Pd nanoparticles catalyzed ligand-free Heck reaction in ionic liquid microemulsion

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The H_2O/TX-100/1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6) microemulsion is a new green medium, in which the Pd nanoparticles were prepared *in situ* for the first time. Surfactant TX-100 served as the reductant and the stabilizer of the nanoparticles. The TEM images presented that the monodispersed Pd nanoparticles have a mean particle size of 3 nm. The new medium containing the Pd nanoparticles was used to catalyse the Heck reaction of butyl acrylate with iodobenzene. The effects of various reaction parameters on the Heck reaction are herein discussed. The results indicate that the reaction temperature and the base play key roles in the product yield. The H_2O/TX-100/[BMIM]PF_6 microemulsion containing Pd nanoparticles was found to decrease the reaction time for the Heck reaction compared with conventional solvent system. After the fourth cycle, the catalytic activity of the Pd nanoparticles decreased. Moreover, other Heck reactions relating to the coupling of iodobenzene and methyl acrylate, ethyl acrylate and styrene were also investigated with the high yields determined. All the results indicated that the H_2O/TX-100/[BMIM]PF_6 microemulsion containing the Pd nanoparticles was a very efficient catalyst system for the ligand-free Heck reaction.

Introduction

Many room temperature ionic liquids (RTILs) can be considered as green solvents, which are air and water stable salts.[1] In the field of green chemistry, there has been a trend for RTILs to replace conventional solvents in organic synthesis and material preparation.[2,3] In order to expand the application for RTILs, a new concept relating to ionic liquid microemulsions was put forward.[4–6] For example, the hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6) was used to substitute for conventional solvent and form an ionic liquid microemulsion with water by the aid of non-ionic surfactant TX-100.[7] Microemulsion is an optically isotropic, transparent and thermodynamically stable system formed by two or more immiscible liquids which are stabilized by a surfactant and occasionally a cosurfactant film at the liquid–liquid interface.[8] Moreover, microemulsions, especially reverse microemulsions, have been considered as convenient and economic templates for preparing nanoparticles, since it can produce homogeneous and monodispersed nanoparticles without the need for specialized instruments and extreme conditions.[9] In view of economic and environmental problems, a new versatile ionic liquid microemulsions medium was produced with high attention, and was used for electrodeposition, biocatalysis and fabrication of hollow silica spheres.[10–12]

The Heck reaction is normally catalyzed by Pd catalysts in the presence of base for the formation of C–C bonds.[13] Conventionally, a higher temperature, a longer time and phosphine ligands are necessary to enhance the product yield. Furthermore, aprotic, polar solvents (such as *N, N*-dimethylformamide (DMF) and dim-ethylacetamide (DMAc)) are often used to overcome the incompatibility of lipophilic substrates. These solvents are toxic and have high boiling points, which cause difficulties in the removal of the products after the reaction. Moreover, the toxicity of phosphine ligands is not consistent with the green chemistry. Therefore, developing a new green system for the Heck reaction is desirable.[14,15]

Herein, we prepared Pd nanoparticles *in situ* in H_2O/TX-100/[BMIM]PF_6 microemulsion. Palladium chloride can be rapidly reduced by a surfactant (TX-100) without any further reducing agents. The catalytic performance of the ionic liquid microemulsion containing Pd nanoparticles for the Heck reaction was investigated without the aid of phosphine ligand.

Experimental

Materials

The ionic liquid [BMIM]PF_6 was prepared according to literature[16], and dried under vacuum at 70 °C for 12 hours before use. Its purity was checked by applying the $AgNO_3$ test, ^1H and ^{31}P NMR, and cyclic voltammetry.[17] Other reagents including TX-100 (CP), $PdCl_2$ (AR), methyl acrylate (AR), ethyl acrylate (AR), styrene (AR), butyl acrylate (AR), iodobenzene

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(AR) were purchased from Shanghai Chemical Reagent Factory (China) and used without further purification. Et_3N (AR), Na_3PO_4 (AR), NaOAc (AR), Na_2CO_3 (AR) were obtained from Tianjin Damao Reagent Co. Water used in the experiments was deionized (DI) and doubly distilled prior to use. Unless otherwise stated, all experiments were performed in nitrogen atmosphere.

