Electronic supplementary information (ESI†)

Catalysis with magnetically retrievable and recyclable nanoparticles layered with Pd(0) of C-C/C-O coupling in water

Alpesh K. Sharma[a], Hemant Joshi[a,b] and Ajai K. Singh[a]*

[a]*Department of Chemistry, Indian Institute of Technology Delhi, New Delhi 110016, India.*

[b]*Present address: Department of Chemistry, School of Chemical Sciences and Pharmacy, Central University of Rajasthan, NH-8, Bandarsindri, Ajmer, Rajasthan 305817, India*

Table of contents

S1. Size distribution graph of Fe_3O_4@SiO_2@SePh@Pd(0) NPs

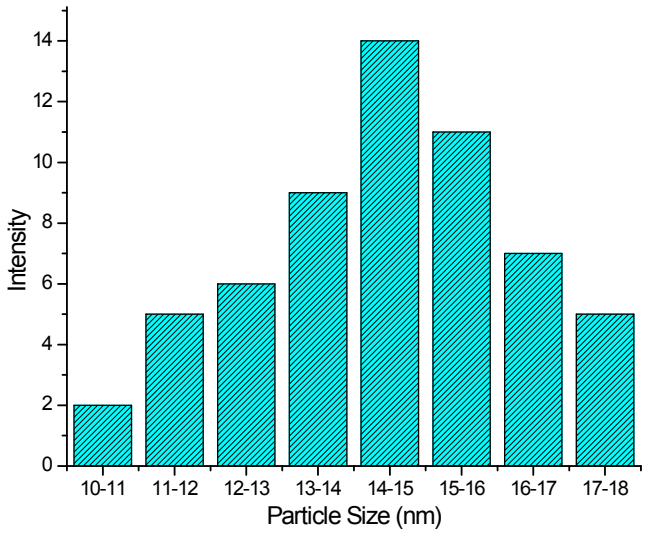

Figure S1 Size distribution graph of Fe_3O_4@SiO_2@SePh@Pd(0) NPs.

S2. SEM–EDX Data

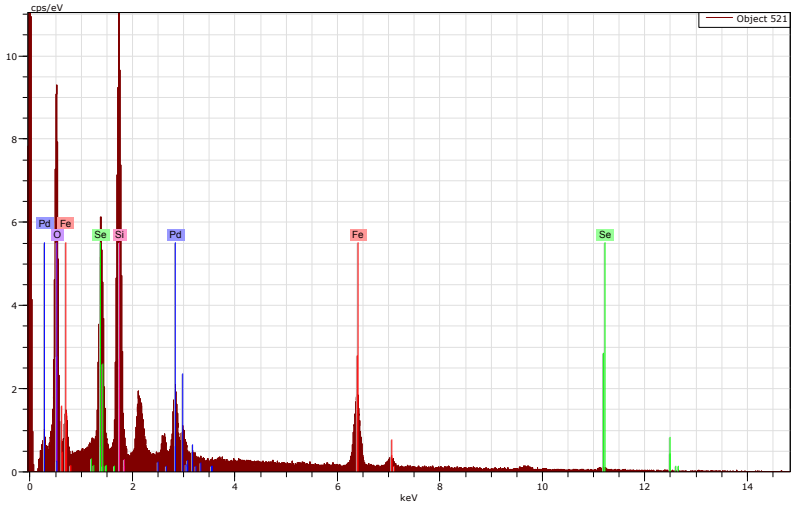

Figure S2 SEM-EDX of Fe_3O_4@SiO_2@SePh@Pd(0) NPs.

