Facile Synthesis of Polyaniline-Supported Pd Nanoparticles and Their Catalytic Properties toward Selective Hydrogenation of Alkynes and Cinnamaldehyde

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We report a facile method toward preparation of conducting polymer-supported Pd nanoparticles by in situ reducing the palladium salt [$Pd(NO_3)_2$] on the surface of polyaniline (PANI) film/membrane. The palladium(0) particles distribute evenly on the PANI surfaces. The size and morphology of Pd particles are dependent on the nature of the substrate surfaces. The palladium (Pd) particles on the PANI membrane surfaces have a rough surface morphology with a size distribution of ~200 nm, and the Pd particles on the PANI film have a smooth surface with a size distribution of ~500 nm. These Pd particles are in fact conglomerates of much smaller nanoparticles with an average size distribution of 13 nm. Pd nanoparticles exhibit efficient catalytic activity toward hydrogenation of alkynes and cinnamaldehyde with high selectivities dominated by a kinetic mechanism. Moreover, our results suggest that the variation in particle morphology resulting from substrates leads to differences in their catalytic efficiency presumably due to the difference in surface area. The PANI-supported Pd nanoparticles are robust and can be reused at least seven times without the significant loss of its catalytic activity and selectivity.

Introduction

Palladium supported on carbon (Pd/C) is one of the most commonly used heterogeneous catalysts for hydrogenation of organic substrates.[1,2] This system is highly efficient but suffers from low catalytic selectivity. In the past decade, there has been increasing interest on the preparation of polymer-supported palladium nanoparticles toward organic transformations due to their much improved catalytic selectivity. Of particular interest is the conducting polymer (ECP) and metal nanoparticle (MNP) composites, which can be prepared via chemical[3,4] and electrochemical means.[5,6] Generally speaking, these ECP/MNP composites are prepared via electrochemical deposition of nanoparticles onto electrodes previously coated with an electrical conducting polymer (ECP), reduction of metal salts by a polymer matrix,[3,4,7] and polymerization of the ECP in the presence of MNPs. As a result of the conducting nature of the ECP/MNP composite, electrocatalytic properties of this material have been demonstrated and show promise in oxidation of methanol and hydrazine.[3,8,9] Incorporation of MNP inside the ECP matrix leads to a new class of materials that often show enhanced electrocatalytic properties.

Among all the ECPs, polyaniline (PANI) is commonly used because of its facile synthesis, lower price tag, and environmental stability. PANI has also been extensively studied for their use as electromagnetic shielding[10–12] and anticorrosion coating.[13–15] PANI possesses secondary amines and tertiary imines in the backbone structure that can bind metal ions; these metal ions can be released by immersing ion-bound PANI into a low pH solution. The ability of binding metal ions and subsequent liberation makes PANI an attractive material for environmental remediation. In the cases where metal ions have a reduction potential higher than that of the PANI, the bound metal ions can be reduced to form zerovalent metals. Therefore, it was long recognized PANI can be used for electrodeless precipitation of metals

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from a metal ion solution.[16] In our laboratory, we have recently demonstrated synthesis of MNPs using conducting polymer colloids.[17] These as-synthesized MNPs can either spread throughout the solution or be embedded in the conducting polymer colloids to form a novel PANI/MNP composite material.[17]

So far, the most efficient PANI/MNP catalyst is prepared through dispersing Pt/Pd nanoparticles on the polymer surfaces and/or inside the polymer matrix.[3,8,18] These Pt/Pd nanocomposites exhibit optimized catalytic properties mainly as a result of their high surface area. Drelinkiewicz and others also demonstrated preparation of Pd *micro*particles onto the PANI/polypyrrole powder and show catalytic properties toward hydrogenation of carbonyl and aromatic rings.[19–21] Despite the fact that it has been long recognized that PANI is capable of reducing metal ions to form zerovalent metals to generate conducting polymer/metal particle composites, there is a need for a robust (reusable) catalytic system with synthetic control over the size and morphology of Pd particles to achieve enhanced catalytic performances. In this work, we report a facile approach toward synthesis of PANI-supported Pd nanoparticles by in situ reduction of $Pd(NO_3)_2$ on the surfaces of PANI thin films prepared by thermal evaporation and PANI membranes prepared by the phase inversion method.[22] These Pd nanoparticles dispersed homogeneously on the PANI surface and have a size distribution of ~200 nm on PANI membrane surfaces and ~500 nm on PANI film surfaces. These metal particles consist of an ensemble of much smaller nanoparticles with an average size distribution of ~13 nm. We observe a difference in catalytic efficiency between Pd nanoparticles grown on top of the PANI thin films prepared by thermally evaporating the solvent and Pd nanoparticles on PANI membrane prepared by phase inversion processes, presumably as a result of the difference in their morphologies. The catalytic properties of these Pd nanoparticles toward hydrogenation of alkynes and cinnamaldehyde are studied. These PANI-supported Pd nanoparticles have a high catalytic efficiency with 0.1 mol % loading. They can be repeatedly used more than seven times without significant loss of the catalytic properties. Moreover, they exhibit high selectivity toward hydrogenation of alkyne and cinnamaldehyde that are not possible with commercially available Pd/C.

