# Separable Catalysts in One-Pot Syntheses for Greener Chemistry

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A method that enables the separation between two different catalytic solids used in one-pot reactions is described. Such separation between the two catalytic solids can facilitate their reuse in other catalytic applications and make the synthesis cheap and greener. The method is based on doping one of the catalysts with magnetic nanoparticles, which can make it magnetically separable while the other solid can be separated by filtration. The magnetically separable catalytic solid is designed by a sol–gel process in which a palladium catalyst is encapsulated in a silica sol–gel-modified polyethylenimine composite in the presence of magnetic nanoparticles modified with ionic liquid groups. The other catalytic solid utilized in this study is a solid acid based on cross-linked polystyrene sulfonic acid and can be separated by simple filtration. The two catalytic solids are utilized in one-pot reactions of dehydration/hydrogenation of benzyl alcohols. After reaction, the palladium-based catalyst is separated by applying an external magnetic field and the solid acid is separated by filtration. The magnetically separable palladium-based catalyst is reused after utilization in a one-pot reaction to catalyze three different types of reactions: carbonylation of iodoarenes, Suzuki, and Heck coupling.

## 1. Introduction

In the past decade, many investigations have been conducted to try to develop greener chemical processes and synthetic methods, due to environmental considerations.[1] Several new methods and novel-designed materials have been developed to make the chemical reactions cleaner and more benign. For example, performing safer and environmentally friendly synthetic processes is now possible by using ionic liquids, supercritical carbon dioxide, water, or perfluorinated solvents as media for reactions instead of the traditional hazard organic solvents.[2] In addition, some catalytic reactions have become less costly and green due to the utilization of recyclable heterogenized catalysts in these reactions that were developed by a variety of heterogenization methods.[3]

One-pot multistep reactions are very attractive since they significantly lower the cost of the synthetic routes, by reducing the number of purification and separation steps, as well as reducing the amount of waste and solvents.[4] However, the application of this type of synthesis is limited since the catalysts utilized in these reactions have to be compatible with each other.

The pioneer work of Patchornik in 1981 showed that it is possible to overcome the limitation of compatibility of catalysts by immobilizing them on solid supports.[5] Recently, Gelman, Blum, and Avnir described an impressive method to overcome the limitation of using incompatible catalysts in one-pot reactions which is based on the concept of "site isolation".[6–10] According to this method, mutually destructive reactants were entrapped separately in sol–gel matrices and then used to catalyze one-pot sequences of reactions in a

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single vessel. Different pairs of opposing reagents or catalysts like acid/base, oxidant/reducing catalyst, and enzyme/metal complex catalyst proved to be effective for the one-pot synthesis. Two other methods that enable the use of acids and bases in one-pot reactions in a single vessel have been reported. Thus, Fréchet and Hawker et al. developed star polymers containing acid and base groups confined in their core for catalyzing homogeneous one-pot reactions.[11] In contrast, Kaneda et al. utilized two types of layered clays as inorganic acid and base catalysts for performing heterogeneous one-pot catalysis.[12] Furthermore, McQuade et al. described a method to use incompatible catalysts in a one-pot multistep reaction that is based on encapsulation of catalysts via interfacial polymerization of an oil-in-water emulsion.[13]

Magnetic nanoparticles (MNP) have received a great deal of attention because of their potential biomedical applications in fields such as drug delivery,[14] magnetic resonance imaging,[15] biomolecular sensors,[16] bioseparation,[17] and magneto-thermal therapy.[18] Additionally, recent studies show that magnetic nanoparticles are excellent supports for catalysts.[19] The supported catalysts proved to be effective and easily separated from the reaction media by applying an external magnetic field. Moreover, quaternary ammonium and phosphonium salts were supported on magnetic nanoparticles and utilized as phase transfer catalysts with good activities.[20] We recently described the highly selective hydroformylation reaction using catalysts supported on dendronized magnetic nanoparticles.[21] In addition, we have developed a new catalytic system for the chemoselective hydrogenation of $\alpha$, $\beta$-unsaturated aldehydes and alkynes, and based on platinum nanoparticles supported on nanomagnetite, $Fe_3O_4$, modified with ionic liquid groups.[22]

Herein, we report a novel method for separation between two solid catalysts after catalyzing one-pot reactions in a single vessel, and then to reuse them for other applications. The method is based on doping of one catalytic solid with a magnetic nanoparticle that enables its separation by applying external magnetic field, while the other catalytic solid can be separated by filtration techniques. The magnetically separable solid catalyst was designed by sol–gel process in which magnetic nanoparticles and palladium catalyst were encapsulated together within silica sol–gel-modified polyethylenimine composite. The second solid catalyst that was chosen for the current study is based on the commercial cross-linked polystyrene sulfonic acid.

## 2. Experimental Section

**2.1. Materials.** Cross-linked polystyrene sulfonic acid (**PS-$\mathbf{SO_3H}$**) (2.2 mmol/g of sulfonic acid groups), polyethylenimine (**PEI**) ($M_w$=28000 g/mol), tetraethoxysilane (TEOS) were purchased from Sigma-Aldrich. Magnetite nanoparticles of 8–12 nm were prepared according to Massart's method.[23] The benzyl alcohols were prepared by reducing the appropriate aromatic ketone with excess of $NaBH_4$ in methanol.