Preparation of microemulsion and Pd nanoparticles

The H_2O/TX-100/[BMIM]PF_6 microemulsion was prepared according to previous work.[7] Palladium chloride was dissolved in the water prior to mixing with TX-100/[BMIM]PF_6 phase. The procedure was carried out as follows: 4.9 g TX-100 and 2.72 g [BMIM]PF_6 were added into a three necks flask, and then the mixture was vigorously magnetically stirred in nitrogen. The resultant solution was heated to 50 °C by the oil bath with 0.5 mL aqueous $PdCl_2$ (30 mg $PdCl_2$ in 25 mL distilled water and 40 µL 1M HCl) injected into the solution. During this process the solution turned from light yellow to dark gray, with no precipitate found to be formed at the bottom of the flask. This indicates the formation of a uniform multiphase system composed of nano-Pd and an ionic liquid microemulsion.

General procedure for the catalytic tests

The cross coupling of alkene with iodobenzene was performed under different reaction conditions. Typically, 1 mmol iodobenzene, 1.2 mmol alkene and 3 mmol base were added to the ionic liquid microemulsion. About 0.003 mmol Pd nanoparticles were dispersed as catalyst in the ionic liquid microemulsion. The reaction was terminated after necessary conditions were achieved. After cooling to room temperature, the products and residual reactants were extracted with 3% ethyl acetate in petroleum ether (7 mL × 5). Products in the resulting mixture were analyzed by a Gas Chromatograph (GC).

Characterization

The particle size and morphology of the Pd nanoparticles were analyzed by transmission electronic microscopy (TEM) with the JEOL 3010 microscope operating at 300 kV. UV-vis absorption spectrum was preformed on the TechLab UV-2100 ultraviolet and visible spectrophotometry. GC analyses were performed on an Agilent GC 6820 N with a 30 m × 0.45 mm × 0.8 µm Agilent DB-WAX column.

Results and discussion

Characterization of the catalysts

Imidazolium ionic liquid ([BMIM]PF_6) was found to be an outstanding medium for the preparation and stabilization of transition metal nanoparticles.[18] However, the ionic liquid must be "dry" in the preparation process of transition metal nanoparticles, as the presence of water and transition metal precursor leads to the imidazolium ionic liquid decomposing with the formation of phosphates, HF and metal fluorides.[19,20] The H_2O/TX-100/[BMIM]PF_6 microemulsion was successfully prepared when H_2O was dispersed in the TX-100/[BMIM]PF_6 and formed a nanosized pool. The interface between the continuous phase ([BMIM]PF_6) and dispersed phase (H_2O) was TX-100 film. TX-100 is polyoxyethylene-type nonionic surfactant, and the ether bond and hydroxyl group are components of its hydrophilic side. For its special structure, TX-100 was regarded as an excellent reducing agent to transition metal salts.[21]

In our work, *in situ* preparation of Pd nanoparticles was completed in the [BMIM]PF_6 microemulsion. Although $PdCl_2$ and water were added into [BMIM]PF_6 together, Pd(II) ions were rapidly reduced after the ionic liquid microemulsion formed. Fig. 1 shows the UV-visible spectra of the $PdCl_2$ in the [BMIM]PF_6 microemulsion before and after reduction. There was no obvious absorption peak of the Pd(II) ion at 360 nm after two minutes which revealed that the transition-metal precursor ($PdCl_2$) was quickly reduced to nano-Pd. Introduction of water and $PdCl_2$ into the ionic liquid microemulsion did not result in the decomposition of [BMIM]PF_6.

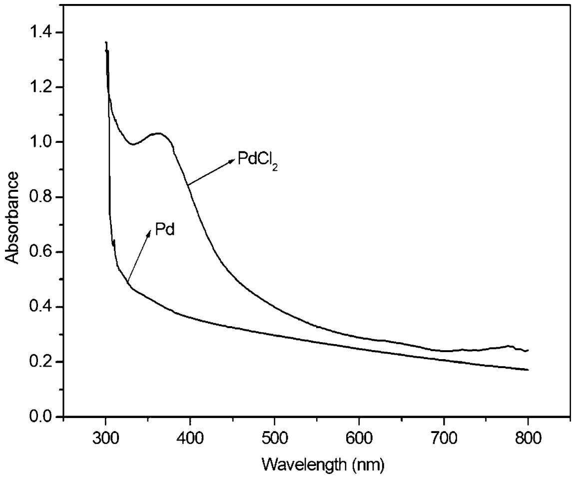


Fig. 1 UV-visible spectra of $PdCl_2$ in the [BMIM]PF_6 microemulsion before and after reduction (reduction time: 2 minutes).