S3. SEM-EDX of recycled Fe_3O_4@SiO_2@SePh@Pd(0) NPs

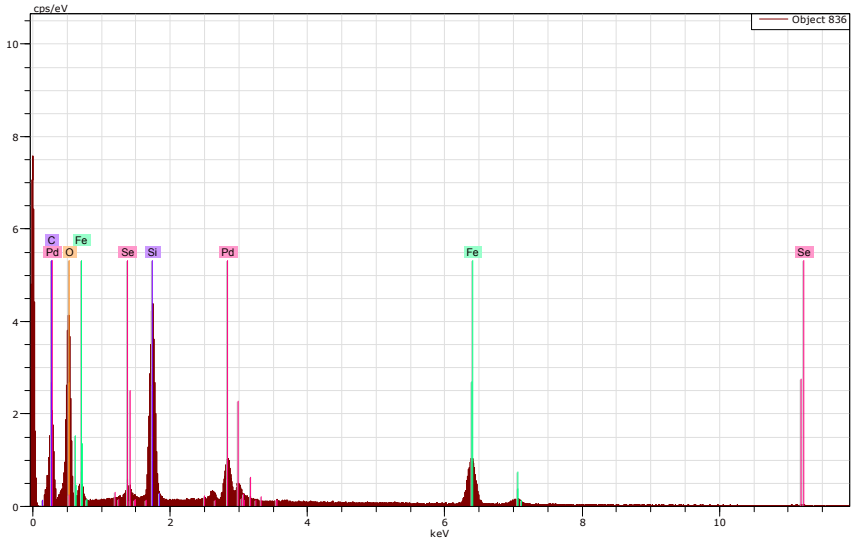

Figure S3 SEM-EDX of recycled Fe_3O_4@SiO_2@SePh@Pd(0) NPs.

S4. Size distribution graph of recycled Fe_3O_4@SiO_2@SePh@Pd(0) NPs

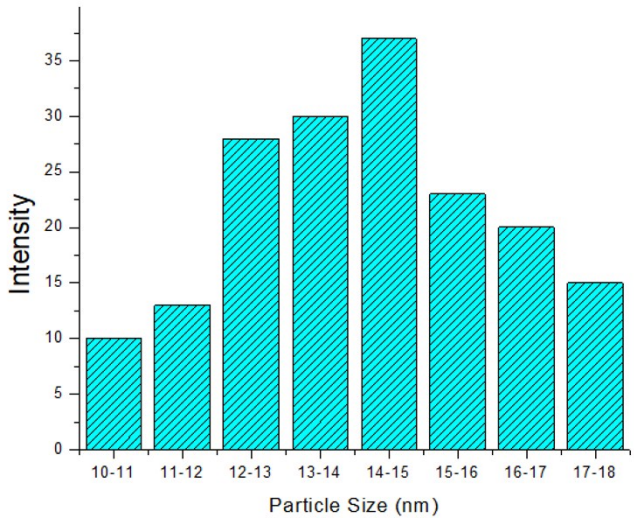

Figure S4 Size distribution graph of recycled Fe_3O_4@SiO_2@SePh@Pd(0) NPs

S5. Comparison table with heterogeneous catalyst

Table S1: Comparison table with heterogeneous catalysts reported in literature for C-O coupling reaction

S. No	Catalyst	Catalyst Loading	Time	Solvent	Substrate
1	Fe_3O_4@SiO_2@SePh@Pd(0) NPs (Present Catalyst	0.01-01 mol%	6 h	H_2O	ArCl/Br/I
2	Pd-$ZnFe_2O_4$	10 mg,	4-5 h	DMSO	ArCl/Br/I
3	Fe_3O_4@SiO_2@PPh_2@Pd(0)	1.5 mol%,	1.5-7 h	H_2O	ArCl/Br/I
4	Maghemite-copper nanocomposites	4.7 mol%,	24 h	DMF	ArI
5	$NiFe_2O_4$	10 mol%,	10 h	1,4 Dioxane	ArI
6	CNT@α-Fe_2O_3@CuO	1.85 mol%,	1-10 h	DMF	ArBr/I
7	$CuFe_2O_3$	10 mol%,	10-24 h	DMF	ArBr/I

Table S2: Comparison table with heterogeneous catalyst reported in literature for SMC