**2.2. Preparation of Acylated Polyethylenimine (PEI-$\mathbf{C_{12}}$).** Polyethylenimine (25 g) was mixed with lauric acid (36 g, 180 mmol) and heated at 160 °C for 36 h while the formed water was distilled off. A bright yellow, very viscous liquid (58 g) was obtained. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.83 $[\mathrm{PEI{-}CH_2{-}NHCO{-}CH_2{-}CH_2{-}(CH_2)_8{-}C\underline{H}_3}]$, 1.23 $[\mathrm{PEI{-}CH_2{-}NHCO{-}CH_2{-}CH_2{-}(C\underline{H}_2)_8{-}CH_3}]$, 1.59 $[\mathrm{PEI{-}CH_2{-}NHCO{-}CH_2{-}C\underline{H}_2{-}(CH_2)_8{-}CH_3}]$,2.15 $[\mathrm{PEI{-}CH_2{-}NHCO{-}C\underline{H}_2{-}CH_2{-}(CH_2)_8{-}CH_3}]$, 2.39–2.83 $[\mathrm{\underline{PEI}{-}CH_2{-}NHCO{-}CH_2{-}CH_2{-}(CH_2)_8{-}CH_3}]$, 3.12–3.45 $[\mathrm{PEI{-}C\underline{H}_2{-}NHCO{-}CH_2{-}CH_2{-}(CH_2)_8{-}CH_3}]$, 3.57–3.71 $[\mathrm{PEI{-}CH_2{-}N\underline{H}CO{-}CH_2{-}CH_2{-}(CH_2)_8{-}CH_3}]$; $^{13}$C NMR (300 MHz, $CDCl_3$) $\delta$ 14.5 $[\mathrm{PEI{-}CH_2{-}NHCO{-}CH_2{-}CH_2{-}(CH_2)_7{-}CH_2{-}\underline{C}H_3}]$, 23.1 $[\mathrm{PEI{-}CH_2{-}NHCO{-}CH_2{-}CH_2{-}(CH_2)_7{-}\underline{C}H_2{-}CH_3}]$, 26.4 $[\mathrm{PEI{-}CH_2{-}NHCO{-}CH_2{-}\underline{C}H_2{-}(CH_2)_7{-}CH_2{-}CH_3}]$, 29.8 and 30 $[\mathrm{PEI{-}CH_2{-}NHCO{-}CH_2{-}CH_2{-}(\underline{C}H_2)_7{-}CH_2{-}CH_3}]$, 32.3 $[\mathrm{PEI{-}CH_2{-}NHCO{-}\underline{C}H_2{-}CH_2{-}(CH_2)_7{-}CH_2{-}CH_3}]$, 37.1 $[\mathrm{PEI{-}\underline{C}H_2{-}NHCO{-}CH_2{-}CH_2{-}(CH_2)_7{-}CH_2{-}CH_3}]$, 47.1–48.8, 49.2–50.6 and 51.8–55.9 $[\mathrm{\underline{PEI}{-}CH_2{-}NHCO{-}CH_2{-}CH_2{-}(CH_2)_7{-}CH_2{-}CH_3}]$, 173.6 $[\mathrm{PEI{-}CH_2{-}NH\underline{C}O{-}CH_2{-}CH_2{-}(CH_2)_7{-}CH_2{-}CH_3}]$. IR (cm$^{-1}$): 3294.6, 2920, 2850, 1648, 1536, 1477. Elemental Anal.: C, 67.47; H, 11.33; N, 13.80.

**2.3. Addition of DL-Glycidol to Acylated Polyethylenimine To Form PEI-$\mathbf{C_{12}}$-GLY.** DL-Glycidol (2.8 mL, 42.2 mmol) was added to a solution of alkylated polyethylenimine (**PEI-$\mathbf{C_{12}}$**) (11.9 g) in dry methanol (250 mL). The solution was stirred for 14 h at room temperature and then refluxed for 6 h. Colorless, very viscous, gel-like product (14.2 g) was obtained. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.88 $[\mathrm{HOCH_2{-}CH(OH)CH_2{-}PEI{-}CH_2{-}NHCO{-}CH_2{-}CH_2{-}(CH_2)_8{-}C\underline{H}_3}]$, 1.26 $[\mathrm{HOCH_2{-}CH(OH)CH_2{-}PEI{-}CH_2{-}NHCO{-}CH_2{-}CH_2{-}(C\underline{H}_2)_8{-}CH_3}]$, 1.59 $[\mathrm{HOCH_2{-}CH(OH)CH_2{-}PEI{-}CH_2{-}NHCO{-}CH_2{-}C\underline{H}_2{-}(CH_2)_8{-}CH_3}]$, 2.1 $[\mathrm{HOCH_2{-}CH(OH)CH_2{-}PEI{-}CH_2{-}NHCO{-}C\underline{H}_2{-}CH_2{-}(CH_2)_8{-}CH_3}]$, 2.4–2.87 $[\mathrm{HOCH_2{-}CH(OH)C\underline{H}_2{-}\underline{PEI}{-}CH_2{-}NHCO{-}CH_2{-}CH_2{-}(CH_2)_8{-}CH_3}]$, 3.2–3.7 $[\mathrm{HOCH_2{-}CH(OH)CH_2{-}PEI{-}C\underline{H}_2{-}N\underline{H}CO{-}CH_2{-}CH_2{-}(CH_2)_8{-}CH_3}]$, 3.47 $[\mathrm{HOCH_2{-}C\underline{H}(OH)CH_2{-}PEI{-}CH_2{-}NHCO{-}CH_2{-}CH_2{-}(CH_2)_8{-}CH_3}]$, 3.87 $[\mathrm{HOC\underline{H}_2{-}CH(OH)CH_2{-}PEI{-}CH_2{-}NHCO{-}CH_2{-}CH_2{-}(CH_2)_8{-}CH_3}]$; $^{13}$C NMR (300 MHz, $CDCl_3$) $\delta$ 14.6 $[\mathrm{HOCH_2{-}CH(OH)CH_2{-}PEI{-}CH_2{-}NHCO{-}CH_2{-}CH_2{-}(CH_2)_7{-}CH_2{-}\underline{C}H_3}]$, 23.1 $[\mathrm{HOCH_2{-}CH(OH)CH_2{-}PEI{-}CH_2{-}NHCO{-}CH_2{-}CH_2{-}(CH_2)_7{-}\underline{C}H_2{-}CH_3}]$, 26.3 $[\mathrm{HOCH_2{-}CH(OH)CH_2{-}PEI{-}CH_2{-}NHCO{-}CH_2{-}\underline{C}H_2{-}(CH_2)_7{-}CH_2{-}CH_3}]$, 29.7 and 30 $[\mathrm{HOCH_2{-}CH(OH)CH_2{-}PEI{-}CH_2{-}NHCO{-}CH_2{-}CH_2{-}(\underline{C}H_2)_7{-}CH_2{-}CH_3}]$,32.3$[\mathrm{HOCH_2{-}CH(OH)CH_2{-}PEI{-}CH_2{-}NHCO{-}\underline{C}H_2{-}CH_2{-}(CH_2)_7{-}CH_2{-}CH_3}]$,36.9$[\mathrm{HOCH_2{-}CH(OH)CH_2{-}PEI{-}\underline{C}H_2{-}NHCO{-}CH_2{-}CH_2{-}(CH_2)_7{-}CH_2{-}CH_3}]$, 47–60

