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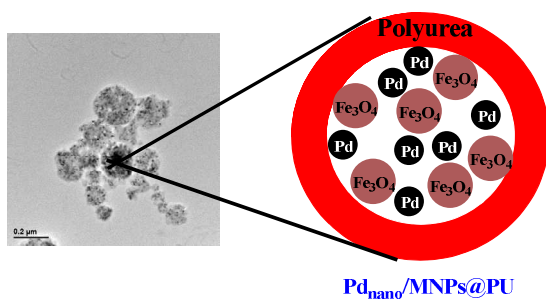


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We report the preparation of magnetically separable catalytic polymeric nanoreactors by simultaneous encapsulation of palladium and magnetite nanoparticles within polyurea nanocapsules. The new catalytic material is applied in aqueous hydrogenation reactions.

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ARTICLE TYPE

# Palladium Nanoparticles Encapsulated in Magnetically Separable Polymeric Nanoreactors

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A method for immobilization of palladium nanoparticles in magnetically separable polymeric nanocapsules is presented. The method is based on co-encapsulation of palladium nanoparticles stabilized by hyperbranched polyamidoamine (H-PAMAM-C<sub>15</sub>) modified with palmitoyl groups and hydrophobic magnetite nanoparticles within polyurea nanospheres. The synthesis of these polyurea nanospheres is based on nanoemulsification of chloroform, containing magnetic nanoparticles and palladium acetate, in water using proper surfactants or dispersants. Then, the chloroform nano-droplets are confined in a polyurea shell formed by interfacial polycondensation between isocyanate and amine monomers. The palladium acetate was reduced with hydrogen to create palladium nanoparticles dispersed in the core of the polyurea nanocapsules. These catalytic polymeric nanoreactors were utilized in hydrogenation of alkenes and alkynes in water. The nanoreactors were easily separated from the reaction mixture via application of external magnetic field. The recyclability of these nanoreactors was examined in hydrogenation of styrene, no significant change was observed in their reactivity for up to four cycles.

## Introduction

In the past decades catalysis by metal nanoparticles (NPs) has been intensively investigated due to their large surface area and their unique properties.<sup>1</sup> The nanoparticles have two major drawbacks; they tend to aggregate and their recovery using trivial procedures is difficult. Employing an electrostatic, steric or electrostatic-steric stabilizer can prevent aggregation of the metal nanoparticles. Common stabilizers are organic polymers,<sup>2</sup> dendrimers,<sup>3</sup> surfactants<sup>4</sup> and organic ligands.<sup>5</sup> Recoverability is achieved by immobilization of NPs that also can prevent their aggregation. Immobilization on solid supports,<sup>6</sup> such as inorganic materials and organic polymers, is used extensively. Other immobilization techniques are based on encapsulation of metallic NPs in sol-gel matrices<sup>7</sup> and in metal organic frameworks.<sup>8</sup> In addition, encapsulation of metal NPs in the shell of polymeric microcapsules has attracted great attention in the past years, because it provides immobilization and protection of NPs from the reaction media.<sup>9</sup> For example, encapsulation of palladium nanoparticles and their application in catalytic hydrodechlorination of chlorophenols was demonstrated.<sup>10</sup> The separation and the recyclability of this encapsulated catalysts was easily enabled by centrifugation.

Magnetic nanoparticles (MNPs) have been recently utilized widely as supports for catalysts, by modification of the MNPs surface.<sup>11</sup> The supported catalysts have proven as effective in numerous organic transformations and were easily separated from the reaction media by applying an external magnetic field. Magnetic nanoparticles have also been utilized recently in immobilization of metal nanoparticles.<sup>12</sup> These magnetically

separable metal nanoparticles are prepared mainly by adsorption of metal ions on the surface of the magnetic nanoparticles. This can be done by using functionalized MNPs with coordinating groups or on MNPs coated with a silica layer, containing specific stabilizing groups. Finally, the loaded ions are reduced with hydrogen, sodium borohydride or hydrazine.

Here, we present a new method for the immobilization of palladium nanoparticles that can be magnetically separable as well. The method is based on encapsulation of palladium nanoparticles and hydrophobic MNPs in the core of polyurea nanocapsules. These nanocapsules were prepared by nanoemulsification and interfacial polymerization techniques between isocyanate and amine monomers.<sup>13</sup> The resulted new materials were characterized and their catalytic activity was explored in hydrogenation of alkenes and alkynes in aqueous medium. By applying an external magnetic field, they were easily separated from the reaction medium and were recycled four times in hydrogenation of styrene in water.

