

Supporting Information

Palladium Catalyst Supported on PEGylated Imidazolium Based Phosphinite Ionic Liquid-Modified Magnetic Silica Core-Shell Nanoparticles: A Worthy and Highly Water Dispersed Catalyst for Organic Reactions in Water

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Experimental Section

Preparation of PEGylated $\gamma\text{-Fe}_2\text{O}_3@\text{SiO}_2$

PEG₆₀₀-silane is synthesized from PEG (MW = 600) and 3-(triethoxysilyl) propyl isocyanate (TESPIC) through hydrogen-transfer reaction.¹ Briefly, 0.01 mol of dried PEG₆₀₀ (at 90 °C for 3 h under vacuum) is dissolved into 50 mL of dry pyridine with vigorous stirring under argon atmosphere for 6 h at 70 °C. Then 0.01 mol of TESPIC is added into the later mixed solution. After 24 h, the solvent is removed by vacuum evaporation. The residue is washed three times with *n*-hexane, and then recrystallized from EtOH at 0 °C. The obtained white **PEG₆₀₀-silane** is filtered at 0 °C and then dried at room temperature (RT) under vacuum.

Then a solution of 0.1 g of PEG₆₀₀-silane in 30 mL of EtOH is added drop-wise to a vigorous stirring solution of 25 mg of $\gamma\text{-Fe}_2\text{O}_3@\text{SiO}_2$ nanoparticles, which is prepared according to the previously reported procedure,² in 30 mL EtOH/H₂O (1:2) and HCl (pH = 4). After vigorous stirring for 24 h, the solution is filtered off and washed thoroughly. The white residue is dried at 100 °C under vacuum for 12 h to obtain [**PEGylated $\gamma\text{-Fe}_2\text{O}_3@\text{SiO}_2$**].

Preparation of PEGylated ImIL- $\gamma\text{-Fe}_2\text{O}_3@\text{SiO}_2$

4 mL conc. H₂SO₄ is added to a solution of [**PEGylated $\gamma\text{-Fe}_2\text{O}_3@\text{SiO}_2$**] (6 g) in 100 ml deionized water (DW). Then a solution of HBr (17.34 g, 10 mmol) in 50 mL DW is added drop-wise to the later mixture during 12 h with vigorous stirring at RT and the mixture is refluxed overnight. Afterwards, the mixture is cooled to RT and a solution of NaOH 1N is added to neutralize the solution. The magnetic solid is separated by an external magnetic device, washed three times with DW and EtOH and then dried under vacuum.

Subsequently, potassium carbonate (1.38 g, 10 mmol), imidazole (0.69 g, 10 mmol) and pyridine

(0.79 g, 10 mmol) are added to a mixture of the later magnetic solid in 50 mL acetonitrile, and then the mixture refluxed overnight. Next the mixture is cooled to RT and the solid residue is separated using an external magnet and washed with DW and EtOH (3×5 ml) to remove the unreacted substrates and give the [PEGylated-ImIL- γ -Fe₂O₃@SiO₂].

Preparation of [PEGylated ImIL-OPPh₂- γ -Fe₂O₃@SiO₂] catalyst

2-chloroethanol (0.4 g, 5 mmol) is poured to a solution of [PEGylated-ImIL- γ -Fe₂O₃@SiO₂] (2 g) in 50 mL toluene and the mixture is stirred at 90 °C overnight. Then the solid residue is magnetically separated, washed with toluene and Et₂O, and dried in a vacuum oven at 50 °C for 24 h. The later dried solid is poured into a solution of NaBF₄ (0.55 g, 5 mmol) in 15 mL dry acetonitrile and is allowed to stir at RT for 4 days. Afterwards, the obtained solid is magnetically decanted and washed and then dried under vacuum. The dried magnetic solid (2 g) and triethylamine (0.505 g, 5 mmol) are added to a solution of chlorodiphenylphosphine (1.1 g, 5 mmol) in dry CH₂Cl₂. The mixture is stirred under argon atmosphere for 12 h at RT. Then the solid residue is separated by an external magnet, washed with CH₂Cl₂ and dried under vacuum at 50 °C for 12 h to give [PEGylated ImIL-OPPh₂- γ -Fe₂O₃@SiO₂].

