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Ionic-Liquid-Grafted Rigid Poly(*p*-Phenylene) Microspheres: Efficient Heterogeneous Media for Metal Scavenging and Catalysis

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Abstract: Novel guanidinium ionic liquid-grafted rigid poly(*p*-phenylene) (PPPIL) microspheres have been developed for metal scavenging and catalysis. The noble-metal nanoparticles supported on the microspheres surface can be used as efficient heterogeneous catalysts. The combination of nanoparticles and ionic liquid fragments on the microsphere surfaces enhance the activity and durability of the catalyst. The PPPIL⋅Pd^0 catalyst has been tested in the Suzuki cross-coupling reaction, and exhibits much higher catalytic activity than Pd catalysts supported on porous polymer matrices. The PPPIL⋅Pd^0 catalyst can be recycled at least for nine runs without any significant loss of activity. The present approach may, therefore, have potential applications in transition-metal-nanocatalyzed reactions.

Keywords: heterogeneous catalysis • ionic liquids • metal scavenging • microspheres • nanoparticles

Introduction

The unique physicochemical properties of ionic liquids (ILs),[1] such as negligible vapor pressure, relatively low viscosity, elevated thermal and chemical stabilities, and differentiated miscibility with organic compounds, make them ideal candidates in the preparation and stabilization of noble-metal NPs (nanoparticles) for biphasic nanocatalysis.[2] However, the agglomeration of NPs in ILs still leads to a loss of activity in some cases.[3] Furthermore, when carried out in a biphasic catalysis system, the reaction occurs primarily at the interphase or in the diffusion layer of the liquid catalyst phase rather than in the bulk solvent. Hence, biphasic catalysis makes use of only a fraction of the ILs and of the NPs dispersed therein. This is interesting because use of relatively large amounts of ILs in biphasic systems is costly and may have toxicological issues.[4] The concept of supported-IL catalysis (SILC) has recently been established to combine the advantages of ILs with those of heterogeneous supporting materials.[5]

In recent years, studies have been performed on the immobilization of ILs onto polymers or porous frameworks with the incorporation of NPs. For example, Vankelecom et al.[6] fabricated hydrogenation catalysts that demonstrated excellent activity by impregnating transition metals and ILs into poly(diallyldimethylammonium chloride). Han et al. reported IL-protected Pd NPs supported on molecular sieves and Ru NPs on montmorillonite, which acted as a highly efficient heterogeneous catalyst for the hydrogenation reaction.[7] Kou et al. prepared ionic copolymers that contained imidazolium IL-like units and incorporated Rh. In this case, the NPs displayed excellent lifetimes and activity for arene hydrogenation in ILs.[8] Recently, Mioskowski et al. employed polyionic gels (PGELs) as efficient heterogeneous media for metal stabilization and catalysis.[9] Generally, the immobilization of NPs in a porous framework or a polymer matrix can facilitate the separation process but may simultaneously lead to a decrease in activity, most probably as a result of the restriction of the geometry of the NPs or due to leaching of the active species.[10] Moreover, it is difficult to completely extract the product from the polymer matrix at the end of the reaction and, therefore, it becomes necessary to develop a suitable scaffold to immobilize the NPs without destroying their activity. The best solution to this problem is to load the NPs onto the surface of the scaffold instead of incorporating them into the polymer matrix. This increases the amount of accessible active sites on the NPs and, therefore, raises the activity of the catalyst.[11]

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The present study involves grafting fragments of ILs onto a rigid poly(p-phenylene) (PPP) surface to form insoluble and non-swelling microspheres. The rigid, non-swelling backbone of the PPP eliminates the issue of solvent compatibility and may be used as a potential scaffold for immobilizing nanocatalysts in heterogeneous reactions. The obtained microspheres were used as an efficient heterogeneous medium for noble-metal sorption and NP immobilization (Figure 1). The combination of NPs and IL fragments on the microsphere surfaces present excellent synergistic effects that lead to enhanced catalyst activity and durability.

