Supplementary Information for

Nano Pd-Fe₃O₄@Alg beads: as an efficient and magnetically separable catalyst for Suzuki, Heck and Buchwald Hartwig coupling reactions

Radheshyam S. Shelkar, Sitaram H. Gund, Jayashree M. Nagarkar*

Department of Chemistry, Institute of Chemical Technology, Matunga, Mumbai - 400019, India.

*Corresponding author. Tel.: +91 22 33611111/2222; fax: +91 22 33611020.

Email: jm.nagarkar@ictmumbai.edu.in

Experimental section

Materials

All reagents were of analytical grade, purchased from M/S S. D. Fine Chemicals Pvt. Ltd. and used without further purification. All products were characterized by MS analysis (GC-MS Shimadzu QP 2010) and ¹H NMR (300 MHz, CDCl₃).

S1. Synthesis of palladium nanoparticles

Pd(OAc)₂ (200 mg) was added into (PEG) (16 g of PEG- 600). The resulting light yellow colored homogeneous solution was stirred on a magnetic stirrer at 80°C for 3h. The solution slowly turned from light yellow to dark grey, signifying the formation of Pd NPs. The PEG stabilized Pd° particles were then allowed to cool at room temperature. The as synthesized Pd° species were then dispersed in dry ethanol under sonication. The dispersion was subjected to centrifuge at 13,000 rpm at room temperature (25°C). The separated particles were washed properly with ethanol and dried under vacuum for further use.

S2. Synthesis of Pd- Fe_3O_4 magnetic nanocomposite (Pd- Fe_3O_4 MNPs)

The Pd incorporated Fe₃O₄ nanoparticles were prepared by adding Pd NPs in to the reaction mixture of Fe₃O₄. The Fe₃O₄ NPs were prepared by sonochemical assisted co-precipitation method. The FeCl₃.6H₂O (2.70g) and urea (1.8 g) were dissolved in water (100 mL) at 80^oC for 2h. to get brown colored solution. To the resultant reaction mixture cooled to room temperature was added FeSO₄.7H₂O (1.39g) and then 0.1M NaOH until pH-10. The mixture was subjected to ultrasonication (frequency 30 kHz and power of 150 Watts). The temperature of the bath was maintained at 60°C and maintained for 30 min in air atmosphere. To this precipitate, the dispersion of the as-synthesized Pd NPs in ethanol was slowly added with continuous stirring. After addition of Pd NPs the reaction mixture changed from brown to chocolate brown colored precipitate. The reaction temperature was slowly brought to 80°C, maintained for 1h and then aged overnight at room temperature. The chocolate brown colored precipitate was then separated by filtration, washed several times with distilled water and finally with ethanol. The solid product was then further dried in an oven at 100°C for nearly two hour and finally calcined at 200°C for 4h. The synthesized sample by this method was denoted as Pd-Fe₃O₄ MNPs.

S3. Synthesis of magnetic beads of nano $Pd-Fe_3O_4$ (a) Alg:

An aqueous Pd-Fe₃O₄ MNPs suspension was first prepared by taking 2g of Pd-Fe₃O₄ nano powder into 10mL distilled water, followed by sonication for about 30 min. Preparation of beads was then accomplished by mixing of 5mL of the Pd-Fe₃O₄ suspension with 20 mL of 4% (w/w) sodium alginate solution, kneading the mixture for 2h by a high speed agitator and dropwise injection of the obtained sol into 0.1 mol/L CaCl₂ solution through a 0.5 mm medical needle to form beads. The formed beads were gently stirred in the CaCl₂ solution for an additional 3h to harden and then they were thrice washed with distilled water followed by drying at 40^oC for overnight. The obtained beads were calcined at 300° C for 3h and the above prepared beads referred as beads of nano Pd–Fe₃O₄@Alg.



Fig. S1 FT-IR Spectra of Fe₃O₄, Pd-Fe₃O₄ and Pd-Fe₃O₄@Alg.



Fig. S2 UV-Visible absorption spectrum of Pd-Fe₃O₄@Alg.



Fig. S3 Thermogravimetric curve for Pd-Fe₃O₄@Alg.



