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Biphasic Hydrogenation of Olefins by Functionalized Ionic Liquid-Stabilized Palladium Nanoparticles

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Abstract: Palladium nanoparticles in the size range of 5–6 nm were prepared conveniently by reducing palladium(II) with atmospheric pressure hydrogen and stabilized by 2,2′-dipyridylamine-functionalized imidazolium cations according to our approach. The efficient catalytic conversion of cyclohexene into cyclohexane by the functionalized ionic liquid-stabilized palladium nanoparticles has been performed under very mild hydrogen pressure (0.1 MPa) and at 35 °C. It was found that the concentration of palladium and the reaction temperature considerably affected the size and degree of aggregation of Pd nanoparticles in ionic liquid, which further changed the performance of the catalyst activity. The synthesized nanocatalysts can be recycled at least five times without any loss of the activity. Finally, the scope of substrates was also investigated. The excellent catalytic activity of the present system can be attributed to good stabilization and high dispersion of palladium nanoparticles.

Keywords: hydrogenation; ionic liquid; nanoparticles; olefins; palladium

Introduction

Recently, the application of transition-metal nanoparticles has attracted large interest because metal nanoparticles can act as the highly efficient catalysts. It has been suggested that the small size of the metal nanoparticles leads to high surface/volume ratio and consequently high numbers of potential active sites available to the substrates, as a result of large enhancement in their catalytic activity while they are used as catalysts.[1,2] However, nanocatalysts are thermodynamically not stable due to their high excess surface-energy, therefore they have a tendency to aggregate unless they are stabilized. The methods for stabilizing nanoparticles mainly involve electrostatic stabilization, steric protection and coordination stabilization by the use of polymers, quaternary ammonium salts, dendrimers, surfactants, polyoxoanions or ligands etc.[3–14]

Among these approaches, particular attention has been paid to the ligand stabilization of metal nanoparticles. By coordinating with the ligand, the entrapped metal nanoparticles can undergo some potential changes of their physical and chemical properties. For example, the electron delocalization of metal nanoparticles can change the extent of the decomposition and solubility in the solvents, thereby offering the possibility that these metal nanoparticles act as homogeneous catalysts which are also called 'soluble' analogues of heterogeneous catalysts and have been characterized by a higher activity and selectivity.[15]

Over the last few years, ionic liquids, as successful alternative solvents for homogeneous biphasic catalysis, have been designed for immobilizing catalysts, facilitating product isolation and recycling the catalyst system. These neoteric solvents have been extensively applied in different reactions such as acylation, hydroformylation, Diels–Alder reaction, olefin dimerization or oligomerization, hydrogenation, oxidation and biocatalysis.[16–23] Ionic liquids have also been named as the 'designer solvents', which offer us a much easier way to find a better ionic liquid with special properties suitable for given reactions. Very recently, Welton's group has employed the designability of the ionic liquids to optimize the nucleophilic aromatic substitution reaction.[24]

It has been reported that he imidazolium ionic liquid (IL) is an interesting medium for the formation and stabilization of catalytically active transition-metal nanoparticles. The pre-organized ‘supermolecular’ structures of imidazolium ionic liquids can create an external layer around the metal nanoparticles to control the growth of the particle size and affect the mass transportation, however, simple imidazolium ionic liquids cannot provide an effective protection to the nanoparticles against aggregation under the catalytic conditions.[21,25] Therefore, there have been some reports about addition of ligands to stabilize metal nanoparticles for biphasic reactions in ionic liquids.[26,27,28] Even if the catalyst/ligand dissolves well in the ionic liquid, there is often a dramatic decrease in its activity after several runs. The main cause of this decrease is that the metal component and/or the ligands might leach successively in the recycling experiments. In addition, the nanocatalyst-ligand complexes are not stable enough in the process of separation, which will also lead to an aggregation of nanoparticles and then a decrease of the catalytic activity,[29,30,31] thus the cations of ionic liquids designed for immobilizing metal nanoparticles have been reported.[32,33] Recently, Han’s group has also reported a kind of guanidinium ionic liquid containing N-donor ligands to stabilize palladium nanoparticles on molecular sieves which showed synergistic effects to enhance the activity and durability of the catalyst.[34]