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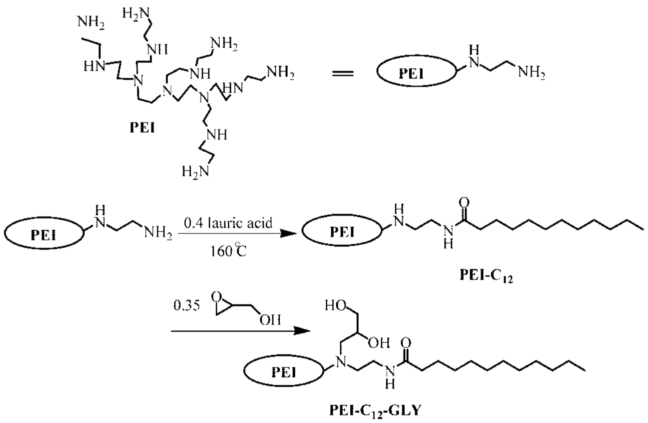
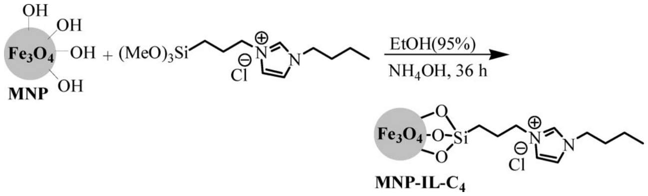
**Scheme 1. Modification Processes on the Hyberbranched Polyethylenimine**



**Scheme 2. Modification of the Magnetic Nanoparticles with Ionic Liquid Groups**



$[HOCH_2\text{-}CH(OH)\underline{C}H_2\text{-}\underline{PEI}\text{-}CH_2\text{-}NHCO\text{-}CH_2\text{-}CH_2\text{-}(CH_2)_7\text{-}CH_2\text{-}CH_3]$, 64.4 $[HO\underline{C}H_2\text{-}CH(OH)CH_2\text{-}PEI\text{-}CH_2\text{-}NHCO\text{-}CH_2\text{-}CH_2\text{-}(CH_2)_7\text{-}CH_2\text{-}CH_3]$, 69.9 and 70.8 $[HOCH_2\text{-}\underline{C}H(OH)CH_2\text{-}PEI\text{-}CH_2\text{-}NHCO\text{-}CH_2\text{-}CH_2\text{-}(CH_2)_7\text{-}CH_2\text{-}CH_3]$, 174.5 $[HOCH_2\text{-}CH(OH)CH_2\text{-}PEI\text{-}CH_2\text{-}NH\underline{C}O\text{-}CH_2\text{-}CH_2\text{-}(CH_2)_7\text{-}CH_2\text{-}CH_3]$. IR ($cm^{-1}$): 3294, 2920, 2850, 1639, 1545, 1459, 1272, 1050. Elemental Anal.: C, 63.83; H, 11.07; N, 10.84.

**2.4. Synthesis of 1-Butyl-3-(3-trimethoxysilylpropyl)-1*H*-imidazol-3-ium Chloride (IL-$C_4$).** (3-Chloropropyl)trimethoxysilane (35 mL, 192 mmol) and 1-butylimidazole (25.2 mL, 192 mmol) were heated under $N_2$ at 120 °C. The progress of the reaction was monitored by $^1H$ NMR, and it was completed after 8 h. The mixture was cooled to room temperature and honey-like, viscous liquid (60.4 g) was obtained (97% yield). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 0.616–0.672 (m, 2H), 0.967 (t, $J = 7.5$ Hz, 3H), 1.352 (dt, $J = 8.1$ Hz, 2H), 1.872–2.075 (m, 4H), 3.571 (s, 9H), 4.334 (dt, $J = 4.2$ Hz, 4H), 7.45 (t, $J = 1.2$ Hz, 1H), 7.568 (t, $J = 1.8$ Hz, 1H), 10.796 (s, 1H). $^{13}C$ NMR (300 MHz, $CDCl_3$) $\delta$ 5.94, 13.48, 19.51, 24.21, 32.21, 49.79, 50.75, 51.7, 121.91, 122.07, 137.84. IR ($cm^{-1}$) 3128, 3044, 2943, 2843, 1560. Elemental anal. Calcd for $C_{13}H_{27}ClN_2O_3Si$: C, 48.35; H, 8.43; N, 8.68. Found: C, 48.78; H, 8.78; N, 9.05.

