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BMIm-PF_6@SiO_2 Microcapsules: Particulated Ionic Liquid as A New Material for the Heterogenization of Catalysts

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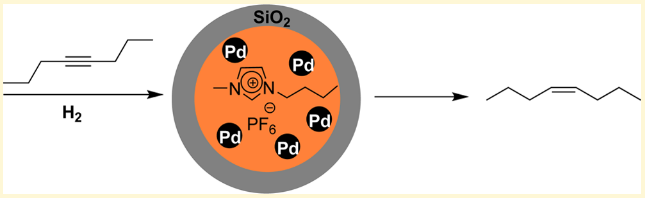
Supporting Information

ABSTRACT: A method for the preparation of silica microcapsules containing a high loading of ionic liquids (ILs) is described. The method paves the way to the conversion of ionic liquids into particulated materials, which results in ILs with new properties without changing their molecular structures. The synthesis of these new materials is based on the emulsification of ionic liquids in water, using surfactants or dispersants, and the resulting ionic liquid droplets are then confined in a silica shell formed via interfacial hydrolysis and polycondensation of tetraethoxysilane. This material can be isolated by centrifugation, followed by drying to yield a fine powder of ionic liquid-silica microcapsules, which are water and organic solvents redispersible. These new materials are utilized in the heterogenization of palladium catalyst and then applied in the hydrogenation of alkynes. The catalyst shows chemoselectivity in the hydrogenation of internal alkynes such as 4-octyne. Comparative studies have shown that the same catalyst loses this selectivity when it is applied under homogeneous conditions.



1. INTRODUCTION

In the last three decades, intensive investigations have been carried out aimed at developing methods and materials for heterogenization of homogeneous catalysts.[1] The goal of these studies was to combine the advantages of homogeneous and heterogeneous catalysis. For this purpose, different materials, such as organic polymer solids,[2] polymeric microcapsules,[3] inorganic solids,[4] metal organic frameworks (MOFs)[5] and nanoparticulated materials[6] were designed and utilized efficiently as support in the immobilization of homogeneous catalysts. In many cases, these heterogenized catalysts could easily be recycled. However, tuning the reactivity and the selectivity of the heterogenized catalysts in organic transformations is still a major challenge.

In recent years, ionic liquids (ILs)[7] have attracted considerable attention due to their potential for application in diverse fields including catalysis,[8] organic synthesis,[9] electrochemistry,[10] and separations.[11] They are nonvolatile, nonflammable, thermally and chemically stable, easily handled and their polar noncoordinating properties allow them to dissolve a broad spectrum of organic, inorganic and polymeric materials. Because of these unique properties, they have been considered as green alternative media to conventional organic solvents. However, their relatively high viscosities lead to difficulties in their separation and practical applications. To overcome or circumvent these limitations, solid state ionic liquid materials have been prepared by immobilization of ionic liquids on porous solids[12] or polymer membranes,[13] and by direct polymerization of ionic liquids functionalized with vinyl groups.[14] In addition, ionic liquids have been recently encapsulated in polymeric shells[15] or carbon shells.[16]

Recently, silica microcapsules prepared by the sol−gel method have been tested in controlled release formulations as an alternative to polymeric microcapsules.[17] The main method employed for the synthesis of these microcapsules is usually based on an emulsion/sol−gel approach. Thus, an oil phase containing silicon tetraalkoxide monomers (e.g., tetraethoxysilane) is emulsified in water using surfactants and then an interfacial polycondensation process takes place to generate a silica shell around the oil droplets. The morphology and the properties of the silica shell can be controlled easily by performing the interfacial polymerization of the silane monomers under different pH or temperature conditions. In addition, the type of the silane monomer employed as a precursor for creating the silica shell has a significant effect on its morphology and porosity.

We describe herein, a method for the synthesis of particulated ionic liquids by preparing silica microcapsules that contain high loading of ionic liquids in their cores. This approach of surrounding microdroplets of ionic liquids with silica shells is regarded to be a powerful tool for designing ionic liquids with new properties. We also demonstrate that the new material, composed of ionic liquid core-silica shell microparticles, can be utilized in entrapment of palladium catalysts.

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These “heterogenized” catalysts are applied in the hydrogenation of alkynes.

