

Supporting Information

Dual Pd and CuFe₂O₄ nanoparticles encapsulated in a core/shell silica microsphere for selective hydrogenation of arylacetylenes

Kyu Hyung Lee, Byeongno Lee, Kyu Reon Lee, Mi hye Yi and Nam Hwi Hur*

Department of Chemistry, Sogang University, Seoul 121-742, Korea

*e-mail: nhhur@sogang.ac.kr

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I. Experimental details

Reagents. Copper nitrate hemi(pentahydrate) ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, 98+%) , cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98+%), iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 98+%), Igepal CO-520, 3-aminopropyltrimethoxysilane (APTMS, 97%), potassium tetrachloro palladate (K_2PdCl_4 , 98 %), and phenylacetylene (98 %) were purchased from Sigma-Aldrich. N-octyl ether was purchased from Tokyo Chemical Industry Co. All solvents (methanol, chloroform, pentane, hexane, cyclohexane) were purchased from Sigma-Aldrich. All the reagents were used without any further purification.

II. Instrumentation

Powder X-ray diffraction patterns were recorded with a Rigaku Miniflex diffractometer ($\text{Cu K}\alpha$) operating at 40 kV and 150 mA. Transmission electron microscope (TEM) analyses were carried out on a JEOL JEM-2100F. Samples were also subjected to chemical microanalysis with an Oxford Instruments INCA TEM 300 system for energy dispersive X-ray (EDX) analysis. Specimens for TEM examination were prepared by dispersing the finely-ground powder in high purity ethanol and then allowing a drop of the suspension to evaporate on a 400 mesh carbon-coated grid. High resolution scanning electron microscope (HR-SEM) analyses were carried out using a Hitachi s-5500. Atomic Weight Percentage (ICP-MS) of the solid catalysts were determined by an inductively coupled plasma-mass spectrometry. The temperature-dependent and field-dependent magnetization measurements were measured with a Quantum Design MPMS-5 SQUID magnetometer. The field-dependent magnetization was measured at 10 and 300 K. The BET (Brunauer-Emmett-Teller) surface areas were calculated from $p/p_0 = 0.05-0.3$ in the adsorption curve using a BET equation.

Hydrogenation products were analyzed using a gas chromatography (GC, Younglin, Acme-6000) equipped with a FID (flame ionization detector) and a capillary column (HP-Innowax, J&W). The ^1H and ^{13}C NMR spectra were recorded on a Varian 400-MHz Gemini operating at 400 MHz for ^1H and 100 MHz for ^{13}C , respectively. All chemical shifts were referenced to tetramethylsilane.

III. Fabrication of Encapsulated Catalysts

Preparation of $\text{SiO}_2@\text{CuFe}_2\text{O}_4$. The core/shell silica microsphere was prepared by slight modification of the Unger procedure^{S1} and the preparation of $\text{SiO}_2@\text{CuFe}_2\text{O}_4$ was done on the basis of our previous report.^{S2} For the synthesis of $\text{SiO}_2@\text{CuFe}_2\text{O}_4$, 1 g of core/shell silica microsphere was added into a 10 mL of ethanol with vigorous stirring, which was then sonicated to disperse the silica microspheres uniformly. To the solution, 0.0573 g of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and 0.1991 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were added. After complete dissolution of the Cu and Fe precursors, 20 mL of n-octyl ether and 1 mL of Igepal CO-520 were sequentially added into the mixed solution. The reaction mixture was sonicated for 20 min, which was then heated at 363 K until ethanol was almost completely evaporated. The mixture was kept for 1 h at 463 K to nucleate CuFe_2O_4 NPs and further refluxed at 573 K for 3 h. The dark brown microspheres were separated by centrifugation (3500 rpm) with a couple of intermediate washing with ethanol. By using a magnet, the microspheres were collected, washed with ethanol, and dried in an oven at 353 K. The dried microspheres are denoted as $\text{SiO}_2@\text{CuFe}_2\text{O}_4$. Some of the microspheres were annealed at 773 K in air for 6 h. The annealed sample is virtually identical in shape but has slightly different magnetic property by comparison with the as-synthesized sample.

Preparation of SiO₂@MFe₂O₄ and SiO₂@CuO. Catalysts with a general formula of SiO₂@MFe₂O₄ (M = Co, Fe) were prepared by incorporating magnetic components (MFe₂O₄) into porous silica shells in the same manner as the synthesis of SiO₂@CuFe₂O₄. The only difference is the precursor complex. For the synthesis of SiO₂@CoFe₂O₄, Co(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O were used as sources of Co and Fe. Fe(NO₃)₃·9H₂O and Cu(NO₃)₂·2.5H₂O were used for the synthesis of SiO₂@Fe₃O₄ and SiO₂@CuO, respectively.

Preparation of SiO₂@CuFe₂O₄-Pd. The SiO₂@CuFe₂O₄ microsphere (0.2 g) was added into a 10 mL of ethanol with vigorous stirring to disperse the microspheres completely, to which a 0.3 mL of 3-aminopropyltrimethoxy-silane (APTMS) was added drop by drop. The reaction mixture was then vigorously stirred for 3 h to bind APTMS molecules on the surfaces of the microspheres. The amine-functionalized SiO₂@CuFe₂O₄ microspheres were separated by centrifugation (3500 rpm) with a couple of intermediate washing with ethanol several times, which were dried in an oven at 353 K. The resulting microspheres were purified by centrifuging them, discarding the supernatant, and re-dispersing them in ethanol. The functionalized microspheres were dispersed in a 10 mL of ethanol. To the solution, 0.0157 g of K₂PdCl₄ dissolved in a 10 mL of deionized water was added. After the reaction mixture was vigorously stirred for 12 h, the resulting microspheres were separated by centrifugation with a couple of intermediate washing with ethanol, which was then dried in an oven at 353 K. The Pd-loaded product is denoted as SiO₂@CuFe₂O₄-Pd.

Preparation of SiO₂@MFe₂O₄-Pd and SiO₂@CuO-Pd. Catalysts with a general formula of SiO₂@MFe₂O₄-Pd (M = Co, Fe) and SiO₂@CuO-Pd were prepared in the same manner as the synthesis of SiO₂@CuFe₂O₄-Pd.

Preparation of SiO₂@Pd. For the synthesis of SiO₂@Pd, 0.2 g of core/shell silica microsphere was first functionalized with AMTMS. The functionalized microspheres were dispersed in a 10 mL of ethanol. To the solution, 0.0157 g of K₂PdCl₄ dissolved in a 10 mL of deionized water was added. After the reaction mixture was vigorously stirred for 12 h, the resulting microspheres were separated by centrifugation with a couple of intermediate washing with ethanol, which was then dried in an oven at 353 K. The product is denoted as SiO₂@Pd.

IV. General Procedure for Catalytic Reactions

Solvent screening experiments (Table S3). To a 5 mL round bottom flask connected to a gas balloon adaptor, phenylacetylene (0.91 mmol), SiO₂@CuFe₂O₄-Pd (10 mg), and solvent (2 mL) were sequentially added. The reaction mixture was thoroughly purged with H₂ through an adaptor and the internal pressure was maintained by a filled balloon of H₂. The progress of the reaction was monitored by ¹H-NMR and the yield was determined by ¹H-NMR. In addition, gas chromatography was also used to confirm the products.

Hydrogenation of phenylacetylene with encapsulated catalysts. To a 5 mL round bottom flask connected to a gas balloon adaptor, phenylacetylene (0.91 mmol), SiO₂@CuFe₂O₄-Pd (10 mg) and hexane (2 mL) were sequentially added. The reaction mixture was thoroughly purged with H₂ through an adaptor and the internal pressure was maintained by a filled balloon of H₂. The reaction mixture was collected at regular intervals by a syringe, which was analyzed by ¹H-NMR. The same experiments were conducted with SiO₂@CuFe₂O₄ and SiO₂@Pd (entries 3, 4 in Table 1).

