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Pd Nanoparticles in Ionic Liquid Brush: A Highly Active and Reusable Heterogeneous Catalytic Assembly for Solvent-Free or On-Water Hydrogenation of Nitroarene under Mild Conditions

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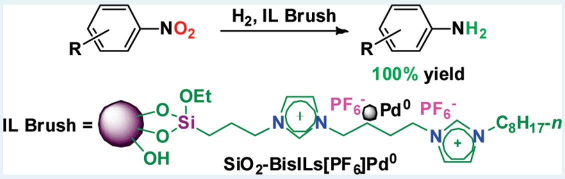
Supporting Information

ABSTRACT: A heterogeneous catalytic assembly of Pd nanoparticles-in-SiO_2 supported ionic liquid brushes has been developed. The catalytic assembly showed uniform Pd particles size distribution. The catalyst allowed the hydrogenation of nitrobenzenes to arylamines to proceed under solvent-free or in neat water, room temperature, and normal pressure, giving nearly 100% yield and selectivity. A clean and energy-efficient process can be thus created over the robust catalysts. The process employing such a catalytic assembly overcomes simultaneously the disadvantages of the requirement for organic solvents in the liquid hydrogenation process and for high temperature in the vapor hydrogenation process.



KEYWORDS: Pd nanoparticle, ionic liquid brush, hydrogenation, solvent-free, nitrobenzene

1. INTRODUCTION

Reduction of energy consumption and chemical waste in chemical transformations is a constant challenge as environmental concerns are increasingly brought into focus. For the production of bulky chemicals, such as aniline, it is more important. Aniline is a bulky chemical of which the world production capacity reached more than 4.3 million metric tons in 2006. To meet the increasing demand of manufacturing 4,4′-methylenedianiline, dyes, pharmaceuticals, pesticides, explosives, fibers, and photographic and rubber chemicals, production capacity of aniline and other aromatic amines needs to further increase.[1−15] Current industrial production of aniline involves the catalytic hydrogenation of nitrobenzene in the vapor phase or the liquid phase. The vapor-phase processes may be performed at 200−300 °C and 1−3 MPa in fixed-bed or fluidized-bed reactors with copper or palladium on activated carbon or an oxide support as the catalyst. The liquid-phase processes, most recently developed by ICI and DuPont, are performed at 90−200 °C and 0.1−0.6 MPa in slurry or fluidized-bed reactors with a finely divided nickel on kieselguhr (ICI) or a platinum−palladium catalyst on a carbon support (DuPont). Obviously, the current industrial hydrogenation processes have some disadvantiges, such as high temperature (vapor-phase processes) and toxic, flammable, environmentally hazardous organic solvents (liquid phase processes). Great efforts have been made to develop a greener hydrogenation catalyst and more cost-effective processes, and numerous methods for the reduction of aromatic nitro have been reported in the literature, such as catalytic hydrogenation,[16−33] catalytic transfer hydrogenation,[34−44] CO/H_2O conditions,[45−48] and other reduction systems;[49−66] however, the problems remain unsolved. Therefore, the development of more effective, less toxic, and handle-convenient catalysts for this transformation is still highly desirable.

Our group has been involved for the past several years in the development of green catalysts and environmentally friendly procedures to organic transformations used in laboratories and industries. Very recently, we disclosed a series of SiO_2-supported, multilayer, ionic liquid brushes that have two or more imidazoliums on each branched chain. We term them "ionic liquid brushes" (Figure 1). The brush extends the immobilized ILs to the upper spaces outside the surface of the supports, forming an immobilized multiple layer IL possessing more prominent three-dimensional characters resembling that of the free ionic liquids. We expect our immobilized multiple layer ILs, in comparison with the monolayer ILs reported previously, should act as highly active catalysts, cocatalysts, or supports on the basis of the following points: (1) more catalysts or precatalysts, such as nanoparticles, anions or coordination anions can be loaded on the unit surface; (2) deeper 3D microenvironment and more flexibility of the longer branched chains containing imidazoliums for more molecules of substrates and reagents to be accommodated and to access the catalytic species; (3) adjustable hydrophobicity via changing the terminal alkyl, spacers, or counteranions would be favorable for the substrates and reagents to "be dissolved" in and for the products—in particular, the water produced in the hydrogenation of nitrobenzene—to move out off the brushes; (4) the fencelike branched chains on the support enable the catalytic species (e.g., Pd nanoparticles) restricted in individual regions where they were generated and protected them from aggregation, and thus lengthen the life span of the catalysts; and (5) the ability to perform the reaction under organic solvent-free conditions or in water without the addition

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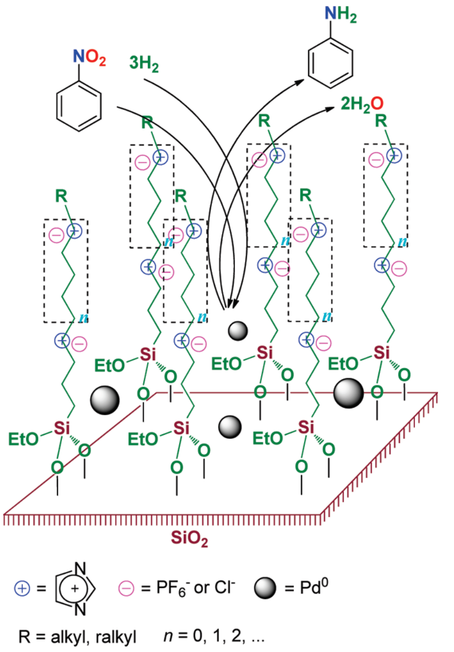


