Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Space and time-resolved probing of heterogeneous catalysis reactions using lab-on-a-chip

Chelliah V. Navin,[†,‡,§,‖] Katla Sai Krishna,[†,‖,†] Chandra S. Theegala,[‡] and Challa S.S.R. Kumar*[,†,‖,†]

[†]Center for Advanced Microstructures and Devices (CAMD), Louisiana State University, Baton Rouge, Louisiana 70806, United States.
[‡]Department of Biological and Agricultural Engineering, Louisiana State University and LSU AgCenter, Baton Rouge, Louisiana 70803, United States.
[§]Engineering Sciences, Louisiana State University, Baton Rouge, Louisiana 70803, United States.
[‖]Center for Atomic-Level Catalyst Design, #324, Cain Department of Chemical Engineering, Louisiana State University, Baton Rouge, Louisiana 70803, United States.

Experimental section:

Chemicals:

Chloroplatinic acid hexahydrate ($H_2PtCl_6.6H_2O$, 99.9%, Strem chemicals), meso-2,3-dimercaptosuccinic acid (DMSA, 97%, Alfa Aesar), Sodium hydroxide (NaOH, 98.6%, Macron chemicals), sodium borohydride ($NaBH_4$, 98%, Aldrich), Ethanol (EtOH, 200 proof), 5-(Hydroxymethyl)furfural (HMF, Aldrich), 5-Hydroxymethyl-2-furancarboxylic acid (HMFCA, Aldrich), 2, 5-Furandicarboxylic acid (FDCA, Aldrich), and *tert*-Butyl hydroperoxide solution (70% in water, Luperox® TBH70X, Aldrich) were purchased. All chemicals were used as received without further purification. Nanopure water was used for all the experiments.

Millifluidic platform set-up:

The uncoated millifluidic reactor chips made of polyester terephthalate (PET) were purchased from Millifluidica LLC. The channel dimensions of the chip were 2 mm wide, 0.15 mm in depth and 220 mm in length. The uncoated millifluidic chip reactor was tested with water as solvent at different flow rates prior to the experiment to optimize the required flow rate.

In-Chip Catalysis experiments:

In a typical reaction, HMF (3 mM), NaOH (12 mM) and 70% TBHP in H_2O (10x diluted) was used for the HMF oxidation reaction.

Nanostructured gold catalyst formation:

The synthesis of Au nanoparticles for batch reactions and coating of nanostructured gold within the millifluidic reactor channel for continuous flow reactions were carried out according to the procedure described by Krishna *et.al.*[1]

Continuous flow oxidation of HMF using millifluidic reactor:

5 mL of 3 mM HMF was mixed in 5 mL of 12 mM NaOH in a vial. To this mixture, 5 mL of 10x diluted 70% TBHP in H_2O was added and vortexed for 10 seconds. This reaction mixture was then transferred to a syringe and injected into the millifluidic reactor chip coated with nanostructured gold catalyst at 0.1 mL/h using a pulsation free syringe pump at room temperature and pressure. Reaction samples were collected at different spatial intervals as the reaction mixture moved within the millifluidic reactor channel as shown in Figure 1. These samples were analyzed using UV-Vis spectrophotometer and HPLC without further processing.

Batch mode oxidation of HMF:

5 mL of 3 mM HMF solution was mixed with 5 mL of 12 mM NaOH solution in a conical flask. To this mixture 5 mL of 10x diluted 70% TBHP in H_2O was added along with 5 mg of Au nanoparticles. The vial was closed and the reaction solutions were mixed using a magnetic stirrer at room temperature and pressure. Samples were taken as the reaction progressed and centrifuged to remove any Au nanoparticles that might have transferred during

the sample collection. The centrifuged samples were analyzed using UV-Vis spectrophotometer and HPLC without further processing.

UV-Visible spectroscopy (UV-Vis):

Optical absorbance of the HMF reaction samples were recorded using Shimadzu, UV-3600 spectrophotometer in a 10 mm Quartz cuvette (sample volume taken is ~ 3 mL) and the absorbance was measured from 200 nm to 350 nm. R-928 photomultiplier tube made of multialkali photocathode 28 mm (1-1/8 inch) diameter, 9-stage, side-on type was used as the detector for the UV-Vis region.