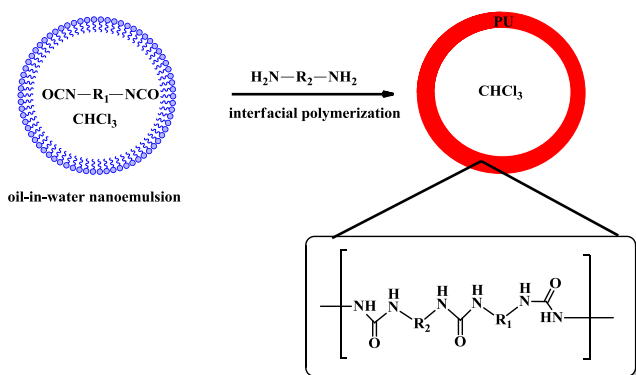
## Results and Discussion

### Synthesis and Characterization of Polyurea Nanocapsules

Generally, the polyurea nanocapsules were prepared in two steps. The first step included nanoemulsification of chloroform, containing the isocyanate monomer, in water. Stabilization of the chloroform nano-droplets in water was done using 4% of surfactant. In the second step, interfacial polycondensation reaction occurred when an amine monomer was added slowly to the chloroform-water nanoemulsion. Polymeric nanospheres were formed after stirring for 16 hours at room temperature. The

preparation process is illustrated in Scheme 1. To optimize the synthesis process of the polyurea nanocapsules, different parameters such as the type of the surfactant, the isocyanate and the amine monomers, were examined and their effect on the polymeric nanocapsules structure was studied.

Initially, different surfactants were employed in the preparation of nanocapsules. The monomers polymethylene polyphenyl isocyanate (PAPI 27) and 1,6-hexamethylenediamine (HMDA) were selected to create the polyurea shells. In particular, the polyoxyethylene (20) sorbitan monooleate (Tween 80), polyoxyethylene (20) stearyl ether (Brij 78), butylated polyvinylpyrrolidone (Bu-PVP), sodium dodecyl sulfate (SDS), cetyltrimethylammonium chloride (CTAC) and the dispersant lignosulfonic acid (Reax 88A) were tested. Phase separation was observed during the interfacial polymerization when Brij 78 was utilized to stabilize the nanoemulsion. When Tween 80 was used, only polyurea chunks were produced. All other surfactants enabled formation of polyurea capsules. However, the desired small-sized polyurea nanocapsules could be obtained only when the surfactant CTAC or the dispersant Reax 88A were utilized. This was indicated by dynamic light scattering measurements (DLS) (Table 1) and scanning electron microscopy (SEM) images (Figure 1). In addition, transmission electron microscopy (TEM) analysis (Figure 2) showed a core shell structure indicating the formation of hollow nanocapsules.



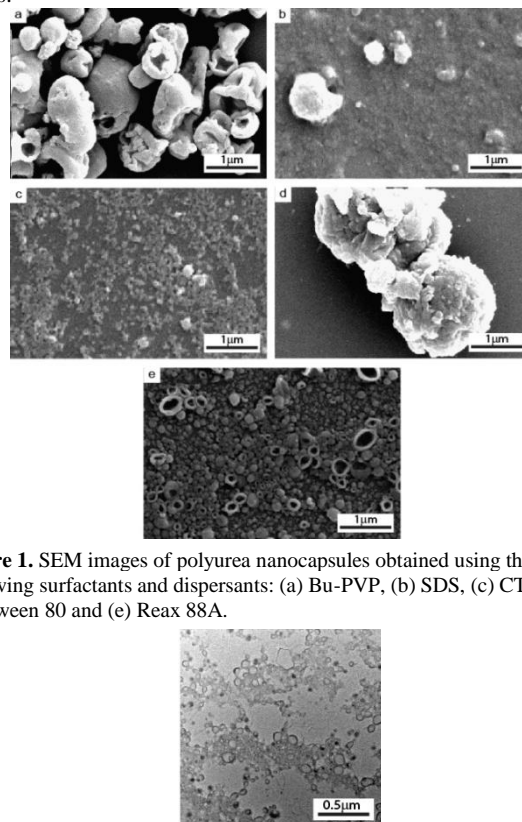
**Scheme 1.** Preparation of polyurea nanocapsules.