To the best of our knowledge, there is no such report on ionic liquid cations tethered to a bidentate nitrogen ligand to stabilize palladium nanoparticles for catalysis. In this work, the N-donor bidentate ligand (2,2′-dipyridylamine) was covalently attached to the imidazolium cation to obtain a novel ionic liquid – 2,3-dimethyl-1-[3-*N*,*N*-bis(2-pyridyl)propylamido]imidazolium hexafluorophosphate ([BMMDPA] [PF_6], Figure 1) in order to prevent aggregation of palladium nanoparticles, on the other hand, the linker (2,2′-dipyridylamine) could also change the surrounding electronic characteristics of the palladium nanoparticles, which may influence the hydrogenation activity of palladium nanocatalysts. 1-*n*-Butyl-2,3-dimethylimidazolium hexafluorophosphate ([BMMIM] [PF_6], Figure 1) instead of 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([BMIM] [PF_6], Figure 1) was intentionally selected as the reaction media for the hydrogenation of various olefins because an N-heterocyclic carbene might form by C-2 deprotonation or oxidative addition of the C-2–H bond of 1,3-dialkylimidazolium ionic liquids, leading to poisoning of the palladium catalyst and decrease of the activity.[35,36] We disclose herein that indeed Pd(0) nanoparticles stabilized by the bidentate nitrogen ligand attached to the imidazolium cations are highly efficient multiphase catalysts for the hydrogenation of various olefins in up to 100% yield. Additionally, the effects of palladium concentration and reaction temperature on catalytic activity were investigated.

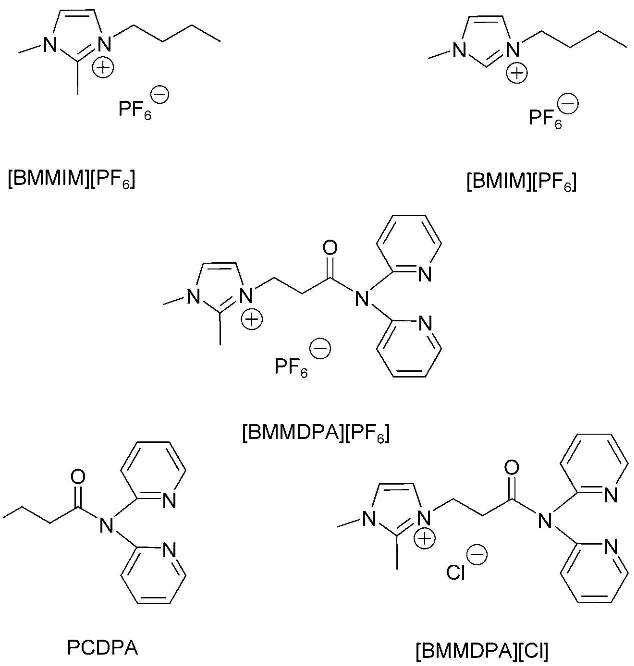
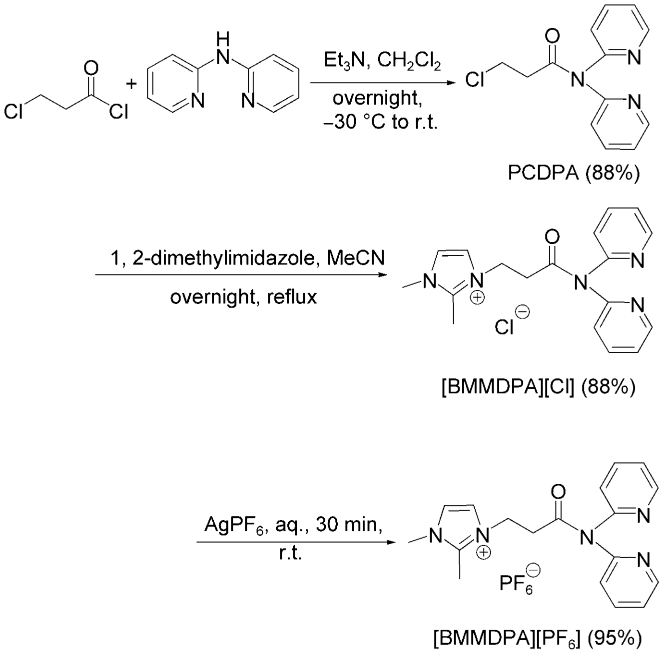


Figure 1. Structures of [BMMIM] [PF_6], [BMIM] [PF_6], [BMMDPA] [PF_6], PCDPA and [BMMDPA] [Cl].

Results and Discussion

The synthetic route to the functionalized ionic liquid [BMMDPA] [PF_6] is shown in Scheme 1. Briefly, it was synthesized according to a conventional method by quaternarization of an imidazole with the corre-



Scheme 1. Synthesis of 2, 3-dimethyl-1-[3-*N*,*N*-bis(2-pyridyl)-propylamido)imidazolium hexafluorophosphate [BMMDPA] [PF_6].

sponding alkyl halide, followed by the step of ion exchange. However, in the step of the synthesis of *N,N*-bis(pyridyl)-3-chloropropanamide (PCDPA, Figure 1), it was found that the reaction of amide formation necessarily started at −30 °C and then was slowly warmed to room temperature. Thermogravimetric analysis (TGA) measurements of the ionic liquids showed that [BMMDPA] [PF_6] started to decompose from 190 °C and was almost completely decomposed at 325 °C, while [BMMDPA] [Cl] started to decompose from 125 °C and was degraded completely at 250 °C. These results indicated that the thermal stability of [BMMDPA] [Cl] was somewhat poorer than that of [BMMDPA] [PF_6] (see Supporting Information, Figures S1 and S2).

