

Electronic Supplementary Material

A Bioinspired Microreactor with Interfacial Regulation for Maximizing Selectivity in a Catalytic Reaction

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Experimental

1. Chemicals

Benzaldehyde (99%, Sigma-Aldrich), Acetone (99.9%, Sigma-Aldrich), Toluene (AR, Fisher Scientific), Cyclohexane (99.5%, Sigma-Aldrich), n-Decane (99%, Sigma-Aldrich), *p*-Xylene (99%, Sigma-Aldrich), Ethanol Undenatured (AR, Chem-supply), Benzalacetone (analytical standard, Supelco), trans, trans-Dibenzylideneacetone (98%, Sigma-Aldrich), Sodium Hydroxide (AR, Chem-supply), Sodium dodecyl sulfate (SDS, 99%, Sigma-Aldrich), Sodium dodecylbenzenesulfonate (SDBS, technical grade, Sigma-Aldrich), Cetyltrimethylammonium bromide (CTAB, 99%, Sigma-Aldrich), Cetylpyridinium chloride (CPC, 99%, Sigma-Aldrich), 4-Chlorobenzaldehyde (97%, Sigma-Aldrich), 3,4-Dichlorobenzaldehyde (95%, Sigma-Aldrich), 2,3-Naphthalenedialdehyde (99%, Tokyo Chemical Industry), 4-Bromobenzaldehyde (99%, Sigma-Aldrich), *p*-Tolualdehyde (97%, Sigma-Aldrich), 2-Methoxybenzaldehyde (98%, Sigma-Aldrich). All chemicals were used as received without further purification. Ultrapure water was used in all experiment (18.2 M Ω ·cm, Synergy UV Water Purification System, Merck Millipore).

2. Partition coefficient measurement

The partition coefficient of a solute is the logarithm of the concentration ratios of the solute between two immiscible phases, which is defined by the following equation:

$$\log P = \log\left(\frac{c_o}{c_w}\right) \quad (1)$$

where $\log P$ is the partition coefficient of the solute, c_o and c_w are the concentrations of the solute in the oil phase and water phase, respectively.^[1] The cyclohexane-water partition coefficient of each compound involving in this reaction was measured at 40 °C. Taking acetone as an example, briefly, 0.5 mmol acetone was added into a mixture of cyclohexane and water (2mL/2mL) and stirred for 1 hour to reach phase equilibrium. Then the concentrations of acetone in the oil phase and water phase were analyzed respectively using a gas chromatograph equipped with an FID and KB-WAX column. The partition coefficient was calculated according to the equation (1).

3. Quantitative analysis of products

The content of benzalacetone and dibenzalacetone was quantified using an Agilent Gas Chromatograph according to corresponding calibration curves (Figure S1). The selectivity of benzalacetone was calculated according to equation (2):

$$\text{Sel.} = \frac{C_{BLT}}{C_{BA(0)} - C_{BA(1)}} \times 100\% \quad (2)$$

where Sel. is the benzalacetone selectivity, %; C_{BLT} is the content of benzalacetone after reaction; $C_{BA(0)}$ and $C_{BA(1)}$ are the content of benzaldehyde before and after reaction, respectively.

4. Materials characterization:

Nikon Eclipse Ni light microscope and Nikon A1R laser scanning confocal microscope were used to image the emulsions. ^1H and ^{13}C NMR spectra of the product obtained after solvent removal were recorded using a Bruker 400 MHz NMR Spectrometer. Interfacial tension was measured by the pendant drop method using a FTÅ200 Contact Angle Analyser. Malvern-Zetasizer Nano ZS was used for zeta potential and drop size distribution measurement. Products were analysed by an Agilent Gas Chromatograph equipped with an FID and HP-5 column. The analysis was performed under the following conditions: injection temperature 250 °C; detector temperature 280 °C; column temperature: initial 100 °C, holding 2 min, programmed at the rate of 20 °C /min to 280 °C, holding 5 min. The gas flows were: hydrogen 40 ml/min, air 400 ml/min, He as a carrier 40 ml/min. Split ratio: 25:1.

5. Reaction procedures

(a) Solvent-free synthesis: 1 mmol benzaldehyde, 1 mmol acetone and 12 mg NaOH was mixed in a mortar and ground for 10 min at 40 °C. After reaction, the mixture was dissolved in 2 mL of toluene and washed with ultrapure water to remove NaOH and then quantitatively analyzed using a gas chromatograph.