The PANI membranes used to support the growth of Pd nanoparticles have one of the best gas separation properties among polymeric materials. Therefore, we expect to develop catalytic membrane reactors (CMR) in which catalytic MNPs are combined with the membranes that are capable of performing chemical separations, for example, gas separation.

Experimental Section

General Details. PANI emeraldine base (EB) powder was obtained from Aldrich. *N*-Methyl-2-pyrrolidone (99% Aldrich), heptamethylenimine (HPMI, 98% Acros), ethyl phenylpropiolate (98% Aldrich), $Pd(NO_3)_2$ (99.99%, 10 wt % solution in 10 wt.% nitric acid, Aldrich), and cinnamaldehyde (96%, Aldrich) were used as received. The NMR spectra were recorded on a Bruker-400 spectrometer. X-ray diffraction (XRD) measurements were made with a Rigka Ultima III diffractometer that uses fine line sealed Cu Kα tube ($\lambda = 1.5406$ Å) X-rays. The generator is a D/MAX Ultima series with a maxmium power of 3 kW. The samples were mounted on a polycrystalline glass slide. Data were collected in continuous scan mode over the 2-theta range from 5 to 90° with sampling width of 0.0500° and a scanning speed of 3.000°/min. The patterns were matched with metallic silver located in the PDF database. Scanning electron microscopy (SEM) micrographs of metals on the PANI membrane surfaces were taken using a JEOL 6300FXV SEM and FEI Quanta FEG ESEM. The infrared spectra are taken by using a Nicolet 550 FTIR spectrometer.

Fabrication of PANI Membranes and Films. Fabrication of PANI porous asymmetric membranes is achieved by employing the phase inversion method using water as the coagulation bath. In a typical procedure, 3.70 g of NMP (99% Aldrich, dried by a 4 Å molecular sieve) was put into a 12.0 mL Teflon vial. Then 0.31 g of HPMI (98% Acros) was added to it. The vial was sealed with a Teflon cap and kept in an oven at 60 °C for 5 min. Then 1.00 g of EB powder was added to the vial. The solution was slowly stirred with a homogenizer and then ramped up to 5000 rpm for 25 min. The EB/HPMI molar ratio was 1:1 (the moles of EB are calculated on the basis of the tetrameric repeat unit). The resulting EB solution was poured onto a glass plate and spread into a wet film using a gardener's blade (Pompano Beach, FL) with a preset thickness. The wet film was then immersed into the water bath and kept in the water bath for more than 24 h. The resulting membrane was then dried under vacuum at room temperature for 12 h before any subsequent processing.

The PANI thin films are prepared by placing the wet film inside a 60 °C oven overnight to thermally evaporate the solvent. The thin films are then immersed in water and methanol to ensure complete removal of the solvent residue.

Preparation of Pd Nanoparticles on PANI Membranes. A piece of preweighed PANI membrane/film prepared above was immersed into a diluted solution of $Pd(NO_3)_2$ [1 mL of $Pd(NO_3)_2$ in nitric acid was mixed with 50 mL of water] for 16 h. A shiny layer of Pd could be clearly seen at this stage. The Pd-coated PANI membrane/film was carefully taken out, repeatedly washed with ammonium water (0.4 M) and distilled water, and then dried under vacuum. The amount of Pd coated on a PANI film was calculated on the basis of the weight difference before and after the deposition.