Preparation of [Pd@PEGylated ImIL-OPPh₂- γ -Fe₂O₃@SiO₂] catalyst

To a mixture of [PEGylated ImIL-OPPh₂- γ -Fe₂O₃@SiO₂] (1 g) in 50 mL dry CH₂Cl₂, palladium acetate (2 mmol) is added and stirred at RT under argon atmosphere for 24 h. The obtained solid is magnetically separated and washed with CH₂Cl₂ (2×10 mL) and Et₂O (2 × 10 mL). Finally, [Pd@PEGylated ImIL-OPPh₂- γ -Fe₂O₃@SiO₂] nanocatalyst is obtained as a dark brown powder after drying under vacuum for 12 h.

General procedure for the Heck coupling reaction

A mixture of aryl halide (1.0 mmol), alkene (1.1 mmol), NaOAc (1.5 mmol) and catalytic amount of [Pd@PEGylated ImIL-OPPh₂- γ -Fe₂O₃@SiO₂] (5 mg) is taken in a round-bottom flask, stirred in H₂O (3.0 mL) at r.t. and the reaction progress is monitored by TLC. At the end of the reaction, liquid is isolated by magnetic decantation. The liquid is poured into DW (10 mL) and the product is extracted with ethyl acetate. The organic phase is dried over Na₂SO₄. Then the combined organic phase is evaporated and the product is purified by column chromatography on silica gel using a mixture of n-hexane/ethyl acetate (5:1) as eluent. The recovered catalyst is rinsed with water and EtOH, and finally dried at RT, and used without any pre-treatment for the next run. The recycling test of the catalyst is performed in the reaction between bromobenzene and n-butyl acrylate according to the above procedure.

General procedure for the Sonogashira coupling reaction

A mixture of aryl halide (1.0 mmol), aryl phenylacetylene (1.0 mmol), NaOAc (1.5 mmol) and the catalytic amount of [Pd@PEGylated ImIL-OPPh₂- γ -Fe₂O₃@SiO₂] (5 mg) in a round-bottom flask is stirred in H₂O (3.0 mL) at RT and the progress of the reaction is monitored by TLC. After the completion of the reaction, the catalyst is separated from the reaction mixture by an external magnet device. Then, the residual mixture is poured into DW (10 mL) and the product is extracted with ethyl acetate. The organic phase is washed with brine and dried with anhydrous Na₂SO₄. The organic phase is evaporated and the residue is purified by column chromatography on silica gel using a mixture of *n*-hexane/ethyl acetate (10:1) as eluent to obtain the corresponding products.

Catalytic reduction of 4NP to 4AP

A mixture of 2.5 mL of fresh aq. solution of NaBH₄ (1.2 M) and 10 mL aq. solution of 0.34

mmol 4NP and 1 mg of nanocatalyst is stirred. The colour of the later solution is faded as the reaction proceeded. The progress of the reaction is monitored by UV-vis spectra of the supernatant (at short intervals). This procedure is repeated for blank experiment to show that the reaction do not proceed without the catalyst only in the presence of NaBH_4 .

References

- 1 L. Ma'mani, S. Nikzad, H. Kheiri-Manjili, S. Al-Musawi, M. Saeedi M, S.Askarlou, A. Foroumadi, A. Shafiee, *Eur J Med Chem.*, 2014, **18**, 646-54.
- 2 L. Ma'mani, A. Heydari, M. Sheykhani *Applied Catal. A: General*, 2010, **384**, 122–127.

