Supporting Information

Highly efficient and stable hydrodechlorination of chlorophenols in flow Pd-Ce/SiO_2/Ni foam reactor

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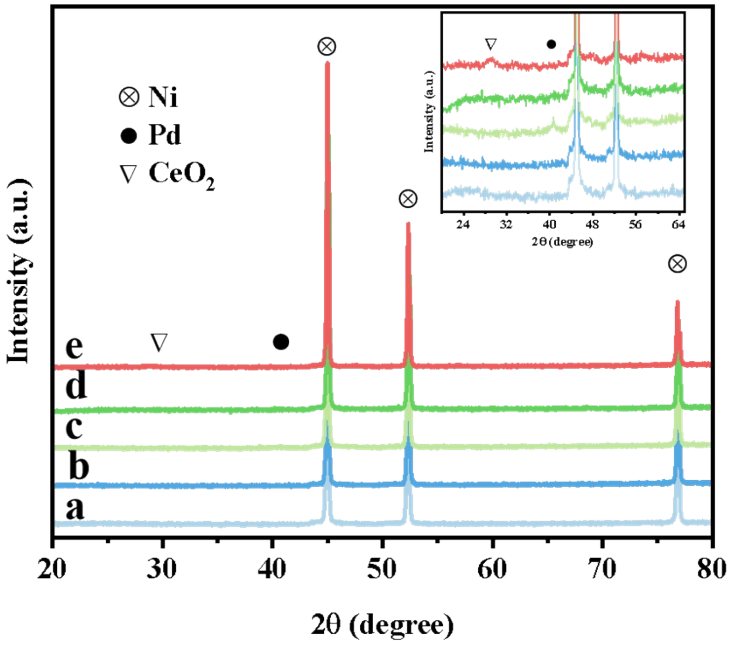

Fig. S1: XRD patterns of Ni foam (a), SiO_2/Ni foam (b), Pd/Ni foam (c), Pd/SiO_2/Ni foam (d) and Pd-Ce/SiO_2/Ni foam (e).

External and internal mass transfer in flow Pd-based Ni foam reactor

External mass transfer limitation

The dimensionless Carberry numbers, defined as the ratio between the observed reaction rate (r_{obs}) and the maximum transfer rate of the reactants were calculated to evaluate the external mass transfer limitation. The overall gas–liquid mass transfer coefficient between the rather insoluble H_2 gas and water is approximately equal to the liquid-side mass transfer coefficient, because the gas phase mass transfer resistance is far less than the liquid phase mass transfer resistance [1]. Therefore, the Carberry numbers for gas-liquid ($Ca_{G\text{-}L}$) and liquid-solid ($Ca_{L\text{-}S}$) mass transport are expressed as follows [2,3]:

$$Ca_{G-L} = \frac{r_{obs}}{(k_L a_{GL})C^*}$$

$$Ca_{L-S} = \frac{r_{obs}}{(k_{LS} a_{LS})C_b}$$

The value of the gas-liquid mass transfer coefficient ($k_L\alpha_{GL}$) was estimated by the correlation consisting of Sherwood (*Sh*), Reynolds (*Re*) and Schmidt (*Sc*) numbers [1]:

$$\frac{a_{GL}\varepsilon_L}{a_p} Sh = 0.0037 Re_L^{1.4} Sc_L^{0.5}$$

$$Sh = \frac{k_L d_p}{D}$$

$$Re_L = \frac{d_p u_L \rho_L}{\mu_L}$$

$$Sc_L = \frac{\mu_L}{\rho_L D}$$

Where α_{GL} is the interfacial gas-liquid area per unit volume of liquid, k_L is the liquid side mass transfer coefficient, ε_L is the liquid hold-up, measured by the method reported previously[1], α_p is the specific surface area of foam bed (per unit of bed volume), d_p is the characteristic length of the foam bed, ρ_L is the liquid density, μ_L is the liquid viscosity, u_L is the liquid superficial velocity, D is the diffusion coefficients evaluated by Wilke-Chang equation [4]:

$$D = 7.4 \times 10^{-8} \frac{(\varphi M_L)^{0.5} T}{\mu_L V_i^{0.6}}$$

Where the volumes of hydrogen and 4-chlorophenol in water at normal boiling temperature (V_i) are 14.3 and 123 cm^3/mol, respectively, φ is association factor (2.6 for water), M_L is the molecular weight of water.

To determine the liquid-solid mass transfer coefficient (k_{LS}) in solid foam, Mohammed et al proposed a modified correlation that considers gas and liquid superficial velocities, fluids physical properties and foam geometric features. A good agreement between the experimental result and predicated data was obtain, for the liquid-solid mass transfer coefficient calculation of polyurethane foam [5]. In this work, the liquid-solid mass transfer coefficient (k_{LS}), in terms of Sherwood number, was also estimated by the correlation mentioned above.

$$\frac{\theta Sh}{Sc_L^{0.33}} = 0.13 Re_L^{0.805} Re_G^{-0.89} \left(a_p d_p \frac{1-\varepsilon}{\varepsilon} \right)^{-1.34}$$

Where θ is the wetting efficiency of solid surface, α_p is the specific surface area of foam bed (per unit of bed volume), d_p is the characteristic length of the foam bed, ε is the porosity of foam. The wetting efficiency of solid surface is approximately equal to 100 %, because the liquid flow regime under experimental condition is similar to the typical low liquid holdup trickle flow with high gas-liquid interaction [6,7].

