ELECTRONIC SUPPORTING INFORMATION (ESI)

High catalytic activity of bimetallic AgPd alloy supported on UiO-66 derived porous carbon for transfer hydrogenation of nitroarenes using formic acid-formate as hydrogen source

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Table S1 Reduction of nitrobenzene to aniline with different hydrogen source over Ag_1Pd_9@NPC-UiO-66-800 catalyst.[a]

Entry	FA (mmol)	Ammonium formate (mmol)	Time (min)	Conversion (%)	Selectivity (%)
1	4	0	12 h	15	86
2	0	4	2 h	99	>99
3	4	4	20	99	>99
4	4	8	15	99	>99
5[b]	4	4	60	98	>99
6[c]	4	4	3 h	87	93

[a] Reaction conditions: nitrobenzene (1 mmol), Ag_1Pd_9@NPC-UiO-66-800 (1 mol%), methanol (5 mL), 25 ^oC. GC analysis using *n*-decane as an internal standard. [b] HCOONa. [c] HCOOK.

Table S2 Various reported catalyst tested for reduction of nitroarenes into anilines.

Entry	Catalyst	Hydrogen source	Temp (^oC)	Time (h)	TOF[h^{-1}][a]	Ref
1	C-Pd-Fe_3O_4	$NaBH_4$	25	0.5	545	[1]
2	Au/TiO_2-EC	10 atm H_2	90-120	2-7	53-279	[2]
3	ZIF-67-derived nanocomposites	NH_3BH_3	25	1.5-4	1.00-2.61	[3]
4	Pd−Pt−Fe_3O_4	NH_3BH_3	25	5	188-1176	[4]
5	Fe-MIL-88A-C	$N_2H_4{\cdot}H_2O$	85	0.75-12	2-53	[5]
6	Ni-MoO_3/CN@SBA-15	$N_2H_4{\cdot}H_2O$	40	0.5-1	357-715	[6]
7	Au/rutile	HCOOH	60	0.67-4	25-149	[7]
8	$[Mo_3S_4H_3(dmpe)_3]BPh_4$[b]	HCOOH-Et_3N	70	18	0.54-1.85	[8]
9	Fe_2O_3/NGr@C	HCOOH-Et_3N	120	20-24	0.74-0.95	[9]

10	γ-Fe_2O_3@HAP-Pd[c]	$HCOONH_4$	60	3	35-30	[10]
11	Ag_1Pd_9@NPC-UiO-66-800	HCOOH-$HCOONH_4$	25	0.33-6	15-300	This work

[a] mol of substrate transformed per mol of catalyst per hour. [b] dmpe = 1,2 (bis)dimethylphosphinoethane. [c] HAP = hydroxyapatite.

Table S3 Reusability of Ag_1Pd_9@NPC-UiO-66-800 catalyst for reduction of nitrobenzene to aniline.[a]

Entry	Time (min)	Conversion (%)	Selectivity (%)
1	20	>99	>99
2	20	>99	>99
3	20	>99	>99
4	25	98	>99
5	30	98	>99

[a] nitrobenzene (1 mmol), FA (4 mmol), $HCOONH_4$ (4 mmol), Ag_1Pd_9@NPC-UiO-66-800 (1 mol% metal), methanol (5 mL); GC analysis using *n*-decane as an internal standard.