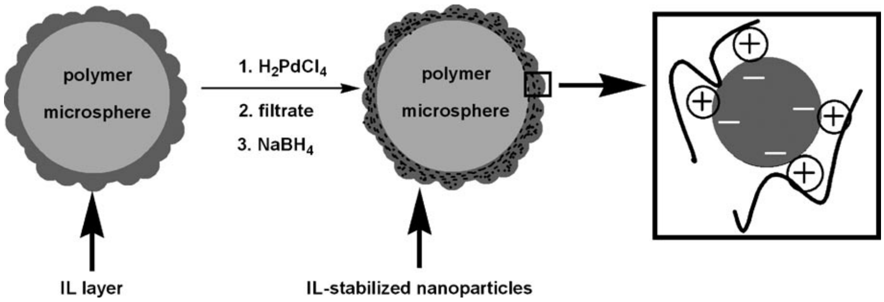
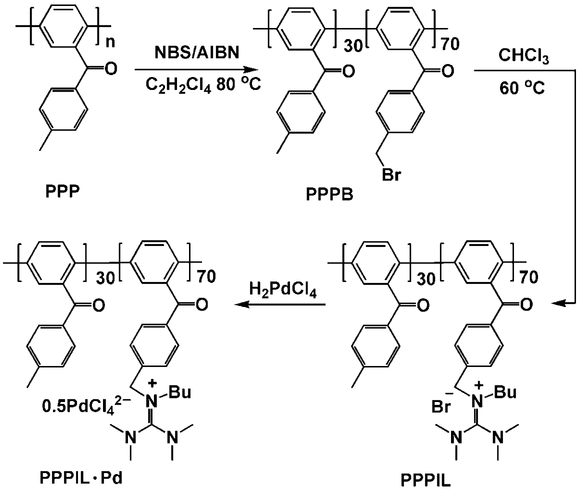


Figure 1. PPPIL particles used as carriers for metal scavenging and NP immobilization.

Results and Discussion

The PPP-supported IL (PPPIL) particles were prepared according to the procedure shown in Scheme 1. Previous work has involved the preparation of a large number of PPPs



Scheme 1. The synthetic route for a polymer-supported guanidinium IL/Pd catalyst.

with various linkers.[12] The physical and chemical properties of PPPIL particles were found to depend on the ratio of the grafted IL and on the type of linker employed.[12] This study concerns polymer-supported guanidinium IL. The PPP was treated with N-bromosuccinimide (NBS) in the presence of 2,2′-azobisisobutyronitrile (AIBN) in $C_2H_2Cl_4$ to give PPPB, which was then treated with pentaalkylguanidine in $CHCl_3$ at 60 °C for 6 h to give the PPPIL particles. Thermogravimetric analysis (TGA) revealed that the PPPIL particles had a high thermal stability (see the Supporting Information). Furthermore, the morphology of the micrometer-scale PPPIL particles was observed by using scanning electron microscopy (SEM; Figure 2a). A thin layer of nanoscale protuberances was observed on the as-prepared microsphere surfaces (Figure 2b), which indicates that the microspheres had more IL units on the surface as compared to a smooth surface.

A predetermined concentration of aqueous H_2PdCl_4 (5.0 mmol L^{-1}) was added to a suspension of PPPIL microspheres. The orange solution lost all its color at a Pd/PPPIL molar ratio of 1:10, and inductively coupled plasma (ICP) analysis confirmed the loading of Pd on the PPPIL particles to be 0.12 mmol g^{-1}, which roughly corresponds to the total absorption of H_2PdCl_4 in solution. The PPPIL microspheres, on the other hand, took on a very dark orange color (Figure 2d). Bleaching of the aqueous H_2PdCl_4 did not occur in control experiments with the PPP and PPPB polymers. This observation clearly illustrated the high affinity of the IL-grafted polymer for metal precursors. Tetrachloropalladate ($PdCl_4^{2-}$) was exchanged onto bromide-sa-