High-performance Liquid Chromatography (HPLC):

HPLC analysis was performed with a Waters 616 pump, Waters 2707 Autosampler, and 996 Photodiode Assay Detector, which are controlled by Waters Empower 2 software. The separation was performed on an Agilent Zorbax 300Extend- C18 column (5 um, 4.6× 150 mm) with guard column (3.2 × 10 mm) by a gradient resulting from mixing eluents A (0.1% TFA in water) and B (0.1% TFA in acetonitrile). The flow rate used was 1.0 mL/min.

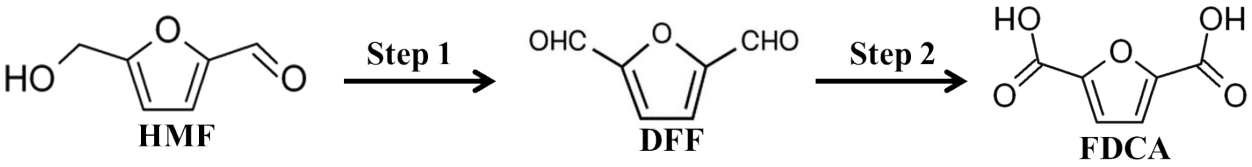

Figure S1: *HMF Oxidation pathway leading to FDCA with DFF as the intermediate product*

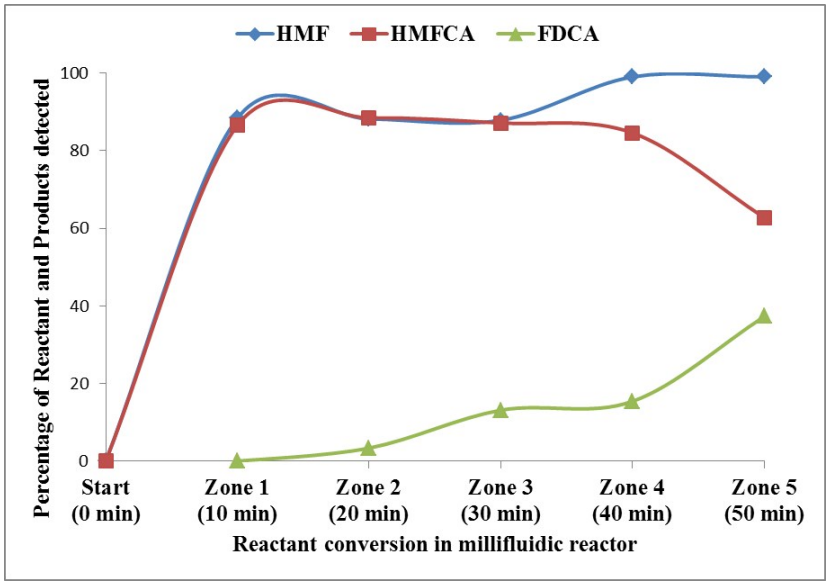

Figure S2: *Oxidation of HMF to FDCA using a millifluidic reactor chip coated with nanostructured gold catalyst.*

Table S1. HPLC data for oxidation of HMF using millifluidic reactor

Volume of sample collected at 10, 20, 30, 40, 50 minutes = 0.016, 0.033, 0.05, 0.066, 0.083 ml respectively

	HMF		HMFCA			FDCA		
Sample	**Peak area**	**Conc. (mM)**	**Peak area**	**Conc. (mM)**	**Total moles of product**	**Peak area**	**Conc. (mM)**	**Total moles of product**
Zone 1 (10 min)	2673	0.349	15549	0.302	$4.83*10^{-9}$	NA	0	NA
Zone 2 (20 min)	6410	0.355	30269	0.314	$1.03*10^{-8}$	3762	0.0106	$3.49*10^{-10}$
Zone 3 (30 min)	3941	0.365	35273	0.318	$1.59*10^{-8}$	11647	0.0418	$2.09*10^{-9}$
Zone 4 (40 min)	NA	NA	43511	0.324	$2.13*10^{-8}$	55491	0.05	$3.3*10^{-9}$
Zone 5 (50 min)	NA	NA	16489	0.303	$2.51*10^{-8}$	155399	0.113	$9.37*10^{-9}$

Table S2. Percentage of HMF converted and yields of HMFCA and FDCA detected at different zones of the millifluidic reactor channel

Exp. No.	Time (min)	Zone	HMF conversion (%)	HMFCA detected (%)	HMFCA Yield (%)	FDCA detected (%)	FDCA Yield (%)
1	0	0	0	0	0	0	0
2	10	1	88.36	86.53	10.06	0	0
3	20	2	88.16	88.45	10.82	3.37	0.35
4	30	3	87.83	87.12	11.99	13.14	1.39
5	40	4	~99	84.57	12.46	15.43	1.66
6	50	5	~99	62.71	13.86	37.29	3.76

