

Palladium Nanoparticles Suspended in an Ionic Liquid as Reusable Catalyst for Alkyne Semihydrogenation

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The reaction of PdCl₂ dispersed in tetra-*n*-butylammonium bromide with tributyl amine at 120 °C under argon leads to stable isolable nanometric particles. X-ray diffraction analysis of the material indicated that it is constituted of Pd(0). Transmission electron microscopy analysis of the particles dispersed in acetone shows the mean particle size distribution (4 ± 1 nm). The isolated palladium nanoparticles can be dispersed in an ionic liquid or in methanol or used in solventless condition for selective hydrogenation of 2-hexyne under mild reaction conditions (0.2 MPa and 20 °C). The commercial variety of the Lindlar catalyst was also studied for comparative investigations.

Key Words: Palladium, Nanoparticles, Semihydrogenation, Ionic liquid, Lindlar catalyst

Introduction

Cis-selective semi-hydrogenation of alkynes on heterogeneous catalysts is the most important method for the generation of *cis*-olefins. Most studies in recent years about hydrogenation of alkynes have focused on the use of supported palladium catalysts. Pd on SiO₂,¹⁻³ Pd on Al₂O₃,⁴⁻⁷ Pd on Carbon,⁸⁻¹⁰ Pd on pumice,^{11,12} Pd on CeO₂¹³ and palladium supported on mesoporous montmorillonite clay^{14,15} and microporous zeolite materials¹⁶ were applied. Much effort has been made to empirical modifications of such palladium based catalysts to improve the desired selectivity. The substrates studied included acetylene, phenyl acetylene, methyl acetylene and various terminal and internal alkynes.

Most of these studies focused on the role of various factors like operating conditions, metal dispersion, metal size, carbon deposits, promoters and additives on semihydrogenation activity. The effect of particle size on the catalytic properties of supported metals is an important issue in heterogeneous metal catalysis and still a subject of much debate.¹⁷ Results of various studies with respect to particle size effects of the transformation of alkynes are rather controversial although most studies showed that alkyne hydrogenation is a structure sensitive reaction at high dispersions.¹⁸⁻²¹ Recent publications have disclosed structure insensitivity or only small changes in activity.²²⁻²⁴ Activity drop with increasing metal dispersion has also been reported.²⁵ Direct comparisons of these results are difficult to make since different substrates were studied under different reaction conditions.

Due to lack of understanding and control, the success of such heterogeneous hydrogenation reactions in organic synthesis is still unpredictable and often unreliable. Although alternative homogeneous systems have been developed, none of these have replaced heterogeneous palladium catalysts for *cis*-selective semihydrogenation which is still widely used in numerous total synthesis of natural products.²⁶⁻²⁸

Transition metal nanoparticles typically of the size less than 10 nm in diameter are now emerging as an important family of

catalysts for various reactions.²⁹⁻³² These metal nano colloids as sometimes called are usually obtained by the reduction of metal compounds in the presence of stabilizing agents such as polymers, surfactants, polyoximes *etc.* Small size of these particles makes them attractive in catalysis due to their large surface to volume ratio. We have previously reported the synthesis and use of tetrabutyl ammonium bromide stabilized palladium nanoparticles in alkene hydrogenation reactions.^{33,34} The present paper reports the use of these nanocolloids as efficient catalysts for alkyne hydrogenation reactions, their superiority over the commercially available Lindlar catalyst and finally their reusability when suspended in an ionic liquid. TEM studies before and after hydrogenation reactions show marked changes in the average size of the particles and this is also reflected in their catalytic activity and recyclability.

Experimental

Catalyst preparation. Palladium nanoparticles were prepared from palladium chloride as per the literature method.³⁵ A mixture of palladium chloride (101.5 mg, 0.58 mmol) and *n*-Bu₄NBr (740 mg, 2.3 mmol) were stirred under vacuum (0.1 mbar) at 120 °C for 2 hours. The mixture was then placed under an argon atmosphere and tributyl amine (300 mg, 1.70 mmol) was injected by means of a syringe through the side arm of the 2-necked round-bottomed flask. After stirring the whole at 120 °C for an additional period of two hours, the mixture was cooled to room temperature. The black mass was washed with diethyl ether (5 mL × 5) and was kept overnight under vacuum. Drying the residue produced the black palladium nanoparticles (740 mg, mp 110 °C) which were stored under vacuum for subsequent use in the characterization process and for catalytic experiments..