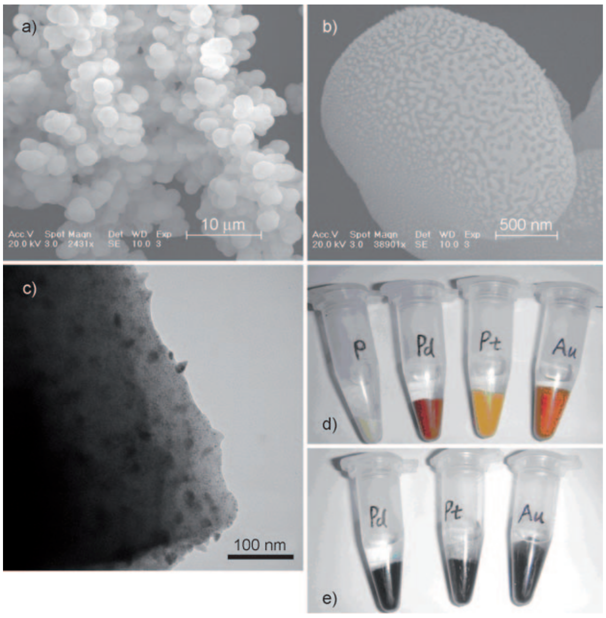


Figure 2. a,b) SEM images of PPPILs. c) TEM image of PPPIL·Pd^0. d) Photograph of PPPIL particles (labeled P) and PPPIL-soaked Pd, Au, and Pt precatalysts. e) Photograph of PPPIL-stabilized Pd^0, Pt^0, and Au^0 NPs.

turated PPPIL particles to obtain dark-brown PPPIL•Pd (Scheme 1). When the Pd/PPPIL molar ratio was increased to 1:2, the loading level of Pd rose to about 0.20 mmol g^{-1}. Furthermore, it was found that the PPPIL particles demonstrated an ability to scavenge $HAuCl_4$ and H_2PtCl_6 onto their surfaces by using the straightforward procedure described above (Figure 2d). The adsorption capacities of Au and Pt were around 0.41 and 0.21 mmol g^{-1}, respectively. The adsorption capacity of $AuCl_4^-$ on the microsphere surfaces also indicated that the amount of supporting guanidinium IL on the microsphere surface was approximately 0.41 mmol per gram of polymer as a result of the exchange molar ratio of $AuCl_4^-$ and Br^- being 1:1. Therefore, it was reasonable to assume that other classes of transition metals (e.g., Rh, Ru, and Ir) could also be scavenged through this method and that the resulting materials could be used as heterogeneous catalysts.

The nitrogen adsorption measurement of PPPIL particles shows that they are non-porous materials (see the Supporting Information), which is consistent with the results of the TEM observations. This indicated that the $PdCl_4^{2-}$ was only exchanged onto the surface of the microspheres. The supported Pd NPs were easily synthesized by reducing the $PdCl_4^{2-}$ with aqueous $NaBH_4$. X-ray photoelectron spectroscopy (XPS) analysis confirmed the presence of Pd^0 NPs on the surface of the PPPIL particles (Figure 3). As shown in Figure 2c, the synthesized Pd NPs were uniformly embedded into the rough IL surface layers of the microspheres, and no free Pd aggregates were observed by TEM. Moreover, the average size of the Pd NPs was found to be 3.1 nm with a deviation of 1 nm. X-ray diffraction (XRD) analysis was also carried out to confirm the crystal phase and to verify the mean size of the Pd NPs (Figure 3). The peak width of the (111) Bragg reflection was chosen to give an estimation of the mean size of the NPs by using the Debye–Scherrer formula,[13] which gives a mean NP size of 4 ± 1 nm. In terms of their size and shape, the Pd NPs were similar to those prepared from the classical ionic liquid $[BMI][PF_6]$ (1-*n*-butyl-3-methylimidazolium hexafluorophosphate), but the Au NPs were smaller than those prepared from $[BMI][PF_6]$.[14] The guanidinium IL appeared to promote the formation of stabilized Pd NPs on the IL layers of the microspheres. A similar phenomenon has already been described regarding the immobilization of a Pd NP catalyst onto the surfaces of molecular sieves in the presence of guanidinium IL.[7]

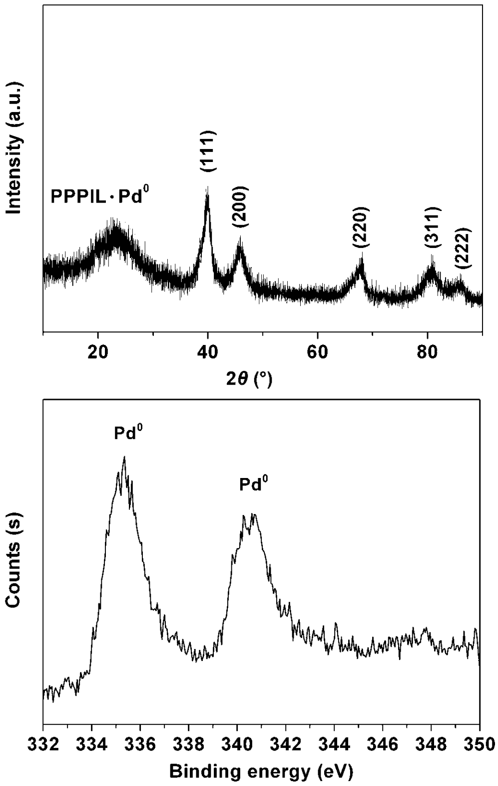
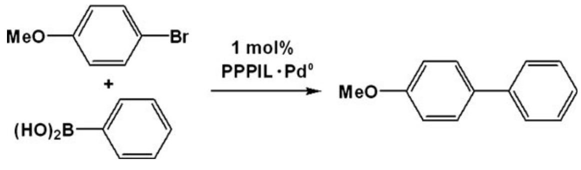