**Table 1.** Average size distribution of capsules formed using different surfactants or dispersants

Entry	Surfactant	Average size distribution (nm)
1	Bu-PVP	1755
2	SDS	245
3	CTAC	114
4	Tween 80	polyurea chunks
5	Reax 88	105

The effect of the amine and isocyanate monomers on the construction of polyurea nanocapsules was examined with Reax 88A as the stabilizer of the nanoemulsions. The monomers used were HMDA and diethylenetriamine (DETA), as the amine monomers, and 4,4'-methylene-bis(cyclohexylisocyanate) (MBDI), 2,4-toluene diisocyanate (TDI), 1,6-hexamethylene diisocyanate (HDI) and PAPI 27, as the isocyanate monomers. SEM images (Supporting Information, Figure S1) and DLS measurements (Supporting Information, Table S1) indicate that nanocapsules were produced when the combinations of PAPI 27

and DETA or HMDA, as well as the combination of MBDI and DETA or HMDA were used. In the presence of PAPI 27 the capsules formed were smaller; therefore, the isocyanate PAPI 27 was chosen as the optimized isocyanate monomer. The monomers PAPI 27 and DETA are trifunctional monomers, and in their presence highly cross-linked shells can be formed. The degree of cross linking affects the diffusion of the substrate into the capsule core. Thus, in order to form strong shells that enable diffusions of the reactants into the nanocapsules, HMDA and PAPI 27 were chosen as the monomers for building the polymeric shells.



**Figure 1.** SEM images of polyurea nanocapsules obtained using the following surfactants and dispersants: (a) Bu-PVP, (b) SDS, (c) CTAC (d) Tween 80 and (e) Reax 88A.

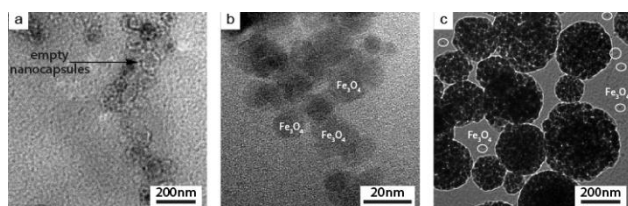
**Figure 2.** TEM images of polyurea nanocapsules obtained using Reax 88A, with an isocyanate amine molar ratio of 1:1.73.

The effect of the PAPI 27:HMDA molar ratios, on the formation of the polyurea nanocapsules, was examined using seven different molar ratio: 1:0.4, 1:0.7, 1:0.9, 1:1.1, 1:1.25, 1:1.5 and 1:1.73, using Reax 88A as the emulsion stabilizer. SEM images (Supporting information, Figure S2) and DLS measurement (Supporting information, Table S2) showed no significant change in the nanocapsule size. Furthermore, Brunauer-Emmett-Teller (BET) measurements were performed for both PAPI 27:HMDA molar ratios, 1:1 and 1:1.73; the pore radius observed was 24.636 Å and 33.028 Å respectively.

### 75 Magnetically Separable Polyurea Nanocapsules (MNPs@PU nanocapsules)

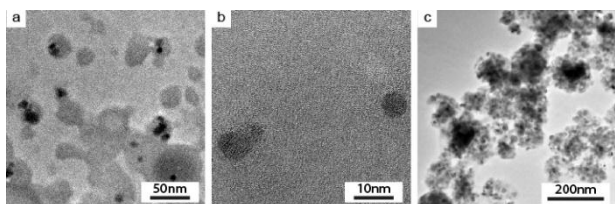
Encapsulation of MNPs in polyurea nanocapsules was performed by a similar procedure utilized in the preparation of the polyurea nanospheres. Therefore, chloroform containing magnetite nanoparticles coated with oleate groups and PAPI 27, was nanoemulsified in water. HMDA was added in order to start

interfacial polymerization, thus yielding magnetically separable polyurea nanocapsules. This process was studied using two different PAPI 27: HMDA molar ratios, 1:1 and 1:1.73, in the presence of CTAC or Reax 88A as stabilizers. Both molar ratios enabled the formation of nanocapsules. According to DLS measurements, when 1:1 molar ratio was applied the average size of the nanocapsules was 106 nm and 110 nm in the presence of CTAC and Reax 88A, respectively. At 1:1.73 ratio, capsules were formed with an average size of 113 nm and 224 nm using CTAC and Reax 88A, respectively. Although when CTAC was used with 1:1 molar ratio, TEM analysis indicated that the MNPs were not encapsulated (Figure 3a and Figure 3b). A shell-core structure was observed, indicating polyurea nanocapsules were formed though no MNPs were found within the core (Figure 3a). MNPs were only seen outside the capsule (Figure 3b). In 1:1.73 ratio, encapsulation of MNPs was partially achieved and MNPs were seen outside the capsules as well as within; as observed in TEM images (Figure 3c). It seems that the MNPs were extracted from the oil droplets during the formation process of the nanocapsules. This may be explained by the ability of CTAC to form micelles in water, which can extract the MNPs and stabilize them in the aqueous medium.