Catalyst characterization. ¹H NMR, ¹³C NMR and FTIR spectral studies on the nanoparticles indicate that the salt tetra-*n*-butyl ammonium bromide is only present in the protecting layer of the palladium(0) particles. ¹H NMR (CDCl₃, TMS) 1.1 (3H, t), 1.4 (2H, m), 1.7 (2H, m), 3.4 (2H, br); ¹³C NMR (CDCl₃)

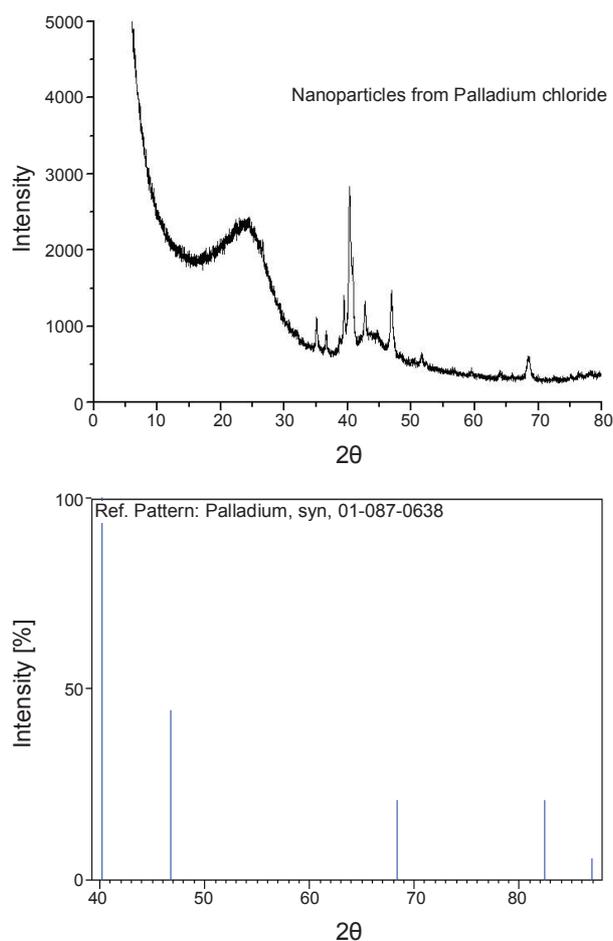


Figure 1. XRD profile of Pd-nanoparticles compared with standard Pd(0).

15.1, 22.8, 26.3, 61.1; FTIR (CDCl_3 dispersion, cm^{-1}) 2962, 2875, 1488, 1467, 1384, 925.

The crystalline phase of the synthesized particles was confirmed by XRD, which revealed the presence of pure palladium with characteristic peaks at 2θ of 40° , 46° and 68° (Fig. 1), corresponding to $\{111\}$, $\{200\}$ and $\{220\}$ planes of an fcc lattice.³⁶ Strong evidence of the existence of nanoparticles in the studied sample comes from Transmission Electron Microscopy (TEM) conducted on the colloidal particles suspended in acetone. The particle size determined has on an average a diameter of 4 ± 1 nm as estimated from ensembles of 200 - 300 particles found in an arbitrary chosen area of the enlarged micrographs (Fig. 2).

General method. Chemicals were purchased from Merck, Aldrich and were used without further purification. The ionic liquid [BMim]PF₆ was prepared according to a known procedure³⁷ and its purity was checked by ^1H and ^{31}P NMR. NMR was recorded on a Bruker 400 spectrometer. Infrared spectra were performed on a Nicolet 800 spectrometer. Gas chromatography analyses were performed with an Agilent Technologies 6890 N network GC system with an FID and a 30 m capillary column with a dimethylpolysiloxane stationary phase. The X-ray diffraction analysis was performed in a Panalytical X'pert MRD diffractometer using curved graphite crystal as monochromator. TEM was performed on a CM30 (FEI make) microscope operat-

