Novel solid-state synthesis of surfactant- and solvent-free Pd tetrahedron nanocatalysts

Kyung Hee Oh^{a,b}, Kwangsoo Kim^c, Jin Gyu Lee^a, Nahyun Park^a, Hack-Keun Lee^a, Shin Wook Kang^a, Jung-II Yang^a, Byeong-Seon An^d, Kang Hyun Park^e, Chang Seop Hong^{b,*}, Byung-Hyun Kim^{f,g,*}, and Ji Chan Park^{a,h,*}

^a Clean Fuel Laboratory, Korea Institute of Energy Research, Daejeon, 34129, Korea. E-mail:

jcpark@kier.re.kr

^b Department of Chemistry, Korea University, Seoul 02841, Korea.

^c Energy AI & Computational Science Laboratory, Korea Institute of Energy Research, Daejeon, 34129, Korea.

^d Analysis Center for Energy Research, Korea Institute of Energy Research, Daejeon 34129, Korea.

^e Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National

University, Busan 46241, Korea

^f Department of Chemical and Molecular Engineering, Hanyang University ERICA, Ansan 15588, Korea.

^g Department of Applied Chemistry, Center for Bionano Intelligence Education and Research,

Hanyang University ERICA, Ansan 15588, Korea.

^h Energy Engineering, University of Science and Technology, Daejeon, 34113, Korea.

E-mail: cshong@korea.ac.kr (C. S. Hong), bhkim00@hanyang.ac.kr (B.-H. Kim), and jcpark@kier.re.kr

(J. C. Park)



Figure S1. (a) A picture of the AIO reactor system and (b) the sequence table for T-Pd/G in the software program.

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Figure S2. Sequence table for Fe_3O_4 -G synthesis in the software program of the AIO reactor system.



Figure S3. (a) HAADF-TEM image and (b-d) elemental mapping images of single Pd nanoparticle in T-Pd/G. All bars represent 10 nm.



Figure S4. (a) N_2 sorption isotherms and (b) pore size distribution diagrams by desorption branches of pristine graphene and T-Pd/G.



Figure S5. (a-c) TEM images of the T-Pd/G at different batches. All bars represent 50 nm.



Figure S6. HRTEM images of (a) T-Pd/AC, (b) T-Pd/Al₂O₃, and (c) T-Pd/SiO₂. All bars represent 10 nm.



Figure S7. Atomic configurations of Pd slab models with full coverage of molecules.



Figure S8. (a) UV–vis spectra and photographs of 4-nitrophenol (4-NP), 4-nitrophenolate anion (4-NPI), and 4-aminophenol (4-AP). (b) UV-vis spectra of the catalytic 4-NP reduction reaction at 30 °C for 4 min using T-Pd/G catalyst.



Figure S9. (a,b) Low-resolution TEM images of C-Pd/G. The bars represent 200 nm (a) and 100 nm (b).



Figure S10. (a) A brief scheme of magnetically separable Fe_3O_4 -G support. (b) TEM image, (c) HRTEM image with the corresponding FT pattern (inset of c), (d) XRD spectrum of Fe_3O_4 -G. The bars represent 50 nm (b) and 5 nm (c), respectively.



Figure S11. UV-vis spectra by the 4-NP reduction reaction at the initial point (0 min) and after reaction (4 min) using Fe_3O_4 -G at 30 °C.

Method	Lattice constant (Å)	Ref.
GGA-PBE	3.94	This work
GGA-PBE	3.98	[1]
GGA-PBE	3.95	[2]
EXPT	3.88	[3]
EXPT	3.89	[4]

Table S1. Comparison of the lattice constant of Pd with those in the recently reported literature.

Table S2. Comparison of the surface energy of the low-index Pd slab model with those found in the

	S	_		
Method	(100)	(110)	(111)	Ref.
GGA-PBE	1.54	1.58	1.30	This work
GGA-PBE	1.54	1.60	1.36	[5]
GGA-PBE	1.49	1.55	1.31	[2]
GGA-PBE	1.51	1.60	1.33	[6]

literature.

Molecule	Facet	# of adsorbate	Adsorption energy (eV)
СО	(100)	1	-1.86
		9 (full coverage)	-0.74
	(110)	1	-1.88
		11 (full coverage)	-0.99
	(111)	1	-2.03
		16 (full coverage)	-0.85
Н	(100)	1	-0.48
	(110)	19 (full coverage)	-0.02
	(110)	1	-0.50
	(111)	19 (full coverage)	-0.22
	(111)	T 27 (full coverage)	-0.06
			-0.00

Table S3. The adsorption energies of CO and H on different Pd facets calculated for both a single molecule and at full coverage.

Catalyst	Reaction conditions	Temperature	Rate constant
		(°C)	<i>k</i> (x10⁻³⋅s⁻¹)
T-Pd/G	Catalyst amount: 2.0 mg	5	6.4
	reaction time: 4 min	10	7.2
		20	9.2
		30	10.1
		40	11.2
	_	50	15.3
S-Pd/G		5	3.4
		10	3.6
		20	5.0
		30	6.2
		40	8.0
	_	50	9.5
commercial Pd/C		5	1.0
		10	1.2
		20	1.8
		30	2.9
		40	4.2
		50	5.9

Table S4. Rate constant data for each catalyst in 4-NP reduction at different reaction temperatures.

*C/N ratio = used catalyst weight (g)/4-NP (mol).

Catalyst	Reaction condition	Rate constant k (x10 ⁻³ ·s ⁻¹)	E _a (kJ·mol⁻¹)	Ref.
T-Pd/G		10.12	13.2	
S-Pd/G	Catalyst amount: 2.0 mg C/N ratio = 2.0 reaction time: 4 min	6.23	17.8	This work
commercial Pd/C	reaction temp.: 30 $^\circ\!C$	2.90	30.3	
Pd NPs	Catalyst amount: 1.3 μg C/N ratio = 3.3 reaction time: 6 min	8.7	14.1	[7]
	reaction temp.: 25 $^\circ\!\!\!C$			
PEI-Pd24	Catalyst amount: 20 mg C/N ratio = 166.7 reaction time: 13 min reaction temp.: room temp.	4	35.3	[8]
Pd/BGO	Catalyst amount: 50 mg C/N ratio = 5 reaction time: 2 min reaction temp.: room temp.	52	37.2	[9]
Pd/GNS-NH ₂	Catalyst amount: 5.0 mg C/N ratio = 250 reaction time: 1 min reaction temp.: room temp.	N.A.	20.8	[10]
Pd/NCB	Catalyst amount: 85 μg C/N ratio = 1.8 Reaction time: 6 min reaction temp.: 30 ℃	6.4	38.9	[11]
Pd-1	Catalyst amount: 1.3 μg C/N ratio = 3.3 reaction time: 6 min reaction temp.: 25 °C	8.57	22.2	[12]
Pd nanocubes	Catalyst amount: 2.4 mg C/N ratio = 750 reaction time: 45 min reaction temp : 30 ℃	0.52	94.6	[13]

Table S5. Comparison of rate constant and activation energies of Pd-based catalysts found in theliterature for catalysts used in 4-NP reduction.

*C/N ratio = used catalyst weight (g)/4-NP (mol).

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