(b) Homogeneous system: In a 5 mL glass vial, 0.1 mmol benzaldehyde and 0.1 mmol acetone (taking 1 equiv. as an example) were dissolved in a mixed solvent (1 mL water/1 mL ethanol), followed by adding 50 μL NaOH solution (6 mol/L). Then the vial was sealed and put in an oven at 40 °C for 3 hours. After reaction, 50 μL HCl solution (6 mol/L) was added to neutralize the base and then the products were quantitatively analyzed using a gas chromatograph.

(c) Micellar system: In a 5 mL glass vial, 0.1 mmol benzaldehyde and 0.1 mmol acetone was dissolved in 1.5 mL SDS aqueous solution (200 mM), followed by adding 50 μ L NaOH solution (6 mol/L). The vial was sealed and put in an oven at 40 °C for 4 hours. After reaction, the products were extracted by 1 mL of toluene and quantitatively analyzed using a gas chromatograph.

(d) Emulsion system: 0.1 mmol benzaldehyde and 0.1 mmol acetone (taking 1 equiv. as an example) was dissolved in 0.3 mL cyclohexane and 1.35 mL water, respectively. In a 5 mL glass vial, the two solution was mixed with 150 μ L SDS aqueous solution (20 mM) and then the mixture was sonicated for 2 min to generate emulsions. Finally, 50 μ L NaOH solution (6 mol/L) was added into the emulsions and the vial was sealed and put in an oven at 40 °C for 6 hours. After reaction, the products were extracted by 1 mL of toluene and quantitatively analyzed using a gas chromatograph.

6. Interfacial tension measurement

The pendant drop method was used for interfacial tension measurement. Prior to the measurement, an oil phase (3 mL, with or without benzaldehyde) was first filled in a quartz cuvette, and a pendant drop of water (with or without SDS) was formed on the end of a stainless-steel needle immersed in the oil phase. An image of the drop was taken automatically after 5 min aging and analyzed through software to give the interfacial tension value. For each data point, the average value of 3 measurements was taken.

7. Zeta potential and drop size distribution measurement

For zeta potential measurement, emulsions (with or without benzaldehyde in the oil phase) were diluted in a ratio of 1:100 with ultrapure water, followed by adjusting pH using NaOH and HCl solutions. The diluted emulsions were filled in a disposable folded capillary cell (DTS1070) which was then inserted into the Malvern-Zetasizer Nano ZS for zeta potential measurement at 25 °C. The instrument calculated the zeta potential from the electrophoretic mobility using the Smoluchowski equation.

Size distribution of emulsions was also performed on the Malvern-Zetasizer Nano ZS. Briefly, 1 mL of diluted emulsions (with or without benzaldehyde in the oil phase) was filled in a quartz cuvette which was then inserted into the instrument. Particle size distribution was measured by dynamic light scattering (DLS) method (scattering angle: 173°).

8. Fluorescence tracer experiment

2,3-naphthalenedicarboxaldehyde was used as a tracer to monitor the location of aromatic aldehyde in cyclohexane-water and toluene-water emulsions. Typically, 0.3 mL 2,3-naphthalenedicarboxaldehyde solution (2×10^{-3} mM, dissolved in cyclohexane or toluene), 1.35 mL pure water and 150 μ L SDS aqueous solution (20 mM) were mixed in a 5 mL glass vial. After emulsification by sonicating, the emulsions were observed under a Nikon A1R confocal laser scanning microscope.

Results and Discussion

Table S1. Cyclohexane-water partition coefficient of each compound in CS reaction

Compounds	Partition coefficient
Acetone	-1.6
Benzaldehyde	2.4
Benzalacetone	> 3
Dibenzalacetone	> 3

Discussion: the partition coefficients of benzaldehyde, benzalacetone and dibenzalacetone are all higher than 2, indicating that the concentrations of these solutes in cyclohexane is more than 100 times higher than that in the water phase. In contrast, the partition coefficient of acetone is -1.6, indicating that the majority of acetone (98%) exists in the water phase.