Table S3. Percentage of HMF converted and HMFCA and FDCA detected using batch reactor as a function of time

Exp. No.	**Time (h)**	**HMF conversion (%)**	**HMFCA detected (%)**	**FDCA detected (%)**
1	0	0	0	0
2	1	84	92.8	7.2
3	2	100	71.7	28.3
4	4	100	69.4	30.6
5	6	100	67.5	32.5
6	24	100	0	~99

Table S4. HPLC data for oxidation of HMF using batch reactor

Volume of sample = 15 ml

	HMF		HMFCA			FDCA		
Sample	**Peak area**	**Conc. (mM)**	**Peak area**	**Conc. (mM)**	**Total Moles of product**	**Peak area**	**Conc. (mM)**	**Total Moles of product**
0 h	-	3	NA	NA	NA	NA	NA	NA
1 h	32161	0.478	1001498	0.369	$5.53*10^{-6}$	34143	0.0266	$3.99*10^{-7}$
2 h	NA	NA	46576	0.326	$4.89*10^{-6}$	126780	0.0924	$1.38*10^{-6}$
4 h	NA	NA	28135	0.312	$4.68*10^{-6}$	131353	0.0956	$1.43*10^{-6}$
6 h	NA	NA	24264	0.309	$4.63*10^{-6}$	138279	0.1006	$1.50*10^{-6}$
24 h	NA	NA	NA	NA	NA	152525	0.1107	$1.66*10^{-6}$

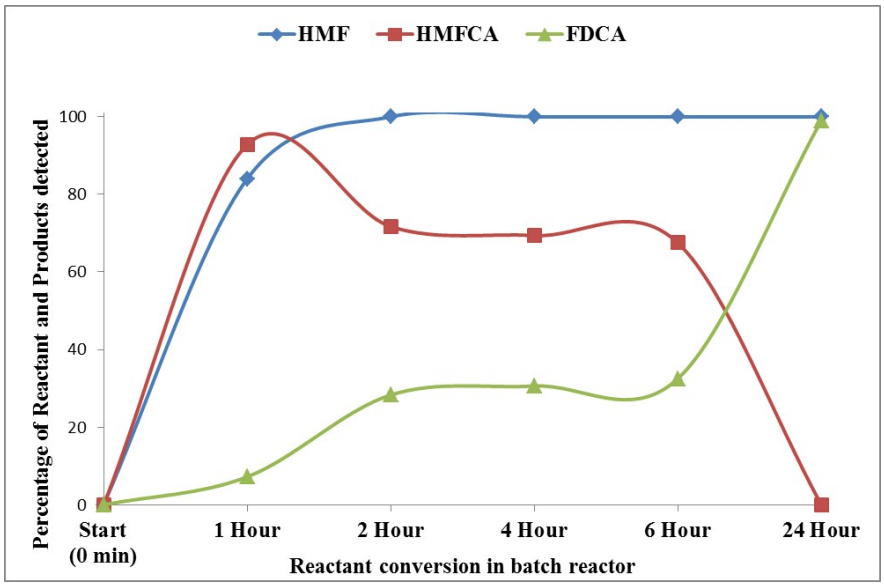

Figure S3: *Oxidation of HMF to FDCA using flask with gold nanoparticles*

Table S5. HPLC data for the control experiment carried out with HMFCA as the initial reactant

	HMFCA		FDCA	
Experiment time (h)	Peak area	Concentration (mM)	Peak Area	Concentration (mM)
t = 0	1452618	1.44	0	0
t = 24	1302451	1.32	0	0

Table S6. HPLC data for the control experiment carried out with HMF as the initial reactant

	HMF		HMFCA		FDCA	
Experiment time (h)	Peak Area	Concentration (mM)	Peak Area	Concentration (mM)	Peak Area	Concentration (mM)
t = 0	313928	1.71	0	0	0	0
t = 24	242761	1.39	0	0	0	0

References

1 K.S. Krishna, C.V. Navin, S. Biswas, V. Singh, K. Ham, G.L. Bovenkamp, C.S. Theegala, J.T. Miller, J.J. Spivey and C.S.S.R. Kumar, *J. Am. Chem. Soc.* 2013**, 135**, 5450.