Hydrogenation of phenylacetylene with Lindlar catalyst. To a 5 mL round bottom flask connected to a gas balloon adaptor, phenylacetylene (0.91 mmol), Lindlar catalyst (5 wt% Pd on CaCO₃ poisoned with lead, Aldrich, 8.3 mg) and hexane (2 mL) were sequentially added. The reaction mixture was thoroughly purged with H₂ through an adaptor and the internal pressure was maintained by a filled balloon of H₂. The reaction mixture was collected at regular intervals by a syringe, which was analyzed by ¹H-NMR. (entry 2 in Table 1).

Hydrogenation of phenylacetylene with SiO₂@CoFe₂O₄-Pd, SiO₂@Fe₃O₄-Pd, and SiO₂@CuO. To a 5 mL round bottom flask connected to a gas balloon adaptor, phenylacetylene (0.91 mmol), SiO₂@CoFe₂O₄-Pd (10 mg) and hexane (2 mL) were sequentially added. The reaction mixture was thoroughly purged with H₂ through an adaptor and the internal pressure was maintained by a filled balloon of H₂. The progress of the reaction was monitored by ¹H-NMR. The reaction mixture was collected at regular intervals by a syringe, which was analyzed by ¹H-NMR. The same experiments were conducted with SiO₂@Fe₃O₄-Pd and SiO₂@CuO (Table S4).

Hydrogenation of phenylacetylene with recycled SiO₂@CuFe₂O₄-Pd. To a 5 mL round bottom flask connected to a gas balloon adaptor, phenylacetylene (0.91 mmol), SiO₂@CuFe₂O₄-Pd (10 mg) and hexane (2 mL) were sequentially added. The reaction mixture was thoroughly purged with H₂ through an adaptor and the internal pressure was maintained by a filled balloon of H₂. The catalyst was separated by a magnet (Fig. S11). The recycle experiments were performed with the separated catalyst under the same conditions (Table S6). The recycle experiments were performed three times under the same conditions.

Hydrogenation of a 1:1 mixture of phenylacetylene and styrene with SiO₂@CuFe₂O₄-Pd. To a 5 mL round bottom flask connected to a gas balloon adaptor, phenylacetylene (0.54 mmol), styrene (0.52 mmol), SiO₂@CuFe₂O₄-Pd (10 mg) and hexane (2 mL) were sequentially added. The reaction mixture was thoroughly purged with H₂ through an adaptor and the internal pressure was maintained by a filled balloon of H₂. The progress of the reaction was monitored by ¹H-NMR. The reaction mixture was collected at regular intervals by a syringe, which was analyzed by ¹H-NMR (Fig. S17).

V. Tables and Figures

Table S1. ICP-MS data for SiO₂@CuFe₂O₄-Pd

Element	Weight (%)
Cu	0.89
Fe	1.61
Pd	4.15

Table S2. BET surface areas of SiO₂, SiO₂@CuFe₂O₄, and SiO₂@CuFe₂O₄-Pd

Sample	Total BET surface area ^a (m ² g ⁻¹)
SiO ₂ ^b	383.1205
SiO ₂ @CuFe ₂ O ₄	298.9725
SiO ₂ @CuFe ₂ O ₄ -Pd	56.9144

^a BET surface areas calculated from N₂ adsorption

^b core-shell silica microsphere

Table S3. Hydrogenation of phenylacetylene to styrene with SiO₂@CuFe₂O₄-Pd^a

Entry	Solvent	Time (h)	Conversion (%) ^b	Selectivity (%) ^b	TOF(h ⁻¹) ^c
1	Methanol	20.0	60	97	7
2	Chloroform	12.0	29	98	6
3	Pentane	3.0	62	99	48
4	Hexane	2.5	98	98	91
5	Cyclohexane	2.0	71	98	83

^a Reaction conditions: phenylacetylene 0.91 mmol, catalyst 10 mg, solvent 2 mL, H₂ balloon (*ca.* 1 atm). ^b Confirmed by ¹H NMR and GC. ^c [mol product]/[mol catalyst][hour].

Table S4. Hydrogenation of phenylacetylene to styrene with various catalysts^a

Entry	Spinel ferrite	Time (h)	Conversion (%) ^b	Selectivity (%) ^b	TOF(h ⁻¹) ^c
1	SiO ₂ @Pd	2.5	3	99	3
2	SiO ₂ @CoFe ₂ O ₄ -Pd	2.5	18	99	17
3	SiO ₂ @Fe ₃ O ₄ -Pd	2.5	60	87	59
4	SiO ₂ @CuFe ₂ O ₄ -Pd	2.5	98	98	91
5	SiO ₂ @CuO-Pd	2.5	-	-	-

^a Reaction conditions: phenylacetylene 0.91 mmol, catalyst 10 mg, solvent 2 mL, H₂ balloon (*ca.* 1 atm). ^b Confirmed by ¹H NMR and GC. ^c [mol product]/[mol catalyst][hour].

Table S5. Hydrogenation of styrene to ethyl benzene with various catalysts^a

Entry	Catalyst	Time (h)	Conversion (%) ^b
1	SiO ₂ @Pd	2.5	99
2	SiO ₂ @CuFe ₂ O ₄ -Pd	2.5	88
3	SiO ₂ @CuO-Pd	2.5	-

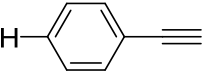
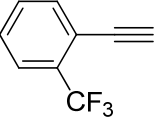
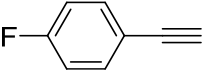
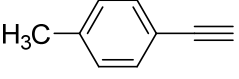
^a Reaction conditions: styrene 0.91 mmol, catalyst 10 mg, solvent 2 mL, H₂ balloon (*ca.* 1 atm). ^b Confirmed by ¹H NMR and GC.

Table S6. Hydrogenation of phenylacetylene with used SiO₂@CuFe₂O₄-Pd catalysts^a

Number of recycle	Time (h)	Conversion (%) ^b	Selectivity (%) ^b
1	2.5	98	98
	1.5	69	>99
2	2.5	99	98
	1.5	66	>99
3	2.5	98	97
	1.5	68	99

^a Reaction conditions: phenylacetylene 0.91 mmol, catalyst 10 mg, solvent 2 mL, H₂ balloon (*ca.* 1 atm). ^b Confirmed by ¹H NMR and GC.

Table S7. Turn over frequency of hydrogenation of phenylacetylene derivatives with SiO₂@CuFe₂O₄-Pd^a

Substrate	Conversion (%) ^b	Selectivity (%) ^b	TOF(h ⁻¹) ^c
	98	98	90
	99	88	203
	99	98	226
	99	73	84

^a Reaction conditions: phenylacetylene 0.91 mmol, catalyst 10 mg, solvent 2 mL, H₂ balloon (*ca.* 1 atm). ^b Confirmed by ¹H NMR. ^c [mol product]/[mol catalyst][hour].

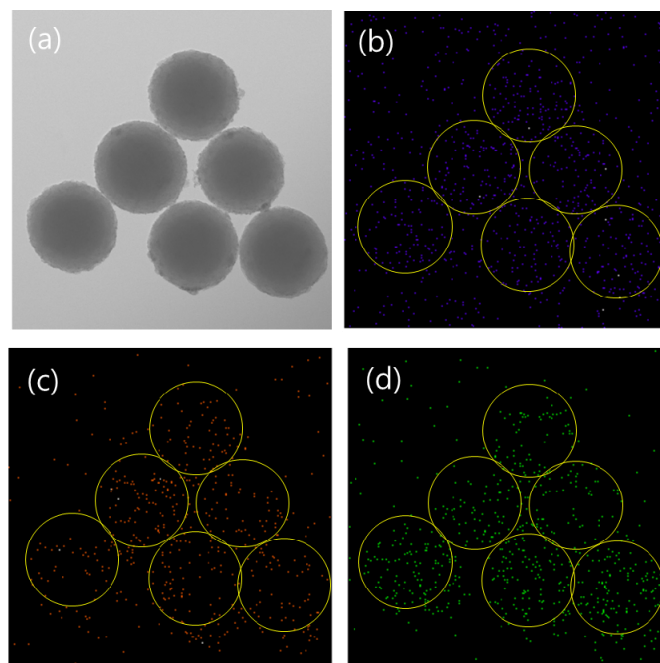


Fig. S1 (a) TEM images of SiO₂@CuFe₂O₄-Pd. Elemental distribution maps of (b) Cu, (c) Fe, and (d) Pd present in SiO₂@CuFe₂O₄-Pd obtained from energy dispersive X-ray analysis.

