

Supplementary Material

The effective synthesis/separation of 5-hydroxymethylfurfural converted from fructose promoted by H₂O–CO₂ biphasic system with solid catalyst: Evaluation from experimental and kinetic modeling approach

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1. Adsorption test for heterogeneous catalysts

Oregon pine powder impregnated with zinc chloride was carbonized under nitrogen, and the resulting carbon material was treated with 11.3 wt% fuming sulfuric acid at 353K for 1 h and then heated at 423 K for 1 h under nitrogen to obtain ZP 150.

Adsorption tests were performed at room temperature (301 K). The solid catalyst (0.25 g) was mixed with the test solution (5 mL) of initial concentration at about 5.0–300 mM (each solute), and the mixture was shaken at 120 rpm for 24 h. Solution concentrations were determined by HPLC. Adsorption capacity W [mmol g⁻¹] was determined as

$$W_i = \frac{V(C_{i,0} - C_i)}{m_{\text{solid}}}, \quad (\text{S1})$$

Where i , V , C , and m are the index referring to the species in question (5-HMF, LA, or FA), solution volume [L], concentration [M], and solid catalyst mass [g], respectively.

The results (Fig. S1) indicated that the adsorption capacity of ZP-150 exceeded that of Amberlyst-45. However, given that ZP-150 may promote the conversion of 5-HMF to LA and FA, Amberlyst-45 was chosen for the reaction/separation of 5-HMF.

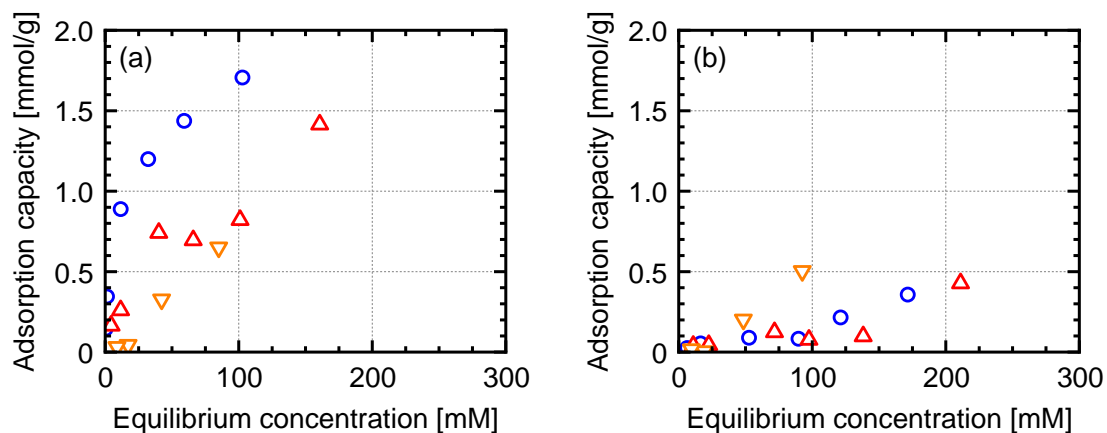


Fig. S1. Adsorption capacities (24 h, 301 K) of (a) ZP-150 and (b) Amberlyst-45 for 5-HMF (○), LA (△), and FA (▽).

2. Determination of vanillin partition coefficients in H₂O–CO₂ for validation purposes

The partition coefficients of vanillin were measured under two different conditions and compared with literature values (Table S1) [1, 2]. The deviations were within uncertainties, which confirmed the validity of the experimental set-up and protocol.

Table S1. Partition coefficients of vanillin in the H₂O–CO₂ biphasic system measured herein and reported previously.

T [K]	P [MPa]	K_{vanillin}	\pm	$u_c(K_{\text{vanillin}})$	Ref [1]	Ref. [2]
313	20	2.02	\pm	0.20	1.94	1.84
333	15	0.81	\pm	0.10	0.76	0.65

3. Detailed explanation of the kinetic model

In this work, we applied a previously reported kinetic model [3]. According to Fig. 4 in the main manuscript, several kinetic equations were considered:

$$\frac{dC_{\text{Fru}}}{dt} = -R_{1\text{F}} - R_{2\text{F}} - R_{3\text{F}}, \quad (\text{S2})$$

$$\frac{dC_{\text{HMF}}}{dt} = R_{1\text{F}} - R_{1\text{H}} - R_{2\text{H}}, \quad (\text{S3})$$

$$\frac{dC_{\text{LA}}}{dt} = R_{1\text{H}}, \quad (\text{S4})$$

$$\frac{dC_{\text{FA}}}{dt} = R_{3\text{F}} + R_{1\text{F}}, \quad (\text{S5})$$

$$\frac{dC_{\text{Hum}}}{dt} = R_{2\text{F}} + R_{2\text{H}}, \quad (\text{S6})$$

where labels Fru, HMF, LA, FA, and Hum denote fructose, 5-HMF, levulinic acid, formic acid, and humins, respectively, while R_{in} [$\text{mol L}^{-1} \text{min}^{-1}$] and C_n [M] are the conversion rate and concentration of component n , respectively. The following equations were used to describe the kinetic model.