Silica-IL[PF$_6$]-Pd^0(1): n=0, R=C_8H_{17}, Pd(wt.%)=1.0
Silica-BisILs[PF$_6$]-Pd^0(2a): n=1, R=C_2H_5, Pd(wt.%)=1.0
Silica-BisILs[PF$_6$]-Pd^0(2b): n=1, R=C_4H_9, Pd(wt.%)=1.0
Silica-BisILs[PF$_6$]-Pd^0(2c): n=1, R=C_8H_{17}, Pd(wt.%)=1.0
Silica-BisILs[PF$_6$]-Pd^0(2c-1): n=1, R=C_8H_{17}, Pd(wt.%)=1.5
Silica-BisILs[PF$_6$]-Pd^0(2c-2): n=1, R=C_8H_{17}, Pd(wt.%)=2.0
Silica-BisILs[PF$_6$]-Pd^0(2d): n=1, R=$C_{12}H_{25}$, Pd(wt.%)=1.0
Silica-BisILs[PF$_6$]-Pd^0(2e): n=1, R=C_7H_7, Pd(wt.%)=1.0
Silica-TriILs[PF$_6$]-Pd^0(3): n=2, R=C_8H_{17}, Pd(wt.%)=1.0

Figure 1. The ionic liquid brush catalytic assembly and its possible working principle.

of any phase transfer catalysts or the use of a surfactant to create the micelles.

Herein, we would like to report the behavior of the brush−Pd nanoparticle catalytic assembly in the hydrogenation of nitroaromatics to aromatic amines.

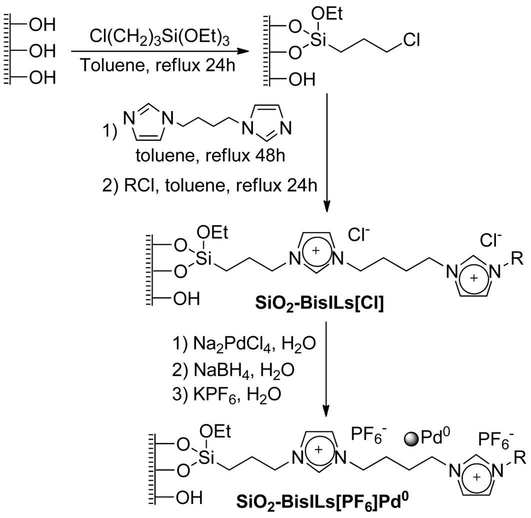
2. RESULTS AND DISCUSSION

2.1. Catalyst Preparation. The silica-supported multi-imidazolium ionic liquid, noted as SiO_2−BisILS[Cl]R, and the brush−Pd nanoparticle catalytic assembly, noted as SiO_2−BisILS[Cl]R−Pd^0, were prepared via the following procedure (Scheme 1).

The multilayer IL−SiO_2 brushes and their catalytic assemblies with Pd nanoparticles were prepared according to the procedure shown in Scheme 1, in which the bis-layer ionic liquid catalyst **2c** was depicted. In a typical experiment, the silanized silica (surface area 385 m^2/g) with (3-chloropropyl)triethoxysilane[67] was refluxed with 1,4-bis(imidazole-1-yl)butane[68] in dry toluene for 2 days and then with 1-chlorooctane for 24 h, giving the brushes, SiO_2−BisILsOc[Cl]. Refluxing the latter and $PdCl_2$ in water for 24 h gave SiO_2−BisILsOc−$PdCl_4$. Then an ethanol solution of sodium borohydride was added, and the suspension turned black, giving the catalytic assemblies, SiO_2−BisILsOc[Cl]−Pd^0 as a gray to black powder, which was further treated with KPF_6 in water for 24 h, yielding the PF_6-containing assemblies, SiO_2−BisILsOc[PF_6]−Pd^0 (1.05 mmol of immidazolium per gram). The catalysts are insensitive to air and moisture.

Because of their heterogeneous nature, the intermediates and the final product can be used in the next step after removal of the unreacted reagents by simple wish or extraction in Soxhlet apparatus with proper solvents.

Scheme 1. Synthesis Route to the Brush Catalyst



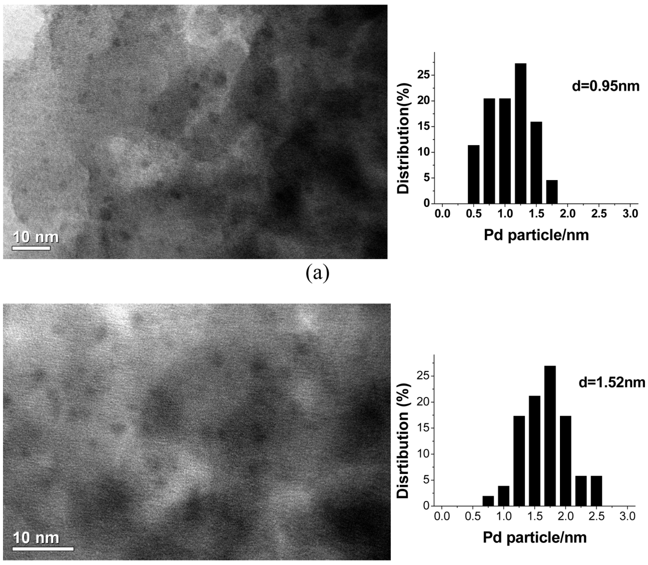
2.2. Catalyst Characterization. The IR spectrum of SiO_2−BisILs[PF_6]−Pd^0 (**2c**) shows bands at 3436 cm^{-1} attributable to the ν (OH) of the silica-gel itself and at 3168 and 3120 cm^{-1} attributable to the aromatic ν (C−H) of imidazolium. In addition, the spectrum also displays ν (C−H) at 2855, 2877, 2902, 2947, and 2965 cm^{-1} of an aliphatic chain and ν (C═C) or ν (C═N) and δ (C−H) at 1567, 1468 cm^{-1} (imidazole ring), similar to that of the monolayer ILs−SiO_2 previously reported.[67]