Fig. S4 N_2 isotherms curve for Pd-Fe₃O₄@Alg.



Fig. S5 Pore size curve of the Pd-Fe₃O₄@Alg.



Fig. S6 XRD of recycled catalyst after fifth cycle.

S4. General experimental procedure for Suzuki cross coupling reactions catalyzed by beads of nano $Pd-Fe_3O_4@Alg$:

Aryl halide (1.0 mmol), boronic acids (1.5 mmol), 2 mmol K₂CO₃ and 2 mg of nano Pd-Fe₃O₄@Alg catalyst were added in a1 mL water and the reaction was carried at 80 °C for 1.5–4h. The progress of the reaction was monitored by Gas Chromatography (GC). After completion of reaction, the reaction mixture was cooled to room temperature and it was extracted with ethyl acetate. The beads of catalyst were easily recovered by simple filtration or by magnetic separation followed by washing with ethanol and drying and preserved for next runs. The pure products were obtained by column chromatography using pet ether: ethyl acetate as the eluent. The preserved catalyst reused in a subsequent run for recyclability study. The conversion of reactant was determined by Gas chromatography (GC). The products were characterized by GC-MS and ¹HNMR. (Table 2, entry 1) White solid, M.p. 69^oC, ¹H-NMR (300 MHz, CDCl₃): $\delta =$ 7.51-7.58 (m, 4H), 7.36-7.43 (m, 4H), 7.25-7.32 (m, 2H). (Table 2, entry 2) White solid, M.p. 85° C, ¹H-NMR (300 MHz, CDCl₃): $\delta = 7.56$ (t, 2H), 7.45 (t, 2H), 7.34 (d, 2H), 7.26 (d, 1H), 6.99 (d, 2H), 3.87 (s, 3H). (Table 2, entry 3) Colorless solid, M.p. 165°C, ¹H-NMR (300 MHz, $CDCl_3$): $\delta = 8.29$ (s, 1H), 7.59 (d, 2H), 7.53 (d, 2H), 7.40-7.48 (m, 2H), 7.26-7.34 (m, 1H), 6.93 (d, 2H). (Table 2, entry 9) White solid, M.p. 119°C, ¹H-NMR (300 MHz, CDCl₃): $\delta = 8.05$ (d, 2H), 7.62-7.71 (m, 4H), 7.41-7.50 (m, 3H), 2.64 (s, 3H).

Table S1. Comparison between some reported works and the present work for Suzuki coupling

 reaction of iodobenzene and phenyl boronic acid.

| Entry | Catalyst | Reaction Conditions | Yield (%) | Reference |
|-------|-------------------------|---|-----------|-----------|
| 1. | Carbon nanocomposite Pd | DMF/H ₂ O, K ₂ CO ₃ , 100°C, 1.5h. | 97 | 1 |
| 2. | Pd/C NPs | DMF, NEt ₃ , 140°C, 2h. | 98 | 2 |

| 3. | Pd-P-300 | EtOH/H ₂ O, Na ₂ CO ₃ , TBAB, 55°C, | 99 | 3 |
|-----|---|--|-----|---------|
| | | 20h. | | |
| 4. | GO-Pd@Ag-AgBr | EtOH/H ₂ O, K ₂ CO ₃ , N ₂ atm., 300W | 97 | 4 |
| | | Xe lamp, 25°C, 0.5h. | | |
| 5. | Pd NPs | IPA, K ₂ CO ₃ , 100°C, 20h. | 88 | 5 |
| 6. | Au/Pd NPs | EtOH/H ₂ O, K ₂ CO ₃ , N ₂ atm., 80°C, | 88 | 6 |
| | | 24h. | | |
| 7. | SBA-15-EDTA-Pd | DMF, K ₂ CO ₃ , 120 °C, 5h. | 98 | 7 |
| 8. | Pd NPs/ PS | DMF/H2O, Na ₂ CO ₃ , 100°C, 12h. | 100 | 8 |
| 9. | GO-NH ₂ -Pd | EtOH/H ₂ O, K ₂ CO ₃ , 60°C, 0.5h. | 87 | 9 |
| 10. | Fe ₃ O ₄ @SiO ₂ @mSiO ₂ -Pd | IPA, K ₂ CO ₃ , 80°C, 6h. | 98 | 10 |
| 11. | Nano Pd–Fe ₃ O ₄ @Alg | H ₂ O, K ₂ CO ₃ , 80°C, 1.5h. | 97 | Present |
| | | | | Work |
| | | | | |