The Pd(0) nanoparticles were simply prepared by stirring a mixture of $Pd(OAc)_2$, the functionalized ionic liquid [BMMDPA] [PF_6] and [BMMIM] [PF_6] in acetone at room temperature in a stainless steel autoclave for 1 h, then evaporating the solvent under vacuum, followed by reduction of Pd(II) with molecular hydrogen (0.1 MPa) at 60 °C for 10 min, which afforded a dark brownish 'solution' and then adjusting the concentration of atomic Pd to 2.5 mmol L^{-1}. After three consecutive recycles of cyclohexene hydrogenation, a black powder could be isolated from the black 'solution' by adding acetone and then centrifuging (4000 rpm, 5 min, 3 times). Washed three times with acetone and dried under reduced pressure, the isolated powder was analyzed by X-ray diffraction (XRD), thermogravimetric analysis (TGA), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS).

The XRD pattern (Figure 2) of the isolated material confirmed the presence of crystalline Pd(0). The most representative reflections of Pd(0) were indexed as face-centered cubic (fcc) with a unit cell parameter $a = 0.39026$ nm. The Bragg reflections at 39.980°, 46.500°, 67.599°, 81.600°, and 86.727° corresponded to the indexed planes of the crystals of Pd(0) (111), (200), (220), (311) and (222).

The previously isolated [BMMDPA] [PF_6]-stabilized palladium nanoparticles were redispersed in acetonitrile, placed as a thin film in a carbon coated copper grid and characterized by TEM. Analysis of the micrographs displayed nearly spherical Pd(0) nanoparticles and a nearly monomodal distribution with an average diameter of 5–6 nm when reaction was performed at 2.5 mmol L^{-1} palladium concentration and 35 °C (Figure 3), but the obvious aggregation of the Pd particles was visually observed when the catalyst was exposed under higher palladium concentration (10 mmol L^{-1}) or higher temperature (50 °C), as shown in Figure 4. Moreover, the presence of N and Pd in the sample by EDS (Figure 5) spectra proved that [BMMDPA] [PF_6] and/or [BMMIM] [PF_6] might coordinate or adsorb strongly on the surface of palladium nanoparticles even if the samples have undergone the previous isolation procedures. This was further verified by a TGA curve of the separated palladium nanoparticles after three consecutive cycles of hydrogenation of cyclohexene. To our surprise, the separated palladium nanoparticles lost *ca.* 23% weight within the temperature range studied (40–600 °C) (Supporting Information, Figure S3), which further proved that the isolated nanoparticles still contained residues of the ILs even if the isolation procedure had been repeated for several times. The Dupont group has also observed a similar phenomenon previously by XPS analysis of the isolated nanoparticles.[25]

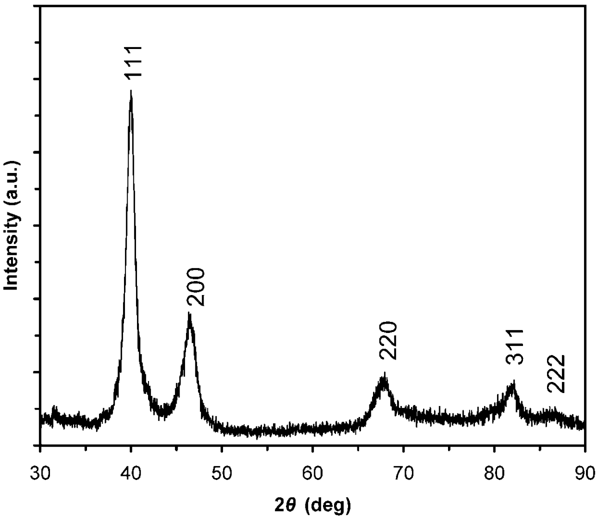


Figure 2. X-ray diffraction pattern of isolated Pd(0) nanoparticles after three consecutive recycles of cyclohexene hydrogenation. The peaks are labelled with the hkl of the planes for the corresponding Bragg angles.

The functionalized ionic liquid [BMMDPA] [PF_6]-stabilized Pd nanoparticles were prepared *in situ* in [BMMIM] [PF_6] and employed directly as catalysts. The catalytic activities under different reaction conditions are shown in Figure 6, Table 1 and Table 2. Cyclohexane was the only product in the hydrogenation of cyclohexene. The hydrogenation of styrene or ethyl acrylate produced only ethylbenzene or ethyl propionate, respectively. Most reactions were carried out at 35 °C under 0.1 MPa of hydrogen pressure for 3 h unless indicated otherwise. The yield of the product was obtained based on the conversion of the substrates and the selectivity of the product determined by gas chromatographic analysis.

