

Electronic Supplementary Information

Cu₂O Hydrides Promote Selective Semihydrogenation of Alkynes on Pd-Cu₂O/TiO₂ under Mild Conditions

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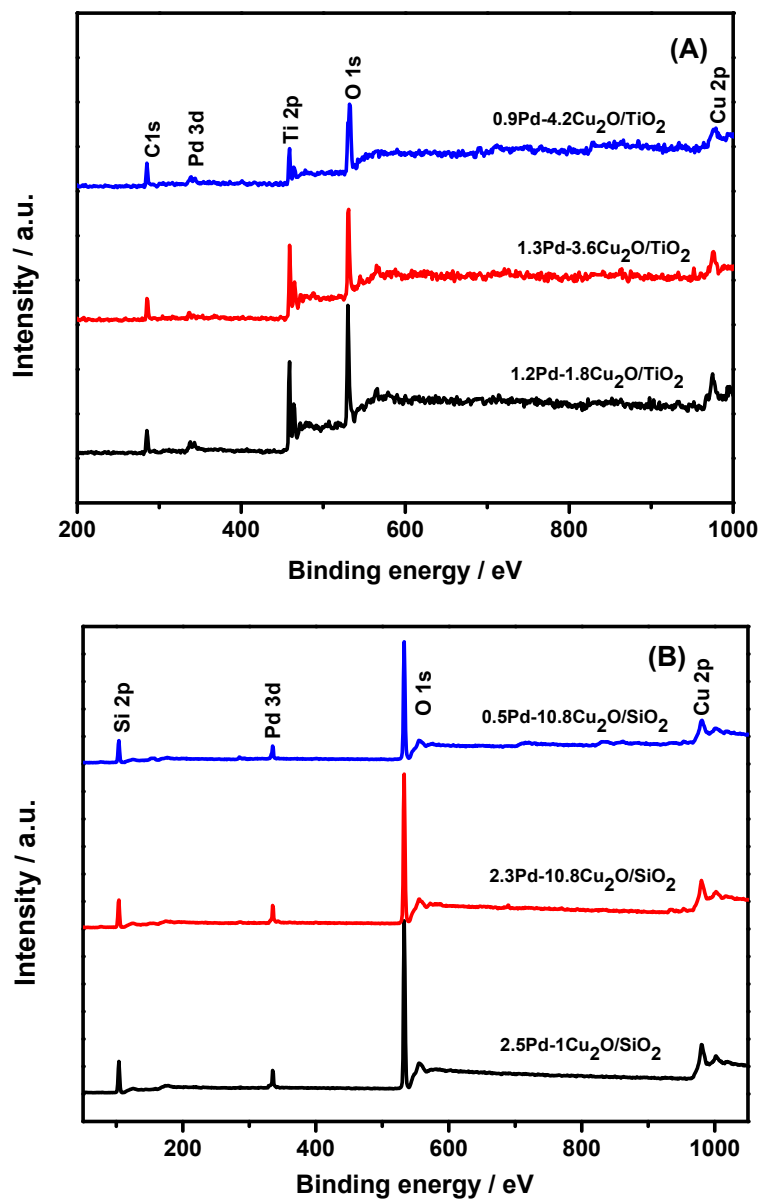


Figure S1. XPS survey spectra. (A) TiO₂ supported catalysts. (B) SiO₂ supported catalysts.

