Supplementary Information

Selenium-modified microgels as interfacial catalysts for the heterophase oxidation of aromatic aldehydes

Anastasiia Pavliuk, [a] Oliver Fiukowski, [b] Jan Wagner, [c] Tetiana Kharandiuk, [d] Volodymyr Ivasiv, [a] Roman Nebesnyi, [a] Uwe Schnakenberg [c] and Andrij Pich [b]

[a] Technology of Organic Products Department, Lviv Polytechnic National University, Ukraine. S. Bandery 12, Lviv-79013, Ukraine. E-mail: roman.v.nebesnyi@lpnu.ua

[b] DWI Leibniz Institute for Interactive Materials e.V., Forckenbeckstraße 50, Aachen-52074, Germany.

[c] Institute of Materials in Electrical Engineering 1, RWTH Aachen University, Sommerfeldstrasse 24, Aachen-52074, Germany

[d] Probiotic Group Luxembourg SA, Henri Koch str. 25, Esch-sur-Alzette, Luxembourg.

Correspondence to: roman.v.nebesnyi@lpnu.ua

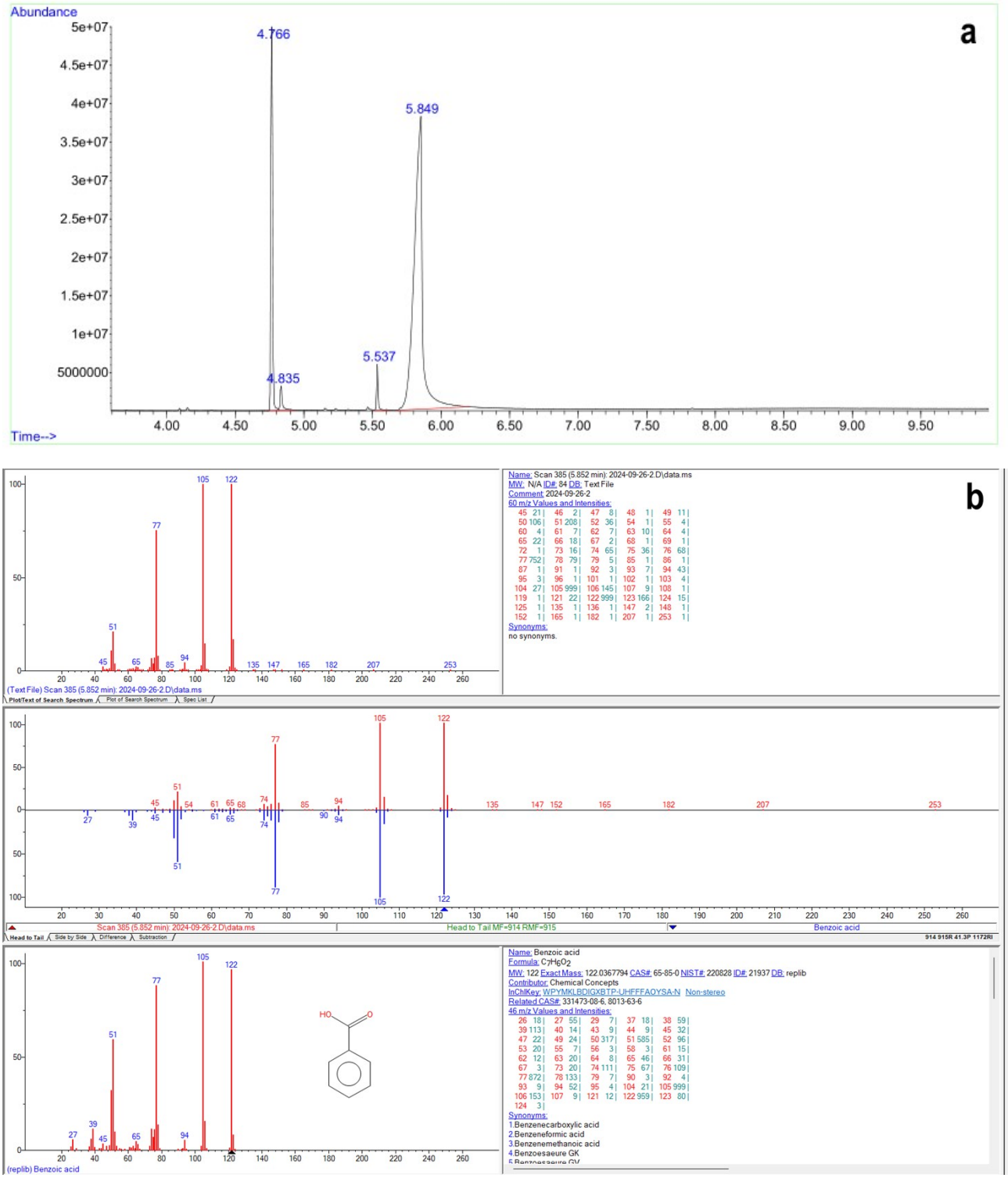

Fig. S1. a) Sample chromatogram; b) Mass spectrum of benzoic acid formed in the benzaldehyde oxidation (top) vs the NIST database (bottom).

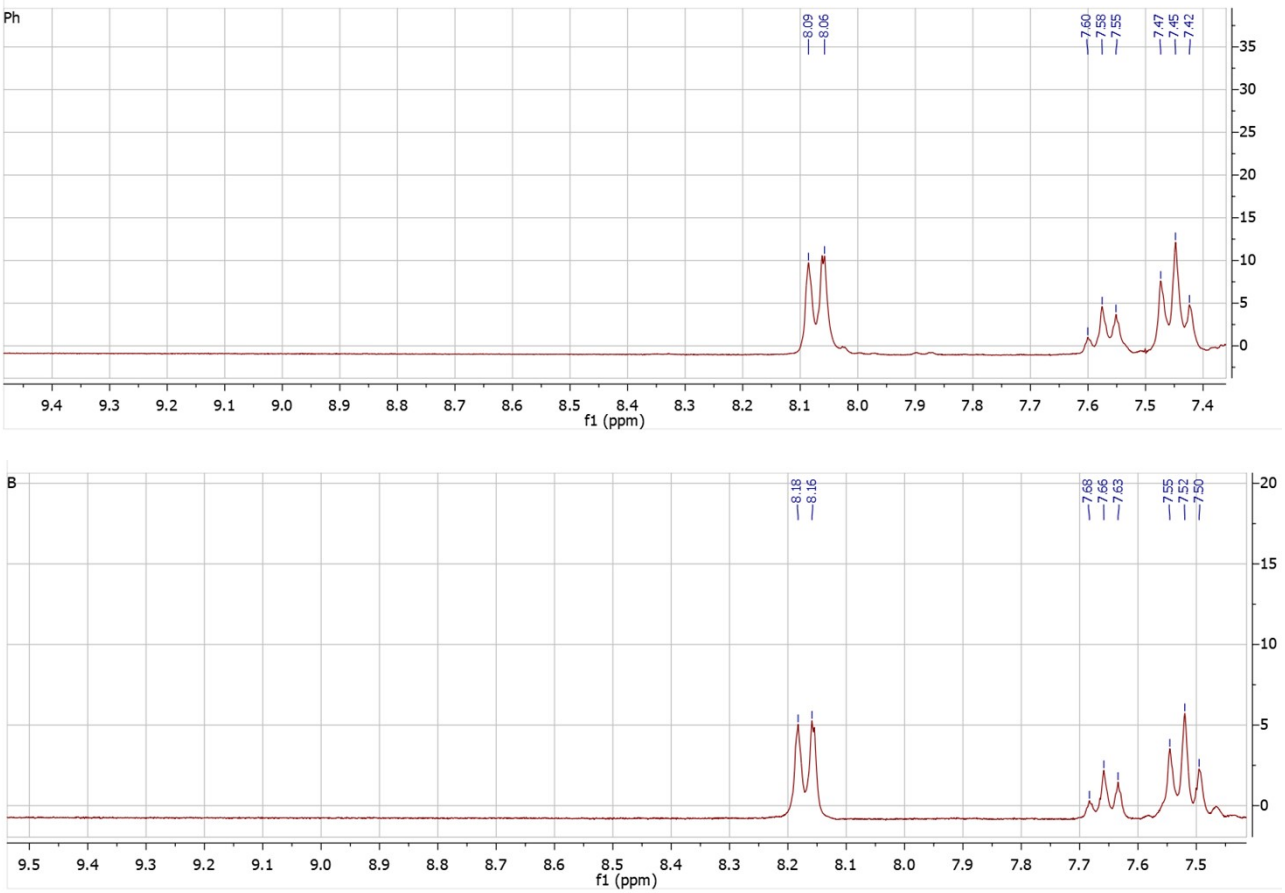

Fig. S2. NMR spectra of benzoic acid formed in the benzaldehyde oxidation (top) and of the sample solution of pure benzoic acid (bottom).