As shown in Figure 6, the effect of Pd(0) concentration on the catalyst activity was firstly investigated. The activity of the catalyst decreased slightly as the palladium concentration increased from 1 mmol L^{-1} to 10 mmol L^{-1} at 35 °C. The TEM images demonstrated that the higher concentration of palladium

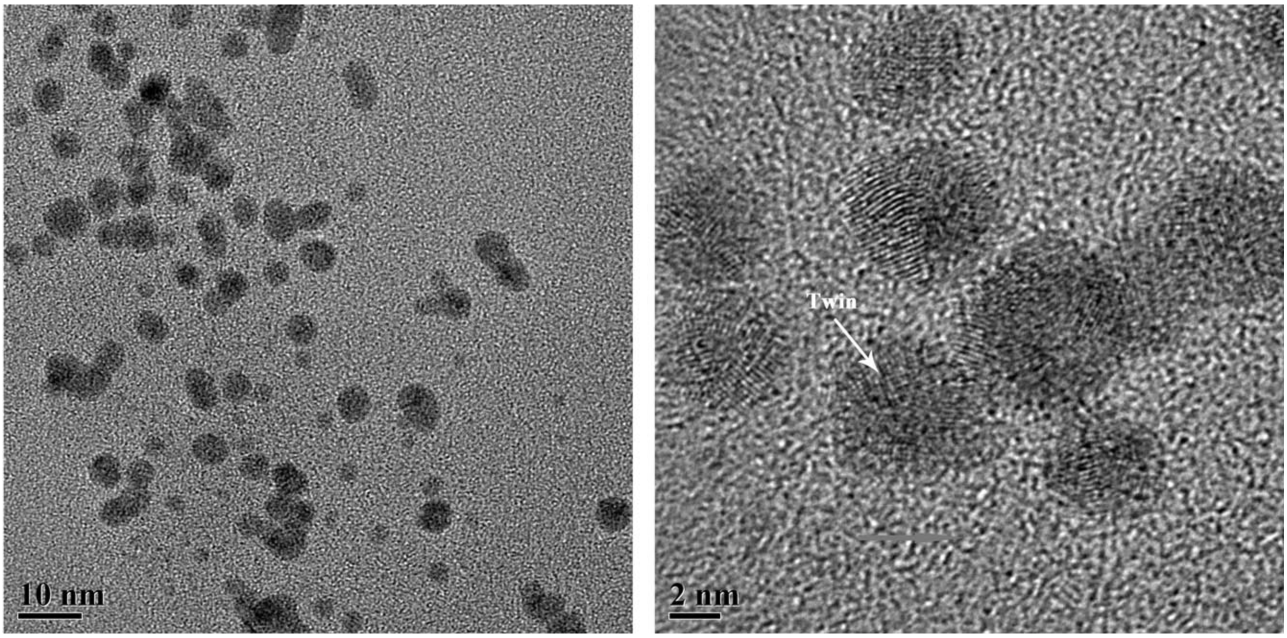


Figure 3. TEM (*left*) and HR-TEM (*right*) images of twinned palladium nanoparticles after three consecutive recycles of hydrogenation of cyclohexene under the conditions of 2.5 mmol L^{-1} palladium concentration and 35 °C reaction temperature, supported on a carbon-coated grid.