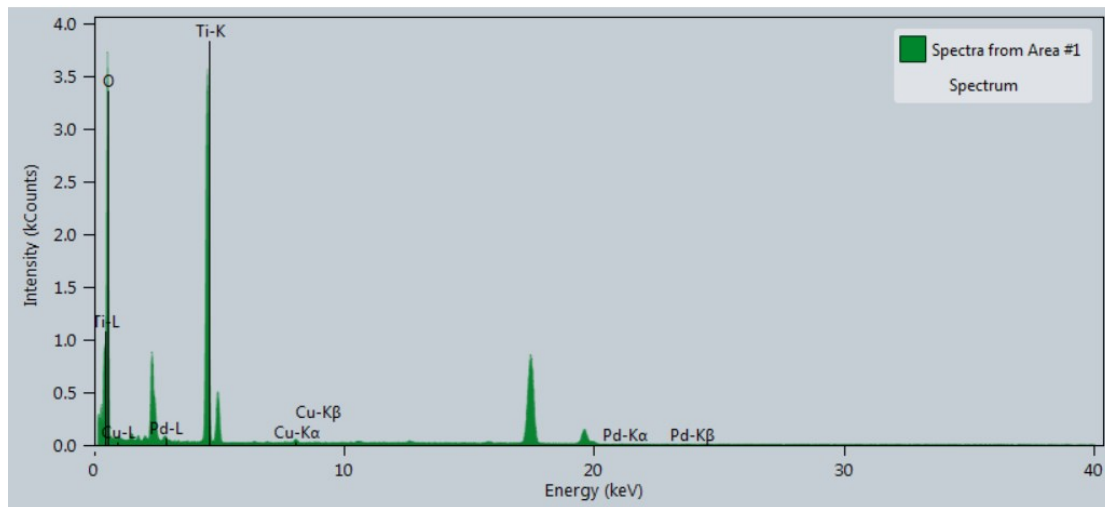


Figure S2. EDS spectrum extracted from the map data.

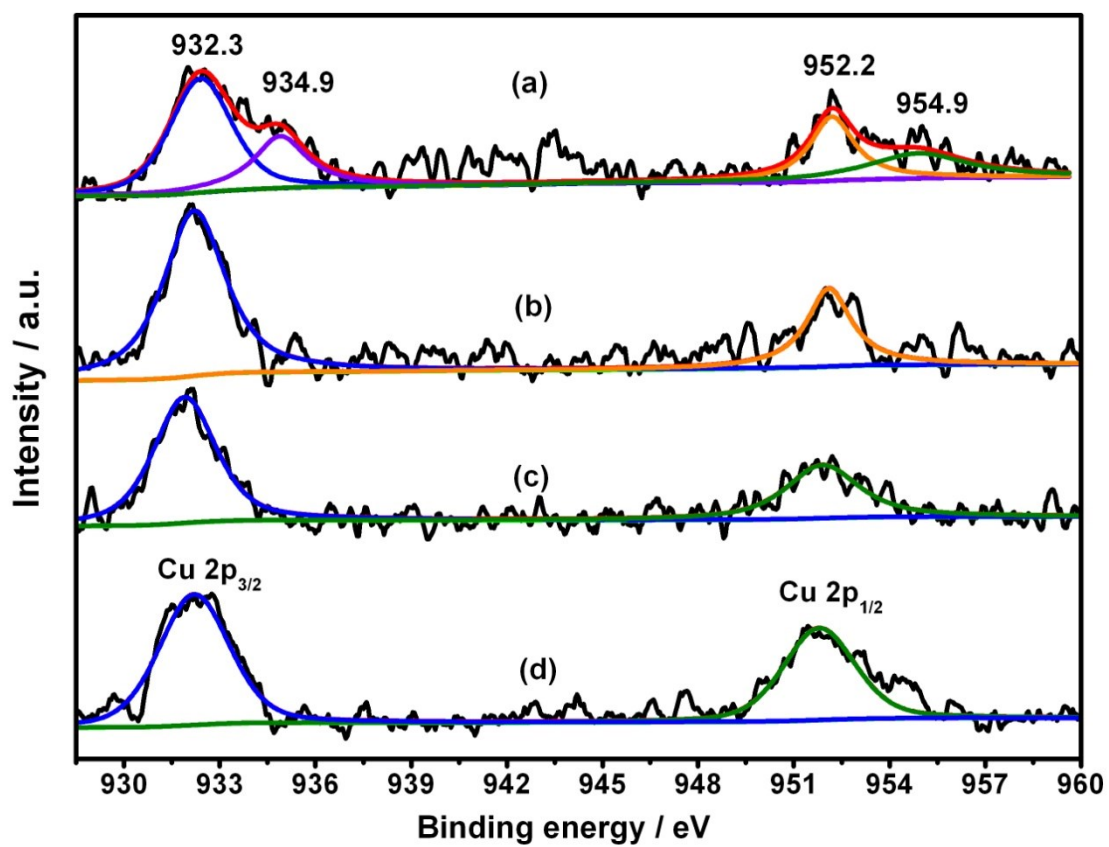


Figure S3. High resolution XPS spectrum of Cu 2p respectively in $3.6\text{Cu}_2\text{O}/\text{TiO}_2$ (a), $1.3\text{Pd}-3.6 \text{Cu}_2\text{O}/\text{TiO}_2$ (b), $0.9\text{Pd}-4.2\text{Cu}_2\text{O}/\text{TiO}_2$ (c), and $1.2\text{Pd}-1.8\text{Cu}_2\text{O}/\text{TiO}_2$ (d).