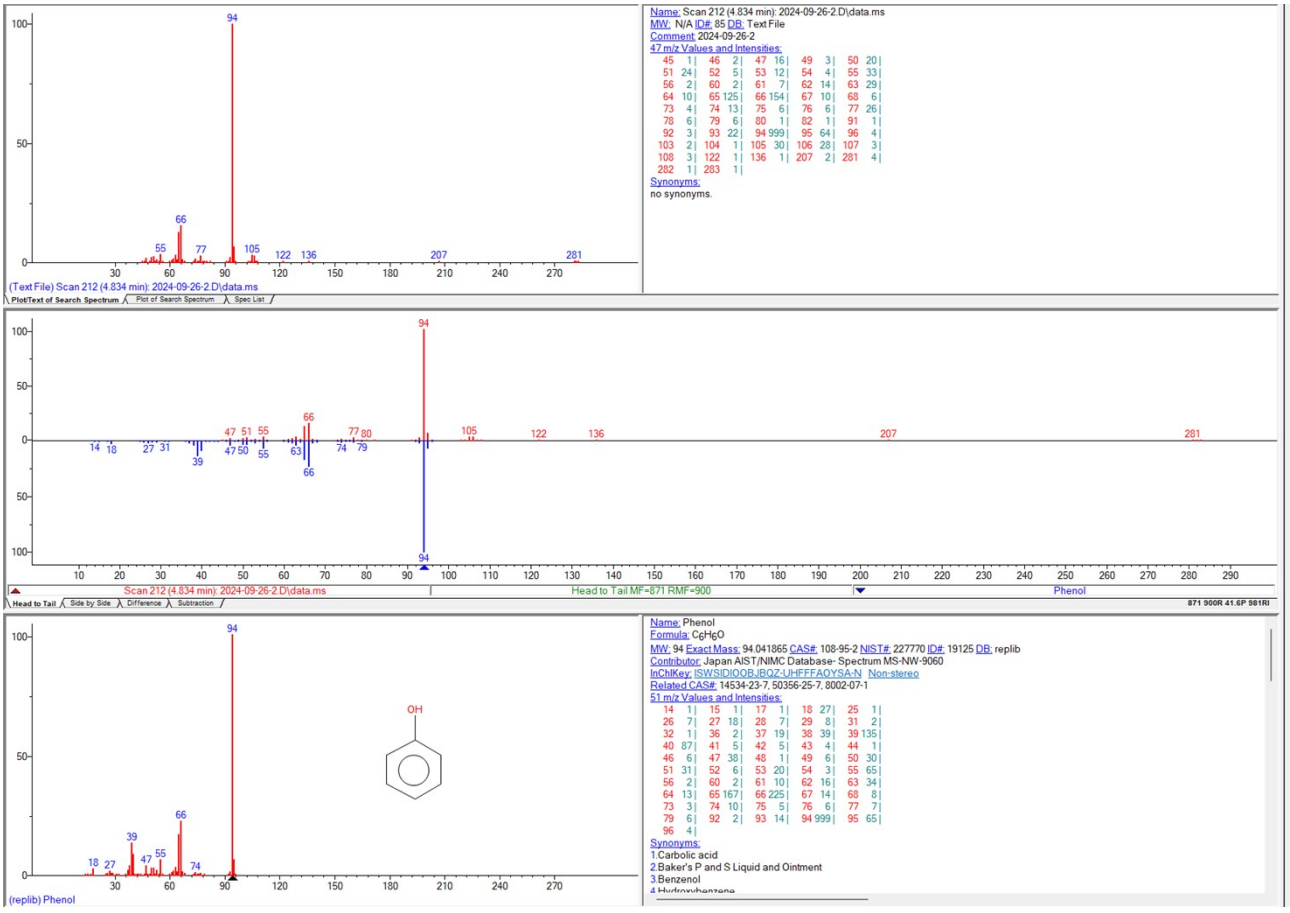

Fig. S3. Mass spectra of phenol formed in the benzaldehyde oxidation (top) vs the NIST database (bottom).

