Na]^+$	317	$[4Fru-7H_2O+H+K]^{2+}$
146	$[2Fru-6H_2O+H+K]^{2+}$	308	$[4Fru-8H_2O+H+K]^{2+}$
527	$[3Fru-2H_2O+Na]^+$	299	$[4Fru-9H_2O+H+K]^{2+}$
525	$[3Fru-3H_2O+K]^+$	398	$[5Fru-8H_2O+H+K]^{2+}$
509	$[3Fru-3H_2O+Na]^+$	389	$[5Fru-9H_2O+H+K]^{2+}$
473	$[3Fru-5H_2O+Na]^+$	380	$[5Fru-10H_2O+H+K]^{2+}$
455	$[3Fru-6H_2O+Na]^+$	371	$[5Fru-11H_2O+H+K]^{2+}$
437	$[3Fru-7H_2O+Na]^+$	362	$[5Fru-12H_2O+H+K]^{2+}$
419	$[3Fru-8H_2O+Na]^+$	353	$[5Fru-13H_2O+H+K]^{2+}$
401	$[3Fru-9H_2O+Na]^+$	515	$[6Fru-5H_2O+H+K]^{2+}$
245	$[3Fru-5H_2O+H+K]^{2+}$	506	$[6Fru-6H_2O+H+K]^{2+}$
236	$[3Fru-6H_2O+H+K]^{2+}$	488	$[6Fru-8H_2O+H+K]^{2+}$
227	$[3Fru-7H_2O+H+K]^{2+}$	470	$[6Fru-10H_2O+H+K]^{2+}$
218	$[3Fru-8H_2O+H+K]^{2+}$	461	$[6Fru-11H_2O+H+K]^{2+}$
209	$[3Fru-9H_2O+H+K]^{2+}$	452	$[6Fru-12H_2O+H+K]^{2+}$
200	$[3Fru-10H_2O+H+K]^{2+}$	443	$[6Fru-13H_2O+H+K]^{2+}$
671	$[4Fru-4H_2O+Na]^+$	434	$[6Fru-14H_2O+H+K]^{2+}$
635	$[4Fru-6H_2O+Na]^+$	425	$[6Fru-15H_2O+H+K]^{2+}$
617	$[4Fru-7H_2O+Na]^+$	416	$[6Fru-16H_2O+H+K]^{2+}$
599	$[4Fru-8H_2O+Na]^+$	407	$[6Fru-17H_2O+H+K]^{2+}$
581	$[4Fru-9H_2O+Na]^+$		

[a] In the above structural formula, $[Fru-3H_2O]$ could also be assigned to [HMF].

Note: structural formulas marked by green represented FA-related species, those marked by pink represented dimerized fructose-related species, those marked by blue represented trimerized fructose-related species, those marked by purple represented tetramerized fructose-related species, those marked by yellow represented pentamerized fructose-related species, and those marked by brown represented hexamerized fructose-related species.

Table S4. Effect of stirring speed on the product distributions of fructose dehydration in the presence of CTAB. [a]

Entry	Stirring speed /rpm	Conv. /%	Yield/%				TCB[b] /%	ACB[c] /%	100-TCB /%	TCB-ACB /%
			HMF	FA	LA	FF				
1	300	97.4	64.8	2.3	1.1	0.3	70.0	69.1	30.0	1.0
2	600	97.8	70.3	1.7	0.8	0.3	74.5	73.7	25.5	0.8
3	1200	97.5	70.2	1.7	0.9	0.4	74.8	74.1	25.2	0.7

[a] Reaction conditions: 50.0 wt.% fructose, 21 mM H_2SO_4, 70 mM CTAB, 5 mL of DIO-H_2O (V_{DIO}/V_{H2O} = 95/5), 140 °C, 15 min, under a N_2 atmosphere. [b] TCB [mol%] = (output of carbon + carbon in degraded fructose) / (input of carbon) × 100%. [c] ACB [mol%] = (output of carbon) / (input of carbon) × 100%.

Table S5. Stability of HMF in the absence or presence of CTAB. [a]

Entry	Modifier /mM	Conv. /%	Yield/%		TCB[b] /%	ACB[c] /%	(100%-TCB) /%	(TCB-ACB) %
			FA	LA				
1	-	12.1	7.3	3.2	95.2	91.8	4.8	3.4
2	CTAB, 70	2.8	2.0	0.9	99.2	98.3	0.8	0.9
3	NaBr, 70	6.9	3.9	1.2	97.0	94.8	3.0	2.3

[a] Reaction conditions: 1.4 M of HMF, 21 mM of H_2SO_4, 5 mL of solvent (V_{DIO}/V_{H2O}=95/5), 140 °C, 15 min, under a N_2 atmosphere. [b] TCB [mol%] = (output of carbon + carbon in degraded HMF) / (input of carbon) × 100%. [c] ACB [mol%] = (output of carbon) / (input of carbon) × 100%.

