

Supporting Information

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

Siew-ping Teong, Guangshun Yi, Huaqiang Zeng and Yugen Zhang*

Institute of Bioengineering and Nanotechnology, 31 Biopolis Way, The Nanos, Singapore 138669

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 H₂SO₄, 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 NH₃ 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/N¹-(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/SiO₂. The prepared SiO₂ (0.57 g), Al(NO₃)₃·9H₂O (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% H₂ 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% AlCl₃ were added and stirred at 150 °C. Aliquots of the reaction mixture were taken out for HPLC analysis.

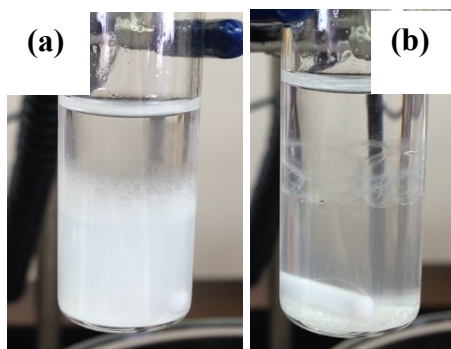


Figure S3 Image of emulsion formed after left standing for 15 mins (a) before and (b) after adding NaCl

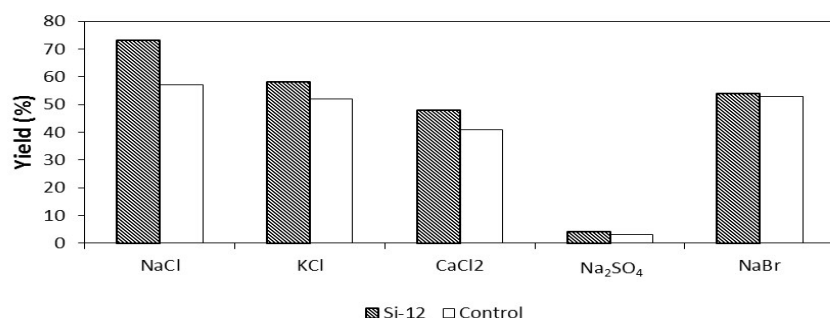


Figure S4 Effect of various salts on emulsion biphasic system. Reaction condition: Fructose (0.5 mmol), salt-saturated aq. HCl (2 mL, 0.25 M), MIBK (6 mL), Si-12 (16 mg), 100 °C, 2 h. For control reaction, no nanoparticles were added.

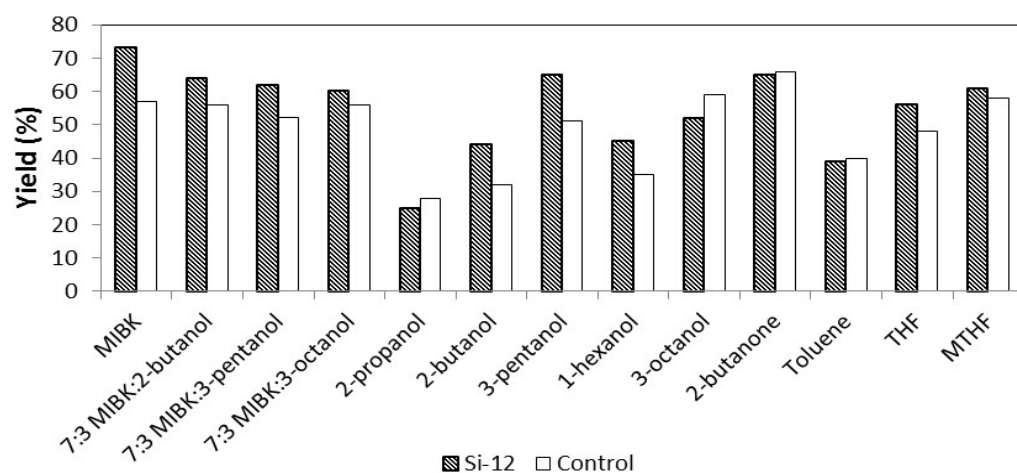


Figure S5 Effect of various solvents on emulsion biphasic system. Reaction condition: Fructose (0.5 mmol), aq. HCl (2 mL, 0.25 M), NaCl (0.7 g), solvent (6 mL), Si-12 (16 mg), 100 °C, 2 h. For control reaction, no nanoparticles were added.

