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Supporting Information

The Effects of Emulsion on Sugars Dehydration to 5-Hydroxymethylfurfural in Biphasic System

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EXPERIMENTAL METHODS

General Information. All solvents and chemicals used were obtained from commercial suppliers and used directly without any pre-treatment, unless otherwise indicated. Conversions of the reaction were typically monitored by SU-300 Sugar Analyzer (TOA-DKK Corp.). Furfural yields were analyzed by HPLC (Agilent Technologies, 1200 series). HPLC working conditions: column (Agilent Hi-Plex H, 7.7 × 300 mm, 8 μm), solvent 10 mM H_2SO_4, flow rate 0.7 ml/min, 25 °C, UV detector 280 nm. The silica nanoparticles sizes were characterized by TEM (FEI Tecnai F20).

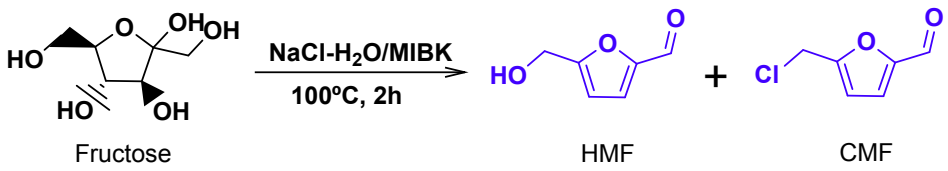
Synthesis and functionalization of silica nanoparticles. The synthesis of silica nanoparticles were modified from the well-established Stöber process. For 200 nm nanoparticles: To a 500 mL round-bottomed flask, ethanol (300 mL), deionized water (90 mL) and aqueous NH_3 solution (28 wt%, 30 mL) were added and placed in a water bath pre-heated to 30 °C. Tetraethyl orthosilicate (30 mL) were then added dropwise to the mixture with stirring for 6 h. The reaction mixture was then washed with ethanol until pH 7, dried under vacuum at 100 °C overnight. For functionalized nanoparticles: To an 8 mL sealed tube equipped with stirrer bars, 1 g of silica nanoparticles were added. Anhydrous toluene (5 mL), appropriate amount of [3-(2-aminoethylamino)propyl]trimethoxysilane/N^1-(3-Trimethoxysilylpropyl) diethylenetriamine and triethoxy(octyl)silane (total organosilane kept at 1.5 mmol) were added and stirred at 110 °C for 24 h under argon atmosphere. The reaction mixture was then washed with toluene, dried under vacuum at 50 °C overnight.

Synthesis of Al/SiO_2. The prepared SiO_2 (0.57 g), $Al(NO_3)_3.9H_2O$ (0.42 g) and acetone (5 – 10 mL) were stirred under open air at room temperature for 24 h to remove the acetone. The resulting mixture was then calcined at 450 °C for 2 h under 5% H_2 with 95% Ar.

Fructose dehydration in biphasic system. In a typical reaction, to a 15 mL sealed tube equipped with stirrer bars, fructose (0.09 g, 0.5 mmol), aq. HCl (2 mL, 0.25 M), NaCl (0.7 g), MIBK (6 mL), nanoparticles (16 mg) were added and stirred at 100 °C for 2 h. Aliquots of the reaction mixture were taken out for HPLC analysis.

Glucose dehydration in biphasic system. In a typical reaction, to a 8 mL sealed tube equipped with stirrer bars, glucose (0.18 g, 1 mmol), NaCl-saturated aq. HCl (1 mL, 0.25 M), MIBK (3 mL), Si-12 (90 mg) and 2.5 wt% $AlCl_3$ were added and stirred at 150 °C. Aliquots of the reaction mixture were taken out for HPLC analysis.

Recycling experiment. After performing the fructose dehydration reaction as described above, the nanoparticles were separated from the solvents by centrifugation. The nanoparticles were then washed with H_2O and MeOH, dried in vacuum oven at 50 °C overnight and used directly for subsequent run.



Scheme S1. Fructose dehydration in NaCl-H_2O/MIBK biphasic system.

