Supporting Information

Long-Term Continuous Co-reduction of 1,1,1-Trichloroethane and Trichloroethene over Palladium Nanoparticles Spontaneously Deposited on H_2-transfer Membranes

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PART II: TABLES

Table S1. Detection methods for analytes in this study

Analytes	Instrument	Model	Column Type	Detector Type	Detection Limit	MCL
Pd	ICP	Thermo Scientific X-Series II	-	MS	0.1 ppb	-
H_2	GC	Shimadzu GC 2010	1010 plot Capillary column 30m× 0.53mm×10 mm (Carboxen®, Bellefonte, PA)	Thermal Conductivity Detector (TCD)	1 ppmv	-
TCE	GC		Rt-QSPLOT column 30m×0.53mm×10 mm (Restek®, Bellefonte, PA)	FID	5 ppb	5 ppb
1,1-DCE	GC			FID	3 ppb	7 ppb
cis-1,2-DCE	GC			FID	3 ppb	70 ppb
VC	GC			FID	2 ppb	2 ppb
Ethene	GC			FID	0.29 ppb	-
1,1,1-TCA	GC			FID	40 ppb	200 ppb
1,1-DCA	GC			FID	5 ppb	-
1,2-DCA	GC			FID	5 ppb	5 ppb
MCA	GC			FID	3 ppb	-
Ethane	GC			FID	0.3 ppb	-

31 **Table S2.** Details of catalysts (type, support, and dosage), conditions (temperature, pH, and substrate concentration), and performance
32 (catalytic activity, products, and selectivity) of Pd-catalyzed 1,1,1-TCA or TCE reduction in previous studies and this study.

Catalyst				Reactant					
Type	**Supporter**	**Dosage** *(g/L)*	**System**	**Type**	**Conc.** *(uM)*	**Temp.** *(K)*	**Conti.**	**Activity** *L/g/min*	**Reference**
Pd	Al_2O_3	0.047	Suspended	TCE	22.8	295	N	34	Lowry and Reinhard [1]
Pd	N.A.	0.017	Suspended	TCE	22.8	295	N	4.4	Lowry and Reinhard [1]
Pd	N.A.	0.025	Suspended	TCE	389	295	N	62	Nutt, et al. [2]
Pd	Al_2O_3	0.025	Suspended	TCE	389	295	N	12	Nutt, et al. [2]
Pd	Al_2O_3	0.039	Suspended	TCE	452	295	N	47	Nutt, et al. [3]
Pd	Biomass	0.05	Suspended	TCE	782	295	12 days	1.37	Hennebel, et al. [4]
Pd	Biomass	0.1~1.0	Suspended	TCE	800	295	0.5 day	0.7	Hennebel, et al. [5]
Pd	Al_2O_3	N.A.	Suspended	1,2-DCA	N.A.	400-600	N	N.A.	Feijen-Jeurissen, et al. [6]
Pd	N.A.	1	Suspended	1,2-DCA	323	295	N	0.0007	El-Sharnouby, et al. [7]
Pd/Au	N.A.	0.025	Suspended	TCE	389	295	N	943	Nutt, et al. [2]
Pd/Au	N.A.	0.039	Suspended	TCE	452	295	N	1956	Nutt, et al. [3]
Ni/Fe	biochar	1 (10% Ni)	Suspended	1,1,1-TCA	1500	295	N	0.7-10	Li, et al. [8]
Pd/Fe	N.A.	0.075-0.75	Suspended	TCE	84	295	N	311	Lin, et al. [9]
Ru/Fe	N.A.	0.075-0.75	Suspended	TCE	84	295	N	3.5	Lin, et al. [9]
Pt/Fe	N.A.	0.075-0.75	Suspended	TCE	84	295	N	0.5	Lin, et al. [9]
Au/Fe	N.A.	0.075-0.75	Suspended	TCE	84	295	N	0.3	Lin, et al. [9]
Pd	Al_2O_3	0.48	Immobilized	TCE	27	295	60 days	0.0008	Lowry and Reinhard [10]
Pd	Al_2O_3	0.095	Immobilized	TCE	140-180	295	N	0.14	Lowry and Reinhard [11]
Pd	Silica	N.A.	Immobilized	1,1,1-TCA	N.A.	358-633	1 day	N.A.	Mori, et al. [12]

