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Pd nanoparticles dispersed on solid supports: synthesis, characterization and catalytic activity on selective hydrogenation of olefins in aqueous media

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Two types of Pd nanoparticle catalysts were prepared having 2–4 nm particle size using silica gel and porous polymer beads as solid supports. 2-Pyridinecarboxaldehyde ligand was anchored on commercially available 3-aminopropyl-functionalized silica gel followed by Pd metal dispersion. Bead-shaped cross-linked poly(4-vinylpyridine-co-styrene) gel was prepared by an emulsifier-free emulsion polymerization of 4-vinylpyridine, styrene and divinylbenzene in the presence of ammonium persulfate and subsequently dispersing the Pd metal on the synthesized polymer. These catalysts were characterized by SEM, TEM and ICP techiniques with respect to appearance, size and possible leaching out, respectively. Furthermore, the reactivity of these catalysts was tested on hydrogenation of various α,β-unsaturated carbonyl compounds using aqueous solvent under a hydrogen balloon (1 atm). The results showed that the Pd dispersed on silica was a more efficient catalyst than Pd dispersed on polymer and the former could be recycled more than 10 times without considerable loss in activity. Copyright © 2010 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: Pd nanoparticle; catalyst; hydrogenation; silica; polymer

Introduction

The synthesis and development of solid-supported metal catalysts has been the subject of most research on catalysis. These catalytic systems have higher reactivity due to their larger active surface area and offer the advantages of heterogeneous catalysis, like ease of handling and recyclability. Nowadays, the development of nano-sized solid supported metal catalysts to make them even more reactive is very popular. For instance, palladium anchored or immobilized on various kinds of supports, such as carbon, clay, silicates, zeolites, amorphous or mesoporous silica, porous biomaterial or polymers, has gained considerable attention due to its remarkable performance in wide range of organic transformations, especially in coupling and in hydrogenation reactions.[1–6] Among these solid supports, polymer and silica are popular among researchers. Many polymer matrices have been developed as solid supports for metals whose macromolecular nature enables the catalytic properties of the complex to be controlled.[7] Furthermore, these polymer matrices stabilize the metal, control its size and avoid agglomeration, making the catalyst robust, highly reactive and recyclable.[8–10] On the other hand, silica as a solid support has been widely used due to its inherent properties such as excellent chemical, mechanical and thermal stability, high surface area and good accessibility for organic groups, which can be easily anchored on its surface via reaction with the surface hydroxyl groups.[11–15] For these reasons, we opted to develop a new type of catalyst tethered on synthesized polymer and end-capped silica as solid supports. These supports enable us to use water as a solvent in an organic reaction. Water as solvent is a promising approach in organic synthesis, primarily for green chemistry reasons. The reaction proceeded well even in water as a solvent because the hydrophobic surface groups tune the transport of hydrophobic substrate to the surface, bringing the substrate and the catalyst into close proximity.[16,17] The reactivity of these catalysts in selective hydrogenation of olefins was checked. Although there are multiple methods for hydrogenation, especially using palladium nano particles on solid supports,[18–22] the catalysts we have developed offer the advantages of using water as a solvent at room temperature and recyclability. We present herein the detailed synthesis and characterization of the catalysts as well as their application for selective hydrogenation reaction.

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Experimental

General Considerations

All chemicals were purchased from commercial suppliers and used without further purification except for cinnamaldehyde and 2-pyridinecarboxaldehyde, which were freshly distilled prior to use. All solvents used were also distilled prior to use. The hydrogenation reaction was carried out using a shaker (Eyela, Mixer CM-1000) at the rate of 12×10^3 rpm. The purity of the products and the progress of the reactions were monitored by NMR spectrometry. ^{1}H and ^{13}C NMR spectra were obtained using a Varian FT-NMR spectrometer (300 and 500 MHz) in $CDCl_3$ or DMSO-d_6 solvents and all were counterchecked with the literature data. The chemical shifts were reported in δ ppm relative to TMS. On the other hand, silica catalyst was prepared using a mechanical stirrer (IKA Labortechnik RW 20.n). The prepared catalysts were characterized thoroughly. The shape and particle dispersion were checked using FE-SEM (Hitachi S-4800 with EDS). The average size of palladium particles was calculated based on the images obtained from HRTEM (JEOL 300 kV). Samples for HRTEM measurements were prepared by grinding the samples, dispersing them on methylene chloride solvent and depositing them on copper grids. Furthermore, the loading value of palladium on the catalysts was checked using ICP-AES (JY Ultima2C).