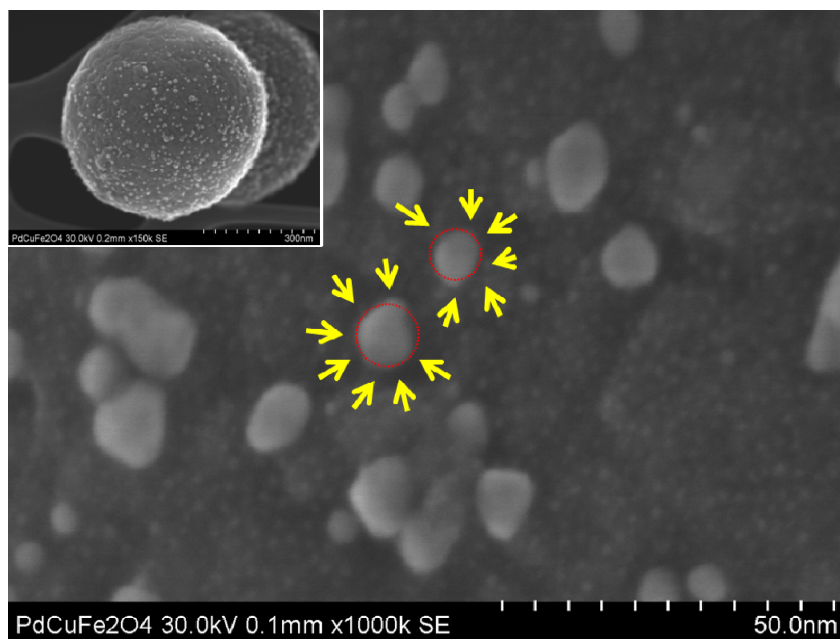


Fig. S2 High resolution SEM images of $\text{SiO}_2@ \text{CuFe}_2\text{O}_4\text{-Pd}$. The inset is an overall image of a $\text{SiO}_2@ \text{CuFe}_2\text{O}_4\text{-Pd}$ microsphere. Yellow arrows and red circles denote Pd and CuFe_2O_4 NPs immobilized on a silica shell, respectively.

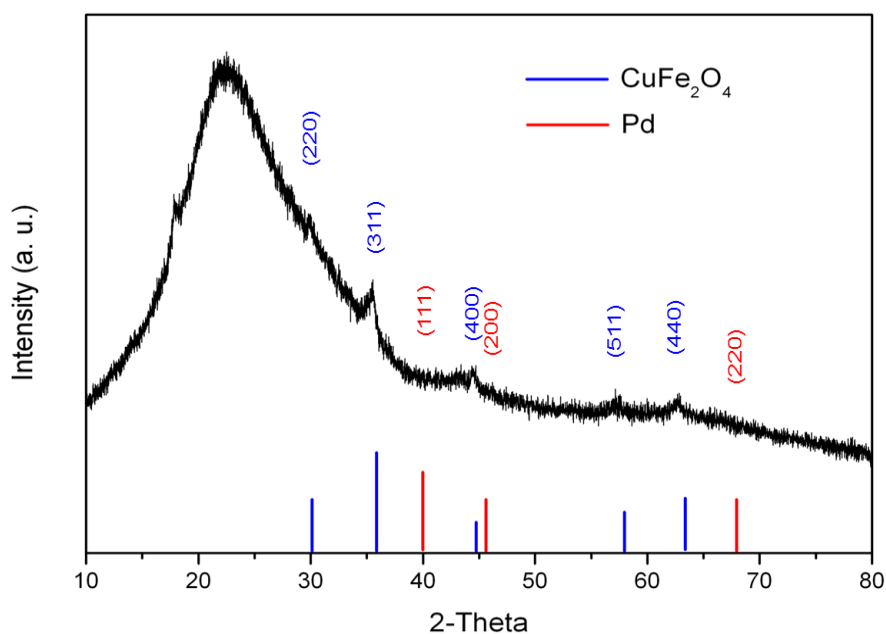


Fig. S3 Powder X-ray diffraction patterns for as-synthesized $\text{SiO}_2@ \text{CuFe}_2\text{O}_4\text{-Pd}$ microspheres. Vertical bars below the XRD patterns are theoretical peak positions of CuFe_2O_4 and Pd.

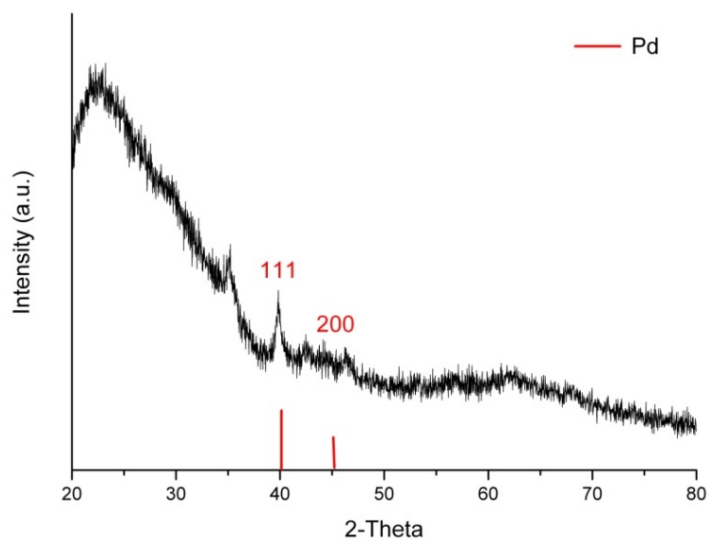


Fig. S4 Powder X-ray diffraction patterns for $\text{SiO}_2@ \text{CuFe}_2\text{O}_4\text{-Pd}$ annealed at 573K. Vertical bars below the XRD patterns are theoretical peak positions of Pd.

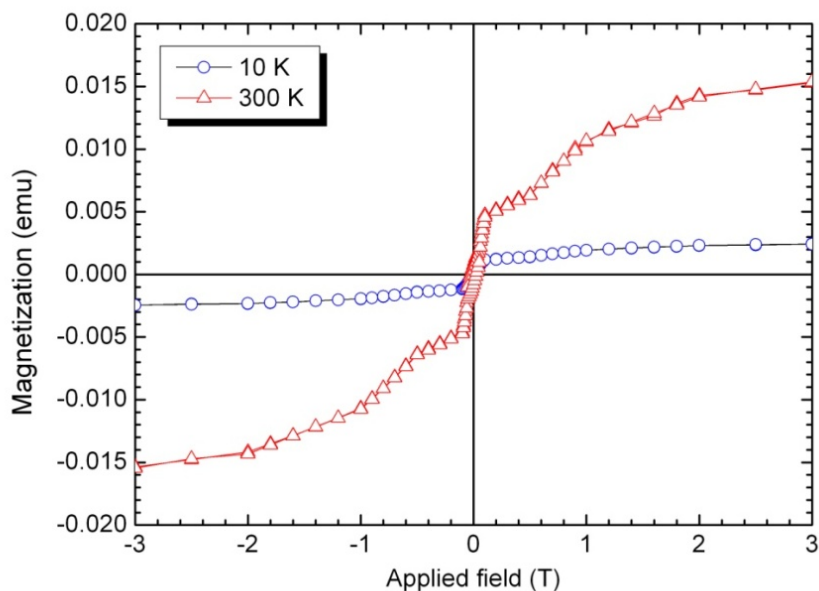


Fig. S5 Field-dependent magnetization curves of $\text{SiO}_2@ \text{CuFe}_2\text{O}_4$. Open sphere and triangle symbols represent magnetization data collected at 10 and 300 K, respectively.