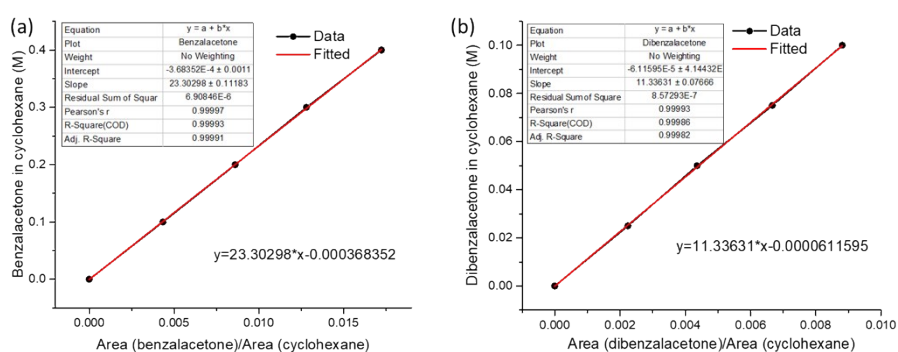


Figure S1. Calibration curves of (a) benzalacetone and (b) dibenzalacetone in gas chromatography measurements.

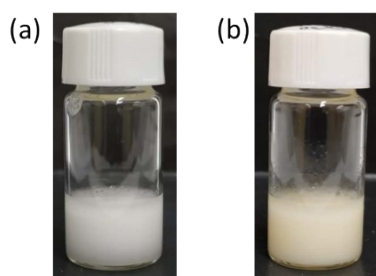


Figure S2. The appearance of the emulsion microreactor (a) before reaction and (b) after reaction.

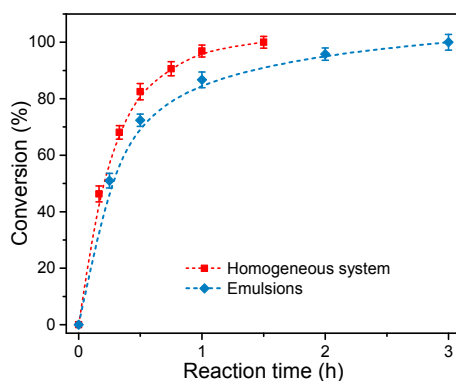


Figure S3. Time-course of benzaldehyde conversion in homogeneous and emulsion microreactor at 2 equiv. acetone.

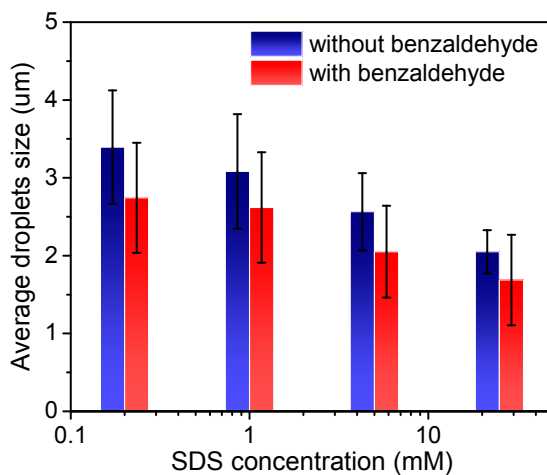


Figure S4. Average drop size of SDS stabilized cyclohexane-water emulsions with or without benzaldehyde in the oil phase.

Discussion: average drop size of emulsions decreases with the increase of SDS concentration and smaller average drop size was observed for emulsions with benzaldehyde in the oil phase at each SDS concentration, indicating that benzaldehyde molecules also hold non-negligible surface activity, enabling them to occupy oil-water interfaces like what a surfactant does.

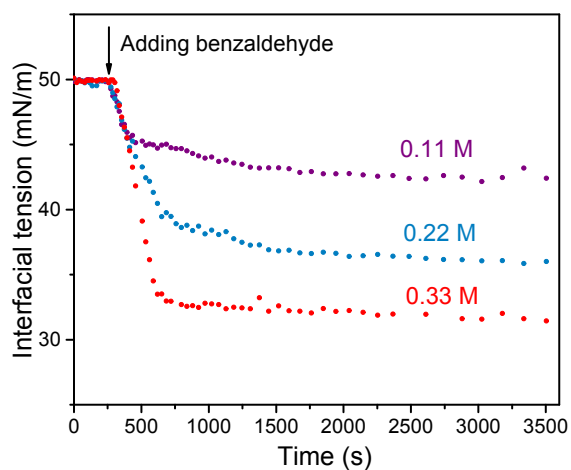


Figure S5. Cyclohexane-water interfacial tension change upon adding benzaldehyde in the oil phase.