$$R_{1\text{F}} = \left(k_{1\text{F},\text{H}^+} C_{\text{H}^+} + k_{1\text{F},\text{Cat}} C_{\text{Cat}} \right) C_{\text{Fru}}, \quad (\text{S7})$$

$$R_{2\text{F}} = \left(k_{2\text{F},\text{H}^+} C_{\text{H}^+} + k_{2\text{F},\text{Cat}} C_{\text{Cat}} \right) C_{\text{Fru}}, \quad (\text{S8})$$

$$R_{3\text{F}} = \left(k_{3\text{F},\text{H}^+} C_{\text{H}^+} + k_{3\text{F},\text{Cat}} C_{\text{Cat}} \right) C_{\text{Fru}}, \quad (\text{S9})$$

$$R_{1\text{H}} = \left(k_{1\text{H},\text{H}^+} C_{\text{H}^+} + k_{1\text{H},\text{Cat}} C_{\text{Cat}} \right) C_{\text{HMF}}, \quad (\text{S10})$$

$$R_{2\text{H}} = \left(k_{2\text{H},\text{H}^+} C_{\text{H}^+} + k_{2\text{H},\text{Cat}} C_{\text{Cat}} \right) C_{\text{HMF}}, \quad (\text{S11})$$

$$k_{in,\text{H}^+} = k_{in\text{R},\text{H}^+} \exp\left(-\frac{E_{in,\text{H}^+}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{R}}}\right)\right), \quad (\text{S12})$$

$$k_{in,\text{Cat}} = k_{in\text{R},\text{Cat}} \exp\left(-\frac{E_{in,\text{Cat}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{R}}}\right)\right), \quad (\text{S13})$$

where k_{inR,H^+} and E_{inR,H^+} are the kinetic rate constant and activation energy for protons, respectively, with the related values listed in Table S2.

Table S2. Kinetic parameters for the conversion of fructose into 5-HMF in biphasic H₂O–CO₂ system.

	R_{1F}	R_{2F}	R_{3F}	R_{1H}	R_{2H}
k_{inR,H^+} [L mol ⁻¹ min ⁻¹] [3]	1.28	0.26	0.06	0.18	0.33
E_{in,H^+} [kJ mol ⁻¹] [4, 5]	123	148	129	92	119

The concentration of protons (C_{H^+} [M]) was determined using the procedure described in previous research [3] based on the acid-base equilibrium relationship as

$$C_{H^+} = \sqrt{K_{CO_2} C_{CO_2} + K_{LA} C_{LA} + K_{FA} C_{FA} + K_w}, \quad (S14)$$

where K_{CO_2} , K_{LA} , K_{FA} , and K_w are the dissociation constants of CO₂, LA, FA, and water, respectively. These values were calculated using previously developed equations as functions of temperature. The determined parameters are summarized in Table S3.

Table S3. pK values of acids used in this work.

T [K]	pK_w [6]	pK_{CO_2} [7]	pK_{LA}^a [3]	pK_{FA} [8]
393	11.88	6.53	4.59	4.03
403	11.75	6.60	4.59	4.09
413	11.64	6.68	4.59	4.14
423	11.54	6.76	4.59	4.20
433	11.45	6.85	4.59	4.26

a) Values at 298 K.