After the Pd(II) ions were reduced by TX-100, a small amount of this microemulsion was centrifuged. The black powder obtained was washed with anhydrous ethanol, dried under reduced pressure and analyzed by TEM. The representative TEM images of Pd nanoparticles are shown in Fig. 2a, 2b. It can be seen that *in situ* reduction of Pd(II) ions leads to monodispersed Pd nanoparticles with a narrow size distribution and the average size of nanoparticles is about 3 nm (Fig. 2d). Moreover, the corresponding electron diffraction pattern is shown in Fig. 2c, with the values of the interplanar distance d_{hkl} calculated from the diffraction rings, indicating that the Pd nanoparticles possess a face-centered cubic structure. The resulting Pd nanoparticles have a very small size and uniform distribution comparing with conventional microemulsion systems (4–10 nm).[22] The small size of Pd nanoparticles is due to the presence of IL and surfactant, which co-stabilized Pd nanoparticles in the ionic liquid microemulsion. Consequently, the H_2O/TX-100/[BMIM]PF_6 microemulsion was considered as a benign medium for preparing ultrafine metal nanoparticles.

Catalytic activities of the catalysts for Heck reaction

In order to investigate the catalytic properties of the Pd nanoparticles dispersed in ionic liquid microemulsion, Heck reaction

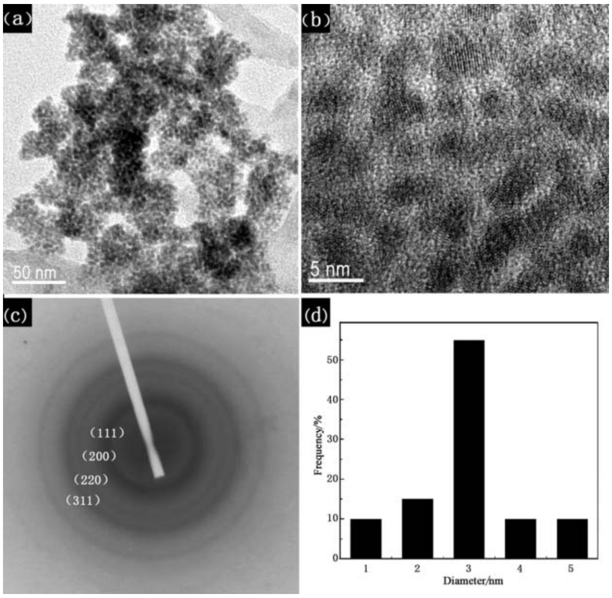


Fig. 2 (a) TEM image, (b) HRTEM image of Pd nanoparticles separated from the [BMIM]PF$_6$ microemulsion, (c) Electron diffraction pattern of the obtained Pd nanoparticles, (d) particle size distribution derived from TEM images, based on 100 randomly selected particles.

Table 1 Influence of base on the Heck reaction of iodobenzene with butyl acrylate[a]

Entry	Base	Yield (%)
1	Et_3N	100
2	Na_3PO_4	70
3	—	66
4	NaOAc	42
5	Na_2CO_3	20

[a] Reaction conditions: 1 mmol PhI, 1.2 mmol butyl acrylate, 3 mmol base, 0.003 mmol $PdCl_2$, the reaction temperature was 100 °C, the reaction time was 2 h. The yield was calculated from the GC of the mixture.

of the cross-coupling of butyl acrylate with iodobenzene was employed. The products and residual reactants were extracted and the ionic liquid microemulsion containing Pd nanoparticles was used for the next cycle without extra treatment. At the end of extraction, the TX-100 and [BMIM]PF$_6$ was not observed in the extraction liquid. In fact, the TX-100 and [BMIM]PF$_6$ that entered into the extraction liquid was inevitable, and was attributed to ethyl acetate (about 1 mL) used in the process of extraction. However, the loss of a thimbleful of TX-100 and [BMIM]PF$_6$ did not destroy the stable structure of the ionic liquid microemulsion.

Fig. 3 presents the effects of the reaction time and temperature on the product yield. It is apparent that the reaction temperature had a marked influence on the yield (Et_3N was used as base). When the reaction temperature increased from 50 °C to 100 °C, the yield increased from 7% to 95% at the same reaction time (0.5 h). When the reaction proceeded under 100 °C, the product yield changed marginally with longer time durations after 0.5 h, with it reaching the maximum 100% after 2 h. The field of reactions catalyzed by Pd nanoparticles in microemulsions, which is sometimes termed “semi-homogenous catalysis”, is located at the frontier between homogeneous and heterogeneous catalysis.[23] Due to the large surface areas employed, Pd nanoparticles possess a high activity under mild conditions. Simultaneously, it is sufficient to employ the comprehensive solubility of an ionic liquid and a suitable surfactant to “solubilize” the reactants as emulsions.[24] Accordingly, the H_2O/TX-100/[BMIM]PF$_6$ microemulsion containing Pd nanoparticles is an excellent green system, and can catalyze the Heck reaction significantly.