Preparation of Catalyst A [Nano-sized Pd(0)dispersed on 3-Aminopropyl Fuctionalized Silica Gel]

The 3-aminopropyl-functionalized silica gel (1.96 g, 2.0 mmol NH_2) was added to a flask containing methylene chloride (10 ml) and 2-pyridinecarboxaldehyde (0.23 ml, 2.4 mmol). After stirring for 3 h at room temperature using a mechanical stirrer, the resulting material was filtered and washed with methylene chloride and dried under reduced pressure at 50 °C giving a white functionalized silica gel (2.01 g). This material (1.5 g) was then added to a flask containing palladium acetate (0.385 g, 1.68 mmol) dissolved in methylene chloride (10 ml). The mixture was stirred for 3 h at room temperature. Afterwards, it was filtered, washed with methylene chloride and dried giving a yellowish Pd immobilized on functionalized silica gel product (1.55 g). The palladium on the silica material (1.3 g) was reduced using sodium borohydride (0.091 g, 2.4 mmol) in tetrahydrofuran (10 ml) for 3 h stirred at room temperature. The product was filtered and washed with tetrahydrofuran and water successively. The dried material gave a black powder of nano-sized palladium (0) immobilized on 3-aminopropyl fuctionalized silica gel (1.32 g).

Preparation of Catalyst B [Nano-sized Pd(0) Dispersed on Cross-linked Poly(4-vinylpyridine-co-styrene] Gel

4-Vinylpyridine (0.03 mol, 3.50 g), styrene (0.03 mol, 3.5 g) and divinylbenzene (0.003 mol, 0.78 g) were mixed in a 300 ml three-neck round-bottom flask equipped with a reflux condenser, thermometer, and nitrogen inlet tube. After 1 h, ammonium persulfate solution (0.023 g in 10.0 ml deionized water) was added. The mixture was stirred at 300 rpm under nitrogen atmosphere for 8 h at 70 °C to complete the polymerization reaction. Afterwards, the resulting microporous beads were filtered, washed with ethanol and dried. These polymer (0.50 g) was added to a flask containing palladium acetate (0.049 g, 0.22 mmol) dissolved in methylene chloride (10 ml). The mixture was stirred for 3 h at room temperature and the resulting material was filtered, washed with methylene chloride and dried. The palladium was reduced using sodium borohydride (0.018 g, 0.48 mmol) in tetrahydrofuran (10 ml) for 3 h stirred at room temperature. The product was filtered and washed with tetrahydrofuran and water successively. The dried material gave a dark gray powder of nano-sized palladium (0) immobilized on cross-linked poly(4-vinylpyridine-co-styrene) gel (0.57 g).

General Procedure for Hydrogenation of Olefins

The starting olefin (1 mmol) and catalyst (5 mol% Pd) were added to a tube-shaped Schlenk flask. It was sealed and kept in a vacuum to remove the air. Afterwards, the aqueous solvent (5 ml) was added using a syringe and the mixture was shaken at room temperature under a hydrogen gas balloon. Upon completion of the reaction based on NMR spectra monitoring, the catalyst was filtered off on celite and the solvent was removed by rotary evaporation. Brine solution was added to the residue and the product was extracted with ethyl acetate as many times necessary. The organic layer was collected, dried with anhydrous magnesium sulfate and concentrated by rotary evaporation. The purity of products was determined by NMR spectra.

In some cases, base was added or reaction solvents were varied to address the solubility problem and thus, further increase the yield. For instance, in some materials (Table 2, entries 1–5) potassium hydroxide (0.059 g, 1 mmol) dissolved in water (5 ml) was used to increase its solubility. For this case, the work-up procedure was varied such that the resulting mixture was acidified with 1.0 M HCl prior to extraction. On the other hand, some material required aqueous organic solvent mixture to increase its solubility and give better yield (Table 2, entries 10–13 and 15–16). The compounds were chatacterized by comparing their ^{1}H NMR spectra with those that have been published in the literature, with, for each compound, a suitable reference.