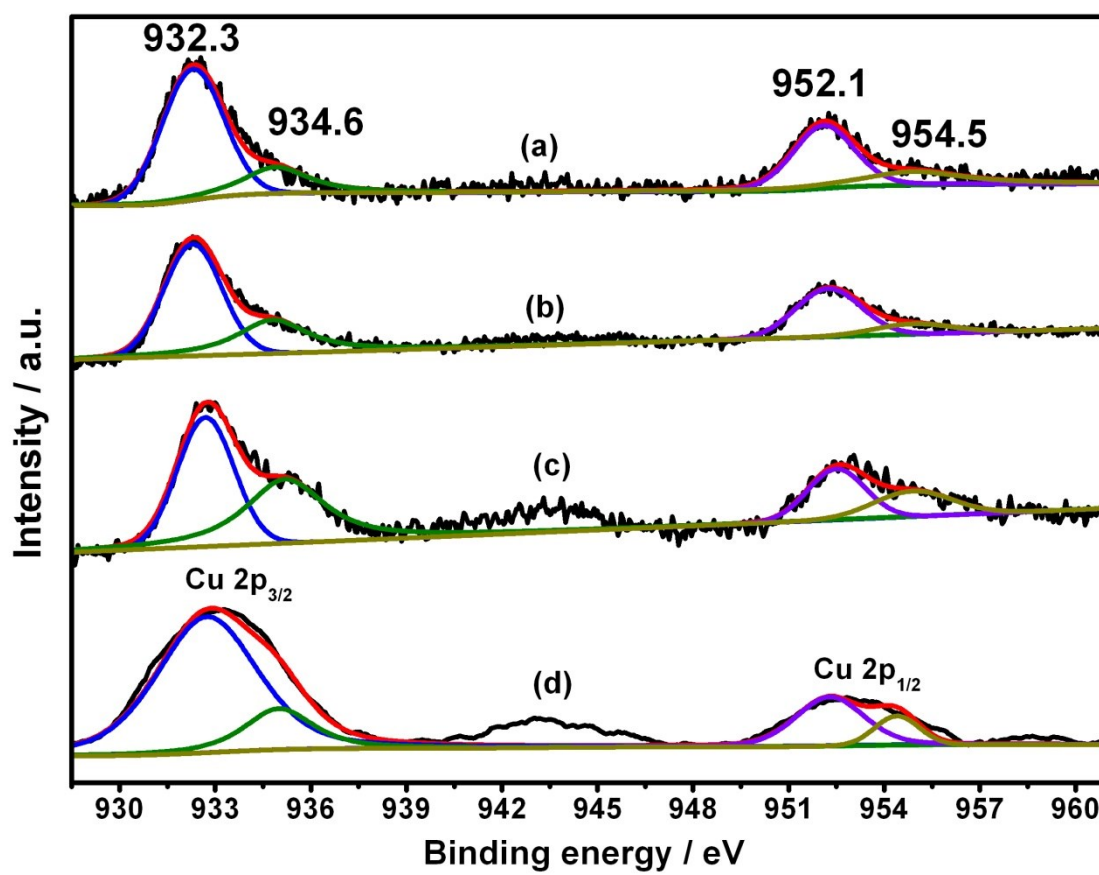


Figure S4. High resolution XPS spectrum of Cu 2p respectively in 10.8Cu₂O/SiO₂ (a), 2.3Pd-10.8Cu₂O/SiO₂ (b), 0.5Pd-10.8Cu₂O/SiO₂ (c), and 2.2Pd-1Cu₂O/SiO₂ (d).