Table S1. Estimated Carberry (Ca) numbers of hydrogen and 4-CP during HDC in flow foam reactor

T(°C)	Pd/Ni foam			Pd/SiO_2/Ni foam			Pd-Ce/SiO_2/Ni foam		
		Ca_{L-S}			Ca_{L-S}			Ca_{L-S}	
	Ca_{G-L}	H_2	4-CP	Ca_{G-L}	H_2	4-CP	Ca_{G-L}	H_2	4-CP
20	1.3×10^{-3}	2.6×10^{-5}	6.9×10^{-5}	1.5×10^{-4}	1.2×10^{-4}	3.1×10^{-4}	9.2×10^{-5}	1.6×10^{-4}	4.3×10^{-4}
40	3.9×10^{-3}	1.1×10^{-4}	6.4×10^{-5}	2.7×10^{-4}	3.2×10^{-4}	1.8×10^{-4}	1.6×10^{-4}	4.0×10^{-4}	2.3×10^{-4}
60	1.9×10^{-3}	1.5×10^{-4}	8.3×10^{-5}	1.2×10^{-4}	3.9×10^{-4}	2.2×10^{-4}	7.2×10^{-5}	5.0×10^{-4}	2.8×10^{-4}

Reaction conditions: gas-liquid volume ratio (4:1), total gas-liquid flow rate (5 $mL\cdot min^{-1}$ at 20 and 40 °C, 10 $mL\cdot min^{-1}$ at 60 °C), 4-CP inlet concentration (10 $mmol\cdot L^{-1}$).

Internal mass transfer limitation

The significance of internal mass transfer limitation was evaluated from the application of the Weisz-Prater criterion (Φ) [4]:

$$\Phi = L_p^2 \frac{r_{obs}}{D_e C^*}$$

Where (D_e) is the effective diffusivity estimated to be 0.1 D in the absence of the tortuosity factor [2, 4]. L_p is the thickness of the active layer, corresponding to 1/6 the Pd particle diameter for Pd/Ni foam and the thickness of the coating Pd layer for Pd/SiO_2/Ni foam and Pd-Ce/SiO_2/Ni foam [3].

Table S2. Estimated Weisz-Prater criterions (Φ) of hydrogen and 4-CP during HDC in flow foam reactor

T(°C)	Pd/Ni foam		Pd/SiO_2/Ni foam		Pd-Ce/SiO_2/Ni foam	
	H_2	4-CP	H_2	4-CP	H_2	4-CP
20	3.8×10^{-9}	3.3×10^{-8}	3.2×10^{-6}	2.8×10^{-5}	3.6×10^{-6}	3.1×10^{-5}
40	4.0×10^{-8}	3.5×10^{-8}	2.1×10^{-5}	1.9×10^{-5}	2.2×10^{-5}	1.9×10^{-5}
60	5.6×10^{-8}	4.9×10^{-8}	2.8×10^{-5}	2.4×10^{-5}	2.9×10^{-5}	2.5×10^{-5}

Reaction conditions: gas-liquid volume ratio (4:1), total gas-liquid flow rate (5 $mL\cdot min^{-1}$ at 20 and 40 °C, 10 $mL\cdot min^{-1}$ at 60 °C), 4-CP inlet concentration (10 $mmol\cdot L^{-1}$).

Parameters of flow Pd-based Ni foam reactor under experimental conditions

Table S3. Parameters of flow Pd-based Ni foam reactor

	Pore density (ppi)	ε	d_p (m)	α_p ($m^2\cdot m^{-3}$)	ε_L	L_p (m)
Pd/Ni foam	110	0.97	3.7×10^{-4}	5.4×10^{5}	0.34	1.8×10^{-8}
Pd/SiO_2/Ni foam	110	0.97	3.7×10^{-4}	1.0×10^{7}	0.43	4×10^{-6}
Pd-Ce/SiO_2/Ni foam	110	0.97	3.7×10^{-4}	1.8×10^{7}	0.44	4×10^{-6}

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Nomenclature

$Ca_{G\text{-}L}$ Carberry number for gas-liquid mass transport

$Ca_{L\text{-}S}$ Carberry number for liquid-solid mass transport

Φ Weisz-Prater parameter

Sh Sherwood number

Sc Schmidt number

Re Reynolds number

D diffusion coefficient ($m^2 \cdot s^{-1}$)

De effective diffusion coefficient ($m^2 \cdot s^{-1}$)

$k_L\alpha_{GL}$ gas-liquid mass transfer coefficient (s^{-1})

k_{LS} liquid to solid mass transfer coefficient ($m \cdot s^{-1}$)

C^* equilibrium concentration ($mmol \cdot L^{-1}$)

C_b bulk concentration ($mmol \cdot L^{-1}$)

r_{obs} observed reaction rate ($mmol \cdot L^{-1} \cdot s^{-1}$)

μ viscosity ($Pa \cdot s$)

ρ density ($kg \cdot m^{-3}$)

u superficial velocity ($m \cdot s^{-1}$)

ε_L liquid hold-up ($m^3_{liquid} \cdot m^{-3}$ $_{bed}$)

α_p the specific surface area of foam bed ($m^2 \cdot m^{-3}$)

d_p the characteristic length of the foam bed (m)

φ association factor, 2.6 for water

V_i volume of species i in water at its normal boiling temperature

M molecular weight ($g \cdot mol^{-1}$)

T temperature (K)

Θ wetting efficiency of solid foam surface

ε porosity of foam.