Pd	PP membrane	0.001~0.013	Immobilized	1,1,1-TCA and TCE	100-1000	295	90 days	3-11	This study

Table S3. Simulation information for the data in Figure 7

Data series	Simulation model	Equation	R^2
1,1,1-TCA Loading vs flux	Exponential, limited growth	$y = 2.7x(1-e^{-0.4x})$	0.993
TCE Loading vs flux	Exponential, limited growth	$y = 5.7x(1-e^{-0.2x})$	0.999
1,1,1-TCA removal vs H_2 ratio	Exponential, limited growth	$y = 93.3x(1-e^{-2.4x})$	0.949
TCE removal vs H_2 ratio	Exponential, limited growth	$y = 98.0x(1-e^{-3.6x})$	0.943
1,1-DCA selectivity vs H_2 ratio	Exponential, limited decay	$y = 2.3+97.7e^{-5.1x}$	0.867
MCA selectivity vs H_2 ratio	Exponential, limited decay	$y = 8.3+91.7e^{-2.0x}$	0.878
Ethane selectivity vs H_2 ratio	Exponential, limited growth	$y = 89.7x(1-e^{-1.9x})$	0.904

Table S4. H_2 supply and discharge at the nine steady states of the continuous operation.

	Supply Pressure [a]	Supply flux [b]	Demand flux [c]	Discharge			
Stage	*atm*	*e- eq/m²/day*		*mg/min* [d]	*mL/min* [e]	*atm* [f]	*μM* [g]
I	1.2	131	11	0.003	0.037	0.342	6.49
II	1.2	131	52	0.002	0.024	0.010	0.18
III	1.2	131	105	0.001	0.008	0.010	0.18
IV	1.2	262	107	0.004	0.047	0.378	7.18
V	1.2	393	105	0.007	0.088	0.785	14.9
VI	1.4	131	108	0.001	0.007	0.012	0.23
VII	1.6	131	105	0.001	0.008	0.012	0.23
VIII	1.2	131	203	0.000	0.000	0.005	0.09
IX	1.2	131	53	0.002	0.024	0.157	2.99

Note:

[a] The supply pressure refers to the H_2 pressure from a gas cylinder or generator to fiber lumens.

[b] Supply fluxes are calculated using Eqn. 1 in the paper.

[c] Demand fluxes are calculated on basis of total reduction of all the TCA and TCE in the influent to ethane.

[d] H_2 discharge flow rates are calculated as $(J_{supply} - J_{demand}) \cdot A$, where J_{supply} is the H_2 supply flux, J_{demand} is the H_2 demand flux, A is the total membrane area.

[e] The unit conversion of the H_2 discharge flow rate is based on the ideal gas law.

[f] These values refer to the H_2 partial pressures detected in the gas sampling port.

[g] These values refer to the aqueous H_2 concentrations in the effluent.