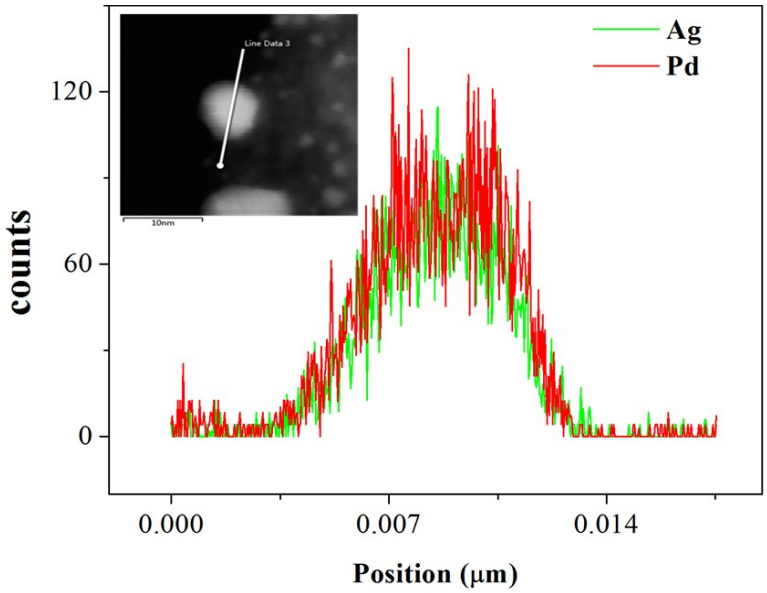

Fig S1. STEM-EDS line-scan of Ag_1Pd_9@NPC-UiO-66-800.

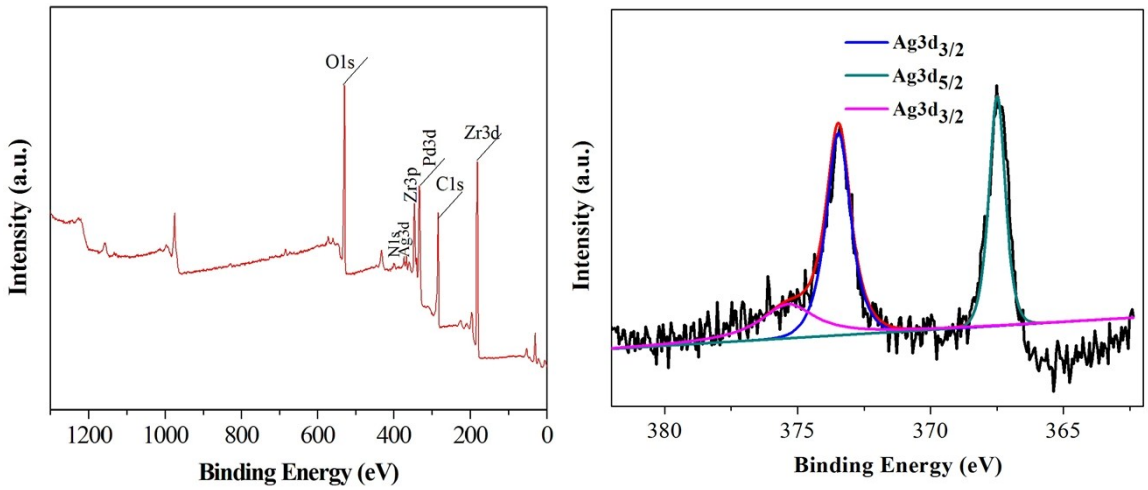

Fig S2. The XPS images of Ag_1Pd_9@NPC-UiO-66-800.