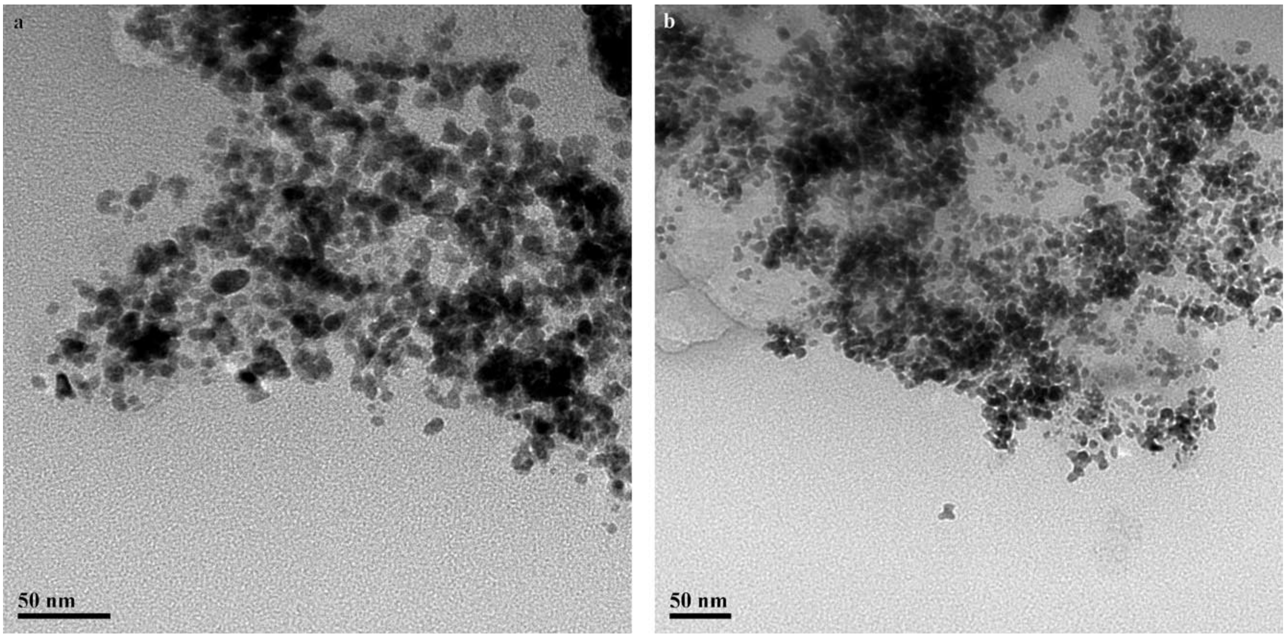


Figure 4. TEM micrographs of Pd(0) nanoparticles after three consecutive recycles of hydrogenation of cyclohexene, supported on a carbon coated grid under different reaction conditions: a (*left*) 2.5 mmol L^{-1} palladium and 50 °C reaction temperature; b (*right*) 10 mmol L^{-1} palladium and 35 °C reaction temperature.

(10 mmol L^{-1}) induced the aggregation of palladium nanoparticles (Figure 4b), leading to a decrease of the activity. The similar results have also been reported by Fink's and Reetz's groups, respectively.[37,38] No significant difference in activity was observed when the concentration of palladium changed from 1 mmol L^{-1} to 2.5 mmol L^{-1}. This phenomenon illustrated that the present palladium nanocatalysts were highly effective even if the concentration of Pd decreased to a very low level since the number of cata-

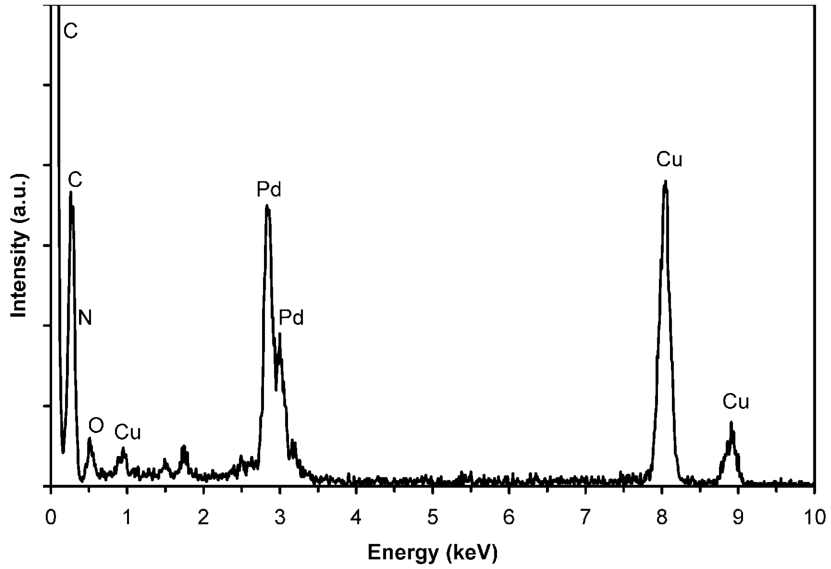


Figure 5. Energy dispersion spectrum (EDS) of the sample as employed for Figure 3 confirming the presence of palladium, [BMMDPA] $[PF_6]$ and/or [BMMIM] $[PF_6]$ in the sample.