Catalyst Testing toward Hydrogenation. All hydrogenations were performed at room temperature in a Schlenk flask. The PANI-supported Pd film was placed in the flask and flushed with N_2 several times to remove any absorbed air in the film prior to use. The desired amount of an alkyne and 15 mL of methanol was then added to the flask. To the stirred solution of such a mixture was charged with ~1 atm of hydrogen gas using the hydrogen balloon. The reaction was stopped at a desired time interval by evacuating the solvent under vacuum. The conversion of the reactant was

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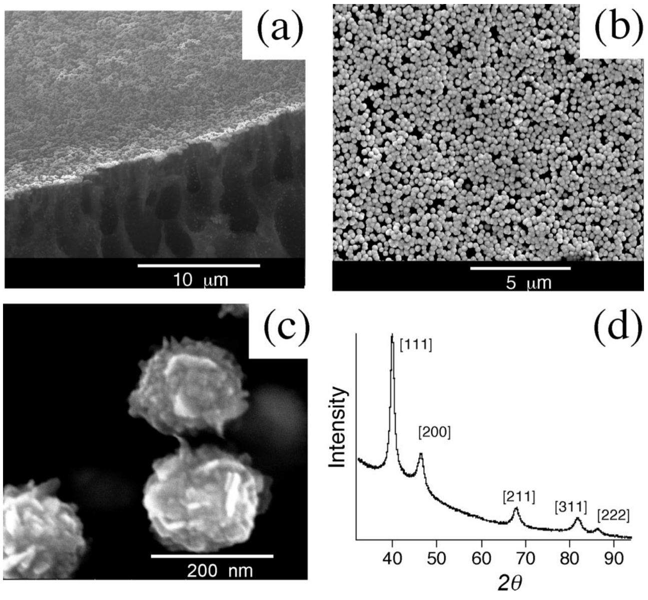

Figure 1. SEM micrographs of Pd nanoparticles on the PANI membrane surface (a, b) show a large number of uniformly distributed Pd nanoparticles, and (c) Pd noanoparticles with a rough surface and very good size distribution of ~200 nm are comprised of many smaller nanoparticles. (d) XRD of Pd nanoparticles grown on PANI membrane.

determined by the integral differences of the starting material and the corresponding products in the ^{1}H NMR spectra.

Results and Discussion

Preparation and Characterization of PANI-Supported Palladium Nanocatalyst. The asymmetric porous PANI membrane was synthesized according to the published method.[22] It features a dense surface layer and a porous substructure. In this case, PANI membranes serve not only as the substrates to support the growth of metal particles but also as reducing agent to convert the Pd^{2+} ions to zerovalent Pd. The Pd particles on the PANI membrane surface have an average size distribution of ~200 nm (Figure 1c). Pd nanoparticles on the PANI membrane surface have a rough surface morphology (see Figure 1). XRD of these Pd nanoparticles on the PANI surfaces are shown in Figure 1d. The entire diffraction pattern belonging to Pd nanoparticles has been identified. We can also determine the size of the nanoparticle by measuring the full maximum of the half-peak width (FMHW), and the results indicate that the particle size is ~13 nm. This result shows very nice consistency with the particle size estimated by SEM. Upon close examination of the high resolution SEM, we can observe that these Pd particles indeed consists of many much smaller nanoparticles.

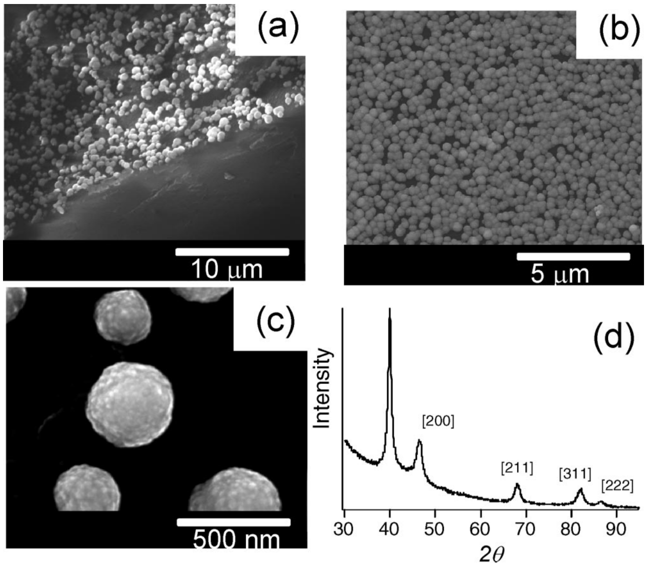

Figure 2. SEM micrographs of the cross section of a thermally cured dense film (a, b) show a large number of uniformly distributed Pd nanoparticles on the PANI thin film surface, and (c) Pd noanoparticles with a relatively smooth surface and size distribution of ~500 nm are comprised of many smaller nanoparticles. (d) XRD of Pd nanoparticles grown on PANI thin film.