L_p thickness of the active layer (m)

L liquid phase

G gas phase

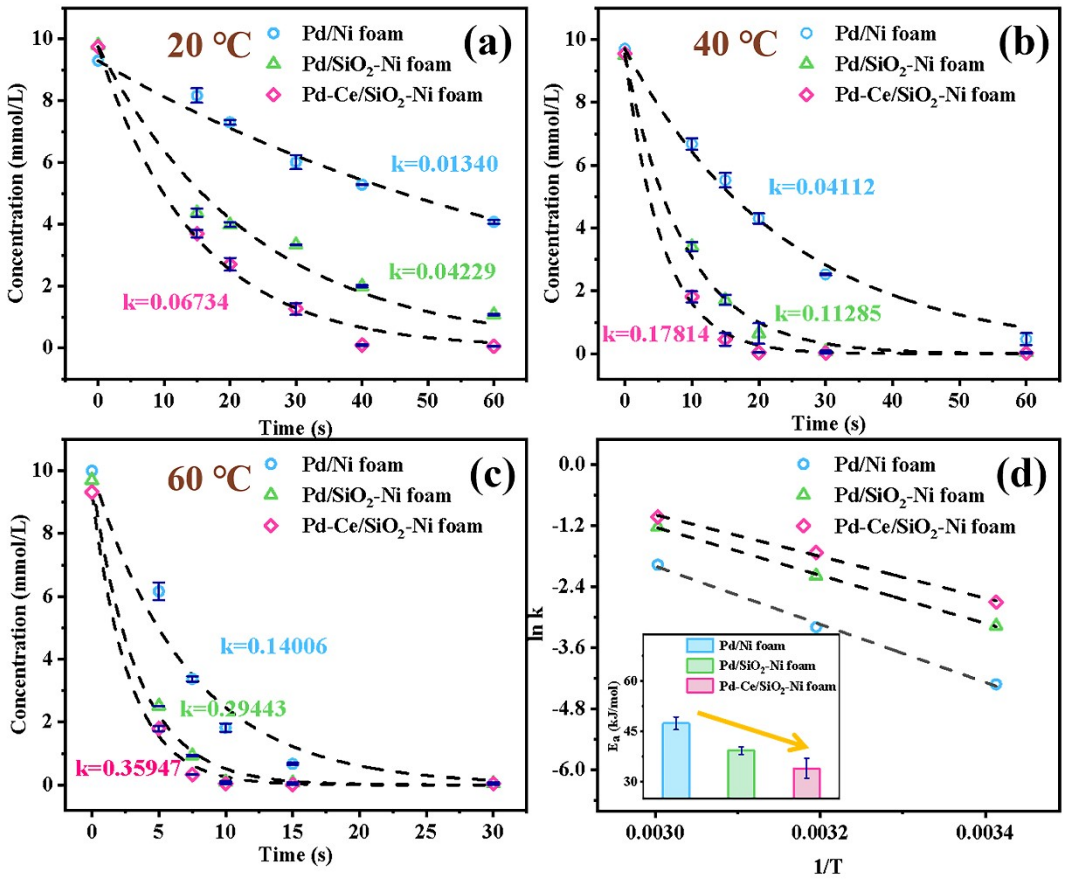

Fig. S2 Concentration-time curves of 4-CP at 20 ℃ (a), 40 ℃ (b) and 60 ℃ (c), and Arrhenius plots of 4-CP (d) during HDC in flow Pd-based Ni foam reactor. Experimental (symbols) and predicted (dash lines) values. Reaction conditions: gas-liquid volume ratio (4:1), 4-CP inlet concentration (10 mmol·L^{-1}).

Table S4. HDC of 4-CP in flow Pd-Ce/SiO_2/Ni foam reactor

Entry	4-CP_{inlet} concentration （$mmol \cdot L^{-1}$)	Total fiow rate ($mL \cdot min^{-1}$)	Residence time (s)	Conversion (%)	4-CP_{outlet} concentration (ppm)
1	10	20	15	59.52%	475.85
2	10	15	20	72.29%	348.49
3	10	10	30	85.95%	162.93
4	10	5	60	99.33%	10.11
5	10	2.5	120	99.45%	9.93
6	20	5	60	91.15%	182.25
7	5	5	60	99.69%	2.06
8	1	5	60	99.57%	0.62
9	0.2	5	60	99.01%	0.36

Reaction conditions: reaction temperature (20 °C), gas-liquid volume ratio (4:1).