2. EXPERIMENTAL SECTION

2.1. Materials. Polyoxyethylene (20) sorbitan monooleate (Tween 80), polyethylene glycol octylphenyl ether (Triton X-100), polyoxyethylene (20) stearyl ether (Brij 78), sodium dodecyl sulfate (SDS), the triblock copolymer poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) (Pluronic P123), Pd/C (10%), the alkyne substrates, *trans*-4-octene, and palladium acetate were purchased from Sigma-Aldrich. Sodium lignosulfonate (Reax 88B), lignosulfonic acid (Reax 88A) and butylated polyvinylpyrrolidone (Bu-PVP) were contributed from FMC Corporation. Tetraethoxysilane (TEOS) was contributed from Sol−Gel Technologies. The ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIm-PF_6) was purchased from Chemada Fine Chemicals.

2.2. Instrumentation. Scanning electron microscope (SEM) was employed to analyze the morphology of the BMIm-PF_6-silica microcapsules. The experiments were performed on high resolution scanning electron microscope (HR SEM) Sirion (FEI company) using Shottky-type field emission source and secondary electron (SE) detector. The images were scanned at voltage of 5kV. Transmission electron microscope (TEM) and electron diffraction spectroscopy (EDS) were performed with (S) TEM Tecnai F20 G^2 (FEI Company, USA) operated at 200 kV. Thermogravimetric analysis (TGA) was performed on Mettler Toledo TG 50 analyzer. Measurements were carried out at temperature range that extended from 25−950 °C at heating rate of 10 °C/min under N_2 atmosphere. Dynamic light scattering (DLS) was utilized to determine the size distribution of the BMIm-PF_6-silica microcapsules. Those measurements were performed on Nano Series instrument of model Nano-Zeta Sizer (Malvern Instruments) model ZEN3600. Gas chromatography (GC) (Aglient Technologies, 7890A) with a capillary column (HP-5, 30 m) was used to analyze the hydrogenation products. ^1H NMR and ^{13}C NMR spectra were recorded with Bruker DRX-400 instrument. Solid-state ^{29}Si MAS, ^{13}C MAS, and ^{31}P MAS NMR spectra were recorded with Bruker DRX-500 instrument. Emulsifications were performed using Kinematica Polytron homogenizer PT-6100 equipped with dispersing aggregate 3030/4EC. Inductively coupled plasma mass spectrometry measurements (ICP) were performed on 7500cx (Agilent company) using an external standard calibration.

2.3. General Procedure for the Preparation of BMIm-PF_6@SiO_2 Microcapsules. 1-Butyl-3-methylimidazolium hexafluorophosphate (1.5−3.75 g) was emulsified with 15.9 g of water containing a proper surfactant (0.6−2.5 g) by milling at 11000 rpm for 2 min. Then, tetraethoxysilane (TEOS) (3.25−5.25 g) was dropped slowly and the resulted mixture was stirred at room temperature for 12 h. The resulted BMIm-PF_6@SiO_2 microcapsules were separated from the mixture by centrifugation, washed three times with water and then analyzed by scanning electron microscope (SEM).

2.4. Preparation of Pd/BMIm-PF_6@SiO_2 Microcapsules. Reax 88A (1.6 g) was dissolved in 15.9 g of water and homogenized for 1 min at 8900 rpm to give the water phase. Then, 30 mg (0.13 mmol) of palladium acetate was dissolved in 3.75 g of 1-butyl-3-methylimidazolium hexafluorophosphate and then emulsified with the water phase by homogenization at 11000 rpm for 2 min. After that, 3.75 g of TEOS was added dropwise and homogenization continued for 2 min, followed by stirring at room temperature for 12 h. The resulted silica microcapsules were separated from the suspension by centrifugation and the brownish precipitate was washed three times with 40 mL of water to remove excess of reagents. The silica microcapsules were dispersed in 50 mL of water and transferred to a glass-lined autoclave, which was then pressurized with 500 psi hydrogen. The mixture was stirred under hydrogen atmosphere for 24 h. Finally, the resulted Pd/BMIm-PF_6@SiO_2 microcapsules were separated by centrifugation and dried to yield 5 g of brown powder. The palladium loading in this material was 0.04 mmol/g.