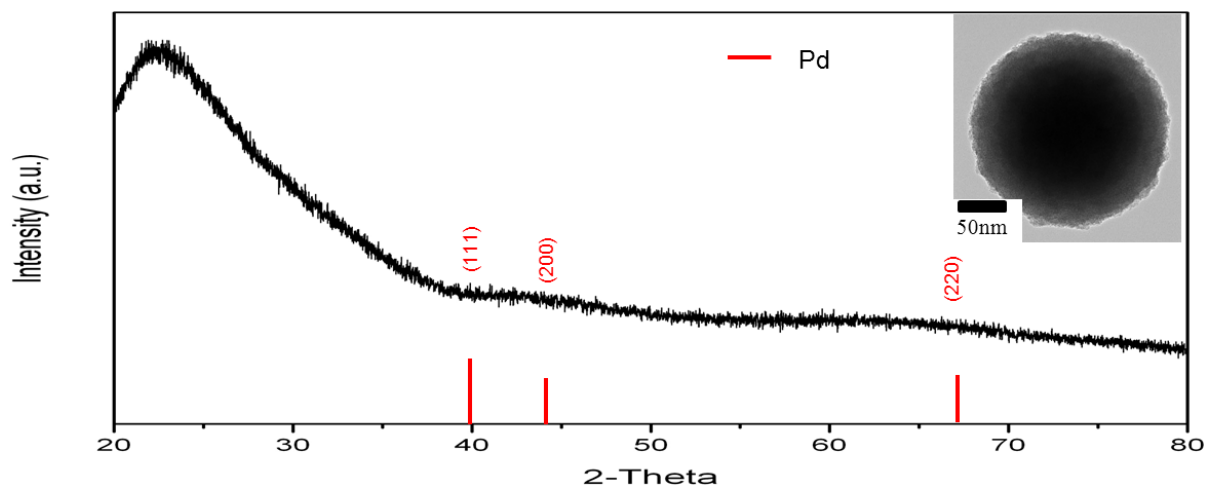


Fig. S6 Powder X-ray diffraction patterns for SiO₂@Pd. Vertical bars below the XRD patterns are theoretical peak positions of Pd. The inset is the TEM images of SiO₂@Pd.

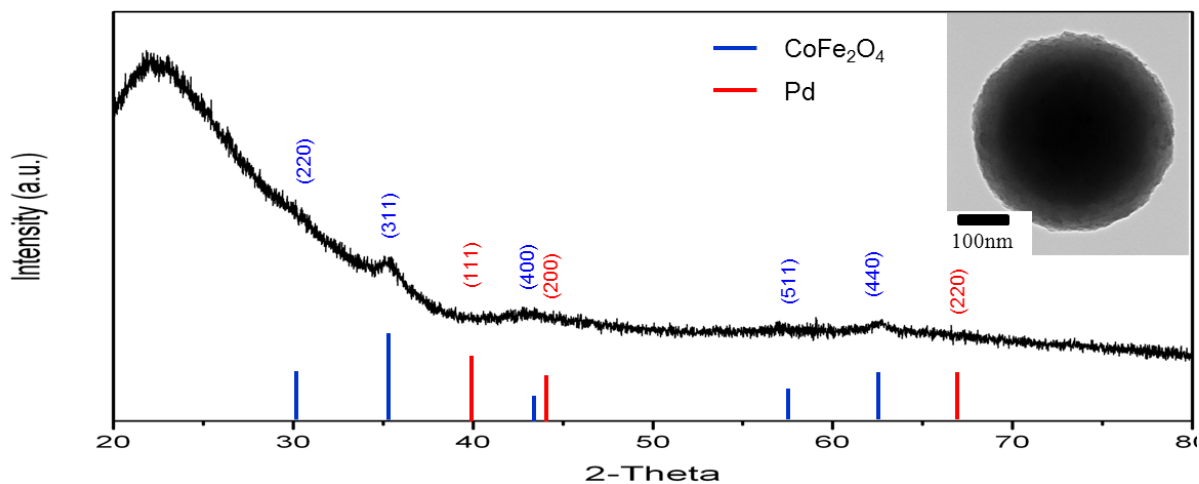


Fig. S7 Powder X-ray diffraction patterns for SiO₂@CoFe₂O₄-Pd. Vertical bars below the XRD patterns are theoretical peak positions of CoFe₂O₄ and Pd. The inset is the TEM images of SiO₂@CoFe₂O₄-Pd.

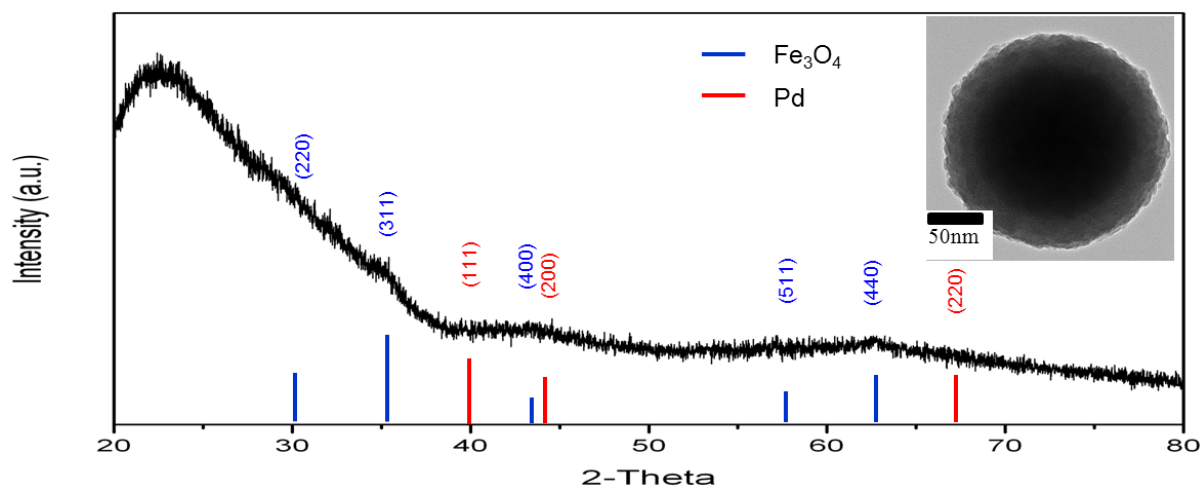


Fig. S8 Powder X-ray diffraction patterns for SiO₂@Fe₃O₄-Pd. Vertical bars below the XRD patterns are theoretical peak positions of Fe₃O₄ and Pd. The inset is the TEM images of SiO₂@Fe₃O₄-Pd.