The TEM image of the brush−Pd nanoparticles assembly **2c** shows that the Pd^0 nanoparticles have an average size of 0.95 nm with a narrow size distribution ranged from 0.5 to 1.5 nm (Figure 2a). This result is consistent with the general idea that the nanoparticles in close proximity to monodispersed particles with a size less than 10 nm in diameter have higher activities in the catalytic reactions.[69−80]

The XRD pattern of SiO_2−BisILS[PF_6]−Pd^0 (**2Oc1**), shown in Figure 3, exhibited typical diffused rings, which could be assigned to (111), (200), and (220) reflections of the face centered cubic structure corresponding to metallic Pd. The particle size calculated from the line-broadening of the (111) reflection using the Scherrer formula was 1 nm, which matched very well with TEM data (Figure 2),[81] indicating that the Pd was deposited in the brush as nanocrystals. A broad reflection (2θ = 10−30°) is also observed in the XRD pattern, which is attributed to the reflection of amorphous SiO_2. Such a high disposition suggests that the catalyst(s) are more active in hydrogenation of nitrobenzene and in other Pd(0)-catalyzed reactions.

The thermogravimetric (TG) analyses (Figure 4) show the catalysts, both of the brush and its Pd^0 loaded catalyst, are stable to 200 °C. The weight loss before 120 °C should be attributable to water absorbed or held in the ionic liquid brushes. The weight loss between 200 and 450 °C may be the decomposition of immobiled ionic liquid. The presence of Pd^0 in the brush seems to have no influence on the thermal stability of the catalytic assembly.

2.3. Catalytic Activity. The catalytic activities of the catalytic assemblies were initially investigated by using nitrobenzene as the standard substrate at room temperature and atmospheric pressure without any solvent.The results were summarized in Table 1.



(a)

(b)

Figure 2. TEM images and Pd particle size distributions of SiO_2−BisILS-$[PF_6]$−Pd^0 (2Oc1) before use (a) and after the 15th recycling (b).

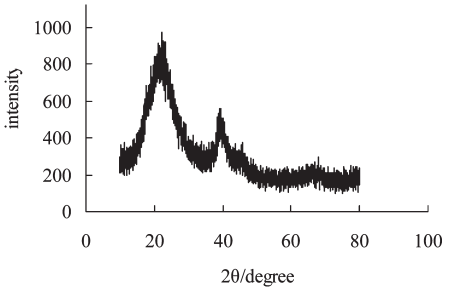


Figure 3. XRD pattern of SiO_2−BisILS$[PF_6]$−Pd^0 (**2Oc1**).

The results, to our great delight, show that in all cases, the hydrogenation of nitrobenzene proceeded smoothly and completely to give aniline in quantitative yields (Table 1, entries 1−14) without any detectable byproducts and unreacted nitrobenzene, except for the control experiments (entries 1, 2, and 9). The catalyst, SiO_2−BisILs$[PF_6]$−Pd^0 (**2c**), bearing two imidazoliums and an octyl as the terminal alkyl group, was found to be the most efficient catalyst (entry 4) as compared with its mono- and trilayer analogues (entries 1 and 9) under reaction conditions. We rationalized the lower activity of the monolayer catalyst resulted from its fewer imidazoliums and, thus, fewer exchangeable anions, although in the trilayer analogue catalyst, the anions near the surface of the support would not be exchanged, at least partially, by the anionic precatalyst, $PdCl_4^{2-}$, or the substrates could not reach the deepest layer of imidazoliums, where the catalytically active species attached, thus rendering these imidazoliums ineffective and, consequently, diminishing the catalytic activity.

In addition, the efficiency of these catalysts is impacted by the terminal alkyl group. A catalyst bearing more or fewer than eight carbons in the chain of an alkyl group is less effective. The explanation may be that octyl is more efficient in balancing the critical hydrophobic and hydrophilic parameters and thus provides a suitable hydrophobic and hydrophilic microenvironment for nitrobenzene and hydrogen to difuse inside the brushes where the catalytically active species are attached. Most importantly, such hydrophobic and hydrophilic microenvironments are helpful for the reduced product and water to move out from the Pd nanoparticles. Even in the case that water was introduced to the reaction mixture before the hydrogenation, a quantitative yield of aniline was obtained (Table 1, entry 17). In sharp contrast, the reactions catalyzed by Pd/SiO_2 without modification of the ionic liquids (entries 18 and 19) or by commercial Pd/C (entries 20 and 21) proceeded rather slowly and stopped at a quite low conversion of nitrobenzene under solvent-free conditions, even worse in water. This result is rationalized by the lack of a suitable hydrophobic environment provided by ionic liquids; the Pd particles are enwrapped by the water film, which prevents the substrates' contact with the catalysts.