Discussion: the cyclohexane-water interfacial tension decreases immediately after adding different concentration of benzaldehyde in the oil phase, indicating that benzaldehyde has non-negligible surface activity.

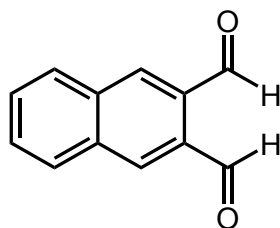


Figure S6. The molecular structure of 2,3-naphthalenedicarboxaldehyde.

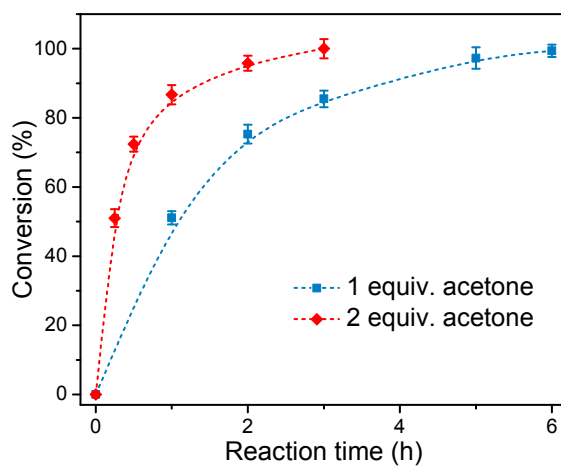


Figure S7. Time-course of benzaldehyde conversion at different acetone equivalents.

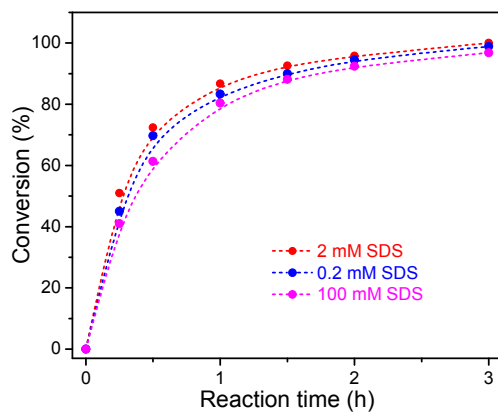


Figure S8. The conversion of benzaldehyde in emulsion reactors stabilized by different concentration of surfactant.

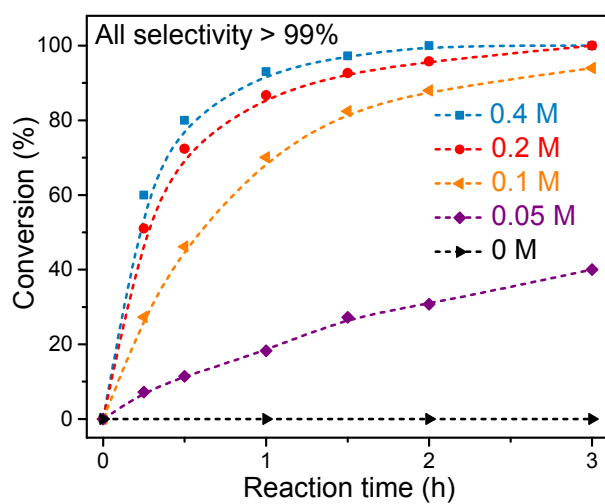
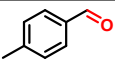
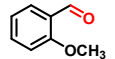
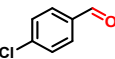
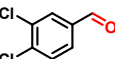
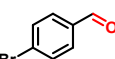


Figure S9. Time-course of benzaldehyde conversion at different NaOH concentrations.

Table S2. The reaction scope of the bioinspired microreactor.

Entry	Substrates	Selectivity/Conversion (%)	
		Homogeneous	Emulsion
1		93/98	> 99/96
2		94/99	> 99/99
3		82/98	> 99/98
4		66/98	> 99/95
5		73/99	> 99/98

Reaction conditions: 0.1 mmol aromatic benzaldehyde, 2 equiv. acetone, 2 mM surfactants, 12 mg NaOH, 40 °C. 2 h for homogeneous systems, 4h for emulsion systems.

References

- [1] I. Moriguchi, S. Hirono, Q. Liu, I. Nakagome, Y. Matsushita, *Chem. Pharm. Bull.* **1992**, *40*, 127-130.