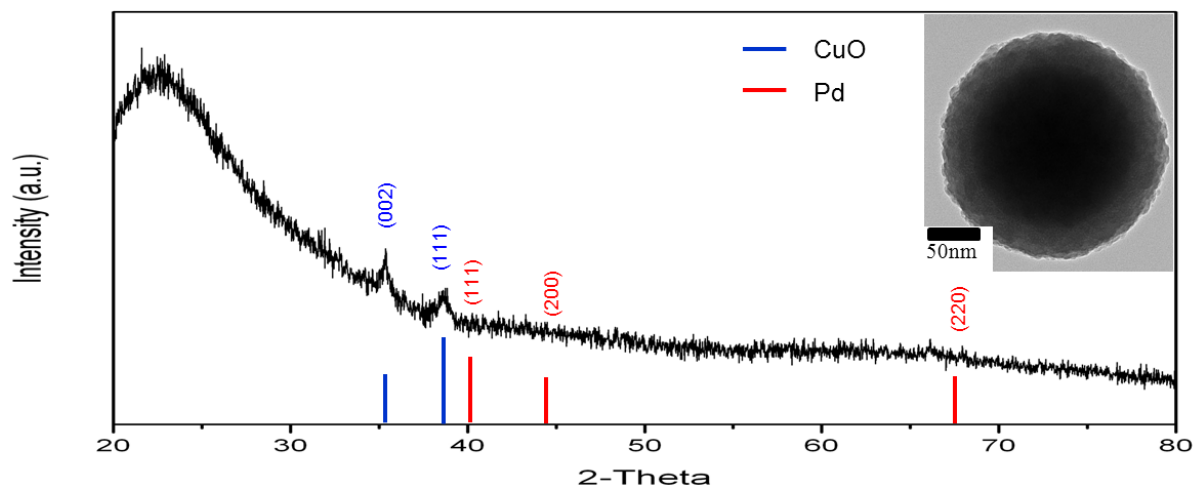


Fig. S9 Powder X-ray diffraction patterns for SiO₂@CuO-Pd. Vertical bars below the XRD patterns are theoretical peak positions of CuO and Pd. The inset is the TEM images of SiO₂@CuO-Pd.

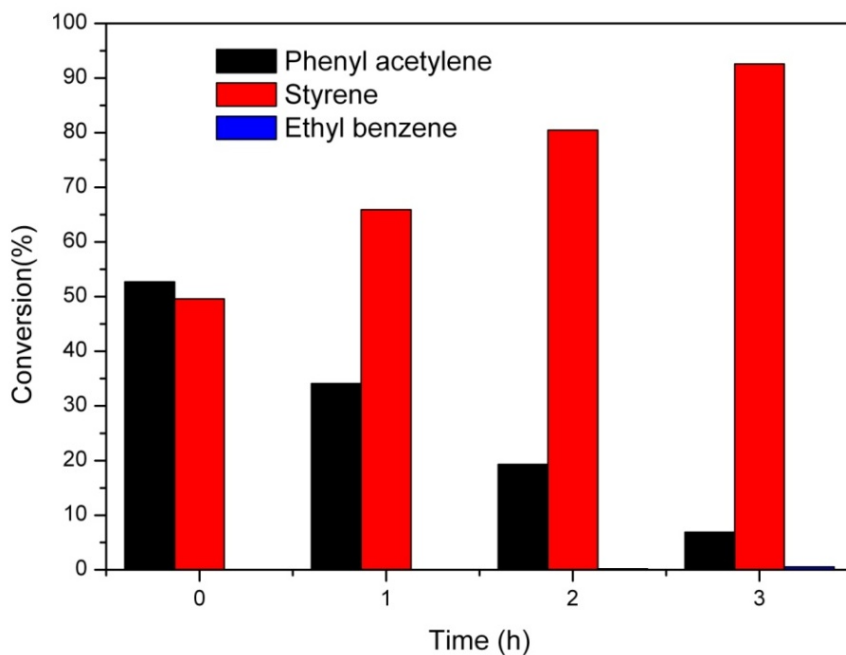


Fig. S10 Hydrogenation product distribution obtained from a 1:1 mixture of phenylacetylene and styrene in hexane using $\text{SiO}_2@\text{CuFe}_2\text{O}_4\text{-Pd}$ as the catalyst. Trace amount of ethyl benzene was detected after 3 h.

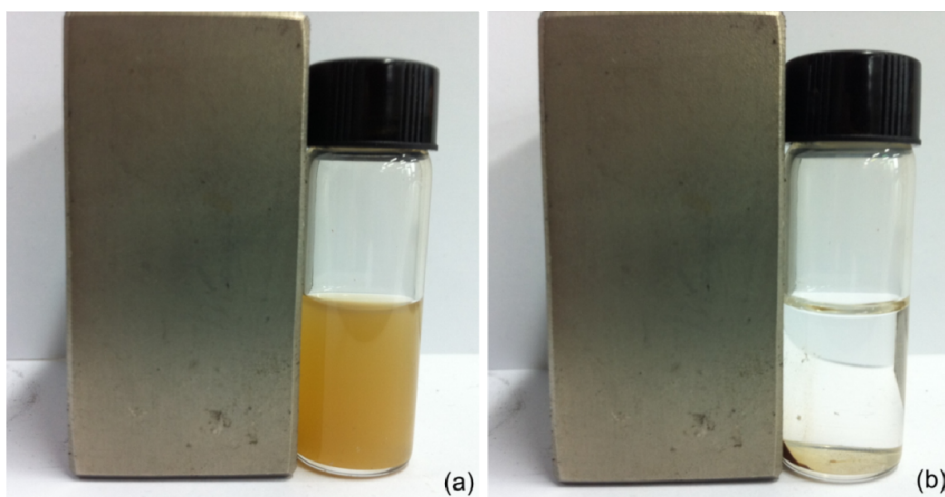
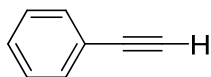


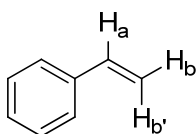
Fig. S11 (a) Initial reaction mixture containing phenylacetylene and $\text{SiO}_2@\text{CuFe}_2\text{O}_4\text{-Pd}$ in hexane. (b) Separation of $\text{SiO}_2@\text{CuFe}_2\text{O}_4\text{-Pd}$ by a magnet after the reaction.

Phenylacetylene.



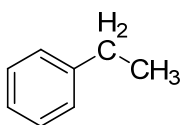
^1H NMR (400 MHz, CDCl_3): δ (ppm) 3.07 (s, 1H, *CH* in alkyne) 7.42 (m, 2H, *CH*-3 and *CH*-5 in phenyl), 7.43 (m, 1H, *CH*-4 in phenyl), 7.55 (m, 2H, *CH*-2 and *CH*-6 in phenyl).

Styrene.



^1H NMR (400 MHz, CDCl_3): δ (ppm) 6.70-6.77 (dd, $J = 17.6$, $J' = 10.8$, 1H, H_a), 5.75-5.79 (d, $J = 17.6$, 1H, H_b), 5.25-5.27 (d, $J = 10.8$, 1H, $H_{b'}$), 7.42 (m, 2H, *CH*-3 and *CH*-5 in phenyl), 7.43 (m, 1H, *CH*-4 in phenyl), 7.55 (m, 2H, *CH*-2 and *CH*-6 in phenyl).

Ethyl benzene.



^1H NMR (400 MHz, CDCl_3): δ (ppm) 1.22 (t, 3H, CH_3), 2.53 (q, 2H, CH_2), 7.42 (m, 2H, *CH*-3 and *CH*-5 in phenyl), 7.43 (m, 1H, *CH*-4 in phenyl), 7.55 (m, 2H, *CH*-2 and *CH*-6 in phenyl).



Fig. S12 ¹H NMR spectra for the hydrogenation of phenylacetylene to styrene with SiO₂@CuFe₂O₄-Pd as a function of time.