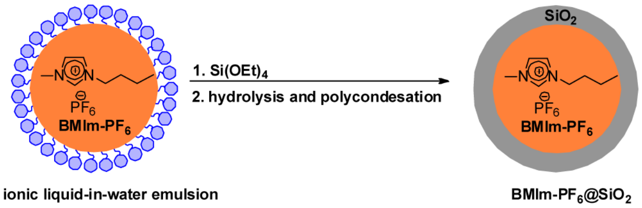
2.5. Procedure for the Preparation Pd/SiO_2 (5%). Palladium acetate (527.4 mg, 2.35 mmol) and 5 g of silica were mixed in 150 mL of chloroform. The mixture was stirred at room temperature for 6 h and then the chloroform was evaporated to dryness affording an orange fine powder. The adsorbed palladium acetate on silica was reduced by 500 psi H_2 and a black powder was obtained.

2.6. General Procedure for the Hydrogenation Reactions with Pd/BMIm-PF_6@SiO_2 Microcapsules. Pd/BMIm-PF_6@SiO_2 (150 mg) containing 6×10^{-3} mmol Pd, was dispersed in 2 mL of proper solvent and 1.0 mmol of substrate were placed in a 25 mL glass-lined autoclave. After sealing, the autoclave was purged three times with hydrogen and pressurized to 500 psi. The mixture was stirred at room temperature for 24 h and then the hydrogen was released. The microcapsules were separated by centrifuge, washed twice with the same medium, and used for subsequent cycles. The products were analyzed by ^1H NMR and GC chromatography. When the medium of the reaction was water, the products were first extracted with ether and then analyzed by ^1H NMR and GC chromatography.

3. RESULTS AND DISCUSSION

3.1. Preparation of Ionic Liquid-Silica Microcapsules. The silica microcapsules filled with an ionic liquid were prepared according to the emulsion/sol−gel approach. To emulsify an ionic liquid in water, we chose an ionic liquid that is immiscible with water. For that purpose, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIm-PF_6) was selected as the water emulsifiable ionic liquid. The formation process of the BMIm-PF_6 silica microcapsules (BMIm-PF_6@SiO_2 microcapsules) is illustrated in Scheme 1.

Scheme 1. Illustration of the Preparation Process of Ionic Liquid−Silica Microcapsules



The first step in this process was based on the emulsification of BMIm-PF_6 in water using a proper surfactant to stabilize the dispersed ionic liquid droplets. Numerous surfactants and dispersants were examined: Tween 80, Triton X-100, Brij 78, SDS, Pluronic P123, Reax 88B, and Reax 88A. The desired spherical BMIm-PF_6@SiO_2 capsules were observed only in the presence of Reax 88A as visualized in the SEM images (Supporting Information, Figure S1). The surfactant should be suitable to interact with both the aqueous phase and the BMIm-PF_6 phase. BMIm-PF_6 is more polar than organic solvents. Therefore, a surfactant with long hydrophobic chains decreases the ability to stabilize the ionic liquid droplets. In the second step, the silane monomer, tetraethoxysilane (TEOS), was slowly added to the ionic liquid-water emulsion, and silica shells confining the ionic liquid droplets were formed after stirring for 12 h, at room temperature. The confinement of BMIm-PF_6 droplets with a silica layer is based on electrostatic interactions. The encapsulation procedure is carried out under pH = 4. Above pH = 2 the silanol groups are partially deprotonated forming negatively charged silanolates. These groups electrically interact with the positively charged imidazolium groups in the ionic liquid. The resulting BMIm-PF_6@SiO_2 microcapsules were isolated and washed by simple centrifugation. This separation process also sheds light on the stability of the formed microcapsules and the robustness of their silica shells. Destruction of the microcapsules yielded a separated layer of the ionic liquid after centrifugation, while the desired products were obtained as a fine brown precipitate. After it was dried, a fine powder of BMIm-PF_6@SiO_2 microcapsules, as particulated ionic liquid, was collected (Figure 1). This powder could be redispersed easily in water or in organic solvents.

Figure 1. Picture of the ionic liquid BMIm-PF_6 (left) versus powder of BMIm PF_6@SiO_2 microcapsules (right).