Table S6. The HMF yields and TOFs for the fructose-to-HMF dehydration with various concentrations of fructose and CTAB. [a]

Entry	Fructose / wt.%	CTAB / mM	HMF yield / %	TOF / h^{-1}
1	10.0	14	68.0	36.0
2	20.0	14	67.5	71.4
3	30.0	14	63.1	100.2
4	40.0	14	62.5	132.3
5	50.0	14	63.3	167.5
6	60.0	14	56.2	178.4
7	50.0	28	64.6	170.9
8	50.0	42	67.2	177.8
9	50.0	56	67.8	179.4
10	50.0	70	70.3	186.0

[a] Reaction conditions: 21 mM of H_2SO_4, 5 mL of solvent (V_{DIO}/V_{H2O}=95/5), 140 ^{o}C, 15 min, under a N_2 atmosphere.

Table S7. Effect of CTAB on the product distributions of fructose dehydration in various organic solvent/water mixed solvents. [a]

Entry	Org.	CTAB /mM	Conv. /%	Yield/%				TCB[b] /%	ACB[c] /%	100-TCB /%	TCB-ACB /%
				HMF	FA	LA	FF				
1	THF	-	80.6	22.3	8.8	0.9	0.5	50.9	44.3	49.1	6.6
2	THF	70	82.5	33.0	5.8	0.6	0.3	56.6	52.2	43.4	4.4
3	NMP	-	82.8	28.7	1.7	0.9	0.1	47.7	47.0	52.3	0.7
4	NMP	70	87.9	45.0	0.6	0.4	0.1	57.7	57.6	42.3	0.1

[a] Reaction conditions: 50.0 wt.% fructose, 21 mM H_2SO_4, 5 mL of solvent ($V_{org.}/V_{H2O}$ = 95/5), 140 °C, 15 min, under a N_2 atmosphere. [b] TCB [mol%] = (output of carbon + carbon in degraded fructose) / (input of carbon) × 100%. [c] ACB [mol%] = (output of carbon) / (input of carbon) × 100%.

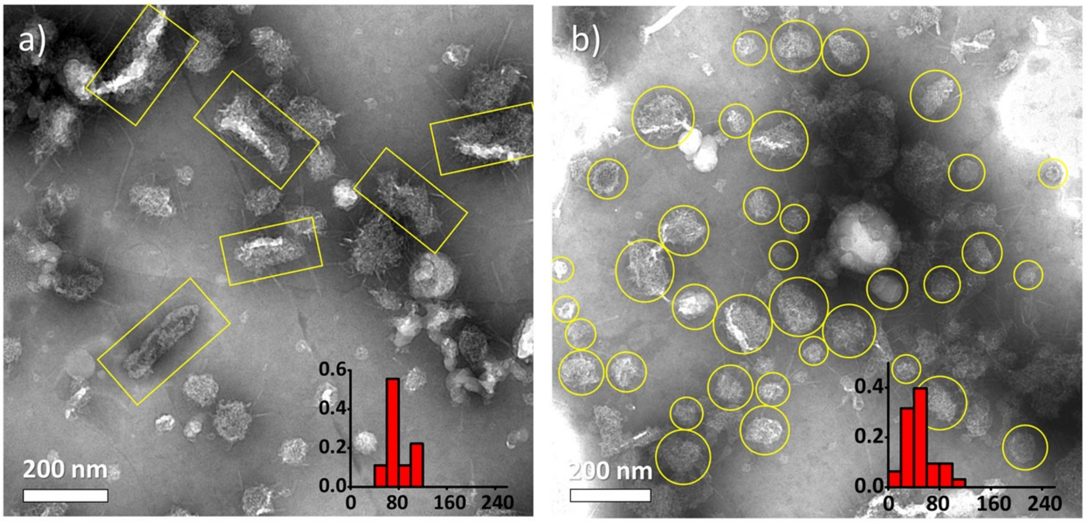

Figure S1. TEM images of a) 28 mM CTAB in DIO-H_2O (V_{DIO}/V_{H2O} = 95/5), and b) 14 mM CTAB in DIO-H_2O (V_{DIO}/V_{H2O} = 80/20) at room temperature. The inset in each image shows the respective histogram of the micellar diameter distribution (abscissa) with percentage as the ordinate.