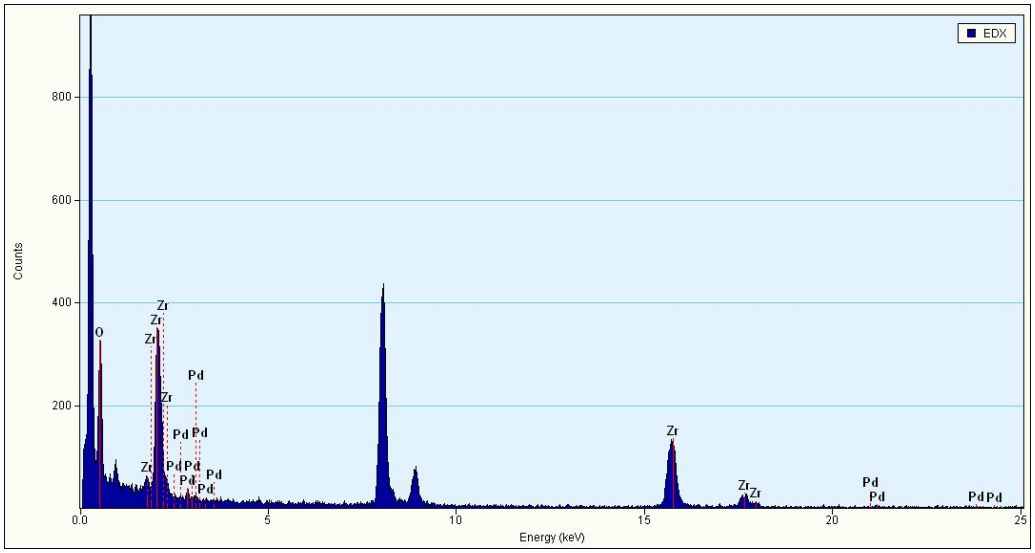

Fig S3. The Energy-dispersive X-ray spectroscopy (EDX) of Ag_1Pd_9@NPC-UiO-66-800.

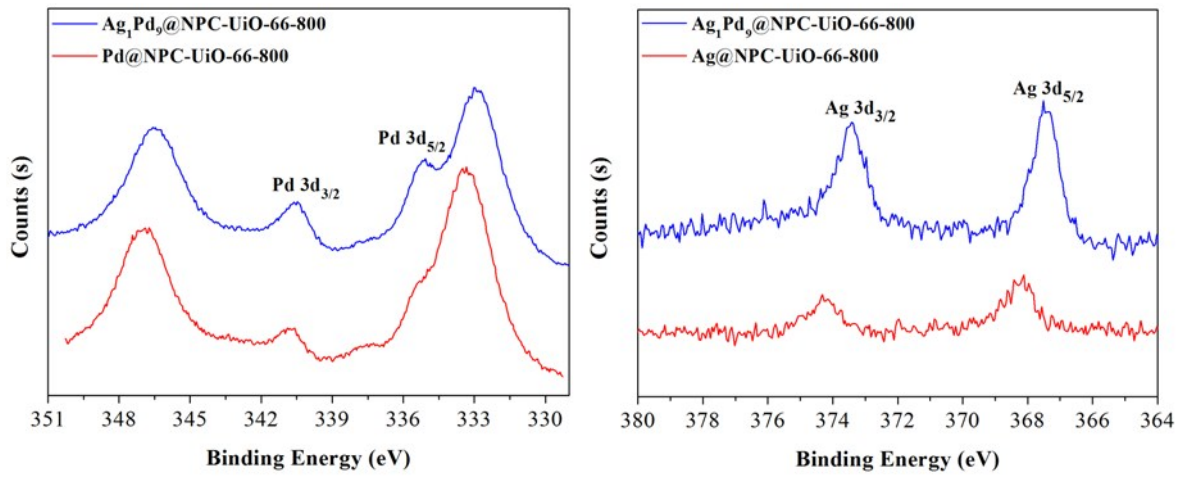

Fig S4. XPS images of Pd 3d and Ag 3d for Pd@NPC-UiO-66-800, Ag_1Pd_9@NPC-UiO-66-800, and Ag@NPC-UiO-66-800.

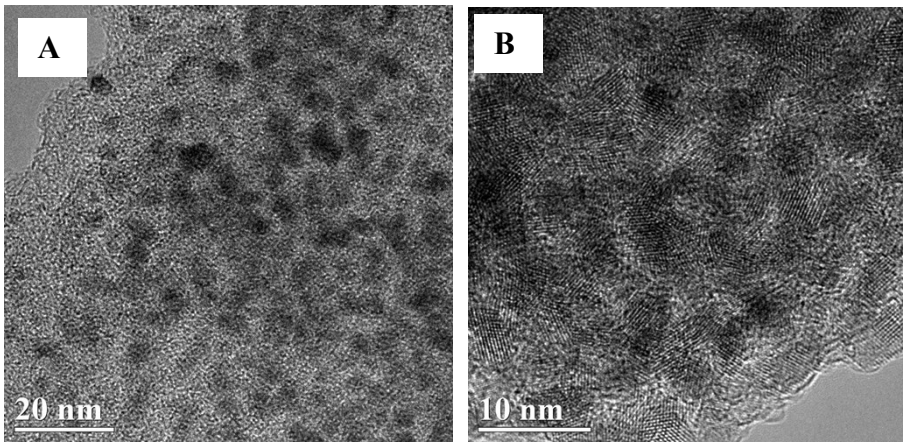

Fig S5. TEM pattern of the reused Ag_1Pd_9@NPC-UiO-66-800.