S.No	Catalyst	Catalyst Loading	Time (h)	Solvent	Substrate
1	**Present Catalyst Fe_3O_4@SiO_2@SePh@Pd(0) NPs**	**0.01-0.1 mol%**	**6 h**	**H_2O**	**ArBr/Cl/I**
2	Pd–Fe_3O_4 heterodimer nanocrystals	1 mol%,	24h	DME:H_2O	ArBr/I
3	Pd@Mag-MSN	1 mol%	6h	1,4 Dioxane	ArBr/I
4	Pd–$CoFe_2O_4$ MNPs	1.6 mol%	6-12 h	Ethanol	ArBr/I
5	iron oxide supported palladium NHC complex	7.3 mol%	12h	DMF	ArBr/I
6	$NiFe_2O_4$-(dopamine)-Pd	8.54 mol%	20-36h	DMF	ArBr/Cl/I
7	silica supported palladium catalyst	2-6 mol%	2h	*O*-xylene	ArBr
8	Pd/C-cetyltrimethylammonium bromide (CTAB)	2.5 mol%	24h	H_2O	ArBr/Cl/I
9	layered double hydroxide (LDH) supported nanopalladium	1 mol%	10h	1,4 Dioxane:H_2O	ArCl
10	Pd-polyoxomatalate nanoparticles	1 mol%	12-16h	EtOH:H_2O	ArBr/Cl

11[1]	mercaptopropyl-modified mesoporous silica supported palladium catalyst	1 mol%	24h	DMF:H_2O	ArBr/Cl

S6. NMR spectral data of compounds

NMR Data of products of C-O coupling reaction-

4-phenoxybenzaldehyde:[1] Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C vs Me_4Si): δ (ppm): 9.92 (s, 1H), 7.84-7.86 (d, 2H), 7.40-7.45 (t, 2H), 7.20-7.26 (m, 1H), 7.05-7.11 (t, 4H).

4-phenoxybenzonitrile:[1] White Solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C vs Me_4Si):7.49-7.55 (m, 2H), 7.30-7.35 (t, 2H), 7.11-7.17 (t, 1H), 6.96-6.98 (d, 2H), 6.90-6.93(d, 2H).

1-Nitro-4-phenoxybenzene:[2] Yellow Solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C vs Me_4Si): 8.11-8.14 (d, 2H), 7.34-7.40 (t, 2H), 7.16-7.21 (t, 1H), 7.01-7.03 (d, 2H), 6.92-6.95 (d, 2H).

1-(4-phenoxyphenyl)ethanone:[1] White Solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C vs Me_4Si): 7.91-7.96 (d, 2H), 7.36-7.42 (t, 2H), 7.19-7.22 (t, 1H), 7.06-7.08 (d, 2H), 6.97-7.02 (d, 2H), 2.57 (s, 3H).

2-phenoxybenzaldehyde:[1] Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C vs Me_4Si): 10.45 (s, 1H), 7.85-7.88 (d, 1H), 7.41-7.47 (t, 1H), 7.30-7.35 (t, 2H), 7.10-7.14 (t, 2H), 6.98-7.01 (d, 2H), 6.81-6.84 (d, 1H).

1-(2-phenoxyphenyl)ethanone:[2] Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C vs Me_4Si): 7.83-7.86 (d, 1H), 7.35-7.45 (m, 3H), 7.15-7.20 (m, 2H), 7.01-7.03 (d, 2H) 6.90-6.92 (d, 2H) 2.64 (s, 3H).

Diphenyl ether:[2] Colorless liquid. ^{1}H NMR(300 MHz, $CDCl_3$, 25°C vs Me_4Si): 7.24-7.28 (t, 4H), 7.02-7.05 (t, 2H), 6.93- 6.95 (d, 4H).

1-Methyl-4-phenoxybenzene:[2] Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C vs Me_4Si): 7.46-7.48 (m, 2H), 7.23-7.26 (t, 2H), 7.06- 7.07 (m, 1H), 6.98-7.04 (m, 2H), 6.89-6.91 (m, 2H), 2.26 (s, 3H).