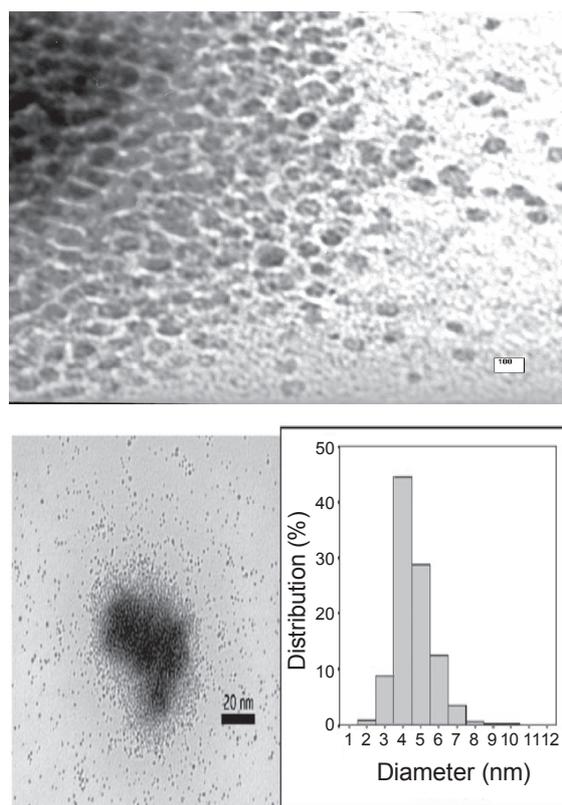


Figure 2. Palladium nanoparticles prepared from PdCl₂.

ing at 200 kV. Particle size distributions were determined once the original negative had been digitalized and expanded to 470 pixels/cm for a more accurate resolution and measurement. TEM pictures were taken at multiple random locations after suspension of the nanoparticles on a carbon film fixed within a copper grid.

Hydrogenation procedure. Hydrogenation of 2-hexyne was performed at atmospheric pressure at 20°C in a 60 mL high pressure glass reactor equipped with a magnetic bar. The reactor was loaded with exactly 5 mL solution of colloidal palladium nanoparticles (20 mg) in methanol and then pressurized with H₂ (0.2 MPa). The catalyst was activated for 10 mins with vigorous stirring (2000 rpm) and the reaction time was monitored after the injection of 0.5 mL of the substrate through a sampling port of the glass reactor. The intermediate samples were withdrawn from the reaction mixture at an interval of 15 mins and analyzed by GC-MS (Agilent Technologies 6890 N network GC system).

Results and Discussion

In continuation of our efforts to investigate new protocols with the palladium nanoparticles prepared from PdCl₂, we report here our investigation on the hydrogenation of 2-hexyne in solventless, organic solvent phase and biphasic (suspended in an ionic liquid) conditions. 2-Hexyne was chosen as a substrate for our hydrogenation study because it is an asymmetrical alkyne whose initial semihydrogenation product *cis*-2-hexene is prone to *cis-trans* isomerization, bond-shift isomerization to produce 1-hexene and 3-hexene and finally overhydrogenation.