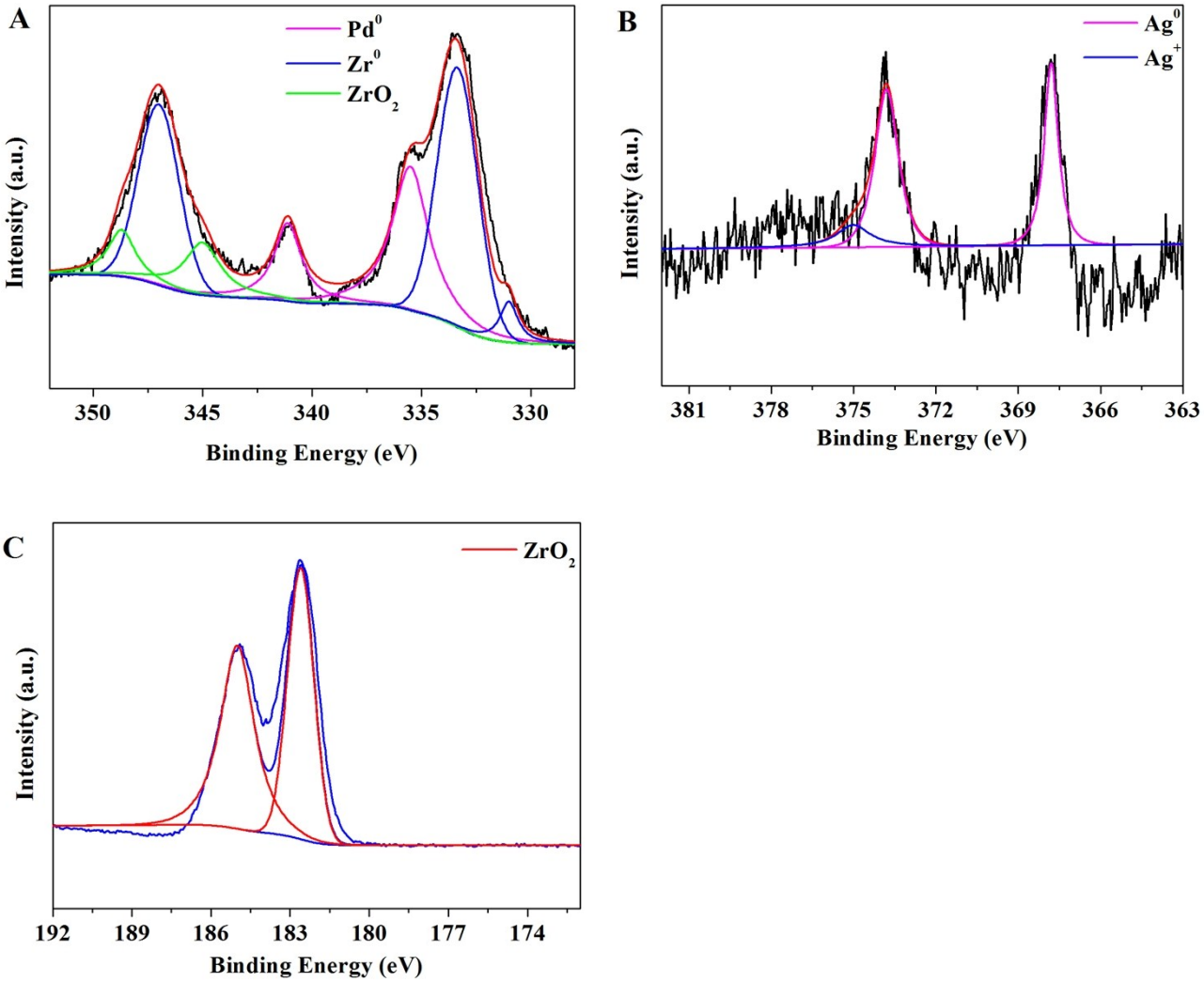

Fig S6. XPS pattern of the reused Ag_1Pd_9@NPC-UiO-66-800.