**2.5. Modification of Magnetic Nanoparticles with IL-$C_4$ To Obtain MNP- IL-$C_4$.** Freshly prepared magnetite nanoparticles[23] (5.3 g) were suspended in ethanol (95%, 500 mL), and sonicated for 60 min. The resulted suspension was mechanically stirred, followed by addition of a solution of ethanol (95%, 100 mL) containing IL-$C_4$ (10.25 g, 30 mmol) and concentrated ammonia (28%, 2 mL). Stirring under $N_2$ was continued for 36 h. The modified magnetite nanoparticles were magnetically separated and washed three times with ethanol (95%, 100 mL) and then dissolved in methanol (400 mL) and stirred mechanically for 30 min. Ether (100 mL) was added and the modified nanoparticles were magnetically separated, washed with ether (100 mL) and dried under a vacuum of 0.2 mmHg for 24 h. Typically, 6–6.5 g of brownish-black powder could be obtained.

**2.6. Preparation of Magnetically Separable Palladium-Based Sol–Gel Catalyst (SG-MNP-PEI-Pd).** Water (4 mL) and HCl solution (0.1 N, 0.1 mL) were added to TEOS (7.6 mL, 34 mmol) and the resulting solution was stirred until a homogeneous solution was obtained (4.5 h). Also, $Pd(OAc)_2$ (0.23 g, 1mmol) and PEI-$C_{12}$-GLY (0.65 g) in methanol (7 mL) were stirred for 30 min, then sonicated for 10 min and MNP-IL-$C_4$ (0.2 g) was added to the solution while sonication continued for additional 5 min. This solution was added to the hydrolyzed TEOS and gelation occurred after stirring for 10 min. The obtained gel was aged for 24 h and

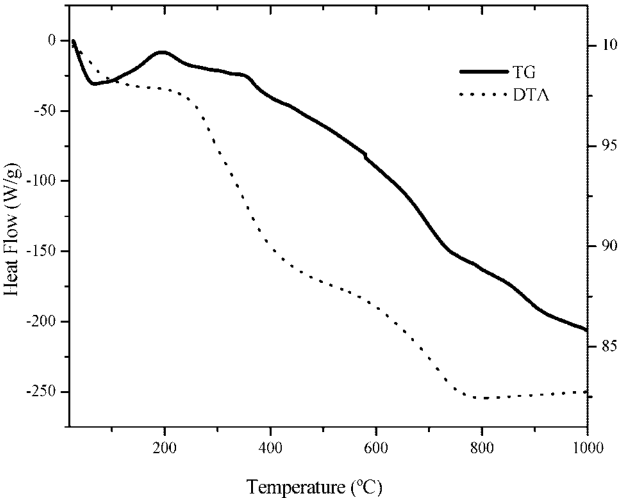


**Figure 1.** DTA-TG curves of the magnetic nanoparticles modified with ionic liquid **IL-$C_4$**.

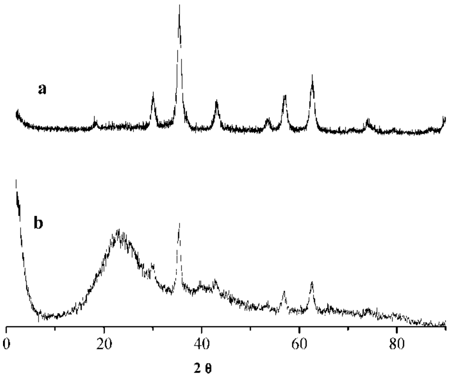


**Figure 2.** XRD patterns of (a) magnetic nanoparticles modified with **IL-$C_4$**, (b) palladium catalyst and magnetic nanoparticles encapsulated within silica sol–gel-modified polyethylenimine composite (**SG-MNP-PEI-Pd**).

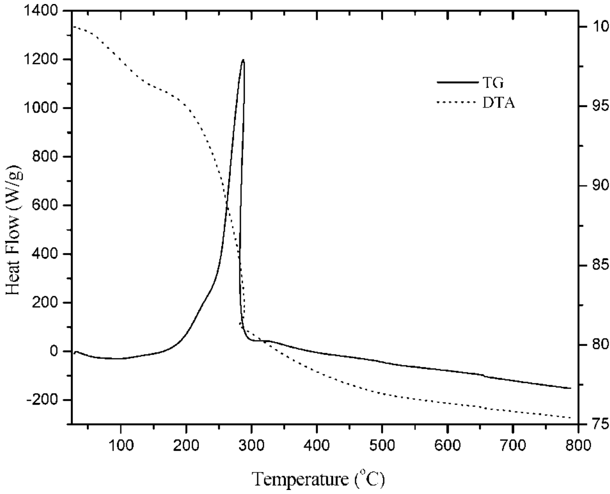


**Figure 3.** DTA-TG curves of the palladium catalyst and magnetic nanoparticles encapsulated within silica sol–gel-modified polyethylenimine composite (**SG-MNP-PEI-Pd**).

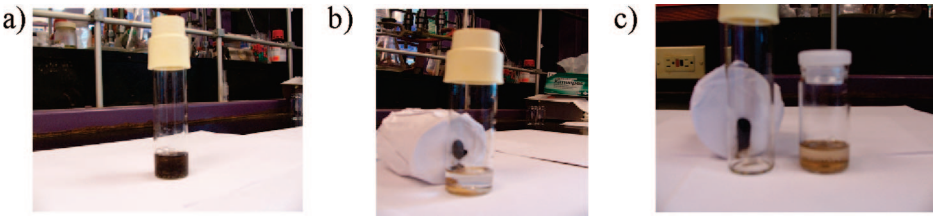


**Figure 4.** Illustration of the separation method between two different catalytic solids mixed together in the same vessel and applied in a one-pot reaction.