Figure 3. The XRD (top) and XPS (bottom) spectra of the PPPIL-supported Pd NPs.

A lot of interest is directed towards Pd-catalyzed carbon–carbon coupling reactions of the Heck and Suzuki type,[15] which are also used in the synthesis of fine chemicals. Therefore, various highly efficient catalytic systems have been developed by our groups.[16] Herein, a Suzuki cross-coupling reaction was adopted as a model reaction to test the catalytic ability and recyclability of the Pd catalyst. Because the IL layers are hydrophilic, the microspheres could be readily dispersed in water. Moreover, due to environmental, economical, and safety concerns, the Suzuki reaction was performed in water. A suitable amount of EtOH was used as a cosolvent to increase the solubility of the substrates.

The Suzuki coupling reaction of 4-bromoanisole with phenyl boronic acid was used as a test reaction. The cross-coupling reactions were carried out with 1 mol % Pd catalyst in H_2O/EtOH (3:1 v/v) at 80 °C. Table 1 shows that the PPPIL•Pd^0 catalyst was highly active for this reaction. A high yield (96 %) of product was observed under the chosen conditions. Furthermore, the catalyst was recycled in the model Suzuki reaction, and the catalytic activity of the preformed PPPIL•Pd^0 catalyst proved to be almost constant,

Table 1. The activity and recycling of the PPPIL•Pd^0 catalyst in the Suzuki coupling of 4-bromoanisole and phenyl boronic acid.[a]



Run	Yield[b] [%]	Run	Yield[b] [%]
1	96	6	90
2	95	7	91
3	92	8	91
4	90	9	89
5	94		

[a] A solution of 4-bromoanisole (1.0 mmol), phenyl boronic acid (1.2 mmol), Pd^0 (0.01 mmol), and K_2CO_3 (2.5 mmol) in H_2O/EtOH (10 mL; 3:1 v/v) was heated at 80 °C under argon for 5 h. [b] Determined by GC analysis (internal standard: dodecane).

with the initial yield of 96 % decreasing to 89 % after nine runs (Table 1). After five catalytic experiments the size and shape of the Pd catalyst were examined by using TEM, XRD, and XPS, and no apparent change in the PPPIL•Pd^0 morphology was observed (Figure 4).

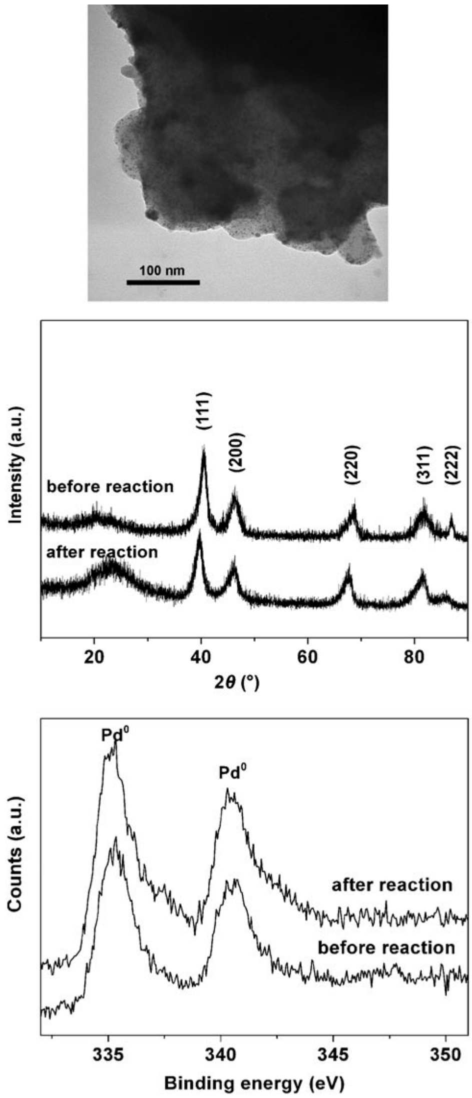


Figure 4. TEM image (top) and XRD (middle), and XPS spectra (bottom) of PPPIL•Pd after five catalytic cycles.