Various analyses were performed to characterize the BMIm-PF_6@SiO_2 microcapsules. The size of the microcapsules was determined using dynamic light scattering (DLS) analysis, which showed an average size of 3.6 μm (Figure 2). To reveal the structure of the resulting microcapsules, they were analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results of the TEM analysis (Figure 3a) confirmed the formation of a core−shell structure of the microcapsules, with an average shell thickness of 90−110 nm. On the other hand, SEM analysis (Figure 3b) indicated that the BMIm-PF_6@SiO_2 microcapsules were spherical, and their surface showing some degree of roughness in addition to high porosity. BET measurements were performed and the surface area obtained was 47.4 m^2/g. Infrared analysis (IR) (Figure 4) revealed the presence of characteristic band at wavelength of 3400 cm^{-1}, which belongs to the Si−OH stretch, and of 1090 cm^{-1}, which was assigned to the Si−O−Si stretch. In addition, the bands at 3120 and 3160 cm^{-1} that are attributed to the C−H ring stretching vibration of the imidazolium indicates the presence of the ionic liquid BMIm-PF_6 within the silica microcapsules. Thermal gravimetric analysis (TGA) was used to investigate the decomposition of BMIm-PF_6, Reax 88A in comparison to BMIm-PF_6@SiO_2 microcapsules in order to evaluate the loading percentage of the ionic liquid (Supporting Information, Figure S2). The analyses were performed under N_2 atmosphere at temperature range of 25−950 °C with 10 °C/min heating rate. It can be seen in the weight loss curve of BMIm-PF_6@SiO_2 microcapsules (Supporting Information, Figure S2) that there are five stages of weight losses. The first, a small weight loss centered at 80 °C, which probably belongs to the desorption of physically adsorbed water molecules on the silica shell. The other four weight losses centered at 185, 240, 330, and 650 °C are ascribed to the decomposition of the encapsulated ionic liquid and the dispersant Reax 88A. This analysis demonstrated a decomposition of about 70% of organic material. To estimate the percentage of ionic liquid in the capsules, additional method was required to determine the proportion of Reax 88A. Therefore, elementary analysis of sulfur was performed, and 1.3% was obtained. Furthermore, elementary analysis of pure Reax 88A detected 11.71% of sulfur. These results indicate that the percentage of Reax 88A within the capsules is 3.6%. Thus, the loading of ionic liquid within the capsule is 66.4% and the percentage of SiO_2 in the capsule is 28%. In the ^{13}C MAS NMR of the BMIm-PF_6@SiO_2 microcapsules (Figure 5b), the

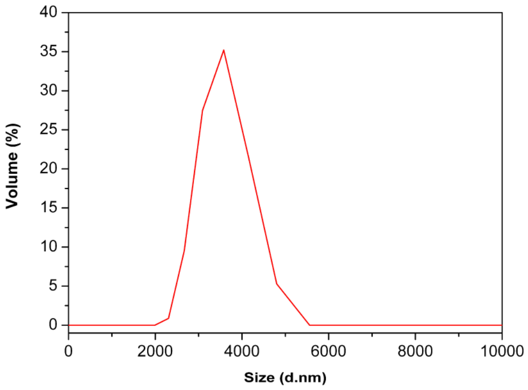


Figure 2. Size distribution of BMIm-PF_6@SiO_2 microcapsules.

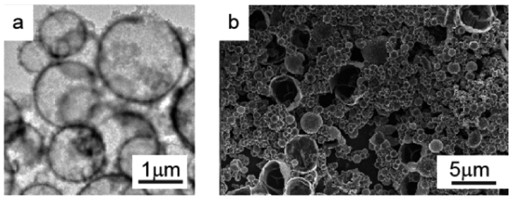


Figure 3. (a) TEM image of the BMIm-PF_6@SiO2 microcapsules. (b) SEM image of BMIm-PF_6@SiO2 microcapsules.

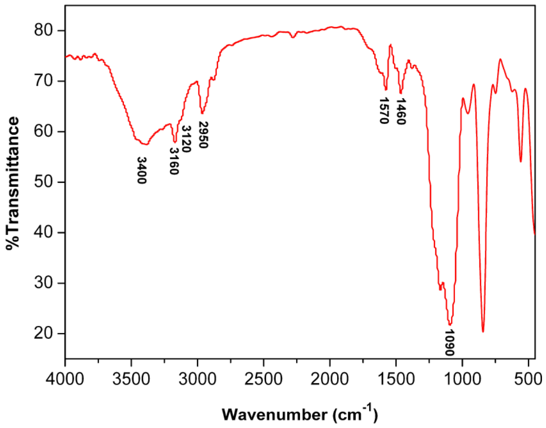


Figure 4. IR spectrum of BMIm-PF_6@SiO_2 microcapsules.