Std proton
Sample: 0524_Lindlar_0.002g_Hydro_2h_30m
File: home/vnmr1/vnmrfsys/data/HNH/LKH/2011/0524_Lindlar_0.002g_Hydro_2h_30m.fid
Pulse Sequence: s2pu1
Solvent: cdcl3
Ambient temperature
Operator: HNH
File: 0524_Lindlar_0.002g_Hydro_2h_30m
VNMRS-400 "hvarlan-NMR2"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.7415174 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
F2 size 65536
Total time 0 min, 55 sec

Table 1, entry 2
2 hour 30min

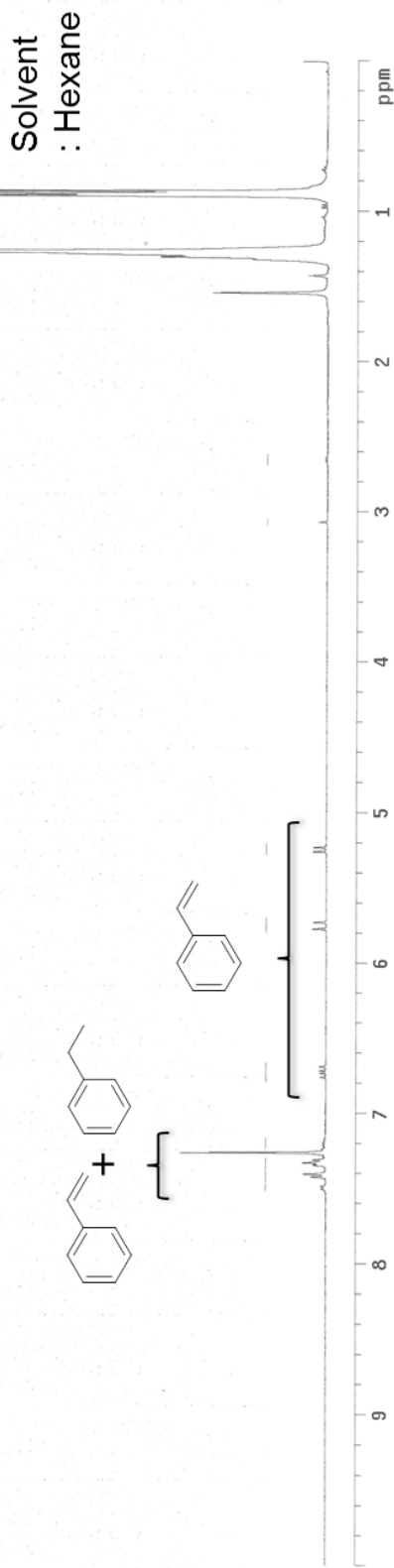


Fig. S13 ¹H NMR Spectra for the hydrogenation of phenylacetylene to styrene with Lindlar catalyst.

Std proton

Sample: 0618_2Pd_mesoSiO2_2h_30m
File: home/vnmr1/vnmrsys/data/HNH/LKH/2011/06/0618_2Pd_mesoSiO2_2h_30m.fid

Pulse Sequence: s2pu1

Solvent: cdcl3
Ambient temperature
Operator: HNH
File: 0618_2Pd_mesoSiO2_2h_30m
VNMR5-400 "vartan-NMR2"

Relax. delay 1.000 sec
Pulse 45.0 degree
Acq. time 2.049 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.7415222 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 55 sec

Table 1, entry 4

2 hour 30min

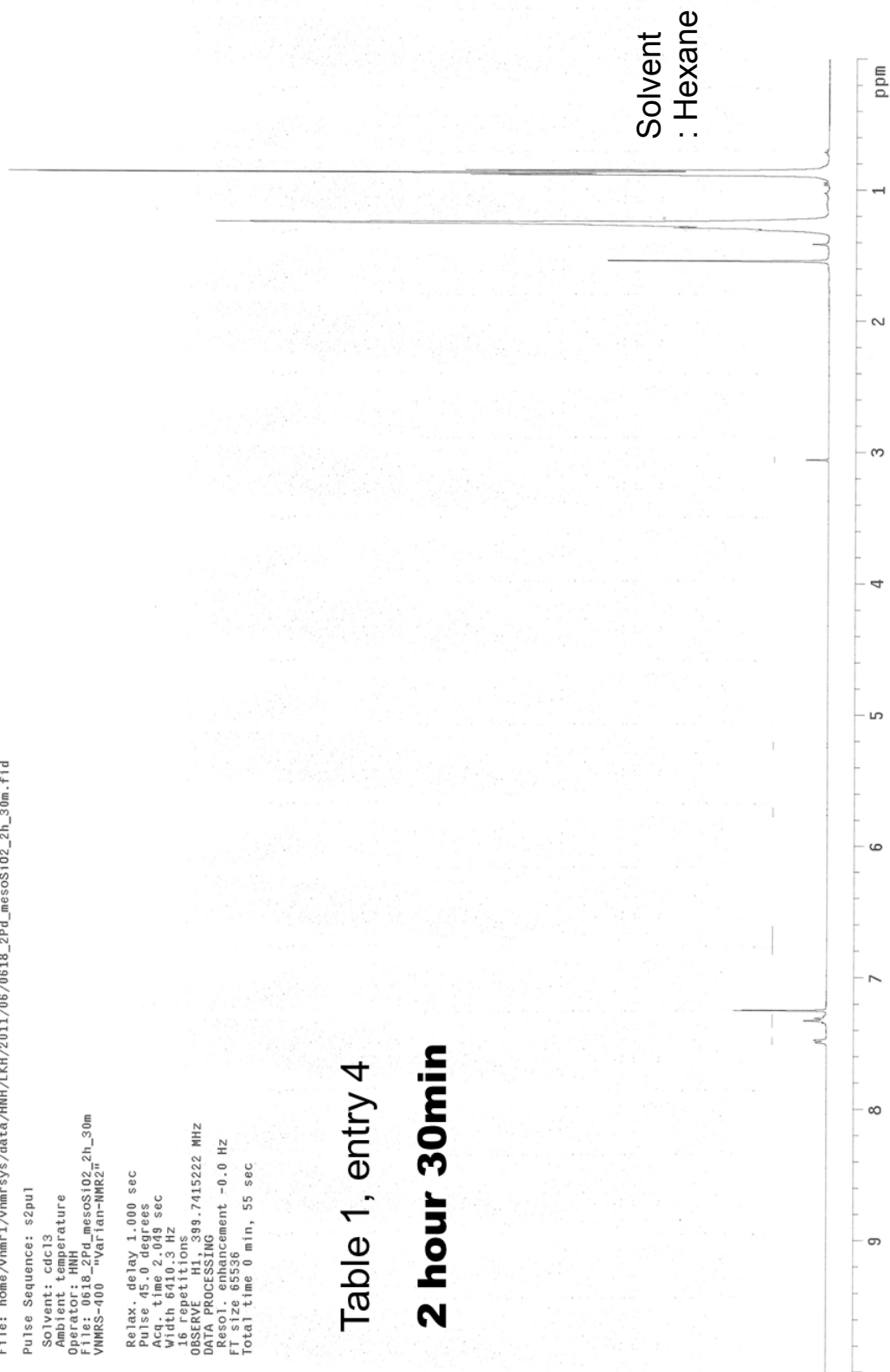


Fig. S14 ¹H NMR Spectra for the hydrogenation of phenylacetylene to styrene with SiO₂@Pd.