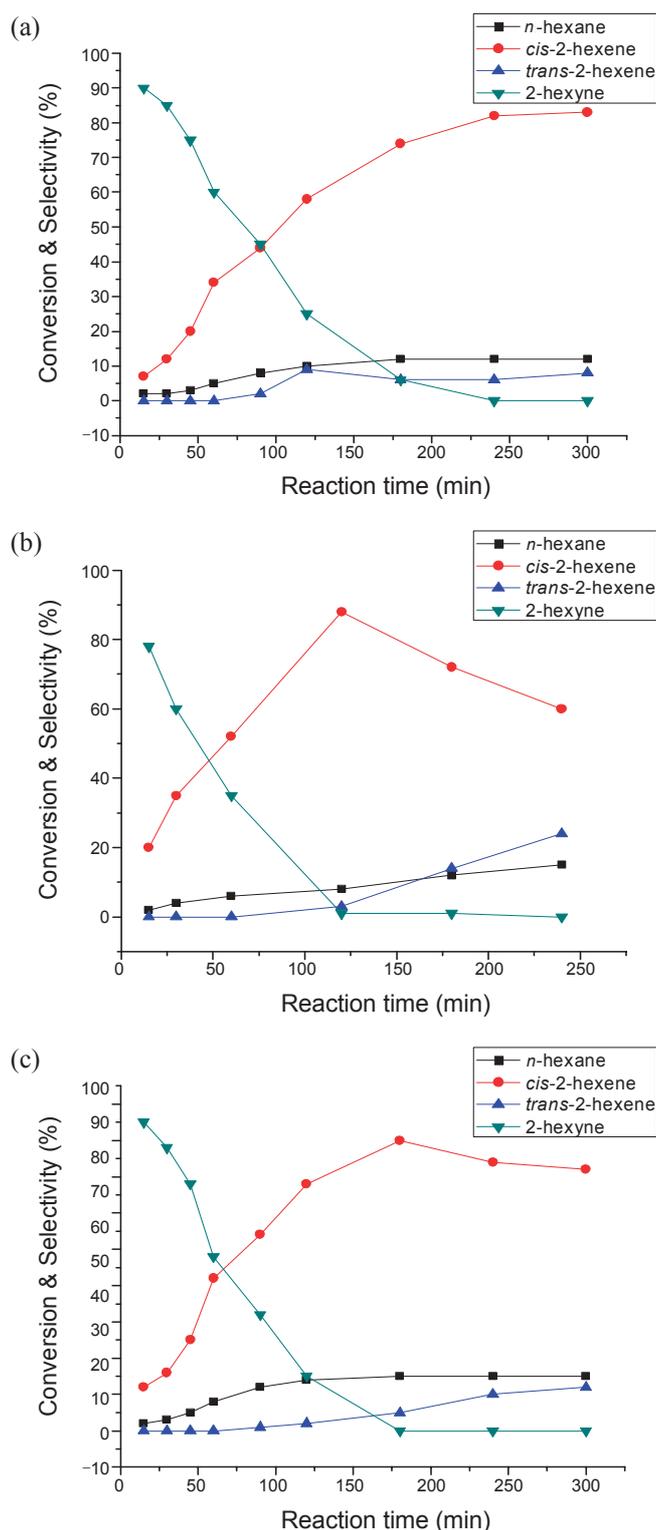


Figure 3. (a) Transformation of 2-hexyne on Pd-nano in methanol. (b) Transformation of 2-hexyne on Lindlar Catalyst in methanol. (c) Transformation of 2-hexyne on Pd-nano in solventless condition.

Hydrogenation of 2-hexyne (99%, Aldrich chemical) under normal pressure and room temperature (20 °C) using the nanoparticles suspended in methanol produced *cis*-2-hexene as the major product (30%) and the saturated hydrocarbon *n*-hexane in minor quantity (8 - 9%). 2-Hexyne was converted to the extent

of 40% after 1 hour of hydrogenation reaction. After 2 hours, the conversion of 2-hexyne was 70% with *cis*-2-hexene still as the main product (56%) and hexane in yield of 12%. No other peaks could be seen in the Gas chromatography profile (intensity vs retention time) recorded in minutes. When the catalytic experiment was conducted for 4 hours under similar conditions and the isolated product subjected to GC analysis, complete conversion of 2-hexyne was noted. Three peaks recorded this time have been attributed to *cis*-2-hexene (82%), *trans*-2-hexene (5 - 6%) and the over-hydrogenation product hexane (12%). Since the yield of hexane remains constant after 4 hours of hydrogenation it can be confirmed that with time the *cis-trans* isomerization reaction occurs and initiates after 2 hours of reaction. The other isomerized products namely 1-hexene and 3-hexene could not be confirmed even by using different columns and changing the GC instrument parameters like flow rate of the carrier gas, column temperature and detector temperature. For comparison, the commercially available Lindlar catalyst (Pd/CaCO₃ modified with Lead acetate) was studied under similar hydrogenation conditions. Reaction profile of the 2-hexyne hydrogenation with the Lindlar catalyst shows almost similar product composition as observed in case of the nanoparticles prepared from palladium chloride. The difference however is evident on the catalytic rate as 2-hexyne is completely reduced after 2 hours of reaction using the Lindlar catalyst (Aldrich chemical). At the end of 2 hour, *cis*-2-hexene (88%) and *n*-hexane (8%) were the two products detected by GC-MS. A small peak accompanying them could be a trace of the isomerized products. At the end of 4 hours of catalytic reaction under similar conditions, the Lindlar catalyst however shows a drastic fall in *cis*-2-hexene product (60%) with concomitant rise in *trans*-2-hexene (25%) and *n*-hexane (15%). The trace of the isomerized product at the end of the 2 hour period has been attributed to *trans*-2-hexene as it has the same retention time as witnessed in case of the nanoparticles suspended in methanol. Conversion curves of 2-hexyne hydrogenation by Pd(0) nanoparticles at 0.2 MPa and 20 °C in methanol has been shown in Fig. 3a. Reaction profile of 2-hexyne hydrogenation using the Lindlar catalyst under identical catalytic conditions has also been given in Fig. 3b for effective comparison.