S5. General experimental procedure for Heck cross coupling reactions catalyzed by beads of nano $Pd-Fe_3O_4@Alg$:

Aryl halide (1.0 mmol), olefins (2 mmol), 2 mmol Et₃N and 4 mg of nano Pd–Fe₃O₄@Alg catalyst were added in a1 mL water and the reaction was carried at 85 °C for 3–8h. The progress of the reaction was monitored by Gas Chromatography (GC). After completion of reaction, the reaction mixture was cooled to room temperature and it was extracted with ethyl acetate. The beads of catalyst were easily recovered by simple filtration or by magnetic separation followed by washing with ethanol and drying and preserved for next runs. The pure products were obtained by column chromatography using pet ether: ethyl acetate as the eluent. The preserved catalyst reused in a

subsequent run for recyclability study. The conversion of reactant was determined by Gas chromatography (GC). The products were characterized by GC-MS and ¹HNMR. (**Table 4, entry 1)** Colorless liquid, ¹H-NMR (600 MHz, CDCl₃): $\delta = 7.68$ (d, J = 16.0 Hz, 1H), 7.49-7.54 (m, 2H), 7.34-7.40 (m, 3H), 6.44 (d, J = 16.0 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H). (**Table 4, entry 5)** White solid, M.p. 139-140°C, ¹H-NMR (300 MHz, CDCl₃): $\delta = 8.25$ (d, 2H, J = 8.8 Hz), 7.73-7.66 (m, 3H), 6.56 (d, 1H, J = 16.1 Hz), 4.29 (q, 2H, J = 7.1 Hz), 1.28 (q, 3H, J = 7.1 Hz). (**Table 4, entry 12)** Colorless liquid, ¹H-NMR (600 MHz, CDCl₃): $\delta = 7.68$ (d, J = 16.2 Hz, 1H), 7.49-7.55 (m, 2H), 7.35-7.40 (m, 3H), 6.44 (d, J = 16.2 Hz, 1H), 3.79 (s, 3H). (**Table 4, entry 16)** White solid, M.p. 121–122°C, ¹H-NMR (300 MHz, CDCl₃): $\delta = 7.54$ (d, J = 7.2 Hz, 4H), 7.40-7.26 (m, 6H), 7.14 (s, 2H).

S6. General experimental procedure for Buchwald-Hartwig amination reactions catalyzed by beads of nano $Pd-Fe_3O_4$ (a) Alg:

Aryl halide (1.0 mmol), secondary amines (1.5 mmol), 2 mmol 'BuONa and 2 mg of nano Pd–Fe₃O₄@Alg catalyst were added in a 1 mL DMSO and the reaction was carried at 110°C for 12h. The progress of the reaction was monitored by Gas Chromatography (GC). After completion of reaction, the reaction mixture was cooled to room temperature and it was extracted with ethyl acetate. The beads of catalyst were easily recovered by simple filtration or by magnetic separation followed by washing with ethanol and drying and preserved for next runs. The pure products were obtained by column chromatography using hexane: ethyl acetate as the eluent. The preserved catalyst reused in a subsequent run for recyclability study. The conversion of reactant was determined by Gas chromatography (GC). The products were characterized by GC-MS and ¹HNMR. (**Table 6, entry 1**) ¹H-NMR (600 MHz, CDCl₃): $\delta = 7.23-7.31$ (m, 2H), 6.84-6.94 (m, 3H), 3.86 (t, J = 4.8 Hz, 4H), 3.16 (t, J = 4.8 Hz, 4H).

| | · · · · · · · · · · · · · · · · · · · | | |
|-------|--|-----------------|--|
| Entry | Reaction | GC Yield (%) | |
| | | Commercial Pd/C | Pd-Fe ₃ O ₄ @Alg |
| 1. | Suzuki reaction ^a | 33 | 97 |
| 2. | Heck reaction ^b | - | 94 |
| 3. | Buchwald Hartwig reaction ^c | 65 | 96 |

Table S2. The comparison of activities of reported Pd-Fe₃O₄@Alg catalyst with conventional Pd/C catalyst.