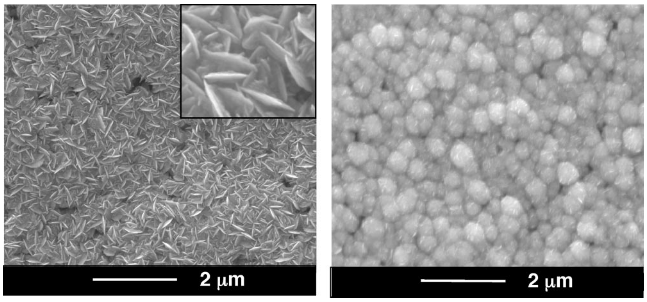

Figure 3. SEM micrographs of a layer of Pd particles grown on top of a PANI membrane (left) and on a thermally cured PANI dense film (right). Inset shows high resolution SEM of the Pd particles.

We follow the same procedure to prepare Pd nanoparticles on the PANI film surfaces. Figure 2a shows the SEM micrograph of the cross section of a dense PANI thin film free of porous structure and the Pd nanoparticles deposited on the thin films surface with near monolayer surface coverage, Figure 2b. In contrast to the Pd nanoparticles grown on top of the PANI membrane, Pd particles grown on a thermally cured dense film are larger in size (~500 nm) and have a relatively smooth surface morphology (Figure 2c). The XRD spectrum clearly identifies the structure of the Pd nanoparticles. It is very interesting to note from the XRD that the size of these much smaller Pd nanoparticles determined by the FMHW is ~13 nm, which is exactly the same as that of the nanoparticles comprised of Pd particles grown on top of the PANI membrane. The XRD results suggest that these large Pd particles (~500 nm) consist of an ensemble of much smaller Pd nanoparticles. In summary, the Pd particles grown on top of the porous membrane (Figure 1) and on top of the dense film (Figures 2 and 3) have different particle size and surface morphology. The difference in substrate, membrane vs film, giving rise to a metal particle with different morphology and size has been demonstrated by in situ reducing AgNO$_3$ and AuCl$_3$ in aqueous solutions.[23]

The amount of deposited Pd particles could also be easily controlled by the reduction time. It is important to note that prolonging the exposure time of PANI membrane to the Pd ion solution does not result in change in the particle size and the morphology. It simply creates more Pd nanoparticle on the PANI surface and, hence, a better surface coverage. As we increase the thickness of the Pd particles on top of

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Table 1. Catalytic Hydrogenation of Diphenylacetylene as a Function of Catalyst Loading and Reaction Time[a]

entry	catalyst	catalyst loading (% mol)	time (h)	conversion (%)	product I (%) *cis*-stilbene	product II (%) Bibenzyl
1	Pd/PANI membrane	1	16	100	0	100
2	Pd/PANI membrane	0.1	16	49	72	28
3	Pd/PANI membrane	0.1	24	72	62	38
4	Pd/PANI membrane	0.1	40	96	39	61
5	Pd/PANI membrane	0.1	48	96	26	74
6	Pd/PANI membrane	0.1	67	97	6	94
7	10 wt % Pd/C	0.1	16	100	0	100
8	Pd/PANI film	1	16	26	86	14
9	Pd/PANI film	1	24	84	88	12
10	Pd/PANI film	1	40	100	60	40

[a] Reaction conditions: diphenylacetylene 1 mmol, MeOH 20 mL, pressure ~1 atm, room temperature.

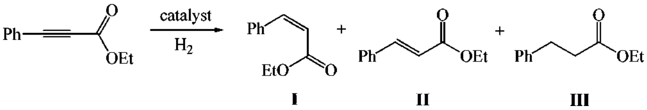
the PANI substrate, the Pd particles eventually evolve into a sheet-like structure on the membrane surfaces and a spherical structure on the film surfaces. Our results indicate that we can effectively control the amount of Pd nanoparticles on the PANI surface and surface coverage without introducing the variables in particle size and morphology.

There are several obvious advantages of our PANI-supported Pd nanoparticle catalyst. First, the method of making Pd nanoparticles is extremely simple. It only requires immersing the PANI film/membranes in a $Pd(NO_3)_2$ solution for a short time period, which is enough to grow a thin layer of Pd nanoparticles. Furthermore, the Pd nanoparticles on the support are chemically stable. After immersing these catalysts in organic solvents for a few days and then repeatedly washing with water and organic solvents (methanol, toluene, and acetone), the SEM and XRD of these nanoparticles before and after the reaction are basically identical. Finally, the amount of Pd nanoparticles on the PANI film could be controlled by adjusting the deposition time. The optimized catalytic properties can be achieved through the monolayer surface coverage and optimized particle morphology.