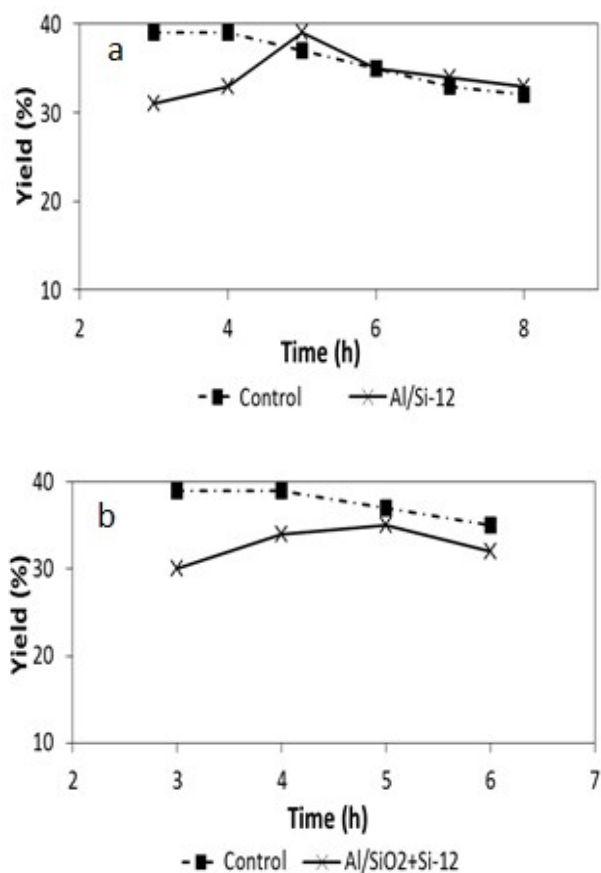


Figure S6. Effect of (a) bifunctional and (b) monofunctional nanoparticles on glucose dehydration to HMF. Reaction condition: Glucose (1 mmol), NaCl-saturated aq. HCl (1 mL, 0.25 M), MIBK (3 mL), Al/SiO₂ (90 mg), Si-12 (90 mg), 150 °C.

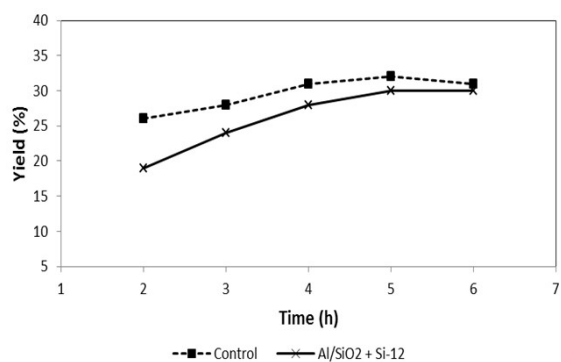
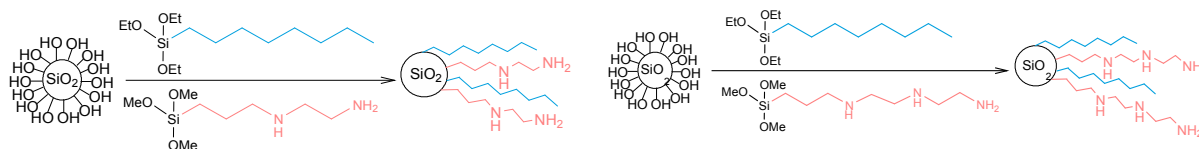


Figure S7 Effect of monofunctional nanoparticles on glucose dehydration to HMF with increased Al/SiO₂ and decreased Si-12. Reaction condition: Glucose (1 mmol), NaCl-saturated aq. HCl (1 mL, 0.25 M), MIBK (3 mL), Al/SiO₂ (180 mg), Si-12 (45 mg), 150 °C.

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/SiO₂ (90 mg), 120 °C, 10 h. ^a 180 mg of Al/SiO₂ 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).