**Scheme 3. One-Pot Dehydration and Hydrogenation Reactions of Benzyl Alcohols**

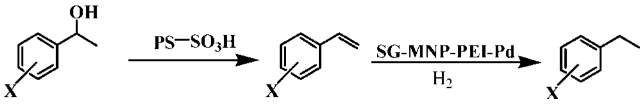
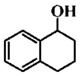
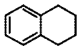
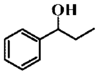
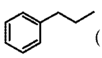
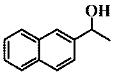
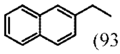
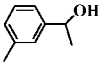
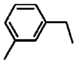
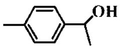
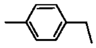
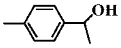
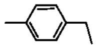
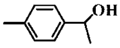
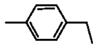


**Table 1. One-Pot Dehydration/Hydrogenation of Benzyl Alcohols Catalyzed by Solid Acid Catalyst and Magnetically Separable Palladium-Based Catalyst**[a]

| Entry | Substrate | Solvent | Conversion (%) | Product (yield %)[b] |
|---|---|---|---|---|
| 1 |  | toluene | 100 |  (100) |
| 2 |  | toluene | 100 |  (97)[c] |
| 3 |  | toluene | 100 |  (93) |
| 4 |  | toluene | 100 |  (70) |
| 5 |  | toluene | 100 |  (14) |
| 6 |  | *n*-heptane | 100 |  (86) |
| 7 |  | cyclohexane | 100 |  (97) |

[a] 100 mg of **PS-SO$_3$H**, 50 mg of **SG-MNP-PEI-Pd**, 1.5 mmol of substrate, 5 mL of solvent, 200 psi $H_2$, 90 °C, 4 h. [b]Determined by GC and $^1$H-NMR, missing percentage belongs to coupling products. [c]Missing percentage belongs to starting reactant.

then dried under a vacuum of 0.2 mmHg at 40 °C for 24 h. The black xerogel (3.1 g) was milled to give fine powder and the loading of the palladium catalyst was 0.323 mmol/g.

**2.7. General Procedure for One-Pot Reaction in a Single Vessel.** Cross-linked polystyrene sulfonic acid (100 mg) and SG-MNP-PEI-Pd (50 mg) were added to toluene (5 mL) containing the appropriate substrate (1.5 mmol) and placed in a 45 mL glass-lined autoclave. After sealing, the autoclave was purged three times with hydrogen and pressurized with 200 psi of hydrogen. The autoclave was placed in an oil bath and heated at 90 °C. After 2.5 h, the autoclave was cooled to room temperature and the hydrogen was released. After separation of the catalysts, the solution was concentrated and the products were analyzed by spectral methods.

**2.8. General Procedure for the Separation between the Two Catalytic Solids.** At the end of the one-pot reaction, the magnetically separable catalyst, SG-MNP-PEI-Pd, was collected aside to the vessel wall using external magnetic field and the solid acid catalyst, PS-SO$_3$H, was decanted with the products solution to another vessel and then collected by filtration. The palladium-based catalyst was washed twice with dichloromethane (10 mL) and then sonicated for 10 min in the presence of $CH_2Cl_2$ (10 mL). After magnetic separation, the catalyst was dried under a vacuum of 0.2 mmHg for 12 h and reused for catalyzing other reactions as described in sections 2.9, 2.10, and 2.11.

**2.9. General Procedure for the Carbonylation Reaction of Iodoarenes.** To a solution of the appropriate iodoarene (1.5 mmol) and triethylamine (0.45 mL, 3.2 mmol) in methanol (5 mL) was added the dried catalyst that was magnetically separated from the one-pot reaction. The mixture was placed in a 45 mL glass-lined autoclave, the autoclave was sealed, purged three times with carbon monoxide, and pressurized with 200 psi of carbon monoxide. The autoclave was placed in oil bath and heated at 110 °C. After 8 h, the autoclave was cooled to room temperature and the carbon monoxide was released carefully. The catalyst was magnetically separated and the solution was decanted and concentrated by evaporation of the solvent. Ether (60 mL) was added to the residue and the ethereal solution was washed with aqueous hydrochloric acid (1N) (2 × 15 mL), saturated sodium hydrogen carbonate (10 mL), and distilled water (3 × 20 mL). The ethereal solution was dried over magnesium sulfate and then concentrated under reduced pressure. The products were analyzed by GC and $^1$H NMR.

**2.10. General Procedure for the Suzuki Reaction.** To a solution of the appropriate iodoarene (1.5 mmol), $Cs_2CO_3$ (0.73 g, 2.2 mmol) and phenylboronic acid (0.238 g, 1.95 mmol) in 1,4-dioxane (5 mL) was added the dried catalyst that was magnetically separated from the one-pot reaction. The mixture was placed in a tube, which was sealed under $N_2$ using a rubber septum, and heated at 90 °C for 16 h. After separation of the catalyst by an external magnetic field, the solution was decanted, filtrated, and concentrated by evaporation of the solvent. Ether (80 mL) was added to the residue and the ethereal solution was washed with aqueous hydrochloric acid (1N) (2 × 20 mL), saturated sodium hydrogen carbonate (10 mL), and distilled water (3 × 20 mL). The ethereal solution was dried over magnesium sulfate and then concentrated under reduced pressure. The products were analyzed by GC and $^1$H NMR.