A hot-filtration test was used to explore possible catalyst leaching and the actual active species.[17] The reaction was terminated after 0.5 h and the conversion was found to be 25 %. At this juncture, the catalyst was separated from the solution by a simple filtration and the resultant filtrate was tested for palladium by using atomic absorption spectroscopy (AAS) analysis (detection limit is 0.03 ppm); the result showed that about 0.09 ppm of the palladium leached into the solution, which corresponds to an original metal loss of less than 1 %. The amount of palladium leaching onto the products was also checked by using ICP; no such leaching was detected. The reaction was continued with the filtrate for an additional 12 h, and the conversion remained almost unchanged. In contrast, the conversion was found to be 19 % for a corresponding heterogeneous reaction conducted with 0.1 ppm PPPIL•Pd^0 catalyst under identical conditions for 12 h. These studies demonstrated that the palladium bound to PPPIL particles was only active during the reaction and that the reaction proceeded on the heterogeneous surface.

It is known that products are easily adsorbed onto a polymer-supported catalyst, especially on a porous polymer matrix. The product must be completely extracted in the next cycle, or product residues may cause contamination of the catalyst. We used the Suzuki coupling reaction of 4-bromoanisole (1 mmol) with phenyl boronic acid (1.2 mmol) as the test reaction in an extraction experiment to investigate the product residue on the catalyst. After the reaction was completed, the product was extracted from the reaction mixture with diethyl ether (30 mL), and the catalyst remaining in the water phase was collected by using filtration. The catalyst was then extracted with diethyl ether, and the product in the diethyl ether phase was determined by using GC analysis with dodecane as the internal standard. The product was found to be easy to extract from the non-porous PPPIL•Pd^0 microspheres, and only 4 mL of diethyl ether was required for complete extraction of the product. However, if a porous PPPIL-gel matrix (developed by us under similar conditions[18] and employed in the same reaction) was used to support the Pd NPs (PPPIL-gel•Pd^0) in the reaction, a small quantity of product was detected in the diethyl ether phase even after four 4 mL extractions with diethyl ether. Similar results were also observed for other porous-polymer-supported Pd catalysts, such as the PNIPAAm-gel•Pd and PGELs developed by Ikegami and Hamamoto[19] and Mioskowski et al.,[9] respectively. A clear advantage of non-porous PPPIL•Pd^0 over porous gel•Pd^0 is that the catalyst requires no further treatment prior to being recycled. Therefore, supporting the Pd NPs on nonporous microspheres not only prevented leaching of the catalyst but also enhanced its activity, thereby facilitating the separation of the products.

To further evaluate the activity of the PPPIL•Pd^0 catalyst, it was compared with four types of Pd NPs under similar conditions. The first catalyst was Pd NPs supported on pore-expanded mesoporous silica (Pd/PE-MCM-41) developed by Sayari et al.[20] The second catalyst consisted of Pd NPs stabilized with poly(*N*-vinyl-2-pyrrolidone) (Pd-PVP), fabricated by Das and El-Sayed.[21] The third consisted of Pd NPs stabilized with polyionic gels (Pd/gel), as reported by Mioskowski et al.[9] Finally, the fourth was a commercially available polyurea-microencapsulated Pd catalyst (Pd^0EnCat) developed by Ley et al.[22] Table 2 compares these catalysts, and it can be seen that PPPIL•Pd^0 was more efficient than Pd/PE-MCM-41 or Pd-PVP in the Suzuki reaction of iodobenzene, providing high turnover frequencies (TOF) of 330 h^{-1} (Table 2, entries1–3). In Suzuki reactions of electron-deficient aryl bromides with benzene boronic acid, the PPPIL•Pd^0 catalyst was again found to be more efficient

Table 2. Suzuki reactions of aryl halides with benzene boronic acid and various Pd catalysts.