**Figure 3.** TEM images of MNP@PU nanocapsules prepared in the presence of CTAC with different amine:isocyanate molar ratios. (a) and (b) ratio of 1:1; (c) ratio of 1:1.73.

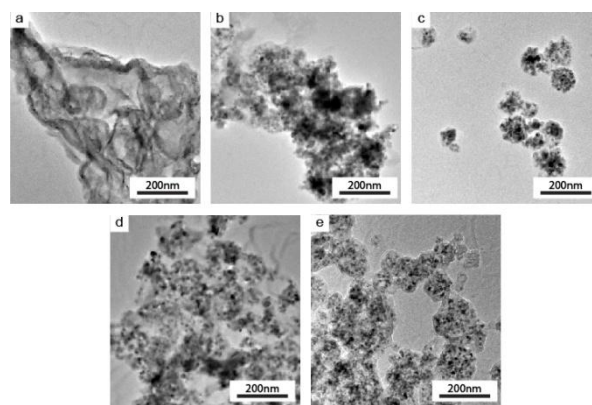
In the presence of the dispersant Reax 88A at 1:1 isocyanate:amine ratio, the MNPs encapsulation was accomplished, although most of the capsules observed by TEM were empty (Figure 4a). Furthermore, a small of non-encapsulated MNPs were observed (Figure 4b). On the other hand, the encapsulation process of MNPs at 1:1.73 isocyanate:amine ratio was successful, and no MNPs were seen outside the nanocapsules (Figure 4c). Energy dispersive X-ray spectroscopy (EDX) measurement (Supporting Information, Figure S3) was performed and coincided with TEM analysis, which demonstrated encapsulation of MNPs nanoparticles, within the polymeric nanocapsules. In addition, X-ray diffraction (XRD) measurements were performed (Supporting information, Figure S4). The XRD pattern shows characteristic peaks of magnetite,  $\text{Fe}_3\text{O}_4$ .



**Figure 4.** TEM images of MNP@PU nanocapsules prepared in the presence of Reax 88A with different amine:isocyanate molar ratio. (a) and (b) ratio of 1:1; (c), ratio of 1:1.73.

The encapsulation of MNPs within the core enables facile

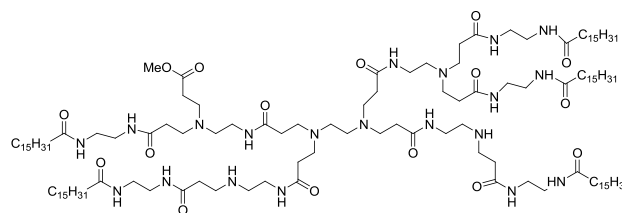
separation of the nanocapsules from the aqueous medium, by applying an external magnetic field. In order to ensure fast and easy separation different loading percentages of MNPs were examined. In all loading percentages polyurea nanocapsules were formed. Though, at low loading percentages, 1.5%, TEM analysis (Figure 5a) revealed that the nanocapsules formed are mostly empty capsules. With loading percentages of 2.5% and up, TEM images (Figure 5) indicate that the nanocapsules formed contain the required MNPs. In order to facilitate fast separation of the polyurea nanocapsules, the loading percentage was chosen to be 9%.



**Figure 5.** TEM images representing different MNPs loading percentage. (a) 1.5%, (b) 2.5%, (c) 5%, (d) 7.5% and (e) 9%.

### Palladium Nanoparticles Encapsulated in Polyurea Nanoreactors ( $\text{Pd}_{\text{nano}}@PU$ nanocapsules)

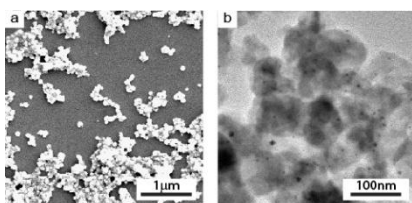
After establishing a method for the formation of magnetically separable nanocapsules, their ability to act as nanoreactors was examined. Thus, palladium acetate and hyperbranched polyamidoamine modified with palmitoyl groups (H-PAMAM- $\text{C}_{15}$ ) (Scheme 2), were dissolved in chloroform and nanoemulsified in water. This was followed by polycondensation to form polyurea nanocapsules. The resulted nanocapsules were treated with hydrogen in order to reduce Pd(II) to Pd(0), and yield the  $\text{Pd}_{\text{nano}}@PU$  catalyst. In order to prevent aggregation of the formed Pd nanoparticles, H-PAMAM- $\text{C}_{15}$  was added. H-PAMAM- $\text{C}_{15}$  can stabilize Pd particles *via* coordinative interaction between the amine groups of the H-PAMAM- $\text{C}_{15}$  and the Pd nanoparticles.