*3-Phenylpropionic acid (**1**)*

The ^{1}H spectrum of 3-phenylpropionic acid (**1**) was found to be in agreement with Brunel.[23]

*2-Methyl-3-phenylpropionic acid (**2**)*

The ^{1}H spectrum of 2-methyl-3-phenylpropionic acid (**2**) was found to be in agreement with Dib *et al*.[24]

*3-(2-Methylphenyl)propionic acid (**3**)*

The ^{1}H spectrum of 3-(2-methylphenyl)propionic acid (**3**) was found to be in agreement with Lemhadri *et al*.[25]

*3-(2-Hydroxyphenyl)propionic acid (**4**)*

The ^{1}H spectrum of 3-(2-hydroxyphenyl)propionic acid (**4**) was found to be in agreement with Cambie *et al*.[26]

*3-(2-Methoxyphenyl)propionic acid (**5**)*

The ^{1}H spectrum of 3-(2-methoxyphenyl)propionic acid (**5**) was found to be in agreement with Lemhadri *et al*.[25]

*4-Phenylbutan-2-one (**6**)*

The ^1H spectrum of 4-phenylbutan-2-one (**6**) was found to be in agreement with Fox *et al*.[27]

*Methyl dihydrocinnamate (**7**)*

The ^1H spectrum of methyl dihydrocinnamate (**7**) was found to be in agreement with Black *et al*.[28]

*3-Phenyl-propan-1-ol (**8**)*

The ^1H spectrum of 3-phenyl-propan-1-ol (**8**) was found to be in agreement with Murphy *et al*.[29]

*3-Phenyl-1-propanal (**9**)*

The ^1H spectrum of 3-phenyl-1-propanal (**9**) was found to be in agreement with Beeson *et al*.[30]

*1,3-Diphenyl-1-propanone (**10**)*

The ^1H spectrum of 1,3-diphenyl-1-propanone (**10**) was found to be in agreement with Mori *et al*.[31]

*3-(4-Methoxyphenyl)-1-phenyl-1-propanone (**11**)*

The ^1H spectrum of 3-(4-methoxyphenyl)-1-phenyl-1-propanone (**11**) was found to be in agreement with Yu *et al*.[32]

*1-(4-Methoxyphenyl)-3-phenyl-1-propanone (**12**)*

The ^1H spectrum of 1-(4-methoxyphenyl)-3-phenyl-1-propanone (**12**) was found to be in agreement with Yu *et al*.[32]

*Dimethyl butanedioate (**13**)*

The ^1H spectrum of dimethyl butanedioate (**13**) was found to be in agreement with Kumar *et al*.[33]

*1,4-Diphenylbutane (**14**)*

The ^1H spectrum of 1,4-diphenylbutane (**14**) was found to be in agreement with Vanier.[34]

*1,2-Diphenylethane (**15**)*

The ^1H spectrum of 1,2-diphenylethane (**15**) was found to be in agreement with Black *et al*.[28]

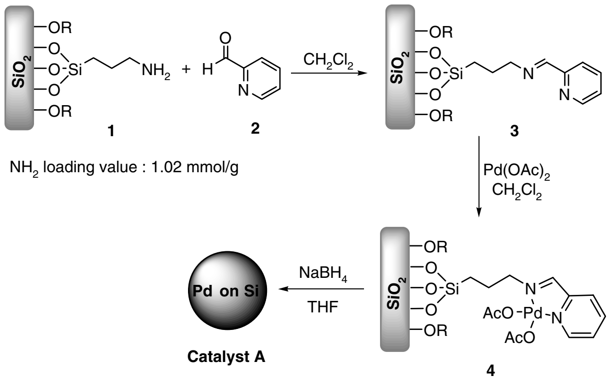
Procedure for Catalyst Recycling

After each reaction, the catalyst was filtered off, washed with ethyl acetate and water alternately and then dried. This catalyst was reused successively 10 times. In the case of catalyst A, cinnamic acid was used as a substrate for the first five recycles and various starting olefin for the succeeding five recycles. For catalyst B, cinnamic acid was used as a substrate during the five times recycle test. The filtrate was also analyzed using ICP-AES to check the possible leaching out of palladium metal into the solution.