Hydrogenation under solventless condition. The isolated Pd nanoparticles were placed in the glass reactor and the substrate (2-hexyne, 6.5 mmol) was added. Hydrogen was then admitted to the system and the whole was stirred at room temperature (20 °C). Samples for GC and GC-MS analysis were also taken at regular intervals under H₂. At the end of the 4 hour period the organic products were recovered by simple filtration and analyzed by GC.

Tests of the catalytic performance of Pd nanoparticles under solventless condition in the transformation of 2-hexyne revealed more or less similar conversion products as witnessed in methanol suspended catalytic experiments (Fig. 3c). Fresh addition of the substrate to the filtered catalyst obtained from solventless condition and those collected from methanol did not yield any product even after 4 hours of hydrogenation. This may be attributed to saturation or complete destruction of the active centers of the nanoparticles responsible for alkyne coordination. Since the adsorption of alkynes on Pd is stronger than that of alkenes

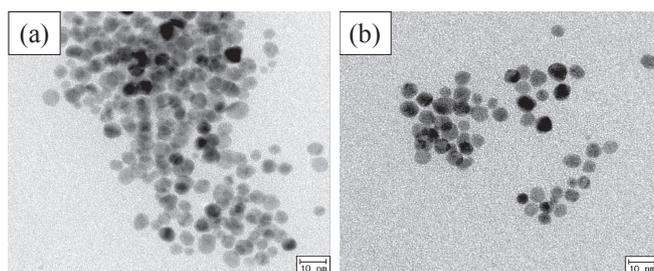


Figure 4. (a) Nanoparticles collected after alkyne hydrogenation in solventless condition. (b) Nanoparticles collected after alkyne hydrogenation in methanol.

and the processes take place on distinct active centers,^{38,39} loss of catalytic activity of the recovered particles may be due to change in particle size because of aggregation of smaller sized particles or carbon deposition during the catalytic reaction. Poisoning of the active sites by the product mixture (saturated and isomerized hydrocarbons) could also be a reason of decreased catalytic activity. Hydrogenation of 2-hexyne with addition of *n*-hexane (2 mmol) as substrate with fresh Pd nanoparticles was next performed under similar conditions. As revealed by GC, presence of hexane in the reaction mixture did not inhibit the catalytic hydrogenation process and reduction of 2-hexyne to *cis*-2-hexene was almost quantitative as noted before. Surface poisoning of the nanoparticles by the hydrogenated products has therefore been ruled out. *Cis* hydrogenation of alkynes is commonly conducted in the presence of modifiers known to compete with olefins for surface interactions and thus increase the product selectivity.^{40,41} To ensure that our data were not obscured by such effects, the catalytic runs were performed in the absence of any additives or modifiers.

Transmission electron microscopy of the nanoparticles collected after the first hydrogenation reaction in both cases (solventless as well as solvent mediated catalytic runs) show marked changes as far as average particle size distribution is concerned (Figs. 4a & 4b). Micrographs reveal considerable aggregation of the palladium particles on use and this is reflected in the increase in average size of the particles. The particles collected after first cycle from the solventless condition had on an average a diameter of 8 ± 1 nm, and those collected after decanting off the solvent methanol and drying under reduced pressure show average Pd size 9 nm with very narrow size distribution. Compared to the freshly prepared catalysts (diameter 4 nm) this marked increase in size due to agglomeration and coagulation is the factor identified for complete loss of catalytic activity of the filtered particles.