**Scheme 2.** Structure of hyperbranched polyamidoamine modified with palmitoyl groups (H-PAMAM- $\text{C}_{15}$ ).

SEM analysis (Figure 6a) of the resulted heterogeneous catalyst revealed aggregates with apparent border lines between each nanocapsules, indicating the aggregation is due to the high vacuum required for imaging. This correlates with the average

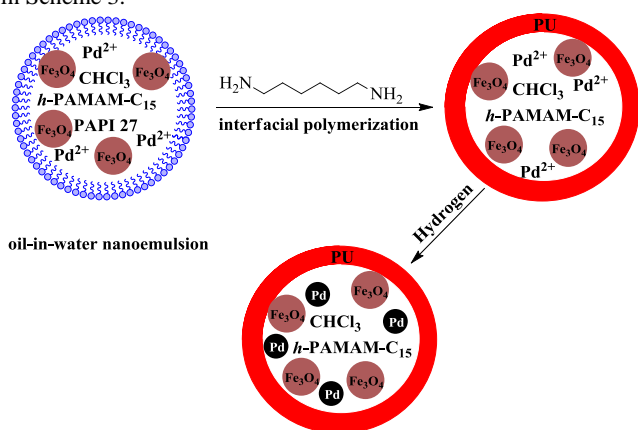
size distribution obtained in DLS measurements. DLS measurements showed an average size of 220nm, an increase of 100 nm in the capsules size (Supporting Information, Table S3, entry 1 and Entry 2), after encapsulation of the palladium nanoparticles. Apparently, encapsulation of H-PAMAM-C<sub>15</sub> and palladium acetate, which was converted to palladium nanoparticles, within the nanocapsules, led to the increase in their size. TEM analysis (Figure 6b) indicates that palladium nanoparticles are formed and encapsulated within the polyurea nanocapsule. The average size of the palladium nanoparticles was 10.3 nm (Supporting Information, Figure S5).



**Figure 6.** (a) SEM image of Pd<sub>nano</sub>@PU nanocapsules after treatment with hydrogen. (b) TEM image of Pd<sub>nano</sub>@PU nanocapsules after treatment with hydrogen.

### Palladium Nanoparticles Encapsulated in Magnetically Separable Nano-reactors (Pd<sub>nano</sub>/MNP@PU nanocapsules)

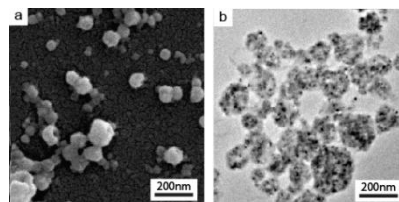
After achieving the ability of polyurea nanocapsules to be easily separated, by encapsulation of MNPs, as well as to perform as heterogeneous catalysts, by encapsulation of palladium acetate and their reduction; our goal was to combine both abilities and form recyclable catalytic nanoreactors. Therefore, MNPs, palladium acetate, H-PAMAM-C<sub>15</sub> and PAPI 27 were dissolved in chloroform and nanoemulsified in water. This was followed by the addition of HMDA, to form a polyurea nanocapsule by interfacial polymerization. The resulted nanocapsules were treated with hydrogen, in order to form the desired heterogeneous catalyst Pd<sub>nano</sub>/MNP@PU. The preparation process is illustrated in Scheme 3.