Characterization of Nanocatalyst

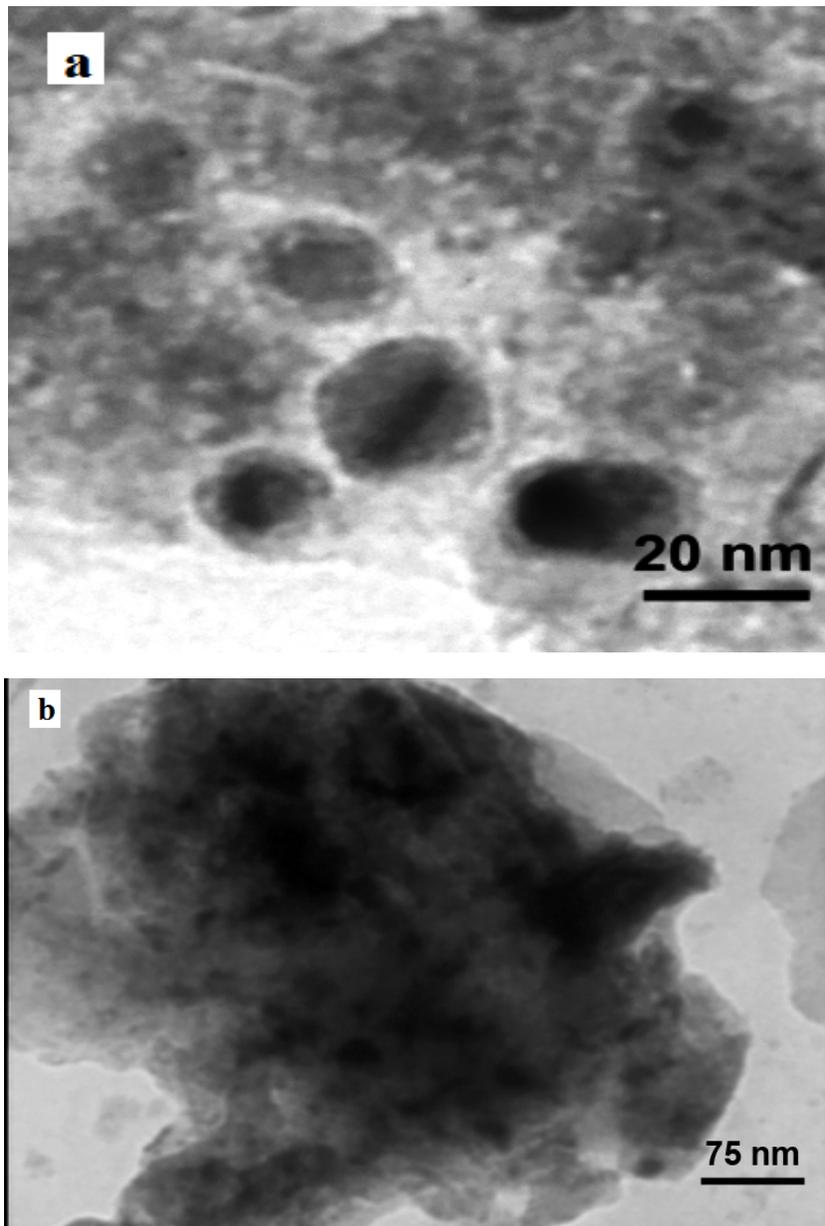


Figure 1. (a) TEM images of [PEGylated ImIL--OPPh₂- γ -Fe₂O₃@SiO₂] and (b) [Pd@PEGylated ImIL--OPPh₂- γ -Fe₂O₃@SiO₂].