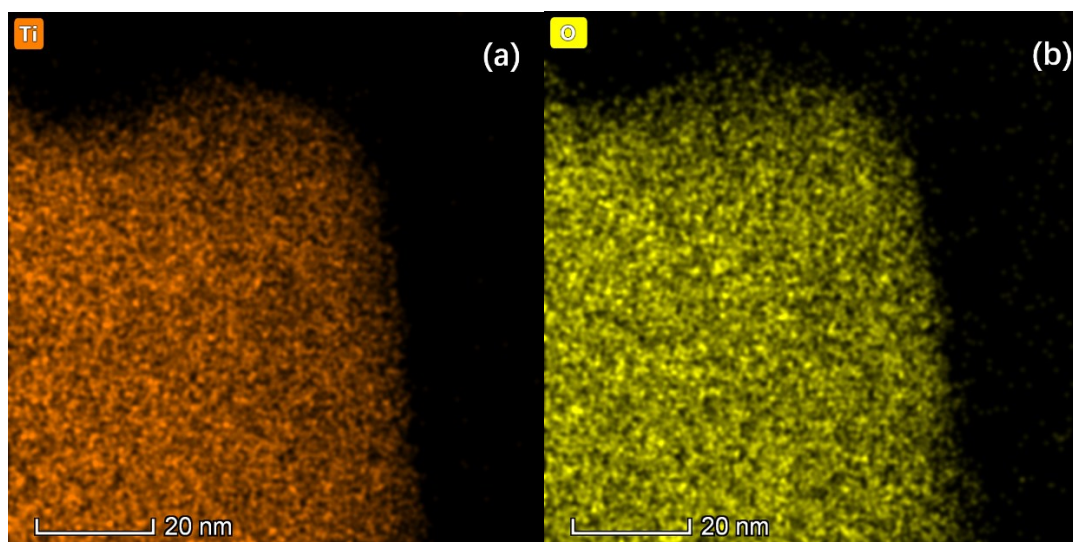


Figure S5. Element mapping images of Ti (a) and O (b) of 1.3Pd-3.6Cu₂O/TiO₂.