**2.11 Procedure for the Heck Reaction.** To a solution of a 4′-iodoacetophenone (0.369 g, 1.5 mmol), triethylamine (0.45 mL, 3.2 mmol) and n-butyl acrylate (0.28 mL, 1.95 mmol) in toluene (5 mL) was added the dried catalyst that was magnetically separated from the one-pot reaction. The mixture was placed in a tube, which was sealed under $N_2$ using a rubber septum, and heated at 90 °C for 16 h. After separation of the catalyst by an external magnetic field, the solution was decanted and concentrated by evaporation of the solvent. Ether (60 mL) was added to the residue and the ethereal solution was washed with aqueous hydrochloric acid (1N) (2 × 15 mL), saturated sodium hydrogen carbonate (10 mL), and distilled water (3 × 20 mL). The ethereal solution was dried over magnesium sulfate and then concentrated under reduced pressure. The products were analyzed by GC and $^1$H NMR.

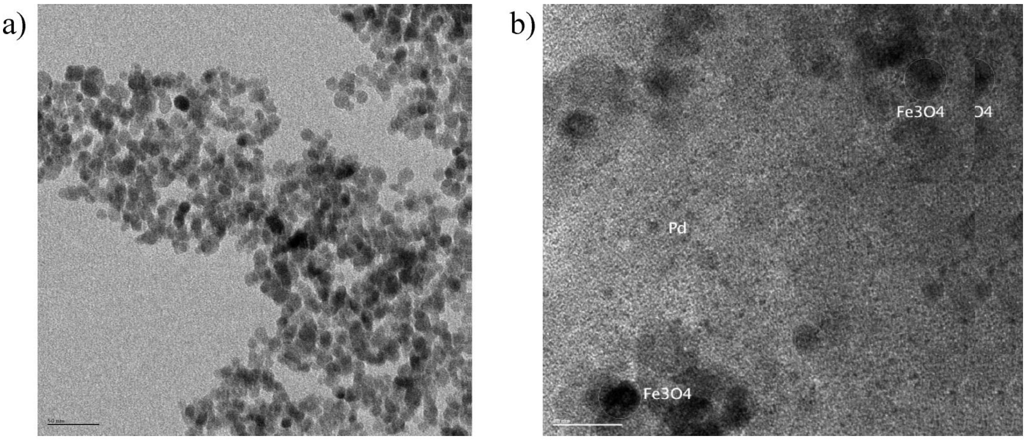
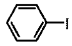
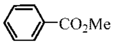
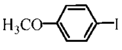
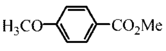
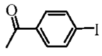
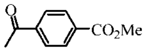
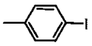
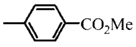
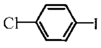
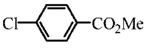
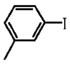
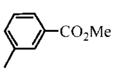


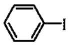
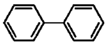
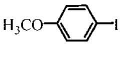
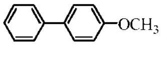
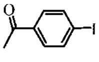
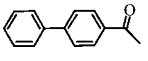
**Figure 5.** (a) TEM micrograph of magnetic nanoparticles modified with ionic liquid–liquid groups (**MNP- IL-C$_4$**), scale bar is 50 nm. (b) TEM micrographs of the magnetically separable palladium-based catalyst (**SG-MNP-PEI-Pd**) after one-pot reaction, scale bar is 20 nm.

**Table 2. Carbonylation of Iodoarenes Catalyzed by Magnetically Separable Palladium-Based Catalyst That Was Separated from the Reaction Mixture for the One-Pot Dehydration/Hydrogenation of α-Tetralol**[a]

| Entry | Substrate | Conversion (%) [b] | Product | Yield (%) [c] |
|---|---|---|---|---|
| 1 |  | 98 |  | 98 |
| 2 |  | 100 |  | >99 |
| 3 |  | 100 |  | >99 |
| 4 |  | 98 |  | 98 |
| 5 |  | 97 |  | 97 |
| 6 |  | 100 |  | >99 |

[a] **SG-MNP-PEI-Pd** (50 mg), 1.5 mmol of substrate, 0.45 mL of triethylamine, 5 mL of dry methanol, 200 psi carbon monoxide, 110 °C, 8 h. [b] Determined by GC. [c] Determined by GC and $^1$H-NMR.

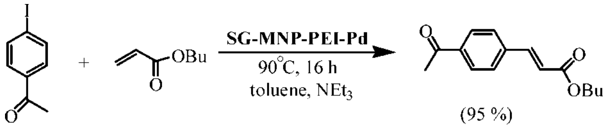
**Table 3. Suzuki Coupling of Iodoarenes and Phenylboronic Acid Catalyzed by Magnetically Separable Palladium-Based Catalyst That Was Separated from the Reaction Mixture for the One-Pot Dehydration/Hydrogenation of α-Tetralol**[a]

| Entry | Substrate | Conversion (%)[b] | Product | Yield (%)[c] |
|---|---|---|---|---|
| 1 |  | 88 |  | 88 |
| 2 |  | 100 |  | >99 |
| 3 |  | 100 |  | >99 |

[a] **SG-MNP-PEI-Pd** (50 mg), 1.5 mmol of iodoarene, 2.2 mmol of Cs$_2$CO$_3$, 1.95 mmol of phenylboronic acid, 5 mL of 1,4-dioxane, 90 °C, 16 h. [b] Determined by GC. [c] Determined by GC and $^1$H-NMR.

## 3. Results and Discussion

**Scheme 4. Heck Reaction Catalyzed by Magnetically Separable Palladium-Based Catalyst**



### 3.1. Modification of Polyethylenimine (PEI).

Hyperbranched polyethylenimine was modified via reactions with its secondary and primary amine groups. First the primary amine groups were reacted with lauric acid without organic solvent at 160 °C for 36 h. During the reaction, water was formed and distilled off. After this amidation reaction the resulted polymer containing hydrophobic alkyl chains in the periphery is soluble in organic solvents but not soluble or dispersible in water. The second modification was obtained by reaction between the remaining secondary amine groups in the alkylated PEI and DL-glycidol. By this modification the percentage of the tertiary amine groups in the polymer is increased, and the core of the polymer becomes more hydrophilic because of the increase in the hydroxyl groups. The whole process for the modifications of PEI is illustrated in Scheme 1.