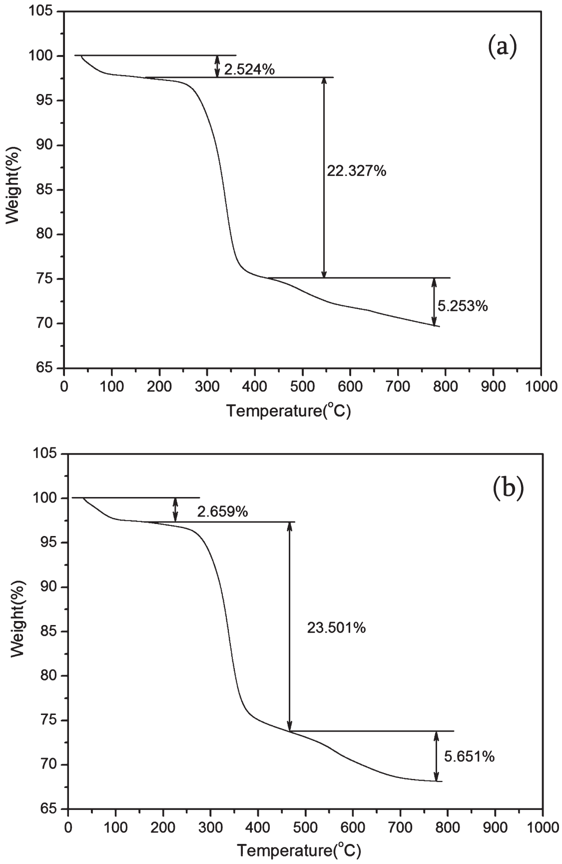


Figure 4. DTA pattern of (a) SiO_2−BisILS (**2Oc1**) and (b) SiO_2−BisILS$[PF_6]$−Pd^0 (**2Oc1**).

The reaction temperature (Table 1, entries 4, 12, 13) has no detrimental effect on the ability of the catalysts to promote this reaction to completion. When the reactions were carried out in ethanol and 95% ethanol, which are commonly used as the solvents for hydrogenation reactions of nitrobenzene, the time for 100% conversion (entries 15 and 16) shortened slightly, reflecting the reaction rate's being determined by the transfer of the reactants[83−86] into the catalytically active center inside the brush.

Accordingly, the role that the brush played in the catalytic system is not only the support of Pd nanoparticles, but also the media or circumstance for the reactants. That is, the brush can catch the molecules of the substrates, even those insoluble in water.

The hydrogen absorption curve of the catalytic hydrogenation of nitrobenzene reveals again that the reaction proceeds

Table 1. Hydrogenation of Nitrobenzene with the Catalysts Synthesized[a]

entry	catalyst[b]	n[e]c	R[f]d	Pd wt %	subs./Pd^0 (mol/g)	solvent	T (K)	t (h)[e]	yield (%)[f]	rate[82] (mol/g·h)[g]
1	**1Oc1**	0	octyl	1.0	33		303	11.0	75	2.26
2	**2Et1**	1	ethyl	1.0	33		303	11.0	88	2.64
3	**2Bu1**	1	butyl	1.0	33		303	11.5	100	2.87
4	**2Oc1**	1	octyl	1.0	33		303	8.5	100	3.88
5	**2Oc1.5**	1	octyl	1.5	33		303	8.5	100	3.88
6	**2Oc2**	1	octyl	2.0	33		303	9.5	100	3.47
7	**2Do1**	1	$C_{12}H_{25}$	1.0	33		303	13.0	100	2.54
8	**2Bz1**	1	benzyl	1.0	33		303	9.0	100	3.67
9	**3Oc1**	2	octyl	1.0	33		303	11.0	92	2.76
10	**2Oc1**	1	octyl	1.0	47		303	15.0	100	3.14
11	**2Oc1**	1	octyl	1.0	57		303	20.0	100	2.83
12	**2Oc1**	1	octyl	1.0	33		323	8.0	100	4.13
13	**2Oc1**	1	octyl	1.0	33		343	8.0	100	4.13
14[h]	**2Oc1**	1	octyl	1.0	33		303	9.0	100	3.67
15	**2Oc1**	1	octyl	1.0	33	EtOH	303	7.0	100	4.71
16	**2Oc1**	1	octyl	1.0	33	EtOH (95%)	303	7.5	100	4.40
17	**2Oc1**	1	octyl	1.0	33	H_2O	303	11.5	100	2.87
18[i−j]i	Pd/SiO_2			1.0	33		303	24.0	54	0.74
19[i−j]i	Pd/SiO_2			1.0	33	H_2O	303	22.0	20	0.30
20[i−j]j	Pd/C			5.0	33		303	26.0	63	0.80
21[i−j]j	Pd/C			5.0	33	H_2O	303	24.0	38	0.52

[a] All reactions were carried out with catalyst [Pd] and 17.5 mmol of substrate under constant hydrogen pressure (1 atm) at 303 K. [b] The catalyst means the number of immidazoliums, terminal alkyl, and wt % of Pd, respectively. [e] Tracking via GC analysis per 0.5 h. [f] Based on GC analysis. [g] The rates based on total metal (moles aniline formed per gram of Pd per hour). [h] Yield of 15 cycles after the experiment described in entry 4. [i−j] Pd/SiO_2 prepared by us without the modification of ILs or commercial Pd on activated carbon (5 wt % Pd) as the catalyst.

smoothly and cleanly (Figure 5). A constant speed of hydrogen absorption was observed before 80% H_2 uptake during the hydrogenation; the reaction slowed down slightly after H_2 uptake exceeded 98%.