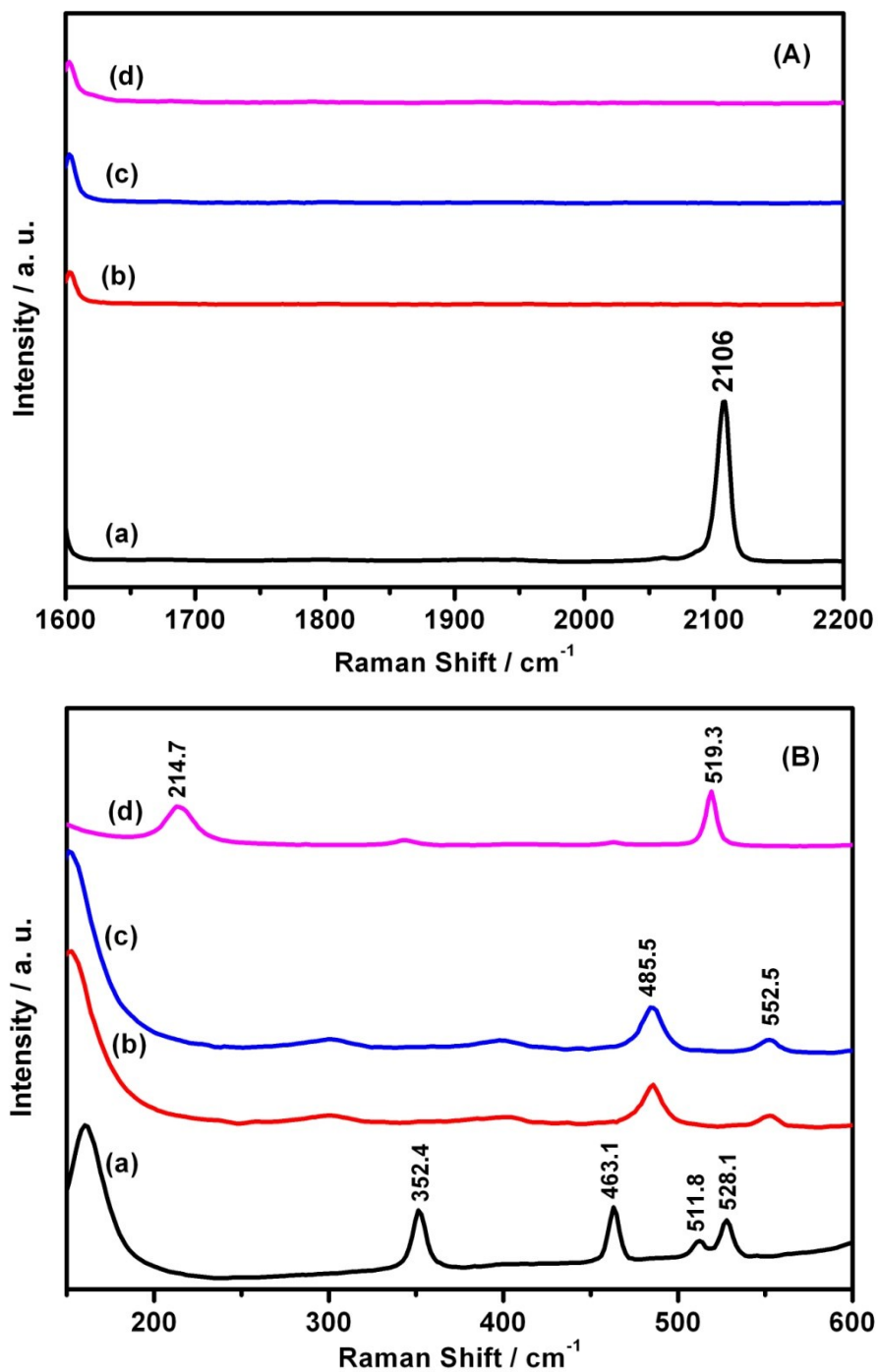


Figure S6. Raman spectra over the spectral range of 1600~2200 cm^{-1} (A) and 150~600 cm^{-1} (B) for phenylacetylene (a), styrene (b), ethylbenzene (c), and toluene (d).