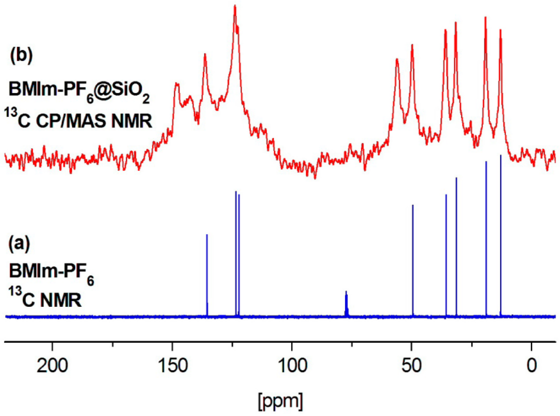


Figure 5. (a) ^{13}C NMR spectrum of the ionic liquid BMIm-PF_6. (b) ^{13}C MAS NMR spectrum of BMIm-PF_6@SiO2 microcapsules.

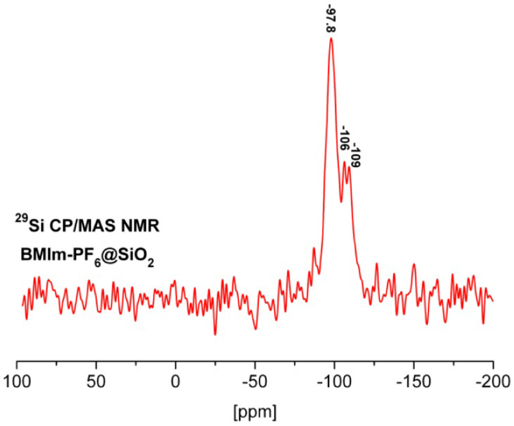


Figure 6. ^{29}Si MAS NMR spectrum of BMIm-PF$_6$@SiO$_2$ microcapsules.

characteristic peaks of the ionic liquid BMIm-PF$_6$ were all present, as was judged by comparing the solid NMR spectrum with the ^{13}C NMR spectrum of the nonencapsulated BMIm-PF$_6$ (Figure 5a). Furthermore, ^{29}Si MAS NMR analysis indicated the presence of Q_3 ([$SiO_3(OH)$], −97.8 ppm) and Q_4 ([SiO_4], −109 ppm) species in the structure of the microcapsules shell (Figure 6). In addition, the peak at −106 ppm belongs to a [$SiO_3(OEt)$] species, which indicates that some of the ethoxide groups were not hydrolyzed. This observation was also confirmed by ^{13}C MAS NMR analysis in which the characteristic peaks of the ethoxide groups appear at 18.8 and 56.5 ppm. The peak of the methyl in the ethoxide groups at 18.8 ppm overlaps with one carbon peak of the ionic liquid BMIm-PF$_6$. Preparing silica by sol−gel process that usually performed under ambient conditions can produce materials that contain alkoxide groups in their structure. These groups can be eliminated by condensation reaction with silanol groups during aging process or treatment at high temperatures. In the case of BMIm-PF$_6$@SiO$_2$ microcapsules, heating at high temperature can affect the structure of the ionic liquid−silica microcapsules and therefore was avoided. The peak at 147.4 is attributed to the aromatic carbons of Reax 88A indicating that some of the Reax 88A is entrapped within the capsule shell. The other characteristic peaks of Reax 88A overlap with the BMIm-PF$_6$ and the ethoxy groups of the silica shell. These results correlate with the elementary analysis mentioned above. ^{31}P MAS NMR was performed in order to establish if hydrolysis of BMIm-PF$_6$@SiO$_2$ occurs during encapsulation. The ^{31}P MAS NMR spectra (Supporting Information, Figure S3) show that the encapsulation process does not affect the BMIm-PF$_6$ chemical structure.