Encouraged by these excellent results, we compared the catalyst **2c** with the Pd catalysts reported in the literature[87−90] for the hydrogenation of nitrobenzene (Table 2). In the result, **2c** has unprecedented activity in nitrobenzene hydrogenation under organic solvent-free, atmospheric pressure, and room temperature conditions, but Pd/SiO_2 cannot promote the reaction to be complete[87] and PS−DVB−Pd catalyzes the reaction with a rather low rate,[82,88] even under rigorous conditions. Although PVPA−Pd exhibits a higher activity, its catalytic activity decreases significantly after reusing for four cycles.[89] $EnPdCl_2Cat$ could be recycled three times without deactivation, but its catalytic activity was too low.[90] In addition, all of these Pd catalysts reported must be employed in methanol, ethanol, or hexane. The reasons might be that the ionic liquid brushes provide a fence protecting nanoparticles from aggregation and a suitable reaction environment, as mentioned above.

2.4. Catalyst Recycling. The potential recyclability of the catalyst **2c** was explored in the model hydrogenation of nitrobenzene. The reaction was carried out under room temperature and normal atmospheric pressure, and solvent-free conditions. The completion of the reaction was monitored by GC analysis. After completion of the reaction, the catalyst was filtered from the reaction stream and then transferred to a new reaction vessel containing fresh nitrobenzene. The aniline was separated from water in a separatory funnel. Gas chromatographic analysis revealed that aniline was obtained in high purity because no other byproducts were detected. This process was repeated for 15 cycles, giving all cycles in quantitative yield and the time required to complete the reaction, as shown in Table 3. Kinetic data for the catalyst **2c** followed by 15 recycles is shown in Figure 6.

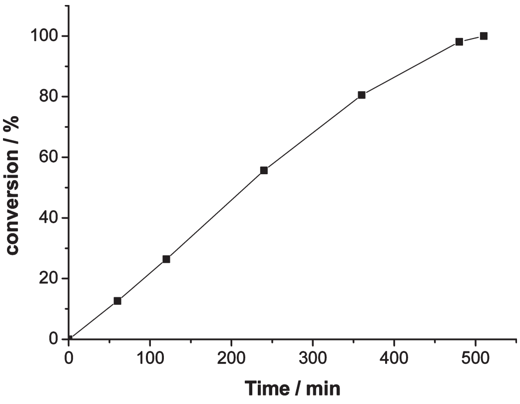


Figure 5. Hydrogen absorption curve of the catalytic hydrogenation of nitrobenzene under atmospheric pressure and room temperature.

The reaction time difference between the catalyst in its first run and after the 15th recycle was only 0.5 h; the kinetic data proved that the catalyst was stable, recyclable, and showed no apparent loss of catalyst efficiency. A TEM study of the used sample showed that the Pd^0 nanoparticles remained unchanged after 15 recycles, suggesting that no palpable aggregation occurred and the Pd nanoparticles kept a narrow size distribution (Figure 2b, 0.95 nm versus 1.52 nm). This might be one of the

Table 2. Comparison of Standard Catalysts versus Catalyst **2c** for the Hydrogenation of Nitrobenzene

catalyst	subs./Pd (mol/g)	solvent	T (K)	P (atm)	t (h)	yield (%)	rate[82] (mol/g·h)[a]	ref
Pd/SiO_2[b]	19.6	ethanol	393	10	4.7	80	3.33	87
PS−DVB−Pd[c]	3.54	methanol	303	1	10.0	100	0.35	88
PVPA−Pd[d]	4.70	ethanol	308	1	1.3	100	3.61	89
$EnPdCl_2Cat$[e]	0.78	hexane	303	1	2	100	0.39	90
SiO_2−BisILs[PF_6]−Pd^0(**2c**)	33		303	1	8.5	100	3.88	this work

[a] The rate based on total metal (moles of aniline formed per gram of Pd per hour). [b] 1.0 g Pd/SiO_2 with Pd loading of 0.5 wt %, 40 mL of ethanol, 10 mL of nitrobenzene. [c] Polymer (styrene divinyl benzene copolymer) anchored 2.58 × 10^{-5} mol Pd, 20 mL of methanol, 9.72 × 10^{-3} mol of nitrobenzene. [d] Palladium complex of a random copolymer of 4-vinylpyridine with acrylic acid. Reaction conditions: 15 mL of ethanol, 0.1 mol/L of KOH. [e] 1.8 × 10^{-5} mol of $PdCl_2$ loaded on the microcapsule, 5 mL of hexane, 1.5 × 10^{-3} mol of nitrobenzene.

Table 3. The Hydrogenation of Nitrobenzene in Recycled Brush[a]

cycle	product yield at 12 h (%)	time for reaction completion (h)
1	100	8.5
2	100	8.5
5	100	8.5
10	100	8.8
15	100	9.0

[a] All cycles were carried out with 5 μmol of catalyst (Pd) and 17.5 mmol of substrate under constant hydrogen pressure (1 atm) at 303 K.