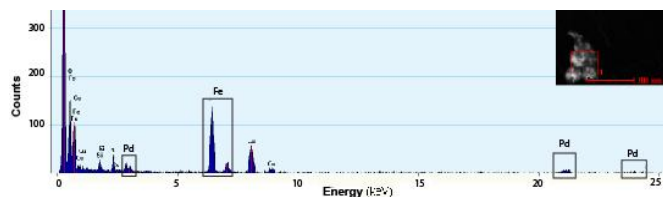
**Scheme 3.** Preparation of Pd<sub>nano</sub>/MNP@PU nanocapsules

SEM and TEM analysis (Figure 7) reveal formation of polyurea nanocapsules, with an average size of 220 nm correlating with data obtained using DLS (Supporting Information, Table S3, Entry 3). EDX measurements show presence of Pd and Fe, demonstrating that simultaneous encapsulation of Pd and MNPs was achieved (Figure 8). Further

indication for the presence of Pd in the nanocapsules was obtained using inductively coupled plasma mass spectrometry (ICP) measurements, in which the Pd concentration was 0.013 mmol/g. In addition, thermal gravimetric analysis (TGA) measurements (Supporting Information, Figure S6) show that the nanocapsules are composed of 9 % non-decomposable materials attributed to the MNPs and the Pd nanoparticles. Furthermore, the TGA curve demonstrates a total weight loss of 5% at 50 °C, ascribed to the removal of volatile compounds, such as chloroform. The sharp mass reduction step at 220 °C (86%) corresponds to the decomposition of the polyurea shell and the H-PAMAM-C<sub>15</sub>.



**Figure 7.** (a) SEM image of Pd<sub>nano</sub>/MNP@PU nanoreactors. (b) TEM images Pd<sub>nano</sub>/MNP@PU nanoreactors.



**Figure 8.** EDX measurements of Pd<sub>nano</sub>/MNP@PU nanoreactors.

### Catalytic Application of Pd<sub>nano</sub>/MNP@PU nanocapsules

The catalytic ability of the magnetically separable catalyst Pd<sub>nano</sub>/MNP@PU was examined in hydrogenation reaction of various alkenes and alkynes, in aqueous media. The reactions were performed under 200 psi of hydrogen for 6.5 hours. After the reactions were completed, the catalyst was easily separated from the reaction medium, *via* an external magnetic field. These results are summarized in Table 2.

The reduction of aromatic alkenes was successful, and saturated products were obtained in excellent yields (Table 2, entry 1-6). No effect of withdrawing and donor groups was observed. The selectivity of Pd<sub>nano</sub>/MNP@PU nanoreactors in reduction of cinnamic aldehyde was examined (Table 2, entry 7); only the C=C could be reduced, and 3-phenylpropanal was obtained in a yield of 66%. In addition, the hydrogenation reaction of aromatic alkynes was effective, and fully saturated products were achieved in high yields (Table 2, entry 8-10). The recyclability of the catalyst was tested in hydrogenation of styrene. The catalyst did not lose its reactivity, and full conversions of styrene to ethylbenzene were obtained in four consecutive cycles. Importantly, no significant change could be observed in the capsule's morphology and size, as was confirmed by SEM analysis of the recycled catalyst (Figure 9). The reaction medium after the separation of the nanoreactors, was analyzed using ICP, in which no palladium was detected.

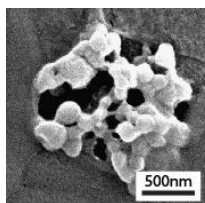


Figure 9. SEM image of the recycled catalyst Pd<sub>nano</sub>/MNPs@PU.

Table 2. Hydrogenation of alkenes and alkynes by Pd<sub>nano</sub>/MNPs@PU nanoreactors.<sup>a</sup>

Entry	Substrate	Product	Yield (%) <sup>b</sup>
1			100
2			100
3			96
4			100
5			100
6			99
7			66
8			87
9			100
10			100

<sup>a</sup> 4 mmol of substrate, 2.6x10<sup>-2</sup> mmol Pd, 2 mL H<sub>2</sub>O, 200 psi H<sub>2</sub>, room temperature, 6.5 hours

<sup>b</sup> Determined by <sup>1</sup>H NMR and GC.

## Conclusion

The design and immobilization of Pd nanoparticles together with MNPs in polyurea nanocapsules was described. These nanoreactors can be easily separated from the reaction medium by applying an external magnetic field, and act as catalysts in hydrogenation of alkenes and alkynes at room temperature, in aqueous medium. The ability to separate these nanoreactors from the reaction media enables the recyclability of the catalyst.

We anticipate that the method for catalyst immobilization in magnetically separable nanocapsules, developed in this work, can be applied in different fields and may lead to new opportunities in the area of green chemistry.

## Experimental Section

**Materials.** lignosulfonic acid, polymethylene polyphenyl isocyanate and butylated polyvinylpyrrolidone were contributed

by FMC Corporation. All other reagents were purchased from either Acros or Sigma-Aldrich, and were used without further purification, with the exception of methyl acrylate, which was purified under reduced pressure.