Results and Discussion

Synthesis and Characterization of Catalysts

Our group developed catalysts **A** and **B** wherein palladium nanoparticles were dispersed on silica and polymer supports. The preparation method for catalyst **A** is outlined in Scheme 1. First 2-pyridinecarboxaldehyde, **2**, was reacted with 3-aminopropyl-functionalized silica, **1**, to make a Schiff base ligand anchored on the surface of silica gel, **3**. Complexation of Pd(II) using $Pd(OAc)_2$ followed by sodium borohydride reduction made catalyst **A** in which the Pd(0) was well dispersed on the surface of functionalized silica. In this catalyst, the silica support has a functionalized hydrophilic surface and alkyl group end capping that renders surface hydrophobicity. These properties make it possible to use water as a solvent in the reaction. We anticipated that water would interact with the hydrophilic surface and facilitate the transport of the hydrophobic substrate towards the hydrophobic surface, making the substrate and the catalyst in close proximity and leading to enhanced reactivity.



Scheme 1. Preparation of catalyst A.

We also considered the direct complexation of Pd(II) on compound **1** wherein the aminopropyl moiety acts as the ligand giving monodentate attachment. This catalyst was slightly more reactive than the former during the first two runs of hydrogenation reaction; however, the yield dramatically dropped after each recycle. We presumed that, although the monodentate Pd was more reactive than the chelated one, the former was more labile, making it unstable. Presumably, this was the reason for the sudden drop in the reactivity of the catalysts prepared without compound **2**.

Catalyst **A** has an irregular shape based on the SEM image (Fig. 1, left) acquired primarily from the shape of the starting silica. Palladium mapping confirmed that Pd was well dispersed on the surface of the silica and because of its nanosize nature it was hardly seen in the SEM image. The Energy Dispersive X-ray Spectroscopy (Fig. 1, right) confirmed that Pd was indeed present. The palladium content on catalyst **A** was determined by ICP-AES and the result showed that it had 0.90 mmol Pd g^{-1} of catalyst. To determine the actual size of palladium particles embedded on catalyst **A**, we checked its High Resolution Transmission Electron Microscopy image (Fig. 2) and found that it had predominantly 2–3 nm sized Pd metal.

Alternatively, we prepared another type of catalyst having cross-linked poly(4-vinylpyridine-co-styrene) gel as the solid support. The bead-shaped cross-linked polymer was synthesized using the

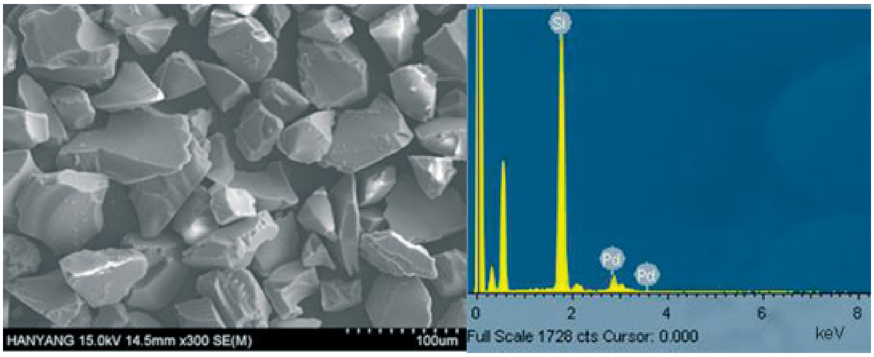


Figure 1. SEM image (left) and EDX (right) analysis of Catalyst A .

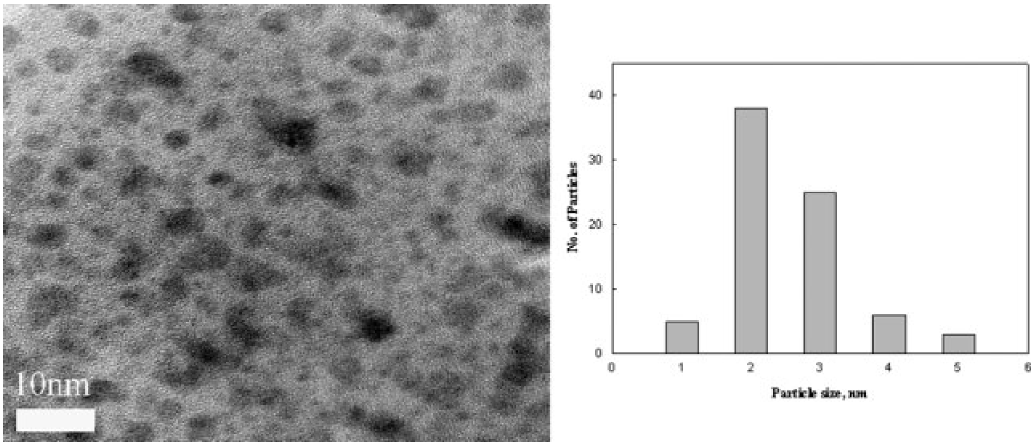


Figure 2. TEM image of catalyst A (left) and Pd particle size distribution (right).