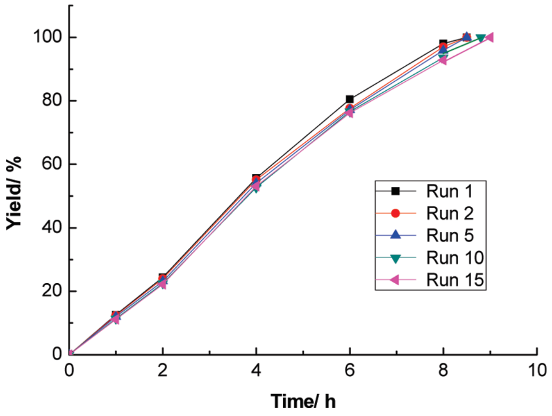


Figure 6. Kinetic data for SiO_2−BisILs[PF_6]−Pd^0 (**2c**) followed by 15 recycles.

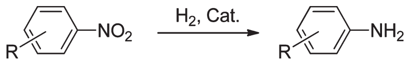
main reasons for the preservation of high activity during recycling experiments. It is noteworthy that the catalyst can be recovered by a simple filtration and reused directly in the next cycle without the need for washing by organic solvents and drying. It is economically viable to the industrial application from a practical point of view.

The reasons that our catalyst has a high activity and maintains such activity in the course of reusing might be that the ionic liquid brushes provide a fence protecting nanoparticles from aggregation (Figure 2) and a suitable reaction environment, as mentioned above (see: Catalytic Activity). To the best of our knowledge, this is the first demonstration that the catalytic hydrogenation of nitrobenzene proceeds efficiently under solvent-free or water and very mild conditions.

2.5. Catalyst Scope. With the catalytic assembly **2c** being identified as the most effective catalyst for hydrogenation of nitrobenzene, the scope of these catalyst systems was explored with a range of substituted nitrobenzene (Table 4). As the data in Table 4 show, the reactions of liquid substrates such as nitrotoluenes under those conditions afforded 100% conversion of the substrates to the corresponding methylanilines (entries 1−3, Table 4).

Other aromatic nitro compounds are suitable to be hydrogenated with **2c**. In most cases, the aromatic nitro compounds were hydrogenated smoothly and cleanly to afford the desired products in quantitative yields in neat water. Either hydrophobic or hydrophilic nitroaromatics could be reduced in excellent

Table 4. Hydrogenation of Various Aromatic Nitro Compounds with SiO_2−BisILs[PF_6]−Pd^0 at Mild Conditions[a]



entry	substrate, R	t (h)[b]	conversion (%)[c]	yield (%)	rate (mol/g·h)[d]
1	*o*-Me	16	100	100	2.06
2	*m*-Me	18	100	100	1.83
3	*p*-Me	16	100	100	2.06
4	*o*-OH	12.5	100	100	2.64
5	*m*-OH	12.5	100	100	2.64
6	*p*-OH	12.5	100	100	2.64
7	*o*-CO_2H	14	100	100	2.36
8	*m*-CO_2H	16	100	100	2.06
9	*p*-CO_2H	15	100	100	2.20
10	*o*-OMe	12.5	100	100	2.64
11	*m*-OMe	12.5	100	100	2.64
12	*p*-OMe	12.5	100	100	2.64
13	2-Cl	15	100	74.7	1.64
14	*m*-NO_2	33	100	100	1.00
15	*p*-$CONH_2$	10	100	100	3.30
16	*p*-CH_2OH	12	100	100	2.75
17	*p*-$COCH_3$	10	100	100	3.30
18	β-nitronaphthalene	12	100	100	2.75
19	*p*-Ph	15	100	100	2.20
20	*m*-Ph	15	100	100	2.20

[a] All reactions were carried out with 5 μmol of catalyst (Pd) and 17.5 mmol of substrate, substrate (mol)/Pd (g) mole ratio = 35, under constant hydrogen pressure (1 atm) at 303 K in distilled water (5 mL). [b] Time for 100% conversion. [c] The conversion/yield of the byproduct dehalogenated. [d] The rate based on total metal (moles of product formed per gram of Pd per hour).

yields by using water as the solvent. 2-Chloronitrobenzene afforded the desired aniline in low yields, perhaps due to the dehalogenation side reaction that was commonly observed in palladium-catalyzed hydrogenation of aryl halides.

It is noteworthy that the catalyst worked well with solid nitrobenzenes as the substrates. Even in the cases that the reduction products are also in solid state and water-insoluble at the reaction temperature (i.e., room temperature) the reactions proceeded completely, but in a lower rate. The slower reaction is rationalized by lattice energy of solid substrates, such as nitrophenols, nitrobenzoic acids, and dinitrobenzenes, which increases the activation energy of the reaction. Addition of a proper organic solvent, such as CH_2Cl_2, to the postreaction mixture resulted in the precipitation of the catalyst. This triphasic mixture can be easily separated by simple filtration and extraction to recover the catalyst and isolate the product.

The heterogeneous system was favorable for product separation, but suffered generally from lower activity. The use of the brush as a heterogeneous catalyst for the hydrogenation of nitrobenzene can simultaneously provide high activity, easy separation of product, and good performance in the recycling of the reaction.

Further studies show that the multiple-layer ILs catalyst systems also work well in the hydrogenation of carbon—carbon, carbon—oxygen, and carbon—nitrogen double bonds in water. Investigations aimed at improving the activity of these catalytic systems and extending the application domains of these ionic liquid brushes systems and their combinations with other catalytic species are now in progress.