Table S1. Effect of toluene:water ratio and reaction temperature on parameters of benzaldehyde oxidation for Fig. 5a. Catalyst – B1.5Se2.0, catalyst concentration – 0.0044 mmol/ml.

T:W ratio	T, °C	Benzaldehyde conversion, %	Benzoic acid selectivity, %	Benzoic acid yield, %
4:1	20	39.4	60.4	23.8
4:1	30	48.6	92.2	44.8
4:1	40	78.3	94.0	73.6
4:1	50	98.9	96.6	95.6
4:1	60	96.0	98.0	94.1
4:1	90	93.0	98.7	91.8
1:1	20	36.2	21.8	7.9
1:1	30	44.8	56.0	25.1
1:1	40	64.2	72.1	46.3
1:1	50	91.5	92.9	85.0
1:1	90	88.2	95.5	84.2
1:4	20	87.5	95.8	83.8
1:4	40	24.5	68.6	16.8
1:4	50	34.4	65.1	22.4
1:4	60	42.8	73.1	31.3
1:4	90	44.1	72.3	31.9
0	20	39.7	77.6	30.8
0	30	36.4	76.9	28.0
0	40	9.7	82.5	8.0
0	50	12.2	85.2	10.4
0	90	20.8	83.7	17.4

Table S2. Kinetic data (time dependence of concentrations) for Fig. 5b. Solvent – Toluene/Water 4:1, catalyst – Se 2.0 microgel.

T, °C	Benzaldehyde concentration, mmol/ml					
	0 h	0.5 h	1 h	2 h	3 h	8 h
20	2.000	1.938	1.879	1.764	1.657	1.212
30	2.000	1.919	1.840	1.694	1.558	1.028
40	2.000	1.818	1.652	1.365	1.128	0.434
50	2.000	1.510	1.141	0.812	0.642	0.022
60	2.000	1.523	1.160	0.672	0.390	0.080
90	2.000	1.536	1.179	0.696	0.410	0.140

Table S3. Kinetic data (time dependence of concentrations) for Fig. 5c. Solvent – Toluene/Water, catalyst – Se 2.0 microgel, temperature – 50 °C.

Toluene/Water ratio	Benzaldehyde concentration, mmol/ml					
	0 h	0.5 h	1 h	2 h	3 h	8 h
4:1	2.000	1.510	1.141	0.812	0.642	0.022
1:1	2.000	1.714	1.470	1.080	0.793	0.170
1:4	2.000	1.948	1.897	1.800	1.707	1.312
Water	2.000	1.984	1.968	1.936	1.905	1.757

Table S4. Effect of reaction time on parameters of benzaldehyde oxidation for Fig. 6a. Solvent – Toluene/Water 4:1, catalyst – B1.5Se2.0, catalyst concentration – 0.0044 mmol/ml.

Time, h	Benzaldehyde conversion, %	Benzoic acid selectivity, %	Benzoic acid yield, %
3	67.9	82.6	56.1
5	97.3	91.2	88.8
8	98.9	96.6	95.6

Table S5. Oxidation of different aromatic aldehydes for Fig. 8. Catalyst – B1.5Se2.0, catalyst concentration – 0.0044 mmol/ml.

Initial Aldehyde	X, %	Products	S, %	Y, %
Cinnamaldehyde	84.1	Cinnamic acid	35.4	29.8
		Hydrocoumarin	11.7	9.8
		Benzoic acid	20.3	17.1
Anisaldehyde	83.0	Anisic acid	34.3	28.5
		Mequinol	42.4	35.2
Veratraldehyde	59.4	Veratric acid	2.9	1.7
		3,4-Dimethoxyphenol	65.7	39.0
Benzaldehyde	98.9	Benzoic acid	96.6	95.6

Table S6. Kinetic data (time dependence of concentrations) for Fig. 9. Solvent – Toluene/Water 4:1, catalyst – Se 2.0 microgel, temperature – 50 °C.