^aReaction Conditions: Iodobenzene (1 mmol), phenylboronic acids (1.5 mmol), K₂CO₃ (2 mmol), Catalyst (0.05 mol%), Water (1 mL) at 80 °C for 1.5h.

^bReaction conditions: Iodobenzene (1 mmol), Ethylacrylate (2 mmol), NEt₃ (2 mmol), Catalyst (0.1 mol%), Water (1 mL) at 85 °C for 3h.

^cReaction conditions: Iodobenzene (1 mmol), Morpholine (1 mmol), ^tBuONa (1 mmol), Catalyst (0.05 mol%), DMSO (1 mL) at 110 °C for 12h.

Table S2 shows that nano Pd-Fe3O4@Alg is also superior to commercial Pd/C. We carried out Suzuki, Heck and Buchwald Hartwig amination reaction with commercial Pd/C under the same optimized reaction conditions. The commercial Pd/C gives only 33% and 65% yield of the product for Suzuki and Buchwald Hartwig amination reactions respectively. The commercial Pd/C does not showed any activity for Heck reaction under the optimized conditions.

S7. Characterization of products by mass spectra (EI, 70 eV):

- (a) Suzuki coupling products.
- 1. (Table 2, entry 1)



MS (m/z/rel.int.): 184(M⁺): 51(4.0), 76(7.5), 115(33.7), 141(47.9), 169(53.5), 184(100).

3. (Table 2, entry 4).



MS (m/z/rel.int.): 168(M⁺): 51(6.8), 83(17.5), 153(49.1), 167(92.3), 168(100).



4. (Table 2, entry 5)

MS (m/z/rel.int.): 199(M⁺): 51(12.0), 76(17.9), 152(99.5), 169(36.7), 199(100).

5. (Table 2, entry 7)



MS (m/z/rel.int.): 170(M⁺): 51(3.8), 115(17.9), 141(25.9), 170(100).

6. (Table 2, entry 8)



MS (m/z/rel.int.): 168(M⁺): 51(4.1), 83(9.8), 152(23.6), 168(100).

7. (Table 2, entry 9).



MS (m/z/rel.int.): 196(M⁺): 43(11.6), 76(20.3), 152(58.2), 181(100), 196(52.7).

8. (Table 2, entry 10).



MS (m/z/rel.int.): 179(M⁺): 51(5.3), 76(12.6), 151(16.7), 179(100).

9. (Table 2, entry 11).



MS (m/z/rel.int.): 172(M⁺): 51(4.0), 76(5.4), 85(10.6), 152(4.6), 172(100).

10. (Table 2, entry 15).



MS (m/z/rel.int.): 155(M⁺): 51(16.8), 77(20.8), 127(19.0), 155(100).

11. (Table 2, entry 16).



MS (m/z/rel.int.): 160(M⁺): 51(5.9), 115(39.5), 128(14.9), 160(100).

12. (Table 2, entry 17).



MS (m/z/rel.int.): 182(M⁺): 51(5.1), 76(7.9), 152(16.1), 167(59.2), 182(100).

13. (Table 2, entry 18).



MS (m/z/rel.int.): 172(M⁺): 51(4.5), 85(10.1), 172(100).

(b)Heck coupling products.



1. (Table 4, entry 1).

MS (m/z/rel.int.): 176(M⁺): 51(18.6), 77(37.1), 103(54.2), 131(100), 176(28.7).

2. (Table 4, entry 2).



MS (m/z/rel.int.): 206(M⁺): 51(5.9), 77(16.5), 134(56.9), 161(100), 206(71.2).

3. (Table 4, entry 3).



MS (m/z/rel.int.): 191(M⁺): 59(20.1), 91(30.3), 119(72.2), 146(100), 191(90.1).

4. (Table 4, entry 4).



5. (Table 4, entry 5).



6. (Table 4, entry 11).



MS (m/z/rel.int.): 182(M⁺): 45(11.1), 65(29.1), 109(42.6), 137(100), 182(48.7).