3. CONCLUSIONS

We have developed an environmentally benign catalyst and procedure for the hydrogenation of nitro aromatics to arylamines. This catalytic assembly combines the advantages of an ionic liquid, Pd nanoparticles, and a heterogeneous catalyst and has proved to be highly efficient, selective, and recyclable in the hydrogenation reactions under solvent-free or neat water conditions. The Pd nanoparticles in the brush have a uniform size. A clean and energy-efficient process can thus be created over the robust catalysts. The processes employing such a catalytic assembly have simultaneously the advantages of no need for high temperature in the vapor hydrogenation and organic solvents in liquid hydrogenation. In view of simplicity in the product separation and in the catalyst recovery and the mild reaction conditions, the present protocol could find industrial applications. Furthermore, the ionic liquid brushes with a deeper three-dimensional feature, enriched homogeneity, and suitable lipophilic ability can be expected to be used as basic catalysts to combine with other catalytic species—especially anions—providing an opportunity to exploit new catalytic materials with good performance from fundamental interests to practical aspects of an environmentally friendly system.

4. EXPERIMENTAL SECTION

^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 300 spectrometer in $CDCl_3$, and tetramethylsilane (TMS) was used as internal standard. TEM images were obtained on a JEM-3010 transmission electron microscope operating at an accelerating voltage of 300 kV. Histograms of the particle size distribution of the Pd nanoparticles were obtained from the TEM images by measuring more than 200 particles in each sample. The surface area was determined from full nitrogen adsorption and desorption isotherms at 77 K using a Sorptometer ST-03A. The catalysts were degassed for 4 h at 573 K prior to measurements. Infrared spectra were recorded with a FT-IR Bruker EQUINX-55 spectrometer equipped with a KBr beam splitter and a TGS detector. The chemical analyses of the content of palladium were carried out with an ICP—OES (inductively coupled plasma—optical emission spectrometer) Vista (Varian). The samples (~10 mg) were digested in a mixture of 1.5 mL of HCl (37%), 0.5 mL of HNO_3 (65%), and 1 mL of HF (40%) by heating. Generally, the solutions were diluted to a volume of 50 mL using a volumetric flask. EDXA measurements were performed on a Philips-FEI Quanta 200 scanning electron microscope. This apparatus was equipped with a Si—Li energy dispersive, and quantitative chemical analysis was performed for Si and Pd. C, H, and N elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The XRD pattern was recorded on a Rigalcu D/Max-3c X-ray diffractometer (Cuka, Ni filter). Gas chromatography was performed on an Agilent GC 6890N with a FID detector equipped with a DB-35 column (30 m long, 0.25 mm i.d.). Parameters were as follows: initial temperature, 70 °C; initial time, 3 min; ramp, 8 $°C \cdot min^{-1}$; final temperature, 180 °C; final time, 2 min; injector temperature, 220 °C; detector temperature, 250 °C; injection volume, 1.0 μL. The high-boiling-point substrates and the products were analyzed by using HPLC. All hydrogenated products were initially identified using authentic commercial samples of the expected products. Melting point is uncorrected.

$PdCl_2$ (AR), imidazole (AR), sodium borohydride, 1-chlorooctane (AR), KPF_6, silica gel (surface area, 385 $m^2 \cdot g^{-1}$), nitrobenzene, 4-nitrophenol, 2-nitrophenol, and other aromatic nitro compounds were used as received. 1,4-Dibromobutane and 3-chloropropyltriethoxysilane were purchased from Alfa Aesar. All organic solvents were dried under standard conditions. 1,4-Bis(imidazol-1-yl)butane was synthesized according to the literature.[91] mp 61—63 °C, ^1H NMR (300 MHz, DMSO-d_6, ppm): δ 1.61 (m, 4H), 3.96 (m, 4H), 6.89 (s, 2H), 7.14 (s, 2H), 7.62 (s, 2H); ^{13}C NMR (300 MHz, DMSO-d_6, ppm) δ 28.1, 39.4, 39.6, 39.9, 40.2, 40.5, 45.7, 119.7, 128.9, 137.7.

1. Example of Preparation of the Brush. *1.1. Preparation of the Silanized Silica with (3-Chloropropyl)triethoxysilane.* The preparation was performed according to the literature.[92] S_{BET} (m^2/g): 385. IR: (KBr disk) 2958, 2930, 2871 cm^{-1} ν(C—H, aliphatic).

1.2. Modification of the Silanized Silica with 1,4-Bis-(imidazole-1-yl)butane. 1,4-Bis(imidazol-1-yl) butane (4.3 g, 22.5 mmol) was added to the suspension of the silanized silica (4.5 g) in 15 mL of dry toluene, and then the mixture was refluxed for 24 h. The solid was then filtered and washed thoroughly with toluene, followed by methanol in a Soxhlet extractor. After drying under high vacuum, 5.1 g of solid was obtained. S_{BET} (m^2/g): 236. IR: (KBr disk) 3155, 3120 cm^{-1} ν(C—H, aromatic), 2947, 2871 cm^{-1} ν(C—H, aliphatic), 1555, 1456 cm^{-1} ν(C=N). Elemental analysis: found (%) C, 14.79; H, 2.574; N, 4.212, revealing that it contained 1.50 mmol of imidazolium/g.