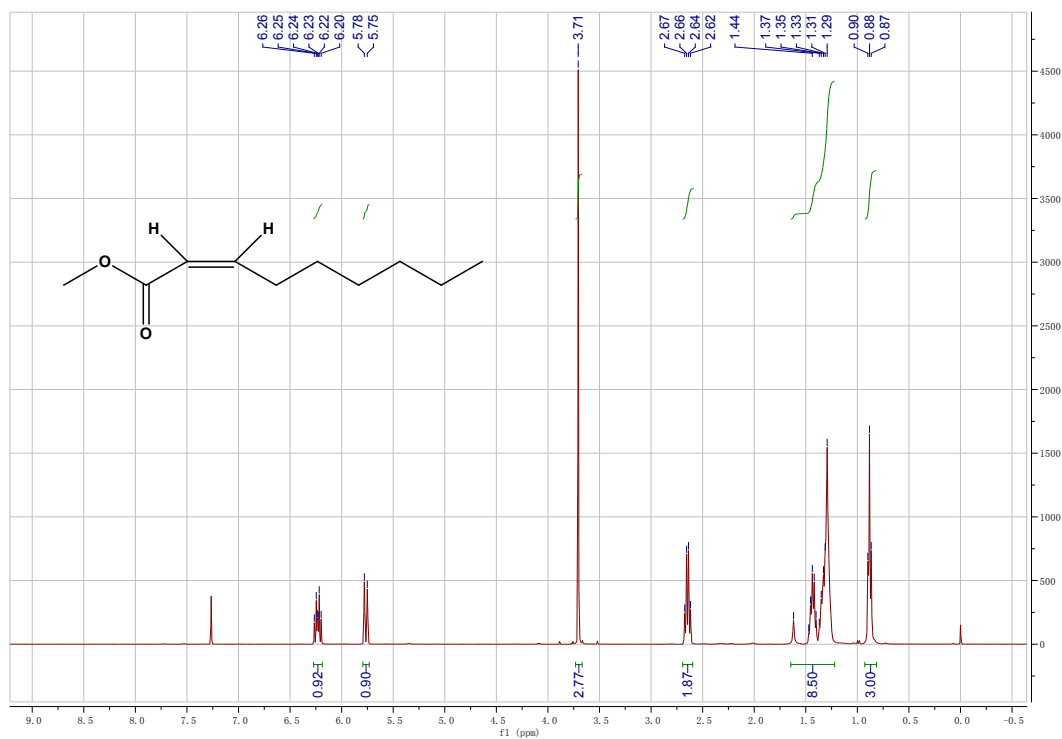


Figure S7. ¹H NMR spectra for (Z)-methyl non-2-enoate obtained from the semihydrogenation of methyl non-2-ynoate. ¹H NMR (400 MHz, CDCl₃): 0.88 (t, 3H, J=4Hz), 1.29-1.44 (m, 8H), 2.62-2.67 (m, 2H), 3.71 (s, 3H), 5.76 (d, 1H, J= 12 Hz), 6.20-6.26 (dt, 1H, J=12, 4 Hz) ppm.