7. (Table 4, entry 12).



MS (m/z/rel.int.): 162(M⁺): 51(27.2), 77(43.5), 103(70.0),131(100), 162(50.6).

8. (Table 4, entry 13).



MS (m/z/rel.int.): 176(M⁺): 51(9.6), 91(30.7), 115(93.8), 145(100), 176(32.9).

9. (Table 4, entry 14).



MS (m/z/rel.int.): 204(M⁺): 43(40.1), 102(19.1), 189(100), 204(32.6).

10. (Table 4, entry 15).



MS (m/z/rel.int.): 147(M⁺): 51(38.5),77(47.8), 103(58.9), 147(100).

11. (Table 4, entry 16).



MS (m/z/rel.int.): 180(M⁺): 51(11.6), 76(20.9), 89(28.3), 165(51.3), 180(100).

(c) Buchwald Hartwig amination reaction products.

1. (Table 6, entry 1).



MS (m/z/rel.int.): 163(M⁺): 51(13.5), 77(31.8), 105(100), 163(55.7).

2. (Table 6, entry 2).



3. (Table 6, entry 3).



MS (m/z/rel.int.): 208(M⁺): 51(13.3), 77(30.0), 120(43.7), 150(100), 208(77.5).

4. (Table 6, entry 4).



MS (m/z/rel.int.): 177(M⁺): 51(5.7), 65(17.1), 91(26.4), 118(100), 177(60.6).

5. (Table 6, entry 5).



MS (m/z/rel.int.): 213(M⁺): 51(3.4), 77(16.5), 127(39.0), 155(100), 213(76.8).

6. (Table 6, entry 6).



MS (m/z/rel.int.): 177(M⁺): 77(9.3), 91(35.8),119(100), 177(58.0).

7. (Table 6, entry 7).



MS (m/z/rel.int.): 181(M⁺): 51(5.5), 75(14.7), 95(27.3), 123(100), 181(52.0).

8. (Table 6, entry 10).



MS (m/z/rel.int.): 208(M⁺): 51(45.2), 77(100), 105(60.9),119(85.3), 191(73.0), 208(48.0).

9. (Table 6, entry 11).



MS (m/z/rel.int.): 163(M⁺): 57(21.8), 77(37.6), 105(100), 163(54.2).





MS (m/z/rel.int.): 164(M⁺): 51(19.2), 79(100), 107(35.7), 133(47.0), 164(32.3).

11. (Table 6, entry 13).



MS (m/z/rel.int.): 160(M⁺): 51(15.1), 77(39.7), 105(37.5), 160(100).

12. (Table 6, entry 14).



MS (m/z/rel.int.): 176(M⁺): 43(100), 71(49.5), 105(64.5), 176(91.9).

13. (Table 6, entry 15).



MS (m/z/rel.int.): 238(M⁺): 51(12.6), 77(42.9), 105(100), 132(56.3), 238(78.4).

14. (Table 6, entry 16).



MS (m/z/rel.int.): 189(M⁺): 77(12.0), 106(100), 189(13.5).

15. (Table 6, entry 17).



MS (m/z/rel.int.): 183(M⁺): 51(23.7), 77(46.3), 104(30.1), 167(29.4), 183(100).

16. (Table 6, entry 18).



MS (m/z/rel.int.): 273(M⁺): 51(7.3), 77(22.5), 91(100), 182(20.2), 273(42.4).

17. (Table 6, entry 19).



MS (m/z/rel.int.): 149(M⁺): 51(11.1), 77(30.1), 106(52.3), 134(100), 149(30.7).

18. (Table 6, entry 20).



MS (m/z/rel.int.): 173(M⁺): 51(25.5), 77(90.5), 104(100), 144(35.8), 158(88.7), 173(56.2).

S8. Characterization of some products by ¹H NMR spectra (300/600 MHz, CDCl₃):
1. (Table 2, entry 1).



2. (Table 2, entry 2).



3. (Table 2, entry 3).



4. (Table 2, entry 9).



5. (Table 4, entry 1).



6. (Table 4, entry 5).



7. (Table 4, entry 12).



8. (Table 4, entry 16).



9. (Table 6, entry 1).



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