### 3.2. Preparation of Magnetic Nanoparticles Modified with Ionic Liquid Groups.

Magnetic nanoparticles were readily prepared via coprecipitation of Fe(II) and Fe(III) ions in basic solution at 85 °C according to Massart's method.[23] Typically, 8–12 nm of magnetite nanoparticles could be formed using this route, as confirmed by TEM analysis. However, the bare magnetite nanoparticles could not be soluble in any medium, including water, and they rapidly aggregate. To overcome this limitation, it was necessary to modify the surface of the magnetic nanoparticles with organic groups that can enhance their solubility in organic solvents. The modification occurred via grafting 1-butyl-3-(3-trimethoxysilylpropyl)-1*H*-imidazol-3-ium chloride (**IL-C$_4$**) on the surface of the magnetite nanoparticles. The **IL-C$_4$**was prepared simply by reaction of (3-chloropropyl)trimethoxysilane with 1-butylimidazole without solvent, and by heating at 120 °C. The grafting process is carried out by reaction of the hydroxyl groups existing on the surface of the magnetic nanoparticles with the trimethoxysilane group of **IL-C$_4$** (Scheme 2). The loading of the ionic liquid groups in the modified magnetic nanoparticles (**MNP- IL-C$_4$**) was 0.6

mmol/g as determined by TGA analysis (Figure 1). The resulted ionic liquid-modified magnetic nanoparticles were highly soluble in polar organic solvents like methanol and water.

**3.3. Preparation of Magnetically Separable Palladium-Based Silica Sol–Gel/PEI-$C_{12}$-GLY Composite.** The sol–gel process is used widely for the heterogenization of catalysts under mild conditions via encapsulation of homogeneous catalysts.[3d] Importantly, the encapsulated catalysts could be recycled after filtration from the reaction mixture. In this study we utilized the sol–gel process to design a heterogeneous catalyst that can be separated by an easier and cheaper method based on applying an external magnetic field. The design is based on coencapsulation of palladium catalyst and ionic liquid-modified magnetic nanoparticles in the presence of the modified PEI within silica sol–gel matrix. The role of the modified PEI in this design is to coordinate with the palladium catalyst via its numerous coordinating sites, and to increase the loading of the catalyst in the final material as well to prevent possible leaching of the catalyst during the reactions. In addition, the modified PEI can increase the hydrophobicity of the silica sol–gel matrix and increase the stability of the magnetic nanoparticles in acidic solutions. Using unmodified PEI caused a rapid and uncontrollable polycondensation of tetraethoxysilane, and partial gelation occurred as a result of this fast condensation.

The preparation of the magnetically separable palladium catalyst was performed as follows: $Pd(OAc)_2$ was mixed with **PEI-$C_{12}$-GLY** in methanol and after sonication a clear yellow-reddish solution was obtained. The resulted solution was mixed with **MNP-IL-$C_4$** and then added to a TEOS solution, which was hydrolyzed under acidic conditions. After gelation and aging steps, the solvents were removed under vacuum at 40 °C and a black xerogel (**SG-MNP-PEI-Pd**) was obtained. The **SG-MNP-PEI-Pd** catalyst was analyzed by Powder XRD (Figure 2), which confirms the presence of the magnetic nanoparticles in the silica sol–gel matrix. Thus, the XRD pattern of **SG-MNP-PEI-Pd** contains the characteristic peaks of the magnetite nanoparticles as well a broad peak between $2\theta = 10°$ and $2\theta = 33°$, which belongs to amorphous silica produced by the sol–gel process. In addition, TGA analysis of the **SG-MNP-PEI-Pd** catalyst (Figure) shows that the organic content in the composite catalyst is 20% and it belongs mainly to the **PEI-$C_{12}$-GLY**.

**3.4. One-Pot Dehydration/Hydrogenation Reactions Catalyzed by Heterogeneous Acid Catalyst and the Magnetically Separable Palladium-Based Catalyst (SG-MNP-PEI-Pd).** The basic idea behind this study is to develop a method to facilitate the separation between two solids functionalized with different catalysts and used in a one-pot reaction. The separation between such catalytic solids enables their reuse in other synthetic applications. The separation method for different catalytic solids, which we developed in the current study, is based on magnetic separation of one of the catalytic solids while the other one can be separated by filtration methods. Such a separation process is illustrated in Figure 4 in which two catalytic solids are mixed in the same vessel (Figure 4 a) and after one-pot reaction, the magnetically separable catalytic solid is accumulated to one side of the vessel wall after applying external magnetic field (Figure 4 b), and then the other catalytic solid is decanted with the reaction mixture to another vessel which can be then separated from the mixture by filtration (Figure 4 c).

The two catalytic solids utilized in this study are the designed **SG-MNP-PEI-Pd** as the hydrogenation catalyst and the cross-linked polystyrene sulfonic acid (**PS-$SO_3$H**) as the solid acid catalyst. These catalytic solids were applied in sequence reactions for the dehydration of benzyl alcohols and then the hydrogenation of the formed olefin intermediates (Scheme 3). The **PS-$SO_3$H** was used to catalyze the dehydration process of benzylic alcohols and the **SG-MNP-PEI-Pd** was utilized to catalyze the hydrogenation of the double bonds formed after the dehydration reaction, giving alkylated arenes as the final products. At the end of the reactions the catalysts were separated from each other by first applying an external magnetic field to separate the **SG-MNP-PEI-Pd**, and then decantation of the solid acid catalyst (**PS-$SO_3$H**) to a second vessel, which was removed from the reaction mixtures by simple filtration.