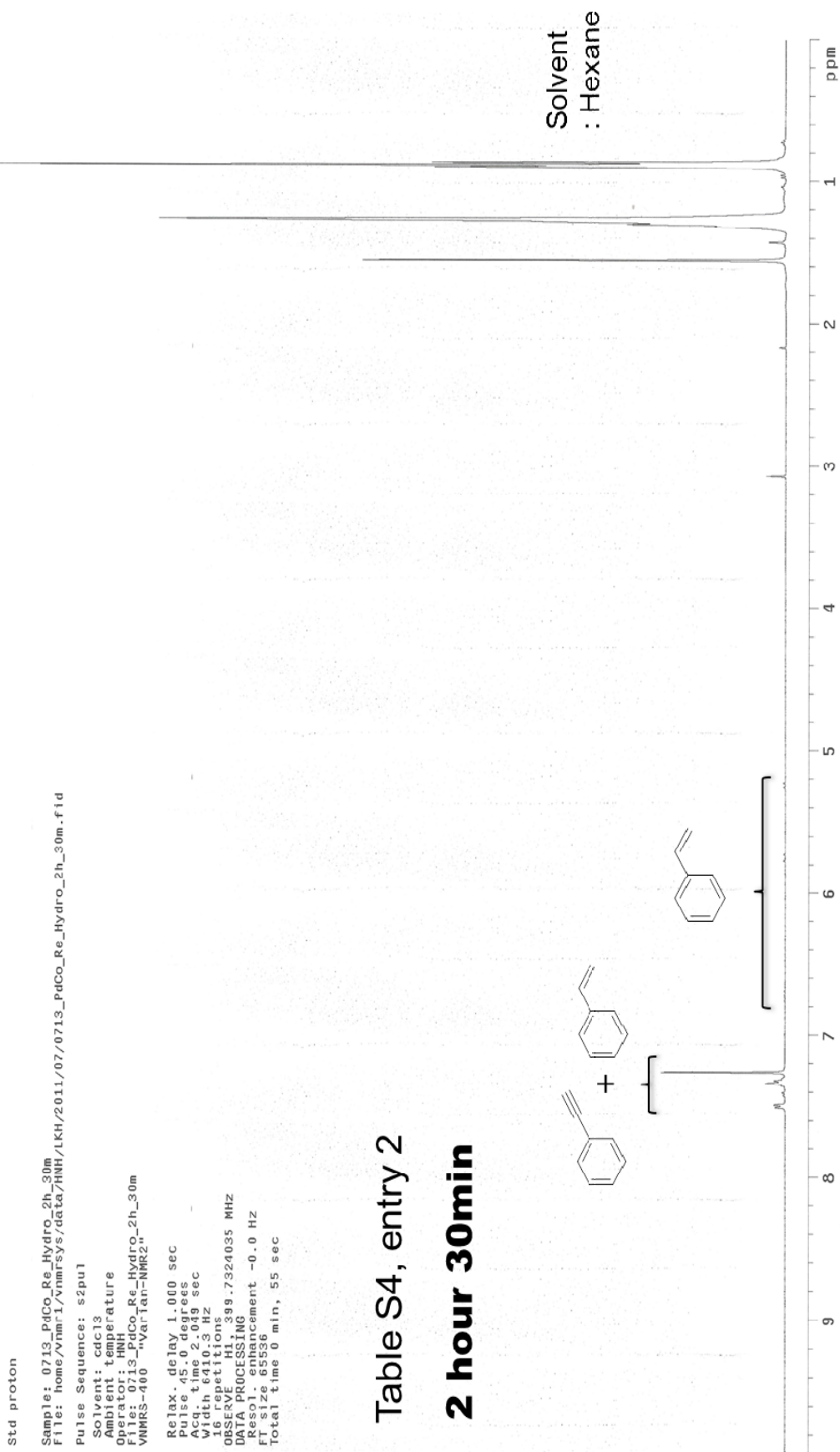


Fig. S15 ^1H NMR Spectra for the hydrogenation of phenylacetylene to styrene with $\text{SiO}_2@\text{CoFe}_2\text{O}_4\text{-Pd}$.

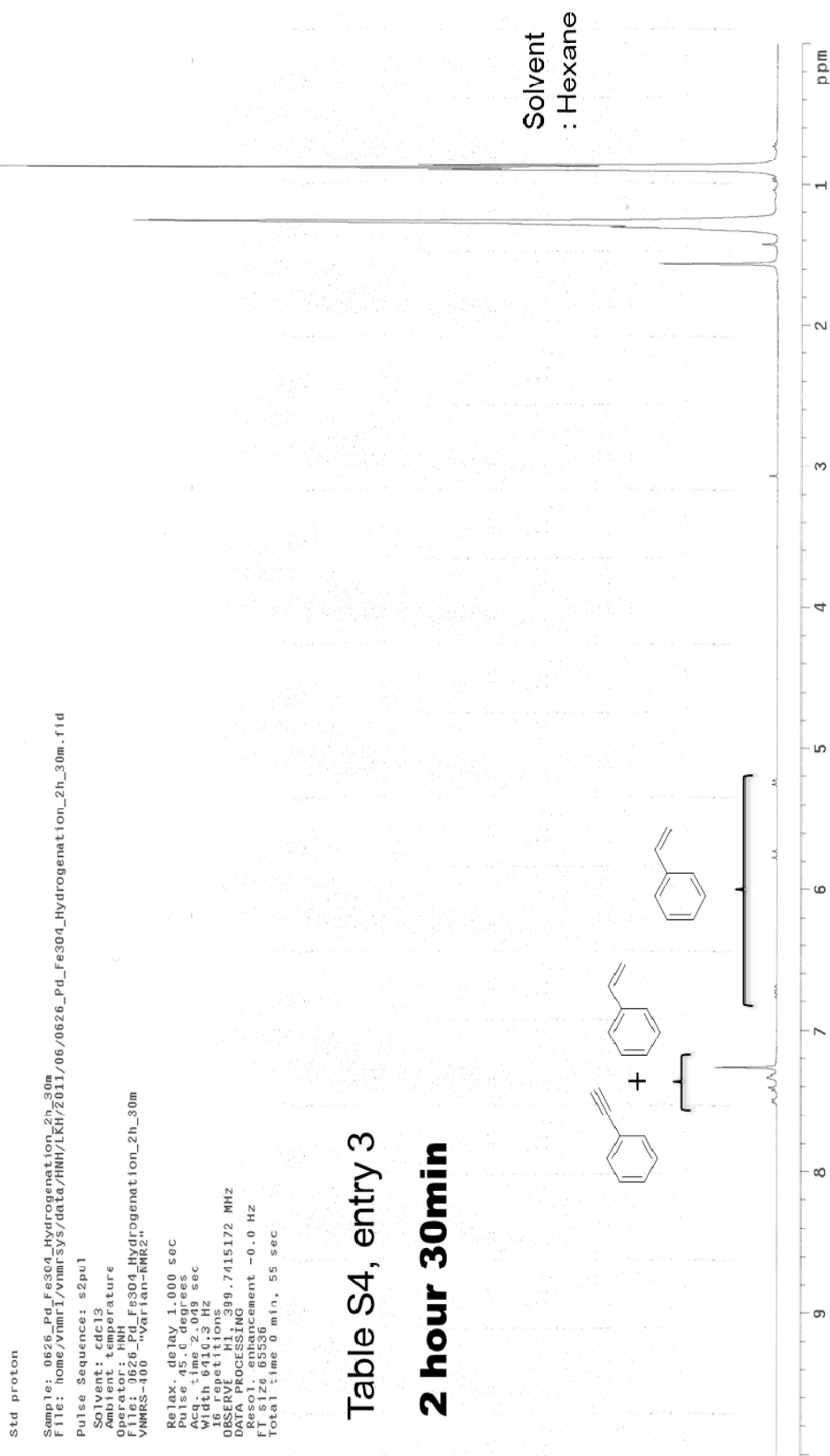


Table S4, entry 3

2 hour 30min

Fig. S16 ^1H NMR Spectra for the hydrogenation of phenylacetylene to styrene with $\text{SiO}_2@\text{Fe}_3\text{O}_4\text{-Pd}$ as function of time.