The concentration of CO₂ (C_{CO_2} [M]) was determined using a similar procedure reported previously [3]:

$$C_{CO_2} = \frac{n_{CO_2}^L}{V_{mix}^L} = \frac{n_{CO_2}^L}{n_{total}^L} \cdot \frac{n_{total}^L}{V_{mix}^L}$$

$$\begin{aligned}
&= x_{\text{CO}_2} \cdot \rho_{\text{m,mix}}^{\text{L}} \\
&= x_{\text{CO}_2} \cdot \frac{\rho_{\text{mix}}^{\text{L}}}{(1-x_{\text{CO}_2})M_{\text{w,H}_2\text{O}} + x_{\text{CO}_2}M_{\text{w,CO}_2}}.
\end{aligned} \tag{S15}$$

In Eq. (S15), $n_{\text{CO}_2}^{\text{L}}$ and $n_{\text{total}}^{\text{L}}$ are the amounts of CO₂ [mol] and total matter [mol] in the liquid phase, respectively, while $V_{\text{mix}}^{\text{L}}$ and M_{w} are the volume of the liquid phase in the mixture [m³] and the molar mass [kg mol⁻¹], respectively, and x_{CO_2} is the mole fraction of CO₂ in the water phase [-] estimated using the Peng-Robinson equation of state (PR EoS) [9]. Herein, the PR-EoS was applied to the experimental data of the H₂O(1)–CO₂(2) biphasic equilibrium as a correlation model [10-13], and the interaction parameters for van der Waals one-fluid mixing rule (vdW1) were determined as

$$a_{\text{mix}} = \sum_i \sum_j x_i x_j a_{ij} \quad a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j}, \tag{S16}$$

$$b_{\text{mix}} = \sum_i \sum_j x_i x_j b_{ij} \quad b_{ij} = (1 - l_{ij})(b_i + b_j)/2, \tag{S17}$$

$$k_{12} = -2.9386 \times 10^{-1} + 5.4501 \times 10^{-4} T, \tag{S18}$$

$$l_{12} = 4.0504 \times 10^{-2} - 1.7523 \times 10^{-4} T. \tag{S19}$$

The average absolute relative deviation for the correlation was determined as 6.5%.

The determined interaction parameters were used to calculate x_{CO_2} and the mixture volume in the vapor phase of the H₂O–CO₂ system (described later). $\rho_{\text{m,mix}}^{\text{L}}$ and $\rho_{\text{mix}}^{\text{L}}$ are the molar density [mol m⁻³] and density [kg m⁻³] of the liquid phase, respectively. In this work, $\rho_{\text{mix}}^{\text{L}}$ was estimated using a previously reported procedure [14] as

$$\rho_{\text{mix}}^{\text{L}} = \frac{\rho_{\text{H}_2\text{O}}}{1 - w_{\text{CO}_2} \left(1 - \frac{v_{\text{CO}_2} \rho_{\text{H}_2\text{O}}}{M_{\text{w,CO}_2}} \right)}, \tag{S20}$$

where $\rho_{\text{H}_2\text{O}}$ is the temperature- and pressure-dependent density of pure H₂O calculated by the method reported in the literature [15], w_{CO_2} is the mass fraction of CO₂ in the liquid phase calculated by the PR EoS, and v_{CO_2} is the molar volume of CO₂ [cm³ mol⁻¹] calculated as reported in the literature [16].

For the semibatch reaction/separation experiment, the liquid volume at high pressure, $V_{\text{mix}}^{\text{L}}$, was changed by the balance of the added water flow rate and the water extraction rate. $V_{\text{mix}}^{\text{L}}$ can be obtained from $C_{\text{CO}_2}^{\text{L}}$ as

$$\begin{aligned}
V_{\text{mix}}^{\text{L}} &= \frac{n_{\text{CO}_2}^{\text{L}}}{C_{\text{CO}_2}^{\text{L}}} = \left(n_{\text{H}_2\text{O}}^{\text{L}} \cdot \frac{x_{\text{CO}_2}}{1-x_{\text{CO}_2}} \right) / C_{\text{CO}_2}^{\text{L}} \\
&= \left(V_{\text{H}_2\text{O,atm}}^{\text{L}} \cdot \rho_{\text{H}_2\text{O,atm}} + m_{\text{H}_2\text{O,cat}} + m_{\text{H}_2\text{O,Flow}} \right) \left(\frac{x_{\text{CO}_2}}{1-x_{\text{CO}_2}} \right) / C_{\text{CO}_2}^{\text{L}} \quad (\text{S21})
\end{aligned}$$

where $V_{\text{H}_2\text{O,atm}}^{\text{L}}$ and $\rho_{\text{H}_2\text{O,atm}}$ are the water volume [m^3] and density [kg m^{-3}] at atmospheric pressure, respectively, and $m_{\text{H}_2\text{O,cat}}$ and $m_{\text{H}_2\text{O,Flow}}$ are the mass of water [kg] derived from the catalyst and the added/extracted water flow, respectively.

4. Extrapolation of 5-HMF partition coefficient by PR EoS

Herein, the van't Hoff equation was used for partition coefficient extrapolation; however, the equation of states could also be applied. For comparison, the results of PR EoS calculations are shown below.