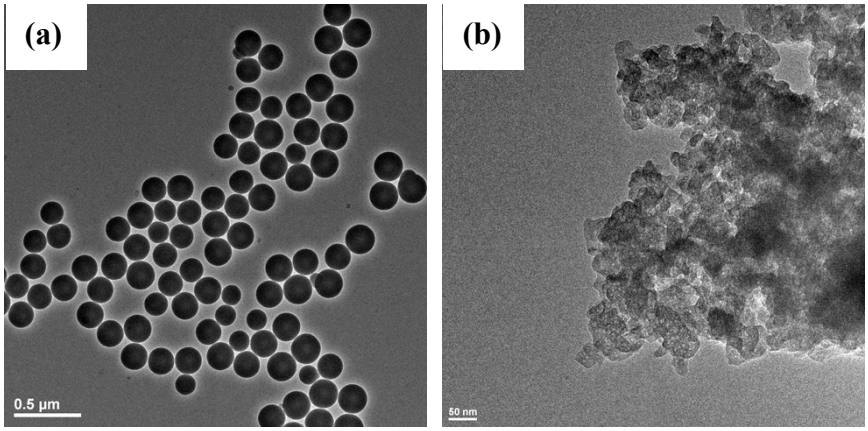


Figure S1. TEM image of (a) synthesized 200 nm silica nanoparticles and (b) commercial silica nanopowder

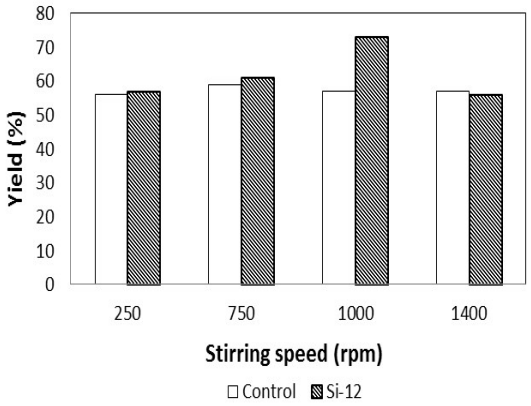


Figure S2. The effect of stirring rate on fructose dehydration to HMF. Reaction condition: Fructose (0.5 mmol), aq. HCl (2 mL, 0.25 M), NaCl (0.7 g), MIBK (6 mL), Si-12 (16 mg), 100 °C, 2 h. For control reaction, no nanoparticles were added.

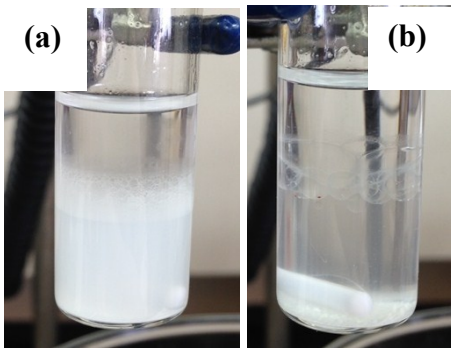


Figure S3 Image of emulsion formed after left standing for 15 mins (a) before and (b) after adding NaCl

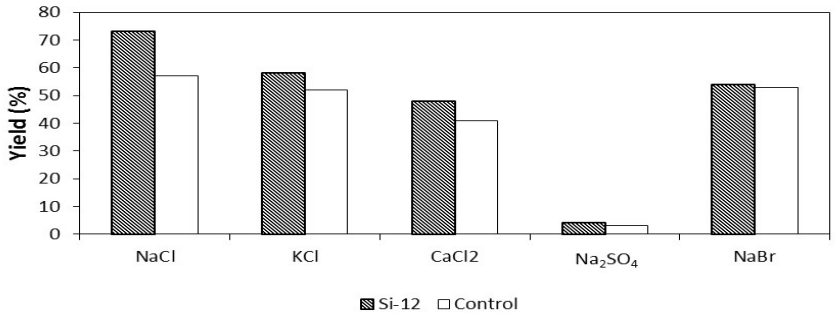


Figure S4 Effect of various salts on emulsion biphasic system. Reaction condition: Fructose (0.5 mmol), salt-saturated aq. HCl (2 mL, 0.25 M), MIBK (6 mL), Si-12 (16 mg), 100 °C, 2 h. For control reaction, no nanoparticles were added.