Morphological changes of metal particles are changes in particle size and shape. The surface structure of a fcc metal particle is essentially composed of three different types of surface atoms that are characterized by the number of nearest neighbor atoms.⁴² These are the terrace atoms with nine nearest neighbours, step atoms with seven and corner or kink atoms with six or less neighbours. The relative distribution and number of these surface atoms changes with particle size. Reaction selectivity and activity is postulated on the availability of these surface intermediates during hydrogenation reactions. Although model of steric interactions of hypothetical surface intermediates to

Table 1. Catalytic performance of Pd(0) nanoparticles and Lindlar catalyst in solventless, with solvent and bi-phasic conditions^a

Entry	Medium	Catalyst	Product(%)	CV (%) ^b	TOF(h ⁻¹) ^c
1	methanol	Pd-nano	<i>cis</i> -2-hexene (58)	75	168
			<i>n</i> -hexane (10)		
			<i>trans</i> -2-hexene (05)		
2	solventless	Pd-nano	<i>cis</i> -2-hexene (68)	85	190
			<i>n</i> -hexane (14)		
			<i>trans</i> -2-hexene (03)		
3	[BMim]PF ₆	Pd-nano	<i>cis</i> -2-hexene (44)	55	122
			<i>n</i> -hexane (08)		
			<i>trans</i> -2-hexene (02)		
4	methanol	Lindlar (Aldrich)	<i>cis</i> -2-hexene (88)	99	222
			<i>n</i> -hexane (08)		
			<i>trans</i> -2-hexene (3)		
5	methanol	Pd/C (5%) (Aldrich)	<i>cis</i> -2-hexene (00)	95	425
			<i>n</i> -hexane (94)		
			<i>trans</i> -2-hexene (00)		

^aReaction conditions; [2-hexyne] = 6.7 mmol; temp. = 20 °C; P_{H₂} = 0.2 MPa (constant pressure). ^bsubstrate (2-hexyne) conversion. ^c[mol product]/[mol cat](hour).

explain catalytic selectivity has been made none of these have yet been identified on a Pd surface during hydrogenation reactions. The surfactant tetra-*n*-butyl ammonium bromide which provided the much needed steric protection in our palladium nanoparticles preventing their aggregation seemed to be modified during catalytic runs. ¹H NMR study of the used Pd particles however shows the existence of the tetrabutyl ammonium salt but their morphological change if any could not be ascertained.

Hydrogenation under biphasic condition. Palladium nanoparticles were dispersed in 1-butyl-3-methylimidazolium hexafluorophosphate ([BMim]PF₆, 1 mL) and placed in the glass reactor to which 0.5 mL of the substrate, 2-hexyne, was added. Hydrogen was admitted to the system and the whole was stirred using a magnetic stirring bar. The reaction mixture forms a typical two-phase system. The lower phase contains the palladium nanoparticles suspended in the ionic liquid and the upper phase contains the organic products. The organic products can be recovered by simple filtration or decantation and analyzed by GC, GC-MS and ¹H NMR.

Tests of the catalytic performance of Pd nanoparticles under bi-phasic condition in the transformation of 2-hexyne revealed more or less similar conversion products as witnessed in methanol suspended catalytic experiments (Table 1). It is clear from the data that reactions performed under solventless and homogeneous (methanol) conditions are completed in less time than those performed with the nanoparticles dispersed in the ionic liquid. The turn over frequency given in terms of [mol of product]/[mol of catalyst] [h] (Table 1) shows a marked fall in catalytic activity although the selective formation of *cis*-olefin is evident from the catalytic experiments. This difference can be attributed to the typical bi-phasic conditions of the reactions performed in the ionic liquid which can be a mass transfer controlled process.^{43,44} The palladium nanoparticles suspended in [BMim]PF₆ are however stable and can be reused at least four