Entry	Substrate[a]	Pd catalyst[b] ([mol %])	T [°C]	t [h]	Solvent	Yield [%]	TOF [h^{-1}]
1	C_6H_5I (1.2)	Pd/PE-MCM-41 (0.1)	78	5	H_2O	93	186
2	C_6H_5I (1.5)	Pd-PVP (0.3)	80	12	EtOH/H_2O	95	26
3	C_6H_5I (1.2)	PPPIL·Pd^0 (0.1)	80	3	EtOH/H_2O	99	330
4	p-nBu-C_6H_4Br (1.2)	Pd-gels (0.7)	85	6.5	MeCN/H_2O	80	17.6
5	p-nBu-C_6H_4Br (1.2)	Pd^{0}EnCat (0.7)	85	6.5	MeCN/H_2O	48	10.5
6	p-MeC_6H_4Br (1.2)	PPPIL·Pd^0 (0.3)	85	6.5	EtOH/H_2O	63	32.3
7	p-MeOC_6H_4Br (1.2)	PPPIL·Pd^0 (1.0)	80	5	EtOH/H_2O	95	19.0
8	p-MeOC_6H_4Br (1.2)	Pd^0/[BMI][PF_6] (2.5)	110	24	[BMI][PF_6]/H_2O	70	1.17

[a] Molar ratio of benzene boronic acid/substrate given in brackets. [b] See ref. [20] for Pd/PE-MCM-41, ref. [21] for Pd-PVP, this work for PPPIL·Pd^0, ref. [9] for Pd-gels and Pd^{0}EnCat, and ref. [23] for Pd^0/[BMI]-[PF_6].

than either Pd/gel or Pd^{0}EnCat (Table 2, entries 4–6) and gave a TOF of 32.3 h^{-1} for the Suzuki reaction of p-bromotoluene.

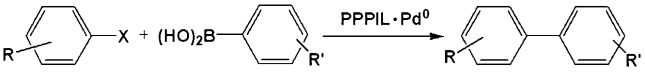
The catalytic activity of PPPIL·Pd^0 in the Suzuki reaction of 4-bromoanisole with phenyl boronic acid was much better than that of [BMI][PF_6]-supported Pd, and the TOF was 16 times greater than that of the [BMI][PF_6]/H_2O biphasic catalysis system. (Table 2, entries 7–8).[23] The main reason for this is that the miscibility of the IL-supported catalysts and the substrates were very poor, so the reaction occurred primarily at the interphase rather than in the bulk solvent. In contrast, the PPPIL·Pd^0 catalyst can be easily dispersed in the reaction mixture with stirring, so PPPIL·Pd^0 has a much greater density of active sites than the Pd^0/[BMI][PF_6] system, which resulted in efficient use of the active sites.

To the best of our knowledge, it is very difficult to give the exact mechanism for the very high activity and stability of the catalytic system. However, highly polar ionic environments allow the electrostatic stabilization of preformed NPs (as for Bu_4N^+ ions in tetrabutylammonium bromide[24]) and could endow PPPIL·Pd^0 with its high activity in the Suzuki cross-coupling reaction. The phase-transfer-catalyzed function of the guanidinium ILs,[25] which increases the amount of accessible active sites on the NPs, may also contribute to the high activity.

The next steps involved investigating the substrate scope of PPPIL·Pd^0-catalyzed Suzuki couplings by using other aryl halides and aryl boronic acids (Table 3). Both electron-rich and electron-deficient aryl bromides and aryl iodides were found to be reactive, and the desired coupling products were even obtained with aryl chlorides in the presence of tetrabutylammonium hydroxide (TBAOH) as the base,[26] despite the fact that Suzuki coupling of aryl chlorides is generally considered difficult.[27] Furthermore, various *meta*- and *ortho*-substituted aryl bromides and aryl boronic acids could be readily obtained in moderate-to-good product yields under these catalytic systems if the catalyst loading was 1.0 mol %.

In addition to Pd NPs, PPPIL microspheres with Au and Pt NPs embedded in the surface IL layers (PPPIL·Au^0 and PPPIL·Pt^0) were also synthesized. Figure 5 shows TEM images of the synthesized Au and Pt NPs, of which the average sizes were 4.9 and 3.6 nm, respectively, uniformly embedded in the surface IL layers of the PPPIL microspheres. No conglomeration of noble-metal NPs was observed. The XRD patterns of PPPIL·Au^0 and PPPIL·Pt^0 are also shown in Figure 5. Four diffraction peaks at 2θ were found for both PPPIL·Au (38.6, 44.1, 64.6, and 78.2°) and PPPIL·Pt (38.8, 44.9, 67.9, and 80.2°), which correspond to diffractions arising from the (111), (200), (220), and (311) lattice planes of the Au and Pt crystals and reveal that the crystals are cubic phase with cell constants of $a=0.4093$ and 0.4005 nm for Au and Pt, respectively. On the basis of the XRD patterns, the average sizes of the Au and Pt NPs embedded in the IL layer of the PPPIL microspheres were calculated to be 4.4 and 3.2 nm, respectively, which are in good agreement with the dimensions observed by using TEM.