To optimize the preparation of the BMIm-PF$_6$@SiO$_2$ microcapsules, different parameters such as surfactant concentration, ionic liquid/water phase ratio and TEOS/ionic liquid ratio, were examined to evaluate their effect on the structure of the microcapsules. Thus, when Reax 88A was applied at concentrations of 2.5%, 5%, 7.5%, and 10% (weight-to-weight, w/w), spherical microcapsules were obtained (Supporting Information, Figure S4). However, the formation of silica particles as byproducts was minimized significantly when the percentage of Reax 88A was 7.5% (w/w). Interestingly, the w/w ratio of the ionic liquid to TEOS had great effect on the synthesis of BMIm-PF$_6$@SiO$_2$ microcapsules. Spherical microcapsules could be achieved when the ratio of BMIm-PF$_6$ to TEOS was increased from 20:80 up to 50:50 (Supporting Information, Figure S5). However, it was very difficult to obtain microcapsules when the w/w percentage of TEOS was greater than 50% (Supporting Information, Figure S5). Furthermore, varying the concentration of BMIm-PF$_6$ in the emulsion from 13% to 21% (w/w) could lead to the production of microcapsules with spherical morphology (Supporting Information, Figure S6). Nevertheless, stable microcapsules without leakage of the ionic liquid were produced only when the concentration of the ionic liquid was 21%.

3.2. Heterogenization of Palladium Catalyst Using Ionic Liquid−Silica Microcapsules. The new materials, based on BMIm-PF$_6$@SiO$_2$ microcapsules, were utilized in the heterogepnization of a palladium catalyst. The procedure for the preparation of this entrapped catalyst was based on dissolving palladium acetate in BMIm-PF$_6$, followed by emulsification in water and construction of the silica shell around the ionic liquid droplets by polycondensation of TEOS. The resulting microcapsules were treated with hydrogen to reduce Pd(II) to Pd(0), which yielded the catalyst Pd/BMIm-PF$_6$@SiO$_2$. TEM analysis (Figure 7) of the resulting heterogeneous catalyst indicated the formation of palladium nanoparticles, with an average size of 7 nm (Supporting Information, Figure S7). In addition, electron diffraction spectroscopy (EDS) measurements supported the presence of palladium in the BMIm-PF$_6$@SiO$_2$ microcapsules (Supporting Information, Figure S8). When the catalyst Pd/BMIm-PF$_6$@SiO$_2$ was analyzed by X-ray powder diffraction (XRD), only a broad peak between 2θ = 10 and 2θ = 33 was obtained, which is attributed to the amorphous silica shell of the microcapsules (Supporting Information, Figure S9). No characteristic peaks of palladium nanoparticles could be detected by the XRD analysis due to their low concentration within the microcapsules. DLS analysis showed an average size of 2.0 μm (Supporting Information, Figure S10). BET measurement demonstrated an increase in the capsule surface area to 97.7 m^2/g after encapsulation of the Pd nanoparticles. This can be explained by the decrease in the capsule size with the palladium encapsulation.

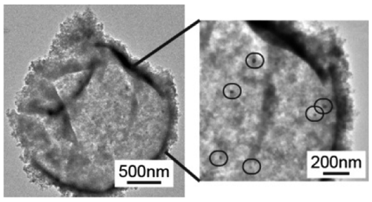


Figure 7. TEM image of Pd/BMIm-PF$_6$@SiO$_2$.

3.3. Catalytic Performance of Pd/BMIm PF$_6$@SiO$_2$. The performance of the catalyst Pd/BMIm-PF$_6$@SiO$_2$ was tested in the hydrogenation of terminal and internal alkynes. The catalyst, Pd/BMIm-PF$_6$ was reacted with different alkynes in diethyl ether under 500 psi of hydrogen for 24 h. Table 1 summarizes the hydrogenation of several of aromatic and aliphatic alkynes. When terminal aromatic alkynes were used, no selectivity was achieved (Table 1, entries 1−3). On the other hand, when terminal aliphatic alkynes were hydrogenated, partial selectivity toward alkenes was observed (Table 1, entries 4−5). In addition reduction of 1-octyne was accompanied by isomerization of the formed 1-octene. Furthermore, hydro-

Table 1. Hydrogenation of Alkynes under Various Conditions[a]

entry	substrate	conversion (%)[b]	products (%)[c]
1	phenylacetylene	100	ethylbenzene (100)
2	4-*tert*-butylphenylacetylene	100	4-*tert*-butyl-4-vinylbenzene (12), 4-*tert*-butyl-4-ethylbenzene (88)
3	4-chlorophenylacetylene	100	1-chloro-4-vinylbenzene (4) 1-chloro-4-ethylbenzene (96)
4	1-octyne	100	1-octene (46), *cis*-2-octene (22), *trans*-2-octene (11), octane (18)
5	cyclohexylacetylene	91	vinyl cyclohexane (62), ethyl cyclohexane (38)
6	diphenylacetylene	95	*cis*-stilbene (100)
7	5-decyne	100	*cis*-5-decene (90), *trans*-5-decene (10)
8	4-ocyne	100	*cis*-4-octene (85), *trans*-4-octene (6), *n*-octane (9)