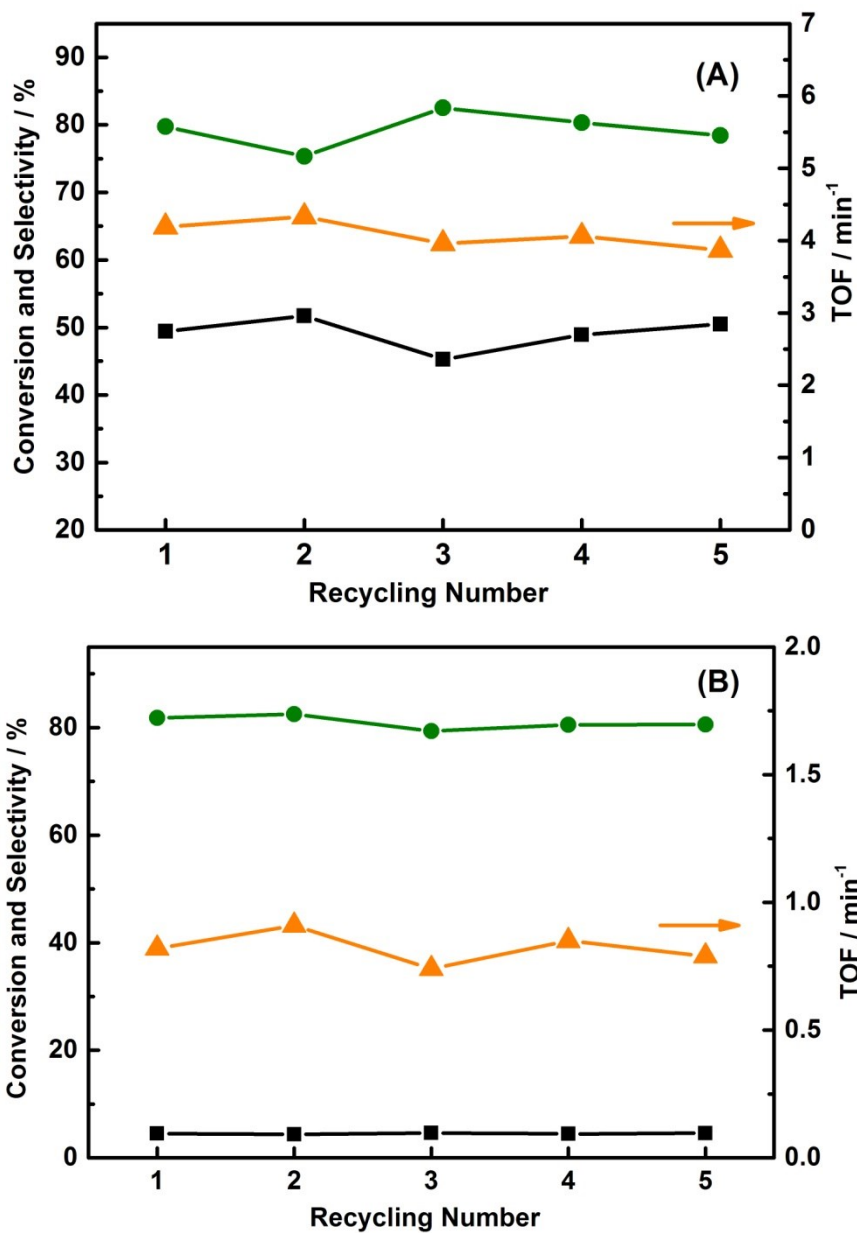


Figure S8. Recyclability of 1.3Pd-3.6Cu₂O/TiO₂ (A) and 2.3Pd-10.8Cu₂O/SiO₂ (B) in the semihydrogenation measured from phenylacetylene conversion (■), styrene selectivity (●), and TOF (▲). Reaction conditions: 9.1×10⁻⁴ mol phenylacetylene, 20.1 mg catalyst, 3 mL toluene, 1 atm H₂, 30°C and 45 min.

Table S1. Metal content and molar ratio of Pd to Cu atoms in Pd-Cu₂O/TiO₂ catalysts detected by ICP-MAS.

catalyst ^a	Pd (wt%)	Cu (wt%)	n _{Pd} /n _{Cu}
0.9Pd-4.2 Cu ₂ O/TiO ₂	0.91	1.85	1.17
0.7Pd-2.5 Cu ₂ O/TiO ₂	0.73	1.11	1.56
1.2Pd-3.6 Cu ₂ O/TiO ₂	1.18	1.61	1.74
0.7Pd-2 Cu ₂ O/TiO ₂	0.68	0.90	1.79
1.3Pd-3.6 Cu ₂ O/TiO ₂	1.27	1.59	1.90
1.2Pd-2.5 Cu ₂ O/TiO ₂	1.19	1.10	2.59
1Pd-2 Cu ₂ O/TiO ₂	1.03	0.90	2.74
1.1Pd-2.5 Cu ₂ O/TiO ₂	1.05	1.10	3.12
1.2Pd-1.8 Cu ₂ O/TiO ₂	1.19	0.81	4.38

a. 0.005g catalysts each used for ICP-MASS.

Table S2. Metal content and molar ratio of Pd to Cu atoms in Pd-Cu₂O/SiO₂ catalysts detected by ICP-MAS.

Catalyst ^b	Pd (wt%)	Cu (wt%)	n _{Pd} /n _{Cu}
0.5Pd-10.8Cu ₂ O/SiO ₂	0.51	4.79	0.06
1.1Pd-6.3Cu ₂ O/SiO ₂	1.11	2.79	0.23
1.7Pd-9.7Cu ₂ O/SiO ₂	1.70	4.29	0.23
1.1Pd-1.4Cu ₂ O/SiO ₂	1.08	0.62	0.27
2.3Pd-10.8Cu ₂ O/SiO ₂	2.25	4.79	0.47
2.9Pd-5.9Cu ₂ O/SiO ₂	2.86	2.62	0.65
1.9Pd-1.5Cu ₂ O/SiO ₂	1.91	0.66	1.05
2Pd-5.5Cu ₂ O/SiO ₂	1.96	2.45	1.74
2.2Pd-1Cu ₂ O/SiO ₂	2.15	0.46	2.83

b. 0.07g catalysts each used for ICP-MASS.

Table S3. Catalysis of 1.3Pd/TiO₂ and 1.3Pd/Cu₂O in the semihydrogenation of phenylacetylene

Catalyst	Conversion ^a (%)	Selectivity ^b (%)
1.3Pd/TiO ₂	85.4%	23.6%
1.3Pd/Cu ₂ O	100%	55.8%

Reaction conditions: catalyst (0.0201g), phenylacetylene (9.1×10^{-4} mol), Toluene (3 mL), reaction temperature: 30°C. ^{a,b} Determined by GC-MS using internal standard technique. H₂ (1atm). Reaction time: 90min.