Table 3. PPPIL·Pd^0-catalyzed Suzuki cross-coupling reactions of aryl halides.[a]



Entry	Aryl halides	Ary boronic acid	Pd^0 [mmol]	Yield[b] [%]
1	C_6H_5I	$C_6H_5B(OH)_2$	0.0005	100
2	p-$NO_2C_6H_4I$	$C_6H_5B(OH)_2$	0.0005	100
3	p-MeC_6H_4I	$C_6H_5B(OH)_2$	0.0005	94
4	p-$NO_2C_6H_4Br$	$C_6H_5B(OH)_2$	0.005	97
5	p-$NO_2C_6H_4Br$	o-Me$C_6H_4B(OH)_2$	0.005	72
6	p-$NO_2C_6H_4Br$	p-Cl$C_6H_4B(OH)_2$	0.005	94
7	p-$NO_2C_6H_4Br$	p-Me$C_6H_4B(OH)_2$	0.005	92
8	C_6H_5Br	o-Me$C_6H_4B(OH)_2$	0.01	80
9	C_6H_5Br	$C_6H_5B(OH)_2$	0.005	85
10	p-(COOH)C_6H_4Br	$C_6H_5B(OH)_2$	0.005	90
11	p-(CH_3CO)C_6H_4Br	$C_6H_5B(OH)_2$	0.005	73
12	p-MeC_6H_4Br	$C_6H_5B(OH)_2$	0.005	71
13	o-MeC_6H_4Br	$C_6H_5B(OH)_2$	0.01	43
14	m-MeC_6H_4Br	$C_6H_5B(OH)_2$	0.01	58
15	p-$NO_2C_6H_4Cl$	$C_6H_5B(OH)_2$	0.01	91[c]
16	C_6H_5Cl	$C_6H_5B(OH)_2$	0.01	36[c]

[a] A solution of aryl halide (1.0 mmol), boronic acid (1.2 mmol), and K_2CO_3 (2.5 mmol) in H_2O/EtOH (10 mL; 3:1 v/v) was heated at 80 °C under argon for 5 h. [b] Isolated yield. [c] TBAOH (2.5 mmol) was used as base, 90 °C, 10 h.

The advantages of this method of generating metallic NPs are obvious: 1) The surface area of the actual catalyst, that is, the Pd particles, is high because the size of the Pd NPs is of the order of several nanometers; 2) the active sites on Pd NPs are not blocked by protective ligands, inferring a high catalytic activity;[28] 3) a facile mass transfer is possible because the Pd NPs are well dispersed on the PPPIL surfaces without aggregation, and the surface IL layer prevents leaching of the active species by steric repulsion; 4) facile