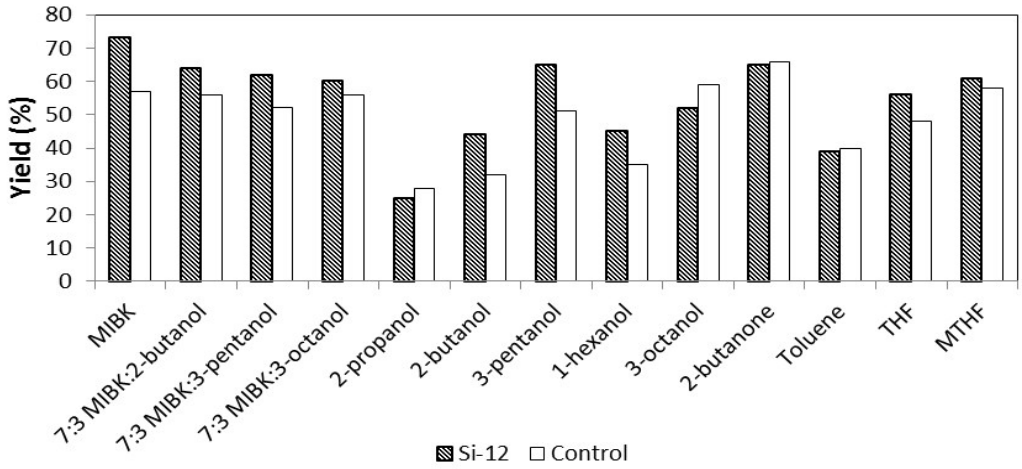


Figure S5 Effect of various solvents on emulsion biphasic system. Reaction condition: Fructose (0.5 mmol), aq. HCl (2 mL, 0.25 M), NaCl (0.7 g), solvent (6 mL), Si-12 (16 mg), 100 °C, 2 h. For control reaction, no nanoparticles were added.

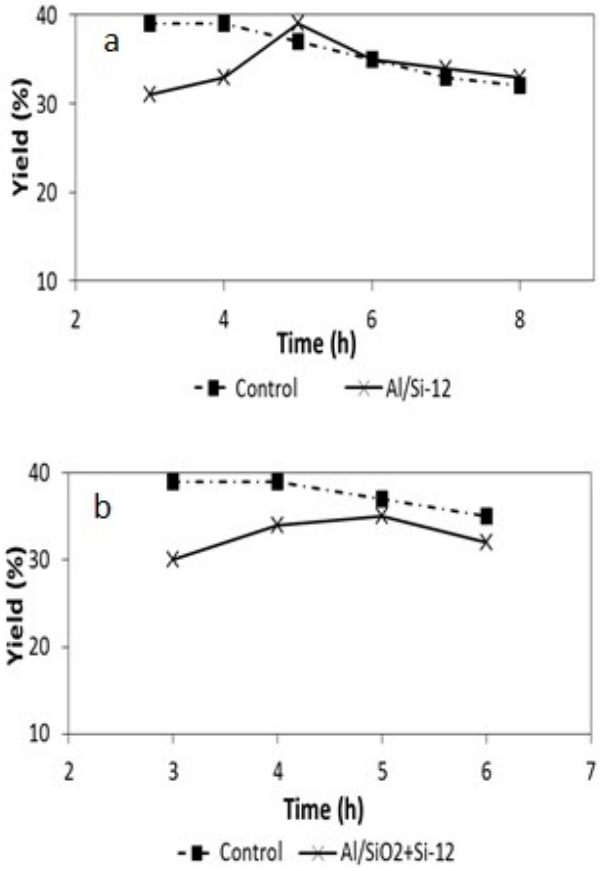


Figure S6. Effect of (a) bifunctional and (b) monofunctional nanoparticles on glucose dehydration to HMF. Reaction condition: Glucose (1 mmol), NaCl-saturated aq. HCl (1 mL, 0.25 M), MIBK (3 mL), Al/SiO_2 (90 mg), Si-12 (90 mg), 150 °C.