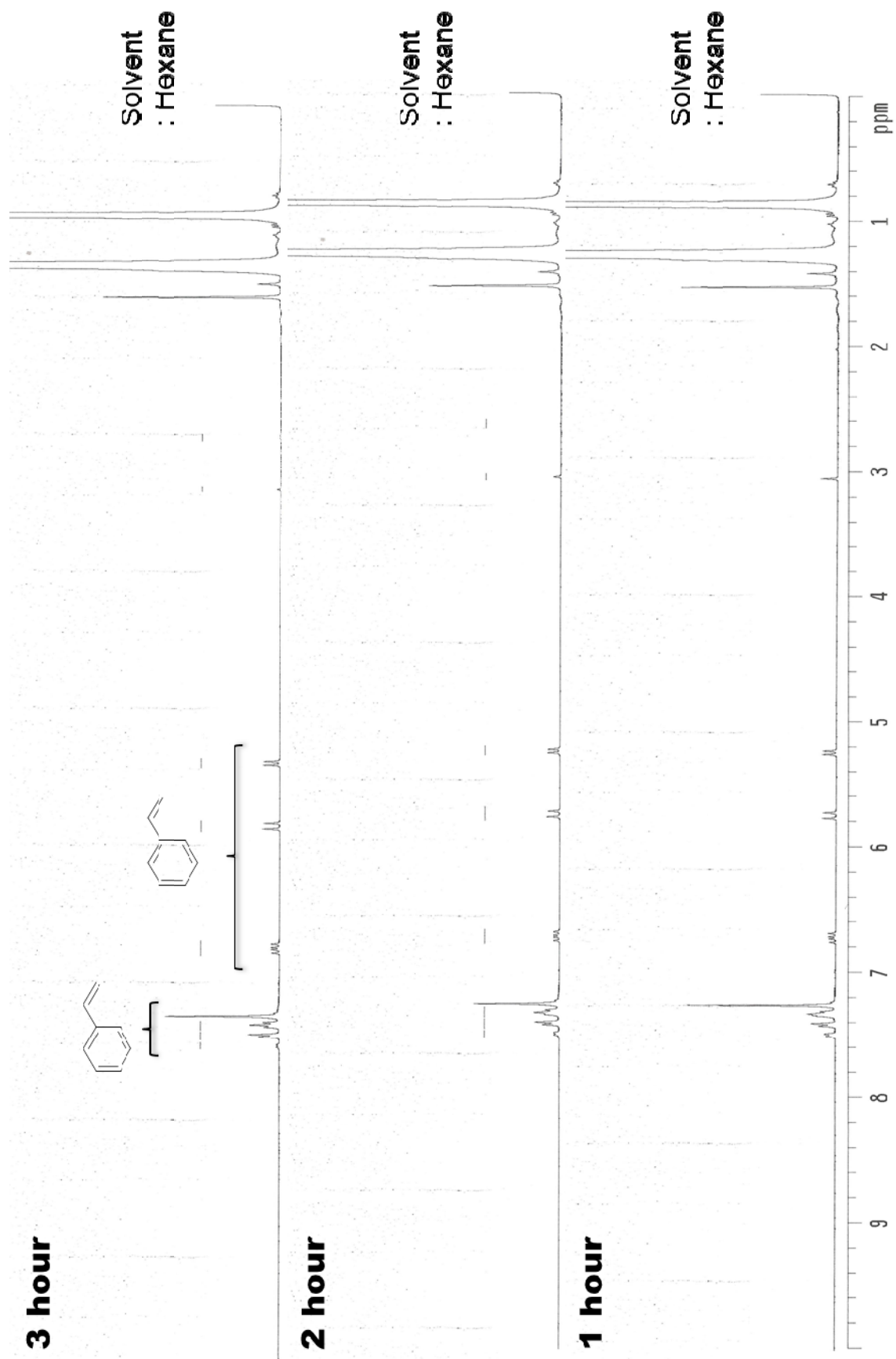


Fig. S17 ¹H NMR Spectra for the hydrogenation of 1:1 mixture of phenylacetylene and styrene with SiO₂@CuFe₂O₄-Pd as a function of time.

Phenyl acetylene

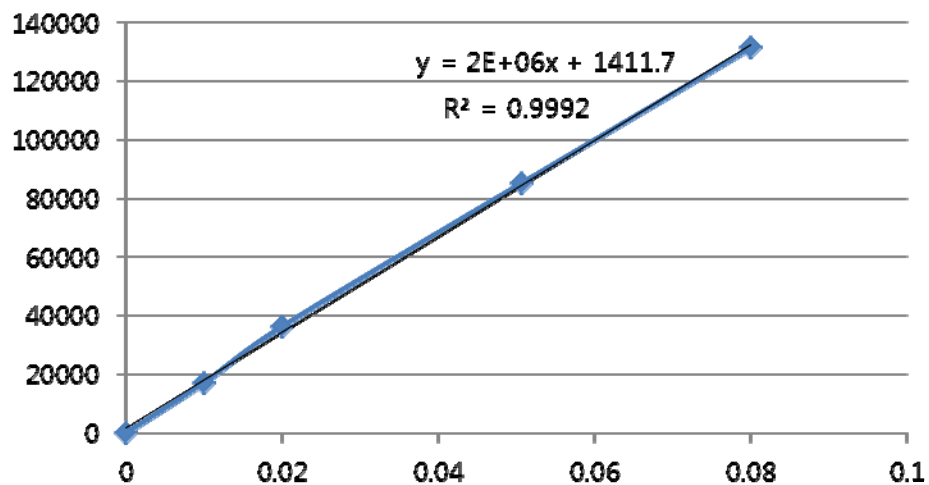


Fig. S18 GC calibration curve of phenylacetylene in hexane.

Styrene

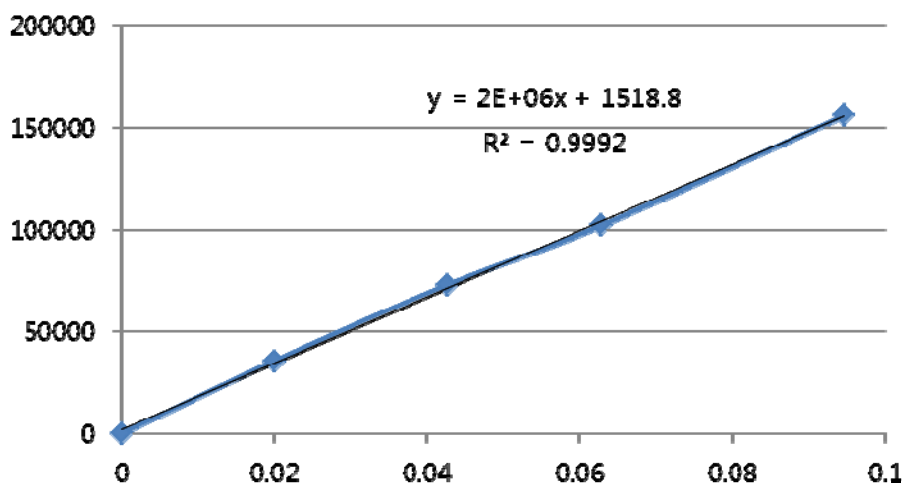


Fig. S19 GC calibration curve of styrene in hexane.

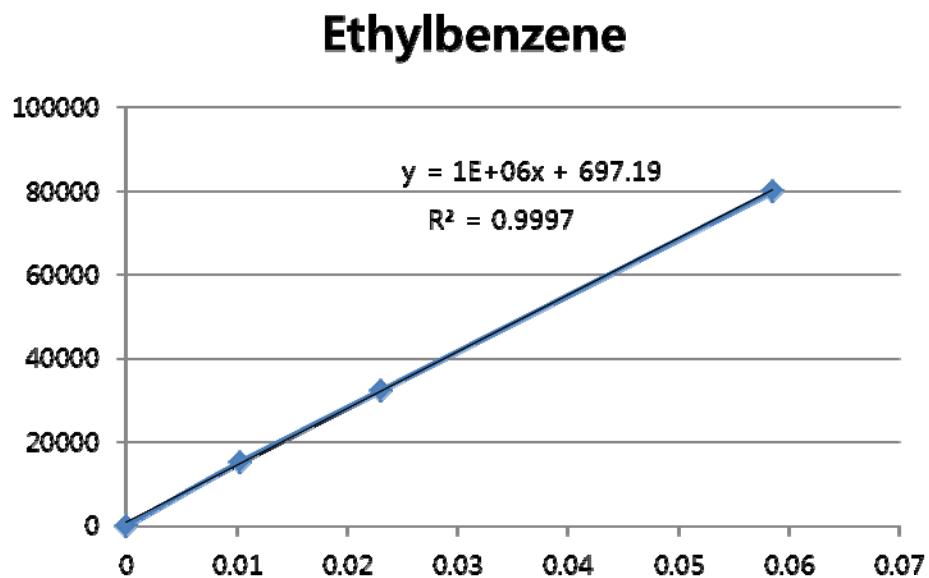


Fig. S20 GC calibration curve of ethyl benzene in hexane.

VI. References

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