Various benzylic alcohols were tested in this sequence of reactions of dehydration/hydrogenation catalyzed by the magnetically separable palladium-based catalyst and the solid acid catalyst (Table 1). Thus, 1,2,3,4-tetrahydronaphthalene was produced exclusively when α-tetralol was mixed with **PS-$SO_3$H** and **SG-MNP-PEI-Pd** catalysts in toluene and heated for 4 h at 90 °C and at a pressure of 200 psi of hydrogen (Table 1, entry 1). On the other hand, the presence of the catalysts together was necessary for a successful reaction; thus, no reaction was obtained when α-tetralol was mixed under the same conditions with **SG-MNP-PEI-Pd**, and only 1,2-dihydronaphthalene was obtained using the catalyst **PS-$SO_3$H**. Moreover, when 1-phenyl-propan-1-ol was used as the substrate, 97% of propylbenzene was obtained (Table 1, entry 2). When the substrates used in this reaction sequence have the possibility to stabilize the carbocation intermediate that is formed during the dehydration reaction, coupling products were also formed. Thus, 1-naphalen-2-yl-ethanol gave 93% of 2-ethylnaphthalene and 7% of coupling products formed by reaction of toluene with the carbocation produced in the first step for the dehydration of 2-ethylnaphthalene (Table 1, entry 3). The attempts to reduce the amount of the **PS-$SO_3$H** or to increase it failed to give better results. These coupling products were increased when 1-*m*-tolyl ethanol or 1-*p*-tolyl ethanol were used as sustrates. In the case of 1-*m*-tolylethanol, 70% of 1-ethyl-3-methylbenzene was produced and 30% of the coupling products (Table 1,entry 4), and only 14% of the desired product was formed when 1-*p*-tolyl ethanol was used as sustrate (Table 1, entry 5). However, it was possible to reduce the amount of the undesired coupling products by changing the solvents to those that can destabilize the intermediate carbocation or can not react with it. Thus, when 1-*p*-tolyl ethanol was reacted in *n*-heptane the percentage of the desired product increased to 86% (Table 1, entry 6) and when it was reacted in cyclohexane, 97% of the desired product was obtained (Table 1, entry 7). After the one-pot reactions, the **SG-MNP-PEI-Pd** catalyst was analyzed by TEM and it was observed that palladium nanoparticles of 2 nm were formed as illustrated in Figure 5.

**3.5. Reuse of the Palladium-Based Catalyst (SG-MNP-PEI-Pd) in Other Reactions after Magnetic Separation from One-Pot Dehydration/Hydrogenation Reactions.** The palladium-based catalyst that was used for the one-pot reactions discussed above was magnetically separated and reused to catalyze successfully three types of reaction: carbonylation of iodoarenes, Suzuki, and Heck coupling reactions. Several iodoarenes were easily carbonylated and converted to aromatic carboxylate esters using the **SG-MNP-PEI-Pd** catalyst that was separated from the reaction mixture for the dehydration/hydrogenation of α-tetralol. Excellent results for this catalytic reaction are presented in Table 2. For example, iodobenzene was converted to methyl benzoate (Table 2, entry 1) when it was heated to 110 °C for 8 h under 200 psi of carbon monoxide and in the presence of the palladium-based catalyst. There is no electronic effect on this reaction. For example, 1-(iodo-phenyl)-ethanone or 1-chloro-4-iodo benzene, which containing electron withdrawing groups, gave quantitative yields of the corresponding aromatic ester (Table 2, entries 3 and 5 respectively). Quantitative yields were also obtained when substrates with electron donating groups like 1-iodo-4-methoxybenzene and 1-iodo-4-methylbenzene were subjected to carbonylation (Table 2, entries 2 and 4 respectively). Also, the position of the electron-donating group did not affect the carbonylation reaction (Table 1, compare entries 4 and 6).

Another reuse of the magnetically separated palladium catalyst was demonstrated by the Suzuki reaction. Thus, three different iodoarenes were coupled with phenyl boronic acid using **SG-MNP-PEI-Pd** that was separated from the reaction mixture of dehydration/hydrogenation of α-tetralol. The results for these coupling reactions are summarized in Table 3. While iodoarenes with electron donating or electron withdrawing group gave quantitative yields of the coupling products (Table 3, entries 2 and 3 respectively), the non-substituted iodobenzene afforded biphenyl in a somewhat lower yield.

The third reuse of the separated palladium-based catalyst was demonstrated for the Heck coupling reaction. Thus, when 4′-iodo acetophenone was reacted with n-butyl acrylate, catalyzed by **SG-MNP-PEI-Pd** that was magnetically separated from the reaction mixture of dehydration/hydrogenation of α-tetralol, 3-(4-acetyl-phenyl)-acrylic acid butyl ester (Scheme 4) was obtained in 95% yield.

## 4. Conclusions

A palladium catalyst was encapsulated in silica sol–gel-modified polyethylenimine composite in the presence of ionic-liquid-modified magnetic nanoparticles. The resulting solid catalyst was easily attracted to an external magnetic field. This new catalyst was applied to one-pot dehydration/hydrogenation reactions of benzylic alcohols. In these reactions, the palladium-based catalyst was mixed together with cross-linked polystyrene sulfonic acid in order to first catalyze the dehydration of the benzyl alcohols and then to hydrogenate the double bonds formed during the first reaction. At the end of these one-pot reactions, the palladium-based catalyst was separated magnetically from the reaction mixture and reused for other applications including the carbonylation of iodoarenes to aromatic esters, as well as the Suzuki and Heck coupling reactions.

We believe that the current findings can be useful for industrial applications where one catalyst can be cheaply and easily separated and used for several other applications. Moreover, the current method of separation between two solids that was developed in this study can be utilized in many other domains.

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