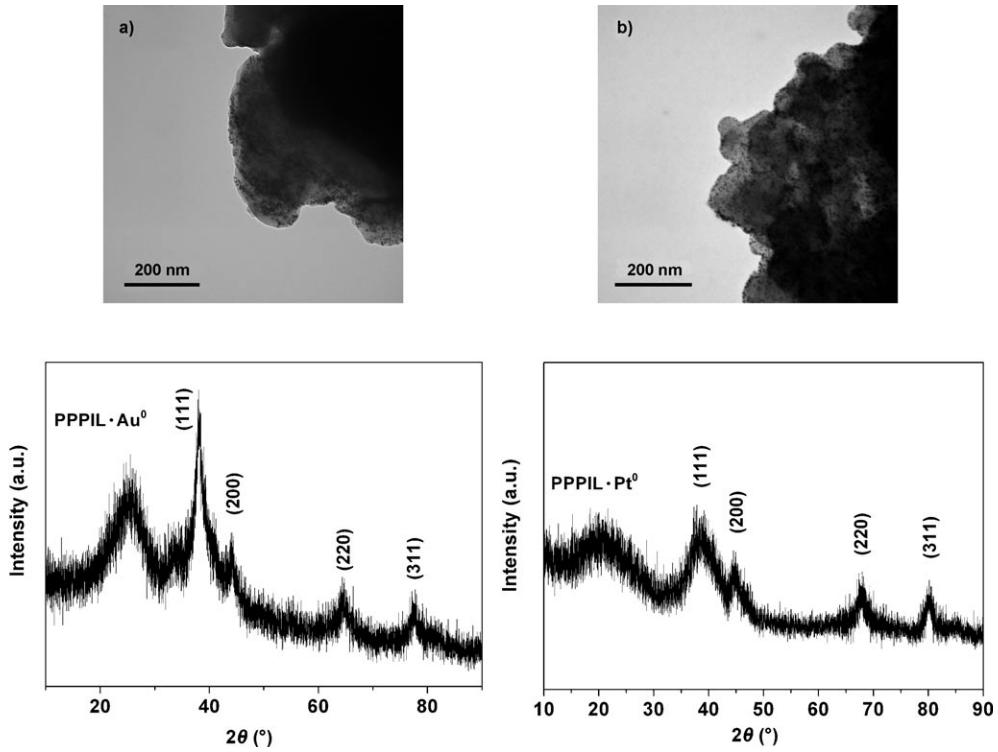


Figure 5. TEM images (top) and XRD spectra (bottom) of a) PPPIL·Au^0 and b) PPPIL·Pt^0.

separation and recycling of the catalyst due to the heterogeneous composite structure; 5) the use of catalysts in aqueous solutions is a top priority for the phase-transfer-catalyzed function of the guanidinium IL.

Conclusions

In summary, IL-grafted rigid poly(*p*-phenylene) microspheres were used as a scaffold to adsorb and immobilize IL-embedded noble-metal catalysts during heterogeneous reactions. The combination of nanoparticles and IL fragments on the microsphere surfaces demonstrated excellent synergistic effects, thereby enhancing the activity and durability of the catalysts. Therefore, the present approach may have potential applications in transition-metal-nanocatalyzed reactions. Further studies into the preparation of other catalytic systems are currently ongoing.

Experimental Section

Preparation of PPPIL particles: Poly(*p*-phenylene) was prepared according to the method described in our previous paper.[12] To prepare the PPPIL particles, PPP (1.94 g, 10 mmol) was dissolved in $C_2H_2Cl_4$ (30 mL), then NBS (7 mmol) and AIBN (5 mol%) were added and the reaction mixture was stirred at 80 °C for 6 h. The reaction mixture was poured into ethanol (100 mL), then the precipitated solid (PPPB) was collected by filtration and washed with ethanol several times, then dried under vacuum at RT for 24 h. PPPB (1 g, 4 mmol) was dissolved in $CHCl_3$ (20 mL), then pentaalkylguanidine (6 mmol) was added and the reaction mixture was stirred at 60 °C for 6 h. The precipitated solid (PPPIL particles) was collected by filtration and washed with $CHCl_3$ several times and dried in a vacuum at RT for 24 h.

Preparation of PPPIL·Pd^0: The PPPIL microspheres were soaked in aqueous H_2PdCl_4 (5.0 mmol L^{-1}) for 24 h to convert the Br^- form into the $PdCl_4^{2-}$ form, and finally washed thoroughly with water to remove any excess H_2PdCl_4. A 10-fold excess of aqueous $NaBH_4$ (0.4 mol L^{-1}) was added dropwise with vigorous stirring, then the mixture was kept at RT for 4 h. The resultant PPPIL·Pd^0 particles were collected by filtration, washed with water several times, and dried under vacuum at RT for 24 h. PPPILs microspheres with Au and Pt embedded in the surface IL layers (PPPILsAu^0 and PPPILsPt^0) were synthesized by using the straightforward procedure described above.

Typical procedures for the Suzuki reaction: Benzene boronic acid (1.2 mmol), base (2.5 mmol), Pd catalyst (0.5 mol%), aryl halide (1.0 mmol), and H_2O/EtOH (10 mL; 3:1 v/v) were added to a screw-capped vial with a side tube under argon. The mixture was stirred at 80 °C for 5 h and then cooled. The product was extracted from the reaction mixture with diethyl ether (2×4 mL), and then the organic phase was collected, washed with water, and concentrated under vacuum. The residue was purified by flash column chromatography (eluent: hexane/ethyl acetate) to afford the final product. The PPPIL·Pd^0 catalyst remaining in the water phase was collected by filtration.

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