In the Heck reaction, the base was used to neutralize the acid ensuing from the exchange of a hydrogen atom with an aryl group. The change of product yield with different base under the same conditions (100 °C, 2 h) is shown in Table 1. All catalytic experiments were completed in a closed container without the loss of components. When organic liquid base (Et_3N) was used in the reaction, it possessed excellent solubility in the microemulsion and did not result in the agglomeration of Pd nanoparticles. The high product yield (100%) was obtained and the whole process was kept in “semi-homogenous catalysis”. Compared with an organic liquid base, the catalytic activity of the system greatly decreased with the use of an inorganic solid base. For example, the product yield for the reactions utilising Na_3PO_4, NaOAc and Na_2CO_3 is 70%, 42% and 20%, respectively. When the inorganic solid bases were used in the reactions, they destroyed the stability of microemulsion and caused the agglomeration of Pd nanoparticles. The catalytic reaction turned into heterogeneous catalysis with lower product yield. According to the theory of “similarity and intermiscibility”, Na_3PO_4 was dissolved better than NaOAc or Na_2CO_3 in the ionic liquid microemulsion. The superior solubility of Na_3PO_4 could efficiently impel the reaction (70%), comparing with when no base was employed in the reaction (66%). It may be that the action of inorganic base Na_3PO_4 could overcome the influence of heterogeneous catalysis. Therefore, the catalytic activity of the system was closely related to the solubility of the base and the stability of the Pd nanoparticles.

In view of the economy of the reaction, the recovery and recycling of the ionic liquid microemulsion containing the Pd nanoparticles was investigated, through the reaction of the iodobenzene with butyl acrylate at 75 °C with Et_3N as the base. In the first cycle, the coupling product was obtained

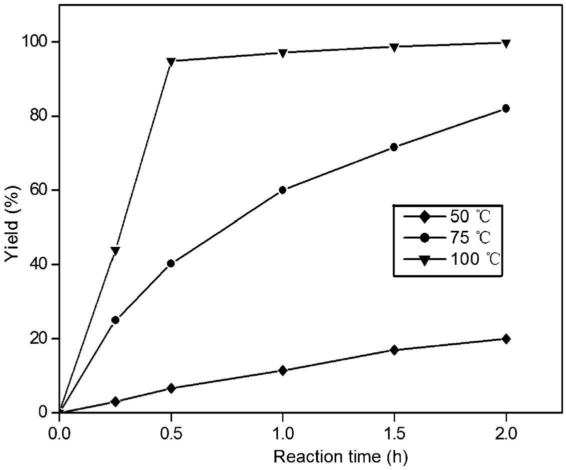
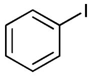
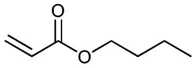
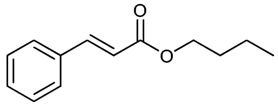
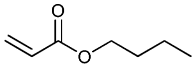
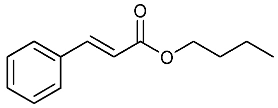
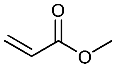
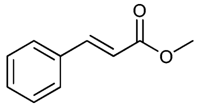
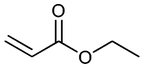
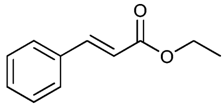
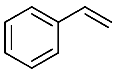
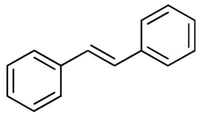


Fig. 3 Effects of reaction time and temperature on product yield of the reaction of butyl acrylate with iodobenzene.

Table 2 Product yields for other Heck reactions in ionic liquid microemulsion[a]

Entry	Aryl halide	Alkene	Product	Time(h)	Yield (%)
1				2	100
2[b]				20	92
3				2	97
4				2	90
5				2	81

[a] Reaction conditions: 1 mmol PhI, 1.2 mmol alkene, 3 mmol Et_3N, 0.003 mmol $PdCl_2$, the reaction temperature was 100 °C, the yield was calculated from the GC of the mixture. [b] Reaction conditions: 1 mol% of 5 wt% Pd/Urea-MCF catalyst with Pd nanoclusters of 2–3 nm, 1 mmol PhI, 1.25 mmol alkene, 2 mmol Et_3N, 5 mL toluene, the reaction temperature was 100 °C, argon atmosphere.