known polymerization procedure for styrene and 4-vinylpyridine having divinylbenzene as cross-linker.[35–37] Using this cross-linked polymer, we prepared catalyst **B** by complexing Pd(OAc)$_2$ into the prepared cross-linked polymer and reducing the complex with sodium borohydride in the same manner as catalyst **A**. Likewise, catalyst **B** was characterized using different methods. The SEM image (Fig. 3, left) of catalyst **B** showed that the bead-shaped nature of the polymer was maintained and EDX (Fig. 3, right) confirmed the presence of palladium metal that was well dispersed on the surface. The amount of palladium metal on catalyst **B** was 0.84 mmol g^{-1} of catalyst based on ICP-AES. The TEM image showed that the palladium particles were predominantly 3–4 nm in diameter (Fig. 4).

Catalytic Activity of Catalysts A and B in the Hydrogenation of Various Olefins

Reduction of organic compounds is considered as one of the most important organic transformations, especially the selective hydrogenation of α,β-unsaturated carbonyl compounds because of its myriad applicattion in the field of pharmaceutial and fine chemicals.[38] Thus, we opted to explore the catalytic activity of our prepared catalysts in this reaction.

First, we chose cinnamic acid as the test substrate. Hydrogenation reaction was done using 5 ml of water and 5 mol% of catalayst **A** at room temperature under hydrogen gas. After 2 h we obtained 98% of 3-phenyl propionic acid. To countercheck

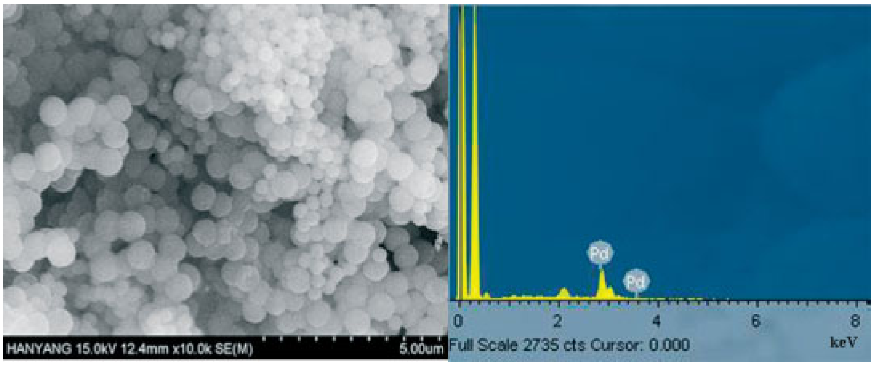


Figure 3. SEM image (left) and EDX (right) analysis of Catalyst B.

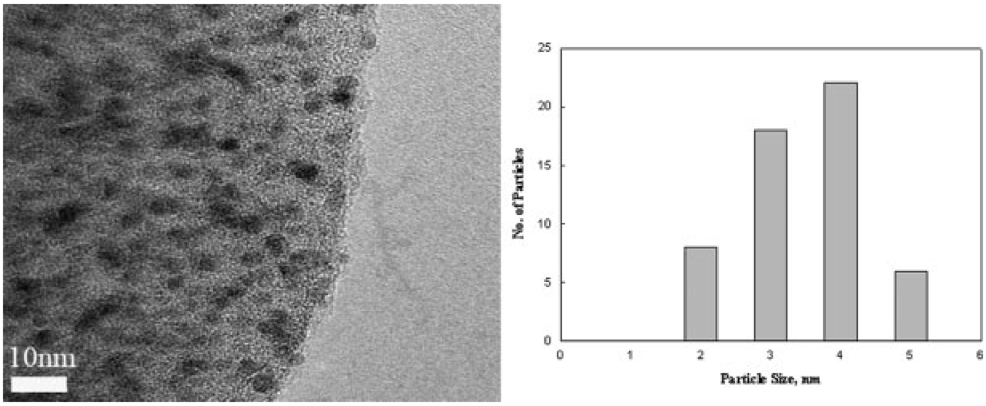


Figure 4. TEM image of catalyst B (left) and Pd particle size distribution (right).