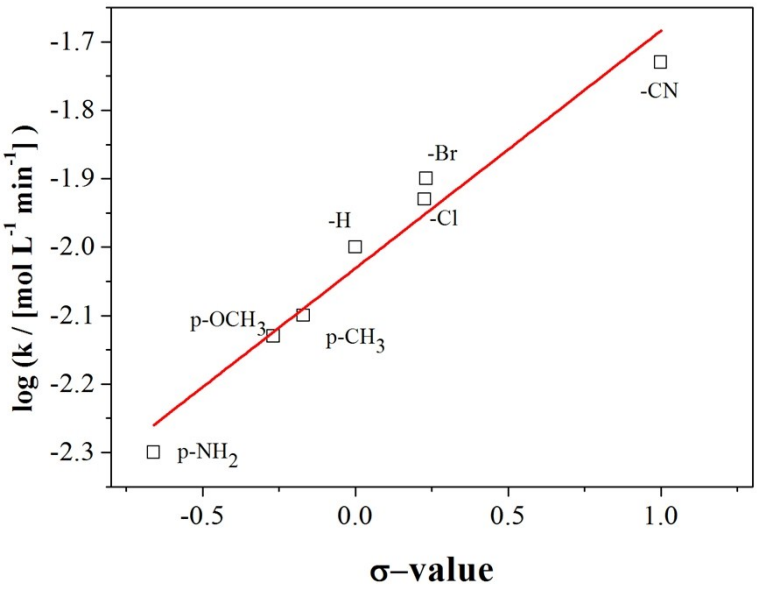

Fig S7. Hammett plot for the catalytic reduction of substituted nitrobenzenes at 25 ^{o}C.

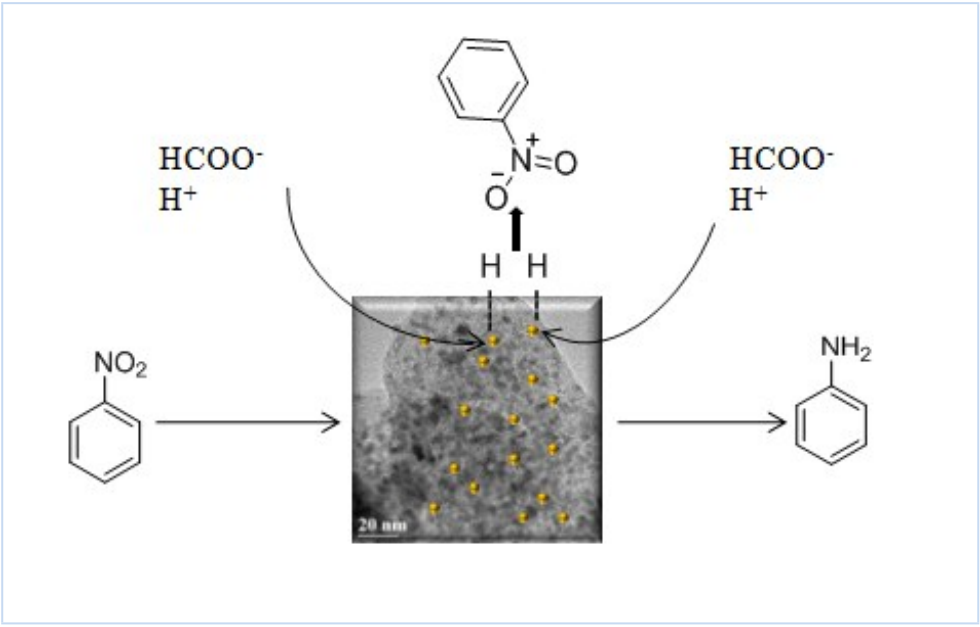

Fig S8. Tentative reaction mechanism for the reduction of nitroarenes over Ag_1Pd_9@NPC-UiO-66-800 catalyst.

Reference

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