**Instrumentation.** NMR measurements were performed on a 400 MHz and 500 MHz Bruker spectrum. Images were acquired using High resolution scanning electron microscopy (HR SEM) Sirion (FEI Company), using Shottky type Field Emission Source and secondary electron (SE) detector. The images were scanned at 5Kv acceleration voltages. Transmission Electron Microscopy and Electron diffraction spectroscopy were performed with (S) Tecnai F20 G<sup>2</sup> (FEI company), operated at 200 kV. Inductively coupled plasma mass spectrometry measurements were performed on 7500cx (Agilent company), using an external standard calibration. Dynamic light scattering measurements were performed using Nano-zeta sizer (Malvern instruments), model ZEN3600. Gas chromatography (GC) was used to analyze the hydrogenation products. GC was performed using Agilent-GC-7890A with a capillary column (HP-5, 30 meters) and a thermal conductivity detector (TCD). Emulsification was performed using Kinematica Polytron homogenizer PT-6100, equipped with dispersing aggregates 3030/4EC. Thermogravimetric analysis was performed on Mettler Toledo TG 50 analyzer. Measurements were carried out at a temperature range that extended from 25 – 950 °C, at a heating rate of 10 °C /min, under air atmosphere. Sonication was performed using Sonics Vibra Cell, model VCX-130 (130 watt). The average molecular mass of H-PAMAM was determined by matrix assisted laser desorption ionization-time of flight (MALDI-TOF) using a Voyager DE PRO MALDI-TOF mass spectrometer (Applied Biosystems). The mass spectra were acquired using a matrix of α-cyano-4-hydroxycinnamic acid, in the linear positive ion mode by using an accelerating voltage of 25000 V, grid voltage of 94%, guide wire of 0.05%, and extraction delay time of 340 msec. Surface areas were determined by N<sub>2</sub> Brunauer-Emmett-Teller method (NOVA-1200e). Pore volume and radius was measured using BJH model. Powder X-ray diffraction analysis was performed using X-ray Diffractometer D8 Advance.

### Synthesis of Hydrophobic Magnetite Nanoparticles.

Magnetite nanoparticles were prepared according to Massart's method.<sup>14</sup> Briefly: 400 mL of H<sub>2</sub>O was degassed for 15 min under nitrogen. Then, 11.6 g (42.9 mmol) of FeCl<sub>3</sub>·6H<sub>2</sub>O and 4.3 g (21.6 mmol) of FeCl<sub>2</sub>·4H<sub>2</sub>O were added and heated at 85 °C. 15 mL of concentrated ammonium (28%) was added and the mixture was heated for additional 30 min. After that, 18 mL (57 mmol) of oleic acid was added, resulting in the formation of a black precipitant. The mixture was stirred for additional 5 min, and then cooled to room temperature. The black precipitant was collected and washed five times with water, five times with acetone, and then dispersed in 50 mL of chloroform.

**General Procedure for the Synthesis of Hyperbranched Polyamidoamine (H-PAMAM).**<sup>15</sup> Ethylenediamine (18.03 g, 0.3 mol) was dissolved in 28 mL of methanol, and added to a 100 mL single neck flask. Then, methyl acrylate (25.83 g, 0.3 mol) was slowly added, with constant stirring, over a period of 20 minutes. After 48 h of room temperature stirring, the methanol was removed under reduced pressure, and the resulted material was

heated at 60 °C for 1h, 100 °C for 2 h, 120 °C for 2 h and 140 °C for 2h, under vacuum. 34.26 g (95%) of a light yellow viscous dope was obtained. Elementary Anal.: C, 51.75; H, 8.56; N, 23.32. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.80-2.32 (NH<sub>2</sub>-NH), 2.30-2.52(COCH<sub>2</sub>), 2.51-3.02 [COCH<sub>2</sub>CH<sub>2</sub>NH, NH (CH<sub>2</sub>)<sub>2</sub>NH, NH (CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>], 3.20-3.50 (NCH<sub>2</sub>), 3.50-4.0 (CH<sub>3</sub>O). <sup>13</sup>C NMR (D<sub>2</sub>O, 125 MHz) δ: 31-59 (CH<sub>2</sub>, CH<sub>3</sub>), 171-178 (C=O). MALDI-TOF: *m/z*=5798.90.