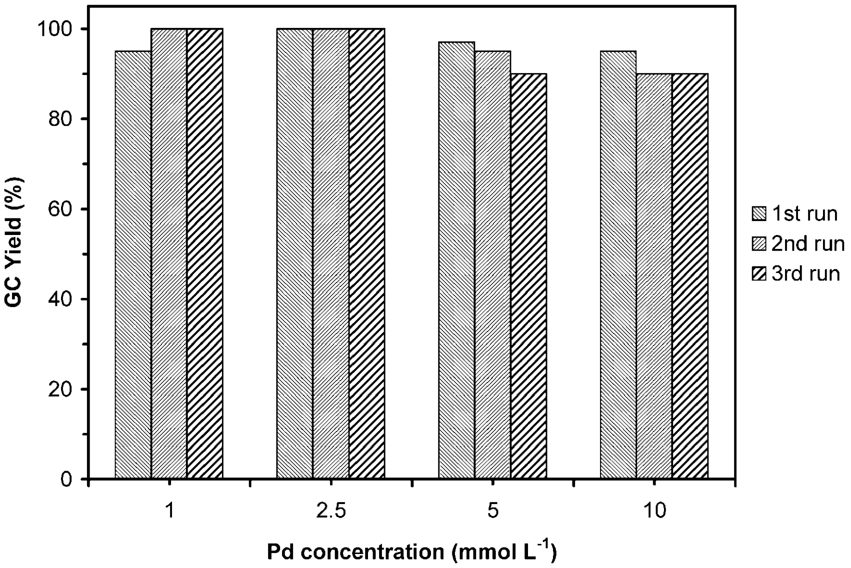


Figure 6. Influence of the concentration of Pd(0) in [BMMIM] $[PF_6]$ on catalytic activity. cyclohexene/Pd = 500 (molar ratio), 0.1 MPa H_2; reaction temperature: 35 °C; reaction time: 3 h.

lytic sites of Pd nanoparticles were enough for the complete conversion of cyclohexene under present conditions.

From Table 1, we see that the activity decreased when the reaction temperature was higher than 35 °C (entries 1, 2; 4, 5). Furthermore, the activity of the catalyst decreased gradually in the consecutive catalytic recycles at a relatively higher temperature (entries 2 and 5). Interestingly, the lower concentration of Pd (2.5 mmol L^{-1}) was beneficial to increasing the durability of the catalysts (entries 1 and 3). It was visually observed that more bulk metal particles were suspended impressively in IL ([BMMIM] $[PF_6]$) with increasing reaction temperature (> 35 °C) or Pd concentration (> 5 mmol L^{-1}), which revealed that the coalescence of palladium nanoparticles into bulk metal particles was accelerated when the unsuitable reaction conditions were adopted, thus leading to lower activity towards the conversion of cyclohexene to cyclohexane correspondingly. However, the nano-sized palladium particles were still in existence (Figure 4a and Figure 4b) even if some of Pd nanoparticles had aggregated and grown up under these conditions. It is worth noting that the low temperature not only pro-

Table 1. Hydrogenation of olefins catalyzed by functionalized ionic liquid-stabilized Pd(0) nanoparticles in [BMMIM] [PF_6].[a]

Entry	T [°C]	Substrate	Substrate/Pd (molar ratio)	$C_{Pd(0)}$ [mmol L^{-1}][b]	GC Yield [%]		
					1st run	2nd run	3rd run
1	35	Cyclohexene	500	10	95	90	90
2	50	Cyclohexene	500	10	77	65	58
3	35	Cyclohexene	500	2.5	100	100	100
4	35	Cyclohexene	2000	2.5	96	95	95
5	50	Cyclohexene	2000	2.5	81	75	72
6	35	Cyclohexene	4000	2.5	50		
7	35	Styrene	500	2.5	100	100	100
8	35	Ethyl acrylate	500	2.5	100	100	100

[a] *Reaction conditions*: 0.1 MPa H_2, reaction time: 3 h.

[b] $C_{Pd(0)}$ denotes the Pd(0) concentration.

Table 2. Influence of different ligands on the activity of cyclohexene hydrogenation.[a]

Entry	Ligands	Ionic Liquid	GC Yield [%]
1	[BMMDPA] [PF_6]	[BMMIM] [PF_6]	96
2	[BMMDPA] [PF_6]	[BMIM] [PF_6]	5
3	2,2′-bispyridineamine	[BMMIM] [PF_6]	83
4	2,2′-bispyridineamine	[BMIM] [PF_6]	8

[a] *Reaction conditions*: Pd (2.5 mmol L^{-1}), Pd/Ligands = 2:1 (molar ratio), cyclohexene/Pd = 2000 (molar ratio), [BMMIM] [PF_6] or [BMIM] [PF_6] (1 mL), 0.1 MPa H_2, reaction temperature: 35 °C, reaction time: 3 h.

moted the formation and dispersion of Pd nanoparticles, but also favored the exothermic hydrogenation reaction. In consideration of the melting point, viscosity of the ionic liquid and the efficient stirring speed, we optimized most of the reaction temperatures at 35 °C.

In summary, low reaction temperature and low concentration of Pd favored better dispersion of Pd nanoparticles which were the actual catalytic active sites. This was the reason why the catalyst showed the best activity at 35 °C and 1–2.5 mmol L^{-1} Pd concentration.