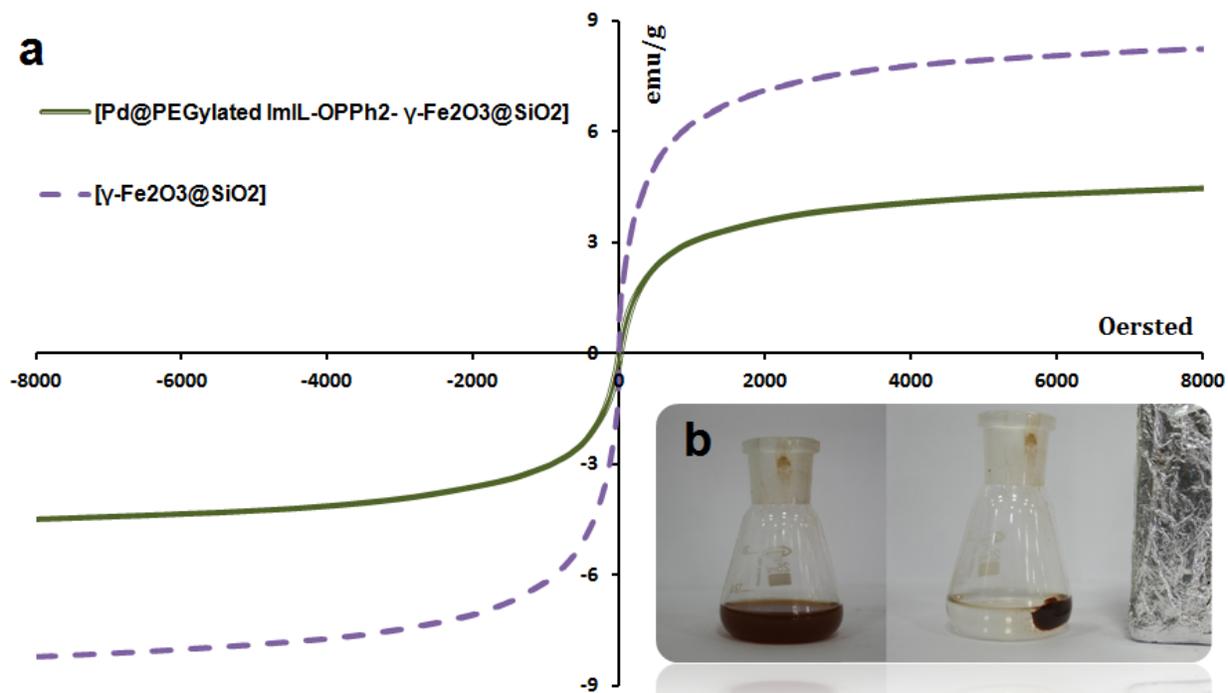


Figure 2. (a) The magnetization hysteresis loop of [γ -Fe₂O₃@SiO₂] and [Pd@PEGylated ImIL-OPPh₂- γ -Fe₂O₃@SiO₂], and (b) high water dispersion and facile magnetic separation of the catalyst.

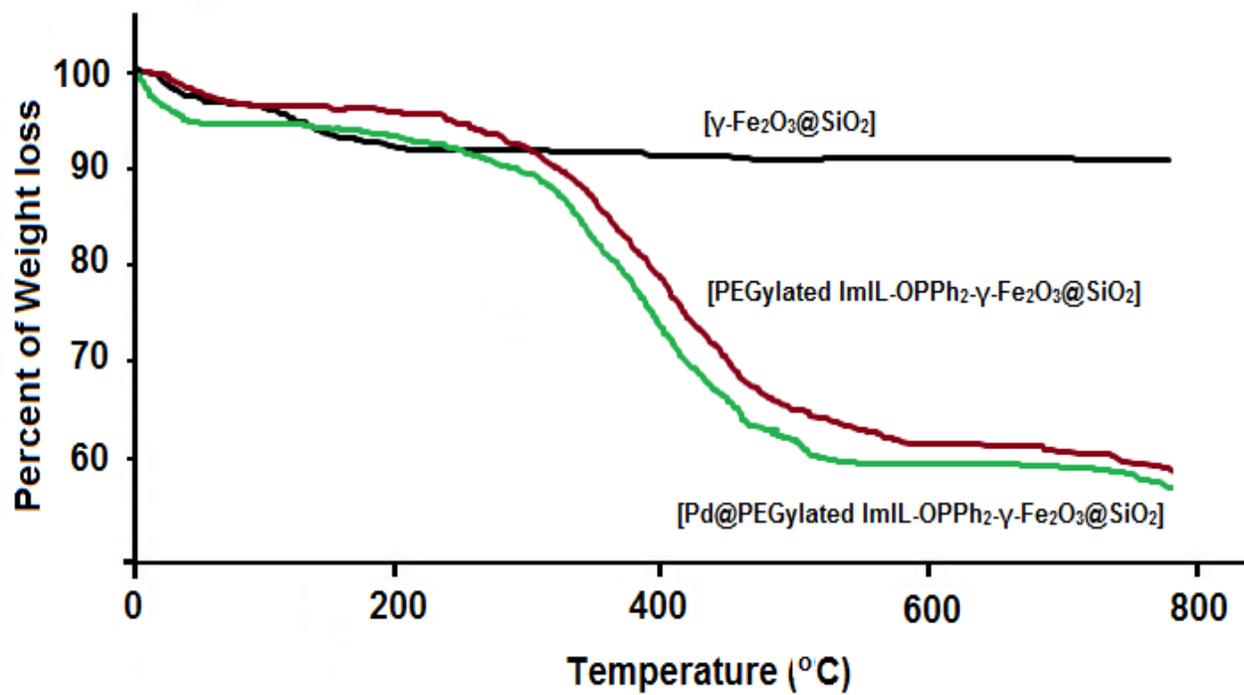


Fig. 3 TG Analysis of synthesized nanoparticles.