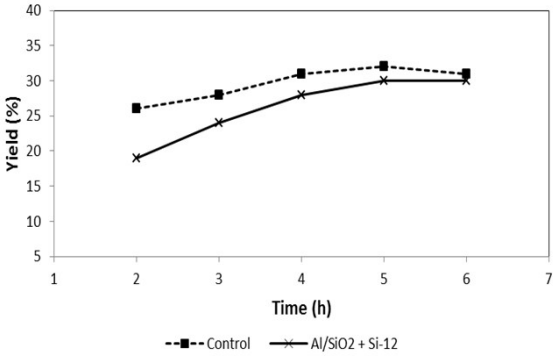


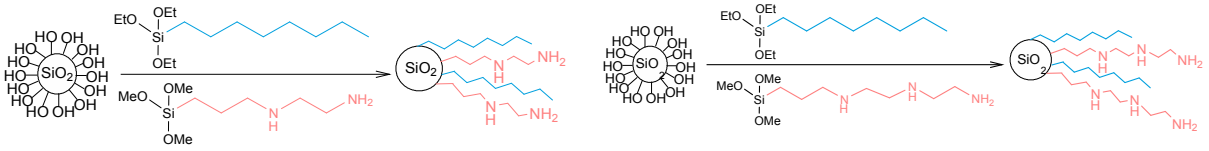
Figure S7 Effect of monofunctional nanoparticles on glucose dehydration to HMF with increased Al/SiO_2 and decreased Si-12. Reaction condition: Glucose (1 mmol), NaCl-saturated aq. HCl (1 mL, 0.25 M), MIBK (3 mL), Al/SiO_2 (180 mg), Si-12 (45 mg), 150 °C.

Table S1. Control reactions for fructose dehydration to HMF

Entry	Nanoparticles	Total HMF Yield (%)	Selectivity (%)
1	-	57	60
2	SiO_2	47	54
3	Si-12	73	90
4	Si-12 *	59	59

Reaction condition: Fructose (0.5 mmol), aq. HCl (2 mL, 0.25 M), NaCl (0.7 g), MIBK (6 mL), nanoparticles (16 mg), 100 °C, 2 h. Si-12: silica particle (200 nm) loaded with diamine (0.76 mmol/g) and octyl (0.30 mmol/g). * Commercial silica particles.

Table S2. Elemental analysis results for the functionalized nanoparticles.



Entry	Nanoparticles (200 nm)	C (wt%)	H (wt%)	N (wt%)	Di- / Triamine loading (mmol/g)	Octyl loading (mmol/g)	Molar ratio (Di-/ Triamine:Octyl)	Yield (%)
1	2N, Si-5	9.89	0.72	<0.50	-	1.030	-	59
2	2N, Si-12	7.51	2.16	2.14	0.764	0.304	2.51	73
3	2N, Si-12 B7	8.32	2.419	2.25	0.803	0.364	2.21	62
4	2N, Si-30	7.82	2.15	2.28	0.813	0.305	2.67	66
5	2N, Si-12 B5	8.27	2.31	2.51	0.896	0.301	2.98	60
6	2N, Si-50	6.05	1.94	1.37	0.489	0.324	1.51	60
7	2N, Si-80	5.21	1.91	1.01	0.360	0.317	1.14	58
8	3N, Si-12	11.07	3.005	3.57	0.849	0.409	2.08	57
9	3N, Si-30	9.32	2.811	2.91	0.692	0.364	1.90	72
10	3N, Si-50	7.13	2.188	1.79	0.426	0.369	1.15	69
11	3N, Si-80	5.07	2.05	0.81	0.193	0.359	0.537	69
12	3N, Si-96	3.72	1.716	<0.5	-	0.389	-	64

Table S3. Various metals screening and calcination conditions for glucose dehydration to HMF

Entry	Metal/SiO_2	Calcination Condition	Glu Conversion (%)	Fructose (%)	Total HMF Yield (%)	Selectivity (%)
1	Cr/SiO_2	450°C, 5%H_2	28	Trace	11	39
2	Ti/SiO_2	450°C, 5%H_2	36	Trace	11	31
3	Al/SiO_2	450°C, 5%H_2	51	13	20	39
4[a]	Al/SiO_2	450°C, 5%H_2	54	18	13	24
5	Al/SiO_2	450°C, air	74	13	21	28
6	Al/SiO_2	700°C, air	69	14	20	29
7	Al/SiO_2	900°C, air	66	14	22	33

Reaction condition: Glucose (0.18 g, 1 mmol), NaCl-saturated aq. HCl (1 mL, 0.25M), MIBK (3 mL), metal/SiO_2 (90 mg), 120 °C, 10 h. [a] 180 mg of Al/SiO_2 added.

Table S4. HMF stability test.

Time (h)	Control			Si-12 (200 nm)		
	HMF added	HMF detected	Loss (%)	HMF added	HMF detected	Loss (%)
2	**1.01**	0.8057	20	**1.09**	0.956	12
3	**1.032**	0.7576	27	**1.07**	0.895	16
4	**0.993**	0.6302	37	**0.983**	0.728	26

Reaction condition: aq. HCl (2 mL, 0.25 M), NaCl (0.7 g), MIBK (6 mL), Si-12 (16 mg).