As shown clearly in Table 1 (entries 3 and 4), the total consumption of cyclohexene took less than 3 h by using the present catalyst which also can be reused at least five times without loss of the activity (not listed) when the molar ratio of cyclohexene to Pd atom was 500, and the palladium nanoparticles were still in an almost monomodal distribution with an average diameter of 5–6 nm (Figure 3) during the catalytic recycles. From high-resolution transmission electron microscopic (HR-TEM) images, it seems that the present Pd nanoparticles (5–6 nm) were aggregates of smaller Pd crystallites (2–3 nm), and the defect in the Pd(0) crystalline lattice was also found. Note that these twin defects are typical for small particles which may be the actual active sites towards the catalytic hydrogenation. The present system was also very active to other substrates such as the hydrogenation of styrene or ethyl acrylate (entry 7 and entry 8), even during three catalytic recycles without the loss of any activity. Actually, this Pd nanocatalyst was far more active than we expected, when the molar radio of substrate to Pd increased from 500 to 2000, the GC yield of cyclohexane could still reach 95% after the two consecutive recycles of hydrogenation (entry 4). Even if we continued to increase the molar radio of substrate to Pd to 4000 (entry 6), the yield of cyclohexane could still reach up to 50%.

We also investigated the roles of [BMMDPA] [PF_6] in the present catalytic system. Some control experiments have been conducted for the hydrogenation of cyclohexene. It was visually observed that the addition of unfunctionalized ligand (2,2′-bispyridineamine) can also effectively stabilize the palladium nanoparticles, but it was much less active than the addition of [BMMDPA] [PF_6] (Table 2, entries 1 and 3). We speculate that the unfunctionalized ligand 2,2′-bispyridineamine has limited solubility in [BMMIM] [PF_6] and/or too strong a coordinating ability compared with [BMMDPA] [PF_6], then the active surface atoms of Pd(0) nanoparticles are strongly coordinated and poisoned,[39] which inhibits the hydrogenation of olefins.

Finally, we testified the effect of the possible formation of carbene on the catalytic reactivity. To our surprise, under the same conditions, after we displaced [BMMIM] [PF_6] with [BMIM] [PF_6] as the reaction medium, and either [BMMDPA] [PF_6] or 2,2′-bispyridineamine was added as the ligand, the yield of cyclohexane was only 5% or 8% even if we repeated the experiments three times in order to avoid the error of the experiments (Table 2, entries 2 and 4). After the reaction, the ionic liquid phase was still slightly yellow-brownish which specified that the Pd(II) complex in the present system was hard to be reduced to Pd(0) species under 0.1 MPa hydrogen pressure at 60 °C for 10 min. This accounts for the fact that the formation of carbene may hinder the reduction of Pd(II) complexes under the present conditions, a similar conclusion has been drawn by the Trzeciak group[40] and the Yokoyama group.[41]

Conclusions

In conclusion, we have first synthesized a new ionic liquid ([BMMDPA] [PF_6]) functionalized by 2,2′-bispyridineamine, and then prepared Pd nanoparticles *in situ* in ionic liquid ([BMMIM] [PF_6]) media. It was found that Pd(0) nanoparticles were stabilized effectively by the bidentate nitrogen ligands attached covalently to the imidazolium cations. The nanocatalyst was a highly efficient multiphase catalyst for the hydrogenation of olefins in up to 100% yield. Furthermore, we have demonstrated that the higher concentration of palladium and reaction temperature did not favor the stabilization of the palladium nanoparticles, which also led to the decrease of catalytic activity in our present catalytic system. We are currently investigating how such ligand-stabilized nanocatalysts catalyze selective hydrogenation and other reactions in the ionic liquid medium.

Experimental Section

Materials

All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen. CH_2Cl_2, CH_3CN (A.R. grade) and olefins (A.R. grade) were distilled from CaH_2. Acetone (A.R. grade) was distilled from molecular sieves. Palladium acetate, 2,2′-bispyridineamine, silver hexafluorophosphate and hexafluorophosphoric acid (60 wt% solution in water) were obtained from Aldrich and used without further purification. The ionic liquids ([BMMIM] [PF_6] and [BMIM] [PF_6]) were synthesized using the procedure reported by other authors.[42] All ionic liquids were dried under a vacuum at 60 °C for 4 h prior to reaction. The chloride content of the ionic liquids was checked by the $AgNO_3$ test and purity by ^1H NMR spectroscopy. The GC analyses were performed in a GC 112 A with FID detector equipped with an HP-5 column (30 m, 0.25 mm i.d.). A Perkin–Elmer Pyris Diamond was used in the current study for the thermogravimetric analysis (TGA). TGA measurements of the ionic liquids and the separated palladium nanoparticles were performed under high-purity nitrogen purge (100 mL min^{-1}) by heating the samples to 400 °C, 500 °C and 600 °C separately at a rate of 10 °C min^{-1} (Figures S1–S3). The XRD analysis was performed in a D/MAX 2550 VB/PC using a graphite crystal as monochromator. The TEM analyses were performed in a JEOL JEM 2010 transmission electron microscope operating at 200 kV with nominal resolution of 0.25 nm.