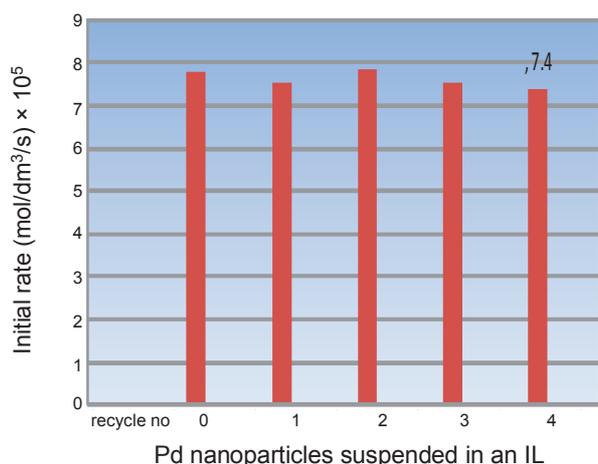
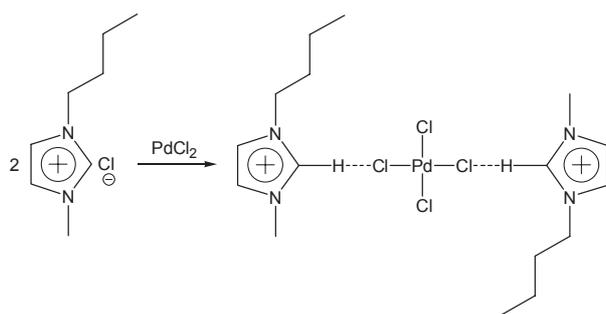


Figure 5. Reusability of palladium nanoparticles in [BMim]PF₆.

times with a minimal loss in catalytic activity or product selectivity (Fig. 5). It is to be noted that the classical Pd supported on carbon (Aldrich product) used as catalyst for 2-hexyne hydrogenation reaction under same conditions produced only the saturated product and did not show selectivity.

PdCl₂ used as the catalyst precursor for preparation of the Pd-nanoparticles was also studied under same reaction conditions. Though we expected formation of metallic palladium under hydrogen atmosphere and subsequently some hydrogenated products, we witnessed complete recovery of the substrate after 4 hours of catalytic reaction. Another attempt to prepare the palladium nanoparticles *in situ* and to study the hydrogenation reaction in biphasic condition was made. In a typical experiment to a glass vial (10 mL) containing [BMim]PF₆ (1 mL) was added PdCl₂ (30 mg, 0.2 mmol), tri-*n*-butyl amine (0.5 mL, 0.02 mmol) and tetra butyl ammonium bromide (480 mg, 1.5 mmol). The whole was stirred at 80 °C for 2 hours under argon atmosphere. After 2 hours a black solution was obtained to which we added 0.5 mL of the substrate 2-hexyne, and conducted the hydrogenation reaction as described earlier. The product at the end of 2 hour was collected by filtration and subjected to GC-MS analysis. To our disappointment no product was detected (not even *n*-hexane) at the end of the catalytic run. The black colloidal solution collected before the hydrogenation reaction was subjected to TEM studies but the micrographs show blurred images with no distinct particle size distribution. Improper and poor dispersion of the particles, if formed *in situ*, in the ionic liquid



Eq. 1

may be the reason or there may be no reduction of PdCl₂ under such conditions. One of the literatures⁴⁵ has cited the existence of (BMim)₂PdCl₄ species during the reaction of PdCl₂ with 2 molar excesses of 1-*n*-butyl-3-methylimidazoliumchloride in acetonitrile (Eq. 1). In our case formation of metallic palladium could be suppressed almost completely by the formation of such catalyst precursor, although no such species could be isolated in our laboratory.

Conclusion

Catalytic activity and selectivity in terms of semihydrogenation of an internal alkyne is high using palladium nanoparticles prepared from palladium chloride. The result corresponded to the highly dispersed state of the nanoparticles. Though the rate of hydrogenation of the alkyne is much higher in solventless and organic solvent dispersed phase, serious drawback of catalyst aggregation and precipitation prevents their reusability in these states. Efforts have therefore been made to suspend the nanoparticles in an ionic liquid medium which suppresses the phenomenon of particle agglomeration and maintain the catalytic activity as well as selectivity of the regenerated forms.

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