Table S4. Catalysis of Pd-Cu/TiO₂ Catalysts in the semihydrogenation of phenylacetylene

Entry	catalyst	n(Pd)/n(Cu) ^a	Conversion ^b (%)	Selectivity ^c (%)	TOF ^d (min ⁻¹)
1	3.6Cu ₂ O/TiO ₂	-	0	0	0
2	0.9Pd-4.2Cu ₂ O/TiO ₂	1.17	19.35	78.46	6.79
3	0.7Pd-2.5Cu ₂ O/TiO ₂	1.56	20.82	94.26	1.78
4	1.2Pd-3.6Cu ₂ O/TiO ₂	1.74	68.46	89.59	4.82
5	0.7Pd-2Cu ₂ O/TiO ₂	1.79	68.58	94.54	3.79
6	1.3Pd-3.6Cu ₂ O/TiO ₂	1.90	100	97.59	5.89
7	1.2Pd-2.5Cu ₂ O/TiO ₂	2.59	74.73	94.26	3.15
8	1Pd-2Cu ₂ O/TiO ₂	2.74	68.67	89.82	2.69
9	1.1Pd-2.5Cu ₂ O/TiO ₂	3.12	67.58	94.54	3.47
10	1.2Pd-1.8Cu ₂ O/TiO ₂	4.38	48.86	82.83	2.95

Reaction conditions: catalyst (0.0201g), phenylacetylene (9.1*10⁻⁴mol), Toluene (3 mL), ^a Determined by ICP-MAS. ^{b,c,d} Determined by GC-MAS using internal standard technique. H₂ (1atm). Reaction time: 90min.

Table S5. Catalysis of Pd-Cu/SiO₂ Catalysts in the semihydrogenation of phenylacetylene.

Entry	catalyst	n(Pd)/n(Cu) ^a	Conversion ^b (%)	Selectivity ^c (%)	TOF ^d (min ⁻¹)
1	10.8Cu ₂ O/SiO ₂	-	0	0	0
2	0.5Pd-10.8Cu ₂ O/SiO ₂	0.06	5.34	88.29	1.00
3	1.7Pd-9.7Cu ₂ O/SiO ₂	0.23	7.90	91.19	2.02
4	1.1Pd-6.3Cu ₂ O/SiO ₂	0.23	11.99	94.13	4.34
5	2.3Pd-10.8Cu ₂ O/SiO ₂	0.27	23.30	94.51	4.68
6	2Pd-5.5Cu ₂ O/SiO ₂	0.47	6.26	90.21	0.92
7	2.9Pd-5.9Cu ₂ O/SiO ₂	0.65	4.35	90.55	0.83
8	1.1Pd-1.4Cu ₂ O/SiO ₂	1.05	4.13	86.37	0.66
9	1.9Pd-1.5Cu ₂ O/SiO ₂	1.74	3.96	85.28	0.68
10	2.2Pd-1Cu ₂ O/SiO ₂	2.83	3.10	84.99	0.60

Reaction conditions: catalyst (0.0201g), phenylacetylene (9.1×10^{-4} mol), Toluene (3 mL), ^a Determined by ICP-MASS. ^{b,c,d} Determined by GC-MASS using internal standard technique. H₂ (1atm). Reaction time: 90 min.

Table S6. Semihydrogenation of methyl non-2-ynoate in the presence of Pd-Cu₂O/TiO₂ or Pd-Cu₂O/SiO₂ Catalyst.

Entry	catalyst	n _{Pd} / n _{Cu} ^a	Conversion ^b (%)	Selectivity ^b (%)	TOF ^b (min ⁻¹)	(Z)/(E)
1	0.9Pd-4.2Cu ₂ O/TiO ₂	1.16	100	92.4	5.98	92:8
2	1.3Pd-3.6Cu ₂ O/TiO ₂	1.90	100	92.4	6.29	95:5
3	1.2Pd-1.8Cu ₂ O/TiO ₂	4.37	100	94.6	5.65	91:9
4	0.5Pd-10.8Cu ₂ O/SiO ₂	0.06	12.3	89.2	2.87	90:10
5	2.3Pd-10.8Cu ₂ O/SiO ₂	0.23	24.6	91.3	3.51	94:6
6	2.2Pd-1Cu ₂ O/SiO ₂	2.29	18.4	90.7	1.10	89:11

Reaction conditions: catalyst: 0.0201g; methyl non-2-ynoate: 5.44×10^{-4} mol, R₁=C₆H₁₃ and R₂=CO₂Me; THF: 3mL; H₂: 1atm; reaction time: 45 min; reaction temperature: 30°C. ^a Determined by ICP-MAS. ^b Determined by GC using internal standard method.