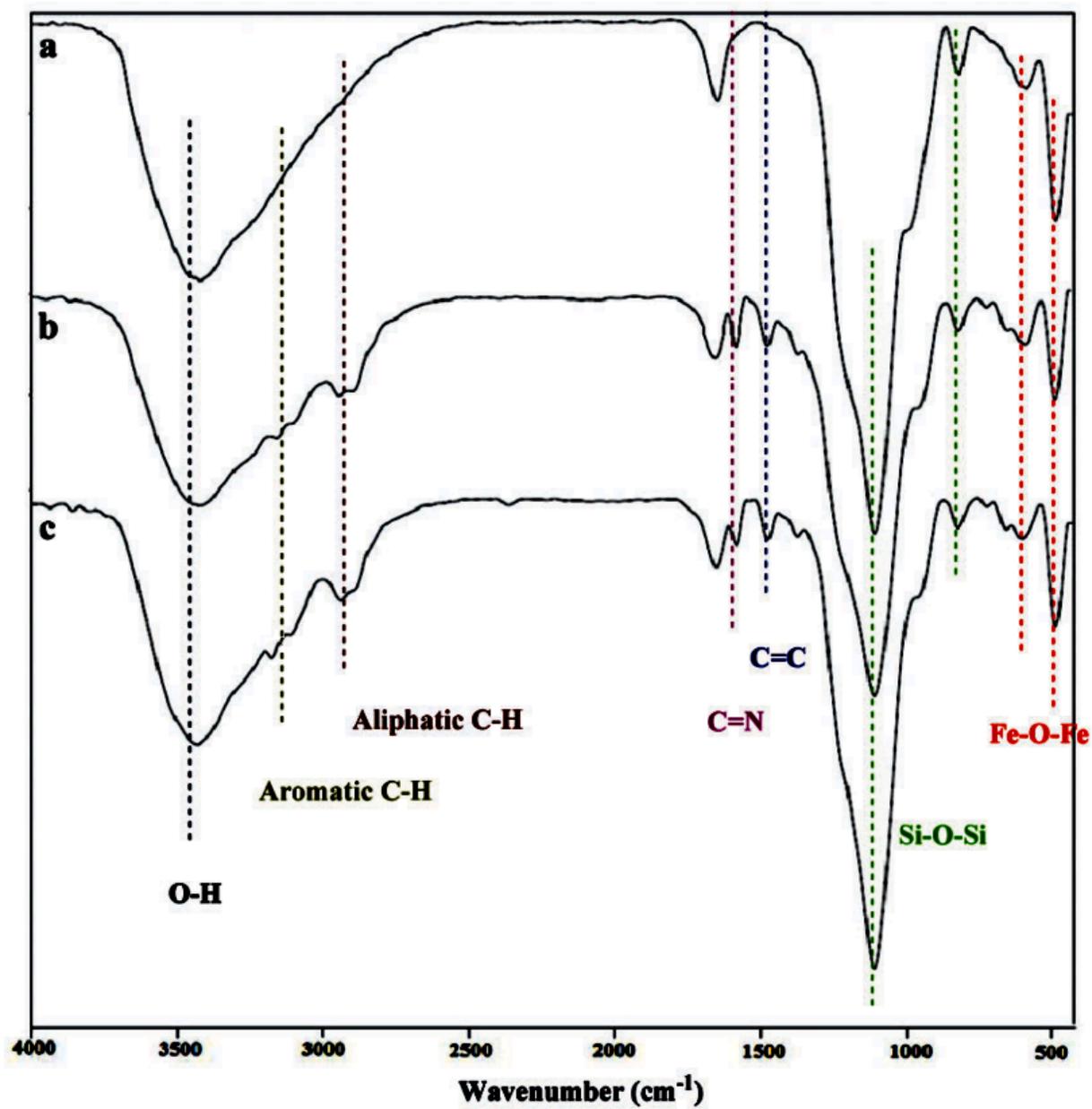


Figure 4. FTIR spectra for (a)[γ -Fe₂O₃@SiO₂], (b) [PEGylated γ -Fe₂O₃@SiO₂], and (c)[PEGylated ImIL-OPPh₂- γ -Fe₂O₃@SiO₂].

¹H NMR Spectra of the selected products

A) Heck Reaction