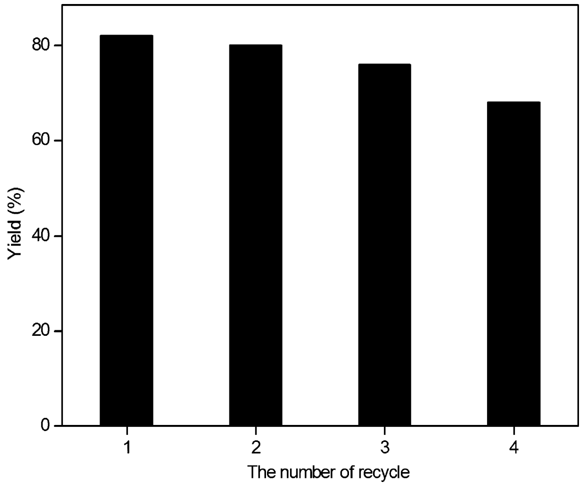


Fig. 4 The recycle experiments by using Pd nanoparticles as catalyst in the coupling of iodobenzene with butyl acrylate.

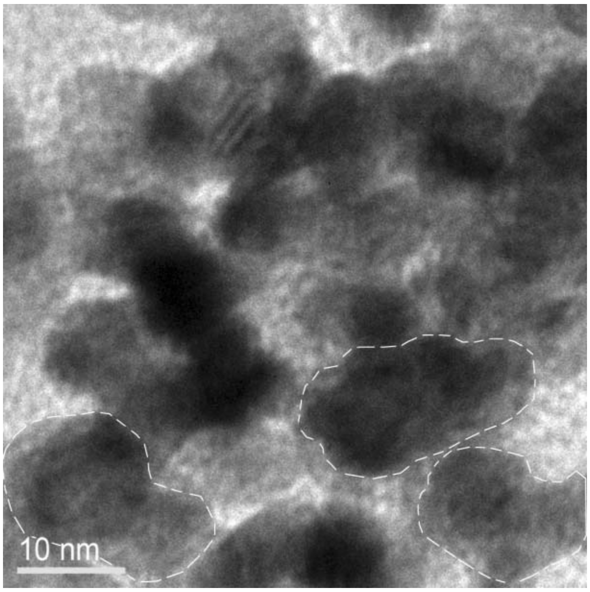


Fig. 5 TEM image of Pd nanoparticles after being reused four times.

with a yield of 82% (Fig. 4). After the products and residual reactants were extracted, new starting materials were added to the remnant ionic liquid microemulsion that contained the Pd particles from the first reaction. After stirring for another 2 h at 75 °C, the product yield was 80% in the second cycle. Similarly, the third cycle afforded a yield of 76%, and the subsequent fourth cycle afforded a 68% yield. The yield of the fourth cycle decreased obviously comparing with the first cycle due to the conglomeration of particles. Fig. 5 presents the TEM image of the Pd nanoparticle after four cycles. It can be seen that after the four cycles, Pd nanoparticles aggregated to a large particle (about 10 nm) in contrast with the clear dispersion before the reaction. Hence, the ionic liquid microemulsion containing the Pd nanoparticles was suitable for reuse, although the product yield was found to decrease slightly with the increase of the recycle number.

Compared with a conventional organic solvent system,[25] the ionic liquid microemulsion containing Pd nanoparticles can obviously shorten the reaction time as shown in Table 2 (Entry 1 and Entry 2). In order to extend the application of the ionic liquid microemulsion containing Pd nanoparticles, we examined other Heck reactions in the system (Entry 3, Entry 4 and Entry 5). It can be seen that the system has good performance for the cross coupling reaction.

Conclusions

In conclusion, Pd nanoparticles were successfully prepared *in situ* in a H_2O/TX-100/[BMIM]PF_6 microemulsion. Thereinto, surfactant TX-100 served as the reductant and stabilized the Pd nanoparticles together with the ionic liquid [BMIM]PF_6. The average size of the monodispersed Pd nanoparticles was about 3 nm. The H_2O/TX-100/[BMIM]PF_6 microemulsion containing the Pd nanoparticles was found to be an excellent catalyst system for the ligand-free Heck reaction. It was consistent with the requirements of green chemistry. The catalytic system could be cycled for four times at least. Investigations of other C–C coupling reactions catalyzed by this green medium are currently underway in our laboratory.

Acknowledgements

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