[a] 1 mmol of substrate, 150 mg Pd/BMIm-PF_6@SiO_2 containing 6×10^{-3} mmol Pd, 2 mL diethyl ether, 500 psi H_2, room temperature, 24 h. [b] Determined by ^1H NMR and GC. [c] Determined by GC.

genation of internal alkynes, (Table 1, entries 6–8), gave higher selectivity to alkenes.

Further performance analysis of the hydrogenation was examined using 4-octyne and different media. The results of these hydrogenation reactions, in addition to results of reactions performed under different condition for comparative studies, are listed in Table 2. To prevent extraction of the ionic liquid from the silica microcapsules, the hydrogenation reactions were performed either in water or organic solvents in which the ionic liquid is immiscible. Thus, the catalyst Pd/BMIm-PF_6@SiO_2 was reacted with 4-octyne in water under 500 psi of hydrogen for 24 h and *cis*-4-octene was formed selectively as the main product (Table 2, entry 1). In addition, only 6% *n*-octane was detected when the same catalyst was utilized to reduce *trans*-4-octene, under the same conditions. On the other hand, when the hydrogenation of 4-octyne was carried out homogeneously using palladium acetate dissolved in BMIm-PF_6, full saturated *n*-octane was generated as the main product (Table 2, entry 10). At the end of this reaction, the formation of palladium black precipitants was observed. We believe the palladium catalyst loses its selectivity because it aggregates to give the black precipitant. Previous reported works demonstrated that selective hydrogenation of alkynes can be obtained when palladium nanoparticles are formed in specific functionalized ionic liquids.[18] These investigations support our assumption that silica microcapsules play a significant role in the stabilization of palladium nanoparticles, after their formation. It seems that producing a microenvironment by confining the ionic liquid droplets with a silica shell prevents the aggregation of the palladium nanoparticles and leads to high selectivity in hydrogenation of 4-octyne. The selectivity of Pd/BMIm-PF_6@SiO_2 in the hydrogenation of 4-octyne was maintained to some extent when it was performed in xylene or diethyl ether (Table 2, entries 3–4). For comparison, hydrogenation of 4-octyne in diethyl ether with palladium on charcoal (10%) and palladium on silica (5%) were conducted, and as expected, only exhaustive hydrogenation occurred (Table 2, entries 6–7). In comparison to BMIm-PF_6, reduction of 4-octyne with Pd/C and Pd/SiO_2 in the presence of BMIm-PF_6 demonstrated lower selectivity (Table 2, entries 8–9). Interestingly, when the hydrogenation of 4-octyne catalyzed by Pd/BMIm-PF_6@SiO_2 was carried out in hexane, the catalyst lost its reactivity (Table 2, entry 2). This result raises the possibility of tuning the reactivity of the same catalyst when it is located in a microenvironment and dispersed in different media. Leaching of the catalyst was examined by separation of the catalytic microcapsules after hydrogenation of 4-octyne via centrifugation at 3000 rpm and reacting the resulted supernatant liquid with 4-octyne. No products were observed indicating that the palladium catalyst did not leach from the silica microcapsules. In addition, ICP analysis was performed, showing that Pd nanoparticles do not leach from the capsules.

Table 2. Hydrogenation of 4-Octyne under Various Conditions.[a]