Table 1. Hydrogenation of various olefins using catalyst A and B[a]

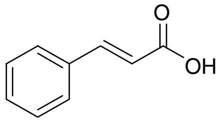
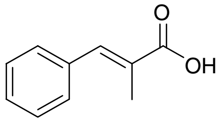
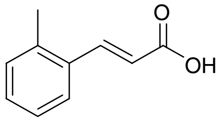
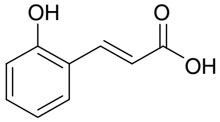
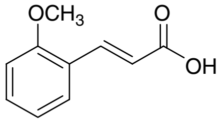
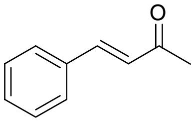
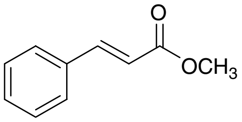
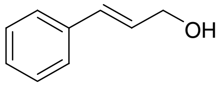
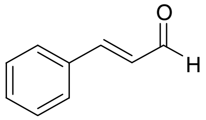
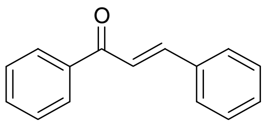
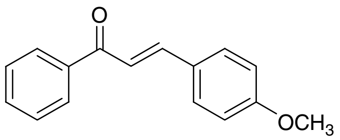
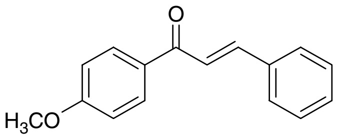
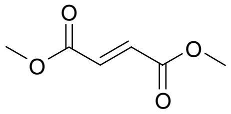
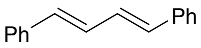
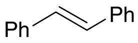
Entry	Starting olefins	Catalyst A		Catalyst B	
		Time (h)	Yield (%)	Time (h)	Yield (%)
1[b]		0.5	98	1	Quant.
2[b]		0.5	98	1	95
3[b]		0.5	Quant.	1	98
4[b]		0.5	Quant.	4	48
5[b]		0.5	96	3	Quant.
6		1	97	2	98
7		1	98	2	97
8		2	Quant.	2	56
9		2	95	2	94

Table 1. (*Continued*)

Entry	Starting olefins	Catalyst A		Catalyst B	
		Time (h)	Yield (%)	Time (h)	Yield (%)
10[c]		2	98	2	98
11[c]		2	98	2	98
12[d]		24	97	24	93
13[c]		2	98	2	95
14[e]		6	97	6	95
15[e]		6	96	6	95

[a] Olefin (1.0 mmol), catalyst (5 mol% of Pd), H_2O (5 ml).
[b] Potassium hydroxide (1 mmol) was added.
[c] CH_3CN (1 ml) and H_2O (4 ml) were used as the solvent.
[d] CH_3CN (2 ml) and H_2O (3 ml) were used as the solvent.
[e] THF (4 ml) and H_2O (1 ml) were used as the solvent.

its effectiveness against Pd/C, a known heteregeneous catalyst for hydrogenation, the same experiment was carried out and we obtained only 83% of the product using 10 mol% of Pd/C. These results showed that our catalyst was superior and thus we considered various substrate for further investigation as shown in Table 1. For the case of α,β-unsaturated carboxylic acids (Table 1, entries 1–5), we used potassium hydroxide to enhance its solubility in water. Although the reaction proceeded in water alone, it took longer (2 h) and gave a slightly lower yield compared with the reaction that used potassium hydroxide. With the use of potassium hydroxide the reaction can be completed in only 30 min with excellent yield. Other types of olefins having various functional groups such as ketones, esters, alcohols and aldehydes (Table 1, entries 6–9 and 13) were also considered. These olefins have low melting point and exist as liquids at room temperature and thus can interact with water; as a result the reaction proceeded excellently without using potassium hydroxide.