PART III: FIGURES

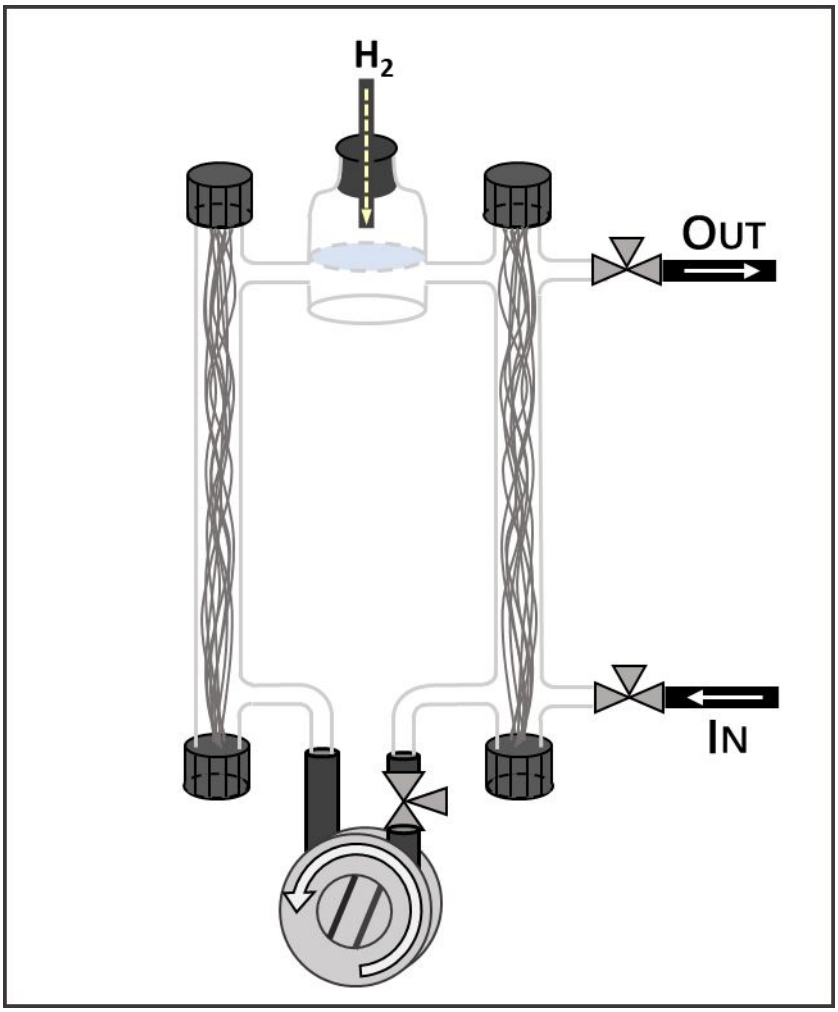

Figure S1. Schematic of H_2 supply exclusively to the headspace via the sampling port in the MPfR.