entry	catalyst	solvent	conversion (%)[b]	products (%)[c]
1	Pd/BMIm-PF_6@SiO_2	water	100	*cis*-4-octene (88), *trans*-4-octene (10), *n*-octane (2)
2	Pd/BMIm-PF_6@SiO_2	hexane	10	*cis*-4-octene (10)
3	Pd/BMIm-PF_6@SiO_2	xylene	100	*cis*-4-octene (84), *trans*-4-octene (5), *n*-octane (11)
4	Pd/BMIm-PF_6@SiO_2	diethyl ether	100	*cis*-4-octene (85), *trans*-4-octene (6), *n*-octane (9)
5[d]	Pd/BMIm-PF_6@SiO_2	diethyl ether	100	*cis*-4-octene (84), *trans*-4-octene (6), *n*-octane (10)
6[e]	Pd/C	diethyl ether	100	*n*-octane (100)
7[e]	Pd/SiO_2	diethyl ether	100	*n*-octane (100)
8	Pd/C	BMIm-PF_6	100	*cis*-4-octene (20), *trans*-4-octene (3), *n*-octane (77)
9	Pd/SiO_2	BMIm-PF_6	100	*cis*-4-octene (68), *trans*-4-octene (9), *n*-octane (23)
10	$Pd(OAc)_2$	BMIm-PF_6	100	*cis*-4-octene (8), *n*-octane (92)

[a] 2.7 mmol of 4-octyne, 6×10^{-3} mmol Pd, 2 mL solvent, 500 psi H_2, room temperature, 24 h. [b] Determined by ^1H NMR and GC. [c] Determined by GC. [d] Reaction was prolonged for 60 h. [e] Reaction was completed after 5 h.

The recyclability of the Pd/BMIm-PF_6@SiO_2 catalyst was tested in three cycles of hydrogenation of 4-octyne. The catalyst was active in all cycles and no significant loss in its selectivity was obtained (Supporting Information, Figure S11). Moreover, the catalytic microcapsules were characterized by SEM and TEM after they were utilized in the hydrogenation reaction and their structure or morphology was not changed (Figure 8a and Figure 8b respectively). In addition, TEM analysis indicates that after reaction, the Pd nanoparticles size does not change (Supporting Information Figure S12). In addition, EDS

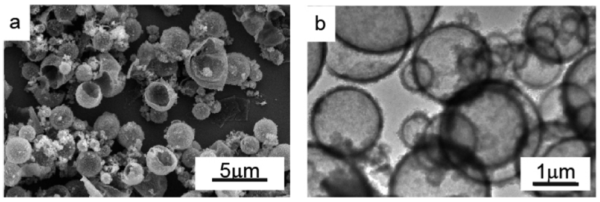


Figure 8. (a) SEM image of Pd/BMIm-PF_6@SiO_2 microcapsules after three cycles of hydrogenation. (b) TEM image of Pd/BMIm-PF_6@SiO_2 microcapsules after three cycles of hydrogenation.

measurement supported the presence of palladium particles after reaction (Supporting Information Figure S13).

4. CONCLUSIONS

We disclosed a method for preparing new materials based on ionic liquids that are encapsulated in silica shells. This method provides particulate ionic liquids in powdered form, and open up opportunities to design ionic liquids with new properties such as lower viscosity. Importantly, the new ionic liquid-silica microcapsules were utilized in the heterogenization of palladium catalyst that show chemoselectivity in the hydrogenation of internal alkynes such as 4-octyne. Remarkably, when the hydrogenation of 4-octyne was performed in ionic liquid under homogeneous conditions, the palladium catalyst lost its selectivity, due to the formation of black aggregates. We believe that the materials developed in this work provide excellent future prospects for many applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

SEM images, XRD pattern, EDS, DLS, and TGA curves of the ionic liquid–silica microcapsules, TGA curves of BMIm-PF_6 and Reax 88A, size distribution of the palladium nanoparticles, and results of the recycling of the catalyst in the hydrogenation reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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■ ABBREVIATIONS

Tween 80, polyoxyethylene (20) sorbitan monooleate; Triton X-100, polyethylene glycol octylphenyl ether; Brij 78, polyoxyethylene (20) stearyl ether; Bu-PVP, butylated polyvinylpyrrolidone; SDS, sodium dodecyl sulfate; Reax 88B, sodium lignosulfonate; Reax 88A, lignosulfonic acid; Pluronic P123, triblock copolymer poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol); ILs, ionic liquids; BMIm-PF_6, 1-butyl-3-methylimidazolium hexafluorophosphate; TEOS, tetraethoxysilane; BMIm-PF_6@SiO_2 microcapsules, BMIM-PF_6-silica microcapsules; Pd/BMIm-PF_6@SiO_2, entrapped catalyst within BMIm-PF_6-silica microcapsules; DLS, dynamic light scattering; SEM, scanning electron microscopy; TEM, transmission electron microscopy; EDX, energy dispersive X-ray spectroscopy; XRD, X-ray powder diffraction

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