Cycle	Benzaldehyde concentration, mmol/ml					
	0 h	0.5 h	1 h	2 h	3 h	8 h
1st cycle	2.000	1.510	1.141	0.812	0.642	0.022
2nd cycle	2.000	1.517	1.151	0.662	0.381	0.037
3rd cycle	2.000	1.523	1.159	0.672	0.389	0.060

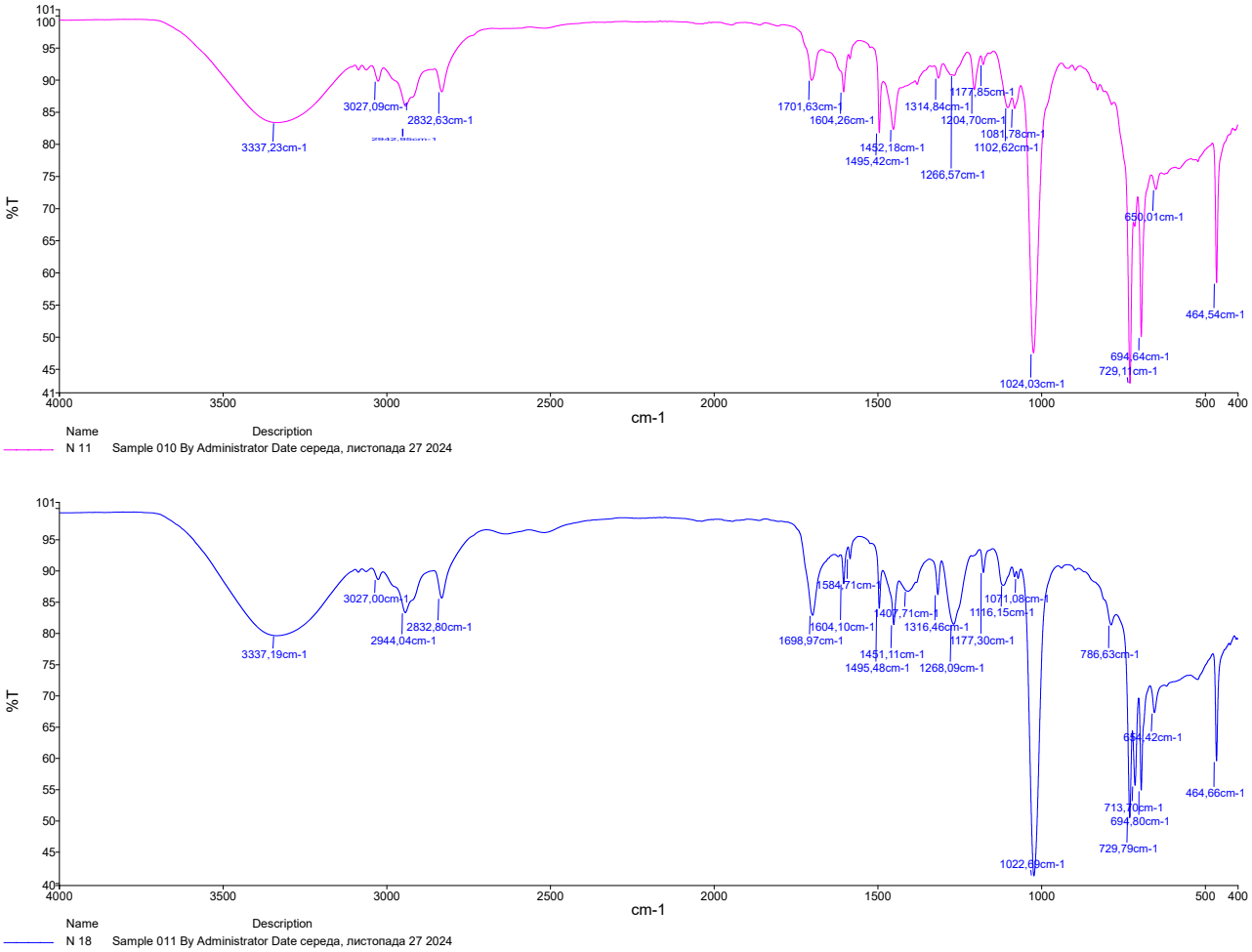

Fig. S4. FT-IR spectrums of microgel: N11 – after first usage cycle (8 h), N18 – after third usage cycle (24 h).