1-Methoxy-4-phenoxybenzene:[3] Colorless liquid. 1H NMR (300 MHz, $CDCl_3$, 25°C vs Me_4Si): 7.25-7.32 (m, 2H), 7.01-7.06 (t, 1H), 6.93- 7.01 (m, 4H), 6.86-6.90 (m, 2H), 3.81 (s, 3H).

NMR Data of products of Suzuki-Miyaura coupling reaction-

4−Phenylbenzaldehyde:[4] Light yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C vs Me_4Si): δ 10.06 (s, 1H),7.95 (d, J = 8.4 Hz, 2H),7.75 (d, J = 8.4 Hz, 2H),7.63−7.65 (m, 2H),7.39−7.51 (m, 3H). 1

4-Phenylbenzonitrile:[5] Pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C vs Me_4Si): δ 7.54−7.61 (m, 4H), 7.49−7.52 (m, 2H), 7.34−7.45 (m, 3H).

4-Nitrobiphenyl:[6] Pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C vs Me_4Si): δ 8.27 (d, J = 9.0 Hz, 2H), 7.71 (d, J = 9.0 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.41−7.51 (m, 3H).

4−Acetylbiphenyl:[6] White solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C vs Me_4Si): 8.02 (d, J = 8.4 Hz, 2H), 7.60−7.68 (m, 4H), 7.38−7.48 (m, 3H), δ 2.62 (s, 3H).

Biphenyl:[6] White solid: ^{1}H NMR (300 MHz, $CDCl_3$, 25°C vs Me_4Si): 7.58 (d, J = 6.9 Hz, 4H),7.42 (t, J = 7.5 Hz, 4H),δ 7.33 (t, J = 7.5 Hz, 2H).

4-Methylbiphenyl:[6] Colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C vs Me_4Si): 7.55−7.58 (m, 2H),7.48 (d, J = 8.1 Hz, 2H),7.38−7.42 (m, 2H),7.27−7.32 (m, 1H),7.23 (d, J = 7.8 Hz, 2H),δ 2.37 (s, 3H).

4-Methoxybiphenyl:[6,7] White solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C vs Me_4Si): 7.50−7.55 (m, 4H), 7.40 (t, J = 7.2 Hz, 2H),7.28−7.31 (m, 1H),6.96 (d, J = 8.4 Hz, 2H),δ 3.82 (s, 3H).

4−Phenylpyridine:[8] Brown solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C vs Me_4Si): 8.65 (d, J = 5.4 Hz, 2H),7.62 (d, J = 8.1 Hz, 2 H),δ 7.40−7.50 (m, 5H).

2−Phenylpyridine:[8] Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C vs Me_4Si) δ 8.70 (s, 1H), 8.00 (d, J = 7.0 Hz, 2H), 7.74 (s, 2H), 7.55–7.38 (m, 4H), 7.24 (d, J = 6.4 Hz, 1H);

S7. References

1 T. Hu, T. Schulz, C. Torborg, X. Chen, J. Wang, M. Beller, J. Huang, *Chem. Commun.*, 2009, 7330.

2 Q. Zhang, D. Wang, X. Wang, K. Ding*, J.Org.Chem*., 2009, **74**, 7187.

3 H. Joshi, K. N. Sharma, A. K. Sharma, O. Prakash and A. K. Singh, *Chem. Commun*., 2013, **49**, 7483.

4 R. K. Arvela, N. E. Leadbeater, *Org. Lett.* 2005, **7**, 2101.

5 B.Tao, D. W. Boykin, *J.Org. Chem.* 2004, **69**, 4330.

6 G. M. Scheuermann, L. Rumi, P.Steurer, W. Bannwarth, R.Mulhaupt, *J. Am. Chem. Soc.* 2009, **131**, 8262.

7 B.V. Martinez, A. G. de Viedma, C.Burgos, B. J. Alvarez, *Org. Lett.,* 2000, **2**, 3933.

8 S. Doherty, J. G. Knight, J P Mcgrady, A M Ferguson, N a B Ward, R W Harrington, W. Clegg, *Adv. Synth. Catal*. 2010, **352**, 201.