Preparation of *N,N*-Bis(pyridyl)-3-chloropropanamide (PCDPA)

The reaction was performed under a nitrogen atmosphere by standard Schlenk techniques. To a solution of 2, 2′-bispyridineamine (0.50 g, 2.92 mmol) and triethylamine (0.30 g, 2.96 mmol) in dry dichloromethane (15 mL) was added 3-chloropropionyl chloride (1.48 g, 11.7 mmol) at −30 °C. The mixture was slowly warmed to room temperature and stirred overnight. For work-up, the mixture was poured into water and extracted with dichloromethane. The dichloromethane extracts were washed with saturated aqueous sodium bicarbonate solution (until the aqueous layer was alkaline), deionized water, following by drying over sodium sulfate, then the solvent was removed under vacuum to gave PCDPA; yield: 0.67 g (88%). The oily product was used in next step without any further purification.

Preparation of 2,3-Dimethyl-1-[3-*N,N*-bis(2-pyridyl)-propylamido]imidazolium Chloride ([BMMDPA] [Cl])

A mixture of PCDPA (0.67 g, 2.56 mmol) and 1, 2-dimethylimidazole (0.27 g, 2.82 mmol) in acetonitrile (15 mL) was refluxed overnight. The solvent was evacuated and the mixture was poured into deionized water (20 mL), washed with small volumes of toluene three times, dried under a vacuum to give the product as a highly viscous orange oil at room temperature; yield: 0.81 g (88%). ^1H NMR (D_2O, 500 MHz): $\delta = 2.55$ (s), 2.70 (t), 3.70 (s), 4.30 (t), 7.20 (m), 7.25 (s), 7.32 (s), 7.98 (m), 8.25 (m); ^{13}C NMR (D_2O, 125 MHz): $\delta = 177.2$, 151.3, 144.7, 143.1, 140.5, 122.5, 120.9, 118.2, 114.1, 45.2, 36.2, 34.5, 9.0.

Preparation of 2,3-Dimethyl-1-[3-*N,N*-bis(2-pyridyl)-propylamido]imidazolium Hexafluorophosphate ([BMMDPA] [PF_6])

Silver hexafluorophosphate (0.20 g, 0.788 mmol) was added to 10 mL of deionized water and stirred for half an hour. The clear solution was poured into a solution of [BMMDPA] [Cl] (0.28 g, 0.788 mmol) in deionized water (10 mL) and stirred for half an hour. The suspension was filtered to remove the silver chloride precipitate, washed with small volumes of water. The filtrate was collected and then carefully evaporated under a vacuum and dried for 3 h which afforded the salt as a highly viscous brownish oil at room temperature; yield: 0.35 g (95%). ^1H NMR (D_2O, 500 MHz): $\delta = 2.70$ (s), 3.00 (t), 3.80 (s), 4.47 (t), 7.52 (m), 7.56 (s), 7.60 (s), 8.19 (m), 8.42 (m).

General Preparation of Catalysts: Ionic Liquid ([BMMDPA] [PF_6]) Stabilized Palladium(0) Catalysts

A mixture of 2.5 mmolL^{-1} $Pd(OAc)_2$ solution in acetone (1 mL), 1.25 mmolL^{-1} [BMMDPA] [PF_6] solution in acetone (1 mL), and [BMMIM] [PF_6] (1 mL) was stirred at room temperature in a stainless steel autoclave (50 mL) for 1 h, then the solvent was evaporated under vacuum, followed by reduction with molecular hydrogen (0.1 MPa) at 60 °C for 10 min which afforded a dark brownish 'solution'. The catalysts with the different concentrations of Pd in the ionic liquid were prepared in a similar way.

After three consecutive recycles of hydrogenation of cyclohexene, to the phase of the ionic liquid was added acetone (5 mL), and then the black powder was isolated by centrifugation (4000 rpm, 5 min, 3 times). The isolated powder was washed with acetone (3×5 mL), dried under reduced pressure, and then analyzed by X-ray diffraction (XRD), thermogravimetric analysis (TGA), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS).

General Procedure for Hydrogenation under Hydrogen Pressure

The stainless steel autoclave containing previously prepared [BMMDPA] [PF_6]-stabilized Pd(0) catalysts was charged with the appropriate substrate (1.25×10^{-3} mol, 500 equiv.), then hydrogen was admitted to the system at a constant pressure up to 0.1 MPa. The mixture was heated to 35 °C and stirred for 3 h. After cooling to ambient temperature, the products were isolated by liquid-liquid extraction with diethyl ether and analyzed by gas chromatography. In all experiments, the molar ratio of Pd to [BMMDPA] [PF_6] was kept at 2:1 and 1 mL of [BMMIM] [PF_6] was used as solvent unless described otherwise.

For the recycling procedure, after reaction for 3 h and then cooling back to ambient temperature, the products were extracted by liquid-liquid extraction with diethyl ether for three times. After evaporating the diethyl ether under a vacuum, the substrate was charged into the autoclave for the next recycling.

Supporting Information

TGA curves of ionic liquids and the Pd nanoparticles are given in the Supporting Information.

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