The same mixing rule as previously (Eqs. (S16) and (S17)) was applied, and the previously determined parameters of H₂O–CO₂ interactions were used (Eqs. (S18) and (S19)). The CO₂(2)–5-HMF(3) interaction parameter was determined by correlation to reference data [17], and the H₂O(1)–5-HMF(3) interaction parameter was determined by correlation to partition coefficient data recorded herein. For both parameters, l_{ij} was assumed to be zero.

$$k_{23} = -2.0178 + 7.6818 \times 10^{-3} T, \quad (\text{S22})$$

$$k_{13} = -2.8015 \times 10^{-1} + 5.7393 \times 10^{-4} T. \quad (\text{S23})$$

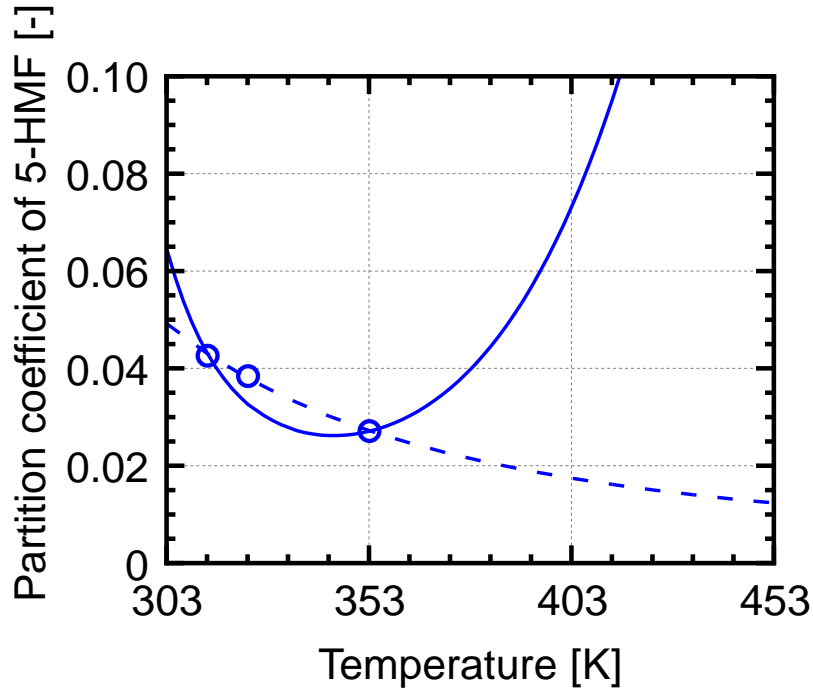


Figure S2. Partitioning coefficient of 5-HMF between H₂O and CO₂ at 25 MPa. Dashed and solid lines refer to data obtained using the van't Hoff equation and the PR EoS, respectively.

5. Experimental and calculated results for batch reaction and kinetic analysis

The experimental and calculated results [M] are shown below.

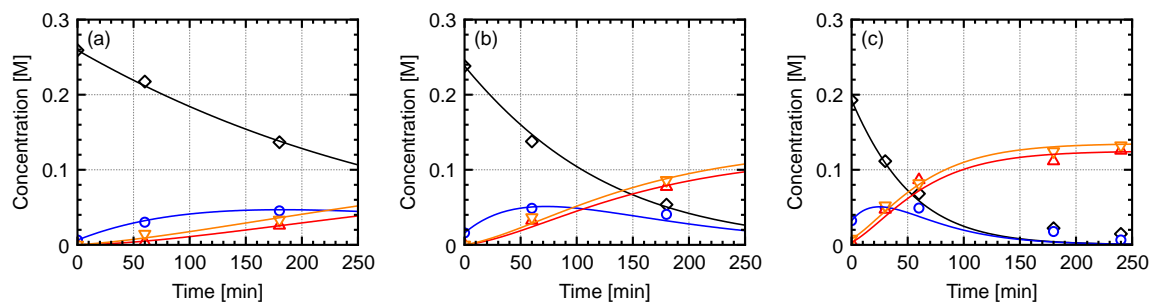


Fig. S3. Experimental and calculated time profiles of concentrations for 5-HMF synthesis. Data refer to batch-mode reactions in biphasic $\text{H}_2\text{O}-\text{CO}_2$ systems with the Amberlyst-45 catalyst at a pressure of 25 MPa and temperatures of (a) 393, (b) 403, and (c) 413 K. (black = Fructose, blue = 5-HMF, red = LA, orange = FA)

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