1.3. Preparation of the Brush (SiO_2—$BisILsC_8H_{15}$). A mixture of the above modified silica (5 g, 7.50 mmol of imidazolium) and 1-chlorooctane (5 g, 34 mmol) in toluene was refluxed for 24 h under nitrogen atmosphere. After the reaction mixture was cooled to room temperature, the solid was filtered off and washed with toluene, followed by ethanol, in a Soxhlet apparatus. Then the solid was dried in vacuum; 5.4 g of solid was obtained. S_{BET} (m^2/g): 181. IR: (KBr disk) 3151, 3084 cm^{-1} ν(C—H, aromatic), 2936, 2855 cm^{-1} ν(C−H, aliphatic), 1568, 1458 cm^{-1} ν(C═N). Elemental analysis: found (%) C, 14.06; H, 2.335; N, 3.545, revealing that it contained 1.27 mmol of imidazolium/g.

2. Preparation of the Pd-in-Brush Catalyst (2 wt % Pd). A typical procedure of the catalysts was as follows: To a yellow solution of $PdCl_2$ (0.017 g, 0.09 mmol) in 10 mL of freshly distilled acetonitrile, the brush (SiO_2−BisILsC_8H_{15}) (1.0 g, 1.27 mmol of imidaloniums/g) was added, and the suspension was refluxed for 96 h under nitrogen atmosphere. The solid material was filtered off and washed repeatedly with methanol in a Soxhlet apparatus and dried under vacuum; 1.013 g of resulting solid was obtained, denoted as SiO_2−BisILs−$PdCl_4$. S_{BET} (m^2/g): 227. IR: (KBr disk) 3167, 3120 cm^{-1} ν(C−H, aromatic), 2948, 2876, 2860 cm^{-1} ν(C−H, aliphatic), 1564, 1522, 1452 cm^{-1} ν(C═N). Elemental analysis: found (%) C, 13.58; H, 2.39; N, 2.85, revealing that it contained 1.02 mmol of imidazolium/g.

1.2.5. Synthesis of SiO_2−BisILs[PF_6]−Pd^0. To the suspension of SiO_2−BisILs−$PdCl_4$ (1 g, 1.02 mmol of imidazolium/g) in EtOH (10 mL), a stoichiometric amount of sodium borohydride ($NaBH_4$) ethanol solution was added dropwise at room temperature under nitrogen atmosphere. The reaction mixture soon changed to black, indicating a reduction of Pd(II) to Pd(0). The resultant solid was filtered, washed with EtOH, and dried under vacuum to give 0.96 g of SiO_2−BisILs[Cl]−Pd^0 as a black solid. S_{BET} (m^2/g): 212. IR(KBr disk): 3168, 3120 cm^{-1} ν(C−H, aromatic); 2935, 2871 cm^{-1} ν(C−H, aliphatic); 1577, 1466 cm^{-1} ν(C−H). Elemental analysis: found (%) C, 13.85; H, 2.615; N, 3.245, revealing that it contained 1.15 mmol of imidazolium/g.

To a solution of KPF_6 (2.1 g, 11.5 mmol) in acetone (50 mL, 0.1 mol/L), SiO_2−BisILs[Cl]−Pd^0 (1.0 g, 1.15 mmol of imidazolium/g) was added, and the mixture was stirred for 48 h under nitrogen atmosphere at room temperature. The solid material was filtered off and washed repeatedly with acetone, distilled water, and acetone; followed by extraction with ethanol in a Soxhlet apparatus; and then dried under vacuum to give 1.2 g of black solid, SiO_2−BisILs[PF_6]−Pd^0 (**2c**). S_{BET} (m^2/g): 110. IR: (KBr disk) 3167, 3120 cm^{-1} ν(C−H, aromatic), 2948, 2876 cm^{-1} ν(C−H, aliphatic), 1567, 1468 cm^{-1} ν(C═N), 838 cm^{-1} ν(P−F). Elemental analysis: found (%) C, 12.62; H, 2.552; N, 2.946, revealing that it contained 1.05 mmol of imidazolium/g. EDXA: Pd, 1.0%.

3. The Typical Procedure for the Hydrogenation of Nitrobenzene under Solvent-Free Condition. All hydrogenation reactions were carried out under standard conditions (30 °C, 1 atm of H_2). A round-bottom flask (25 mL), charged with the supported Pd^0 catalyst (10 μmol) and a magnetic stirrer, was connected to a gas buret (500 mL) with a flask to balance the pressure. The flask was closed by a septum, and the system was filled with hydrogen. Nitrobenzene (3.5×10^{-2} mol) was injected through the septum, and the mixture was stirred (1500 min^{-1}). The reaction was monitored by the volume of gas consumed and by gas chromatography. After the completion of the reaction, the catalyst was filtered from the reaction mixture. The reaction stream was separated, and the organic layer was collected and analyzed by GC. ICP analysis indicated the absence of any palladium within the detection limits (i.e., less than 0.1 μg/mL). The rates were determined for 100% conversion. The products were checked by GC.

4. Recycling and Reuse of SiO_2−BisILs[PF_6]−Pd^0. The hydrogenation reaction of nitrobenzene was selected for testing the recyclability of the catalyst and was carried out under standard conditions by same procedure described above. The recovered catalyst after each cycle was transferred to a vessel charged with fresh nitrobenzene, and the reaction was started. After 15 cycles, no deactivation of the catalytic activity was observed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. The spectral data and copies of ^{1}H and ^{13}C NMR spectra for all the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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