**General Procedure for the Synthesis of Hyperbranched Polyamidoamine (H-PAMAM-C<sub>15</sub>).** Palmitoyl chloride (6 g, 0.0218 mol) was dissolved in 15 mL CHCl<sub>3</sub>, and added to a solution of H-PAMAM (2 g, 0.083 mol) in 30 mL CHCl<sub>3</sub> and of triethylamine (6.1 mL, 0.044 mol). The reaction was stirred for 24 h at 35 °C, under nitrogen. Then, the mixture was cooled to room temperature and washed with 50 mL water three times. The organic layer was collected and dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The material was poured in 100 mL methanol and the precipitate was collected, washed with methanol and dried under vacuum. 3.5 g (40%) of a yellow wax were obtained. Elementary Anal.: C, 72.19; H, 12.93; N, 10.97. FTIR (KBr, cm<sup>-1</sup>) 3311, 2924, 2852, 1644, 1376, 1219, 722, 586. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ: 0.87-0.89 (t, 3H, CH<sub>3</sub>), 1.24-1.26 (2H, -CH<sub>2</sub>), 1.52-1.58 (2H, -CH<sub>2</sub>), 2.29-2.40 (2H, -NCH<sub>2</sub>), 3.34-3.67 (2H, -NCH<sub>2</sub>, -OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ: 14.1, 22.68, 23.90, 29.27-29.72, 31.92-31.93, 42.82, 211.

**General Procedure for Preparation of Polyurea Nanocapsules.** Isocyanate monomer (0.7-1.1 g) was dissolved in 8.9 g of CHCl<sub>3</sub> and later emulsified with 33.5 g of water, containing proper surfactant (2.0 g), by milling at 14,000 rpm for 1 min. Then 5 drops of 1M HCl were added, the emulsion was sonicated for 17 min and the amine monomer (0.9-1.3 g) was dropped slowly. The resulted mixture was stirred for 16 h at room temperature.

**General Procedure for Preparation of Pd@PU Nanoreactors.** 2.0 g of Reax 88A were dissolved in 33.5 g of water and homogenized for 1 min at 14,000 rpm. Then, 1.1 g of PAPI 27, 0.3 g H-PAMAM-C<sub>15</sub>, and 0.15 g palladium acetate were dissolved in 8.9 g of chloroform and emulsified with the water phase for 1 min. After that, 5 drops of 1 M HCl were added, and the emulsion was sonicated for 17 min, and 0.9 g of HMDA (70% in water) was slowly added. Then the solution was stirred for 16 h at room temperature. The next step was to reduce the palladium acetate to Pd nanoparticles, using a glass-lined autoclave. After sealing, the autoclave was purged 3 times with hydrogen and pressurized to 500 psi. The autoclave was stirred at room temperature for 24h.

**General Procedure for Preparation of Pd/MNPs@PU Nanoreactors.** The oil phase containing 1.1 g PAPI 27, 1.0 g of MNPs dispersed in 8.9 g of chloroform, 0.3 g H-PAMAM-C<sub>15</sub> and 0.15 g palladium acetate. Later it was emulsified with the water phase, 2.0 g Reax 88A in 33.5 g water, at 14,000 rpm for 1 min. Then, 5 drops of 1 M HCl were added, the emulsion was sonicated for 17 min and 0.9 g HMDA (70% in water) was slowly added. The solution was stirred for 16 h at room temperature. The formed capsules were separated using a magnetic field, washed three times each with water, ethanol, and water again. The capsules were dispersed in 50 mL of water, and

the palladium acetate was reduced to Pd nanoparticles using a glass-lined autoclave. After sealing, the autoclave was purged 3 times with hydrogen and pressurized to 500 psi. The autoclave was stirred at room temperature for 24h.

**General Procedure for the Hydrogenation Reaction.** 2.0 g of dispersed nanoreactors containing 0.026 mmol of palladium, 2 mL of water and 4 mmol of the appropriate substrate were placed in a 25 mL glass-lined autoclave. After sealing, the autoclave was purged 3 times with hydrogen and pressurized to 200 psi. The autoclave was stirred at room temperature for 6.5 h, and then the gas was released. The capsules were separated by a magnetic field, washed with water, and used for subsequent cycles. The product was extracted with chloroform and passed through Celite layer before analysis with NMR and GC.

## Notes and references

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† Electronic Supplementary Information (ESI) available: SEM images and DLS measurements of polyurea nanocapsules formed from different amine and isocyanate monomers, EDS analysis of MNPs@PU capsules, TGA curve of Pd<sub>nano</sub>/MNPs@PU. See DOI: 10.1039/b000000x/

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