Some olefins are solid and totally insoluble in water thus interaction was difficult. This necessitated a small amount of organic co-solvent in order to give higher yield at shorter reaction time. Several organic co-solvents were tested as shown in Table 2. Among these solvents acetonitrile was the best organic co-solvent for water. This solvent was used for entries 10–13 in Table 1. Noticeably, entries 11 and 12 showed different reactivities. We expected that the higher reactivity of entry 11 was brought about by the electronic effect via conjugation. Moreover, we also considered reduction of conjugated alkene and simple substituted alkene (entries 14 and 15 respectively); both gave excellent yields in reasonable times using THF as water co-solvent.

Table 2. Reaction of *trans*-chalcone in various solvents[a]

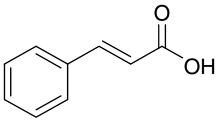
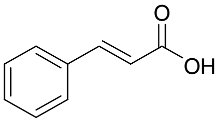
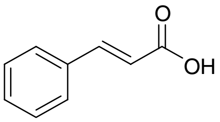
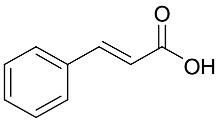
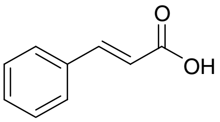
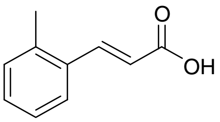
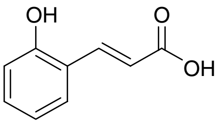
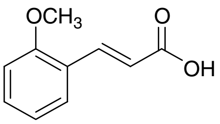
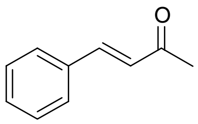
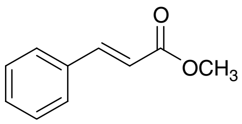
Entry	Solvent	Yield (%)	Entry	Solvent	Yield (%)
1	H_2O	38	6	$H_2O:CH_2Cl_2$	14
2	$H_2O:CH_3CN$	98	7	H_2O : THF	81
3	H_2O : IPA	62	8	H_2O : DMF	67
4	H_2O : MeOH	63	9	$H_2O:Et_2O$	84
5	H_2O : EtOAc	41	10	H_2O : Acetone	79

[a] Co-solvent system ratio is 1 : 4 (H_2O : organic solvent, v/v).

Both catalysts **A** and **B** gave excellent yield of hydrogenation product; however catalyst **B** exhibited lower reactivity. In some cases, catalyst B required a slightly longer reaction time and gave lower yields in some cases. We presumed that the lower reactivity of catalyst **B** was attributed to its structure. Presumably, the pyridyl units of the polymer surrounded the Pd metal, making it less exposed for catalysis.

To check further the merit of our catalyst, we checked its recyclability. Catalyst **A** was recycled 10 times using various olefins. In the first five recyles we used cinnamic acid and

Table 3. Recycle test[a]

Run	Starting olefins	Catalyst A		Catalyst B	
		Time(h)	Yield (%)	Time (h)	Yield (%)
1st[b]		0.5	97	1	Quant.
2nd[b]		0.5	94	1	80
3rd[b]		0.5	96	1	53
4th[b]		0.5	95	4	32
5th[b]		0.5	93	3	35
6th		0.5	98	–	–
7th		0.5	95	–	–
8th		0.5	97	–	–
9th		1	95	–	–
10th[c]		1	92	–	–

[a] Olefin (1.0 mmol), catalyst (5 mol% of Pd), H_2O (5 ml).
[b] Potassium hydroxide (1 mmol) was added.
[c] CH_3CN (1 ml) and H_2O (4 ml) was used as a solvent.

on the next five recycles various α,β-unsaturated carbonyl compounds. As shown in Table 3, the yield did not change appreciably after 10 recyles. This means that the catalyst did not lose its catalytic activity. Furthermore, we also checked the filtrate after removal of the catalyst and negligible amount of palladium was detected based on ICP-AES. On the other hand, the recycle test of catalyst **B** was not favorable. Its catalytic activity decreased dramtically after five recycles, as depicted in Table 3. Analysis of its filtrate showed that negligible amount of palladium leached out.

Conclusion

We have successfully prepared Pd nanosize particles dispersed on two types of solid supports, namely 3-aminopropyl functionalized silica gel and cross-linked poly(4-vinylpyridine-co-styrene) gel. These catalysts exhibit catalytic activity for hydrogenation reaction using aqueous media and, above all, these catalysts are recyclable. We are currently considering other applications of these catalysts on other organic transformations, which we are will report in due course.

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Supporting information

Supporting information may be found in the online version of this article.

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