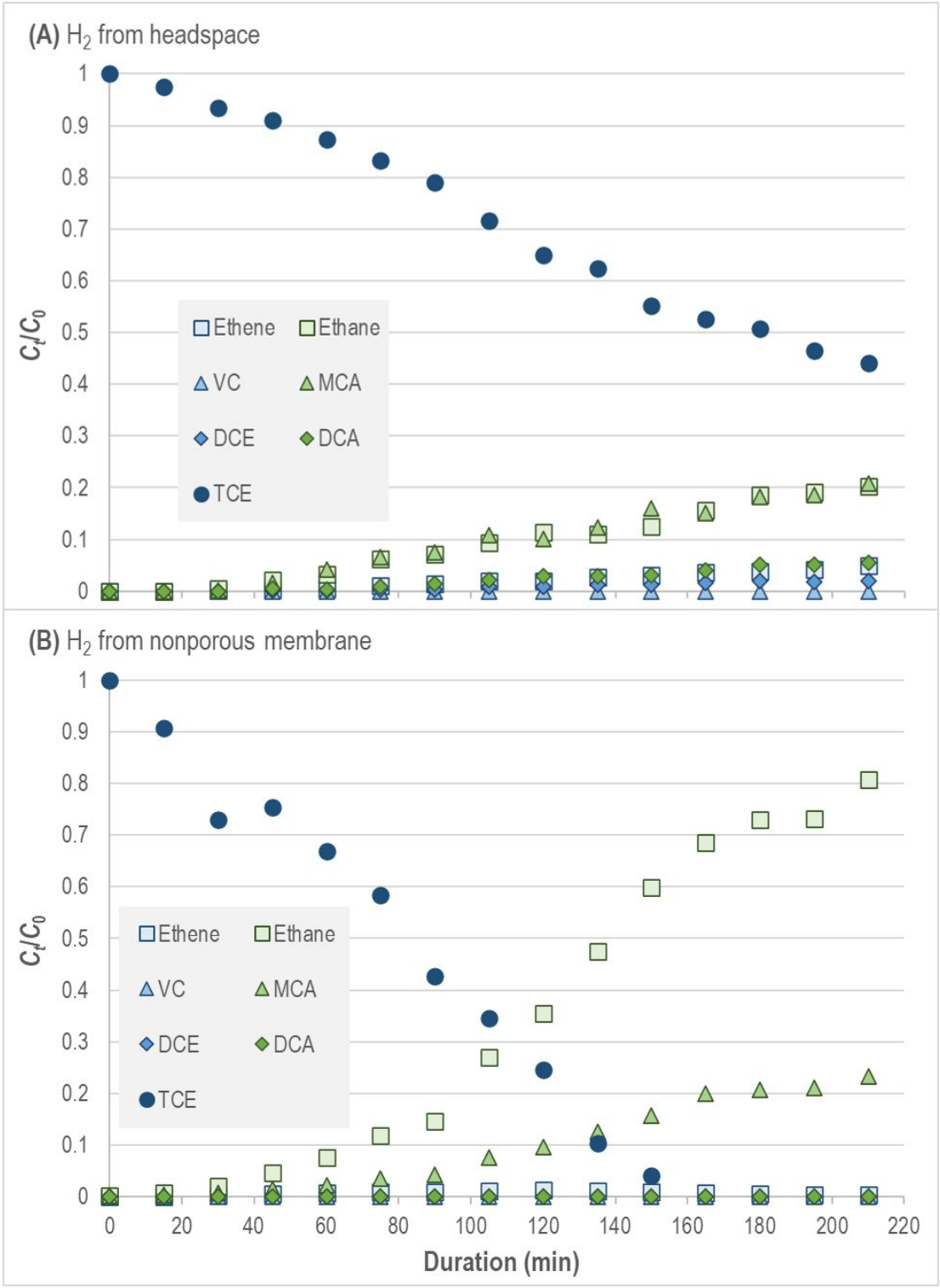

Figure S2. TCE and product concentrations in the supplementary batch tests of TCE reduction catalyzed by 25.1 mg /m^2 PdNPs in the MPfR for 10 psig H_2 supplied to (A) the headspace of the sampling port (Fig. S1) and (B) the nonporous membranes where the PdNPs were anchored.

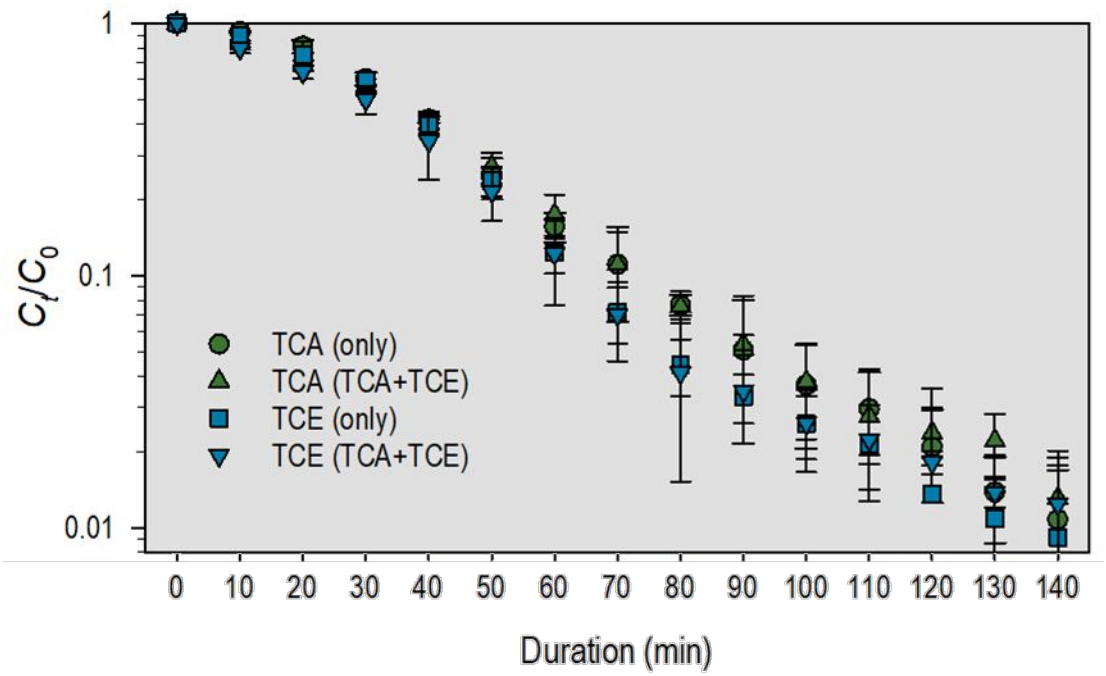

Figure S3. Separated and combined 1,1,1-TCA/TCE depletions over time in the batch tests shown in Figure 3.

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