Catalyst Testing. Synthesis of MNPs with enhanced catalytic properties is of great interest to chemical and pharmaceutical industries. It has been reported that several key factors such as polymer support, particle size, and morphology of Pd particles, have a huge impact on the catalytic properties of supported Pd in organic transformations.[24–28] The homogeneous dispersion of Pd nanoparticles on PANI surfaces and their unique particle morphology prompted us to investigate its corresponding catalytic activities.

The studies of the catalytic properties of the as-prepared PANI-supported Pd nanoparticles were focused on the hydrogenation reactions of several unsaturated organic molecules. Two different alkynes, PhC≡CPh, and PhC≡CC(O)OET, and the cinnamaldehyde were selected in our study. The hydrogenation of these substrates has been extensively studied by employing palladium catalysts prepared by other methods.[29–33] These prior studies allow the characterization of hydrogenation products of these substrates at different stage of the reaction to be much easier; the comparison of catalytic activity between PANI-supported Pd nanoparticles and the known catalysts is more reliable.

Scheme 1



The catalytic hydrogenation reactions were carried out at room temperature under an atmosphere of H_2 maintained by an inflated balloon. Using 1 mol % of PANI-supported Pd catalyst, diphenylacetylene was completely converted to bibenzyl within 16 h (Eentry 1, Table 1). No *trans*-stilbene was observed, and only trace amount of *cis*-stilbene was detected when monitoring the reaction by NMR, indicating the high catalytic efficiency and selectivity of this type of catalyst toward the C═C bond. It is worth noting that the catalytic efficiency of PANI membrane-supported Pd nanoparticles is higher than that of the commercially available palladium nanocatalyst Pd-EnCat (Aldrich), which gives the complete hydrogenation product in 18 h with the catalyst loading of 5 mol %.[29] The PANI-supported Pd nanoparticles could be easily recovered and repeatedly used at least seven times without significant loss of catalytic activity and selectivity. Further testing on the minimum amount of catalyst on a mole percent basis suggests that catalyst loadings of Pd on PANI could go as low as 0.1 mol percent, while still maintaining its catalytic activity. Although relatively slow compared to the commercially available Pd on carbon (Pd/C) hydrogenation catalyst (entry 7, Table 1) under such low loading, one obvious advantage of this catalytic system is the significantly improved catalytic selectivity. Under such a low catalyst loading, *cis*-stilbene could be clearly identified, and its ratio could be controlled by simply varying the reaction time. For example, a 72% selectivity of *cis*-stilbene was obtained with the 50% total conversion of diphenylacetylene after 16 h under such

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Table 2. Catalytic Hydrogenation of Ethyl Phenylpropiolate as a Function of Catalyst Loading and Reaction Time[a]

entry	catalyst	catalyst loading (% mol)	reaction time (h)	conversion (%)	product I cis (%)	product II trans (%)	product III (%)
1	Pd/PANI membrane	5	4	70	65	0	35
2	Pd/PANI membrane	5	16	96	26	0	74
3	Pd/PANI membrane	5	24	100	0	0	100
4	Pd/PANI membrane	0.1	16	23	>75.5	<0.5	24
5	Pd/PANI membrane	0.1	40	83	44	<1	>55
6	Pd/PANI membrane	0.1	60	>97	6	<1	>93
7	Pd/C (10 wt %)	0.1	16	80	17.5	15.5	67
8	Pd/PANI film	5	16	100	30	17	53
9	Pd/PANI film	5	24	100	0	0	100

[a] Reaction condition: ethyl phenylpropiolate 1 mmol, MeOH 20 mL, pressure ~1 atm, room temperature.

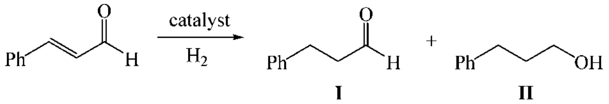
conditions (entry 3, Table 1). The nearly complete hydrogenation (96%) of diphenylacetylene to afford the bibenzyl was achieved within 48 h (entry 5, Table 1).

A similar study using 1 mol % of PANI film-supported Pd catalyst demonstrates an inferior catalytic efficiency as compared to the PANI membrane-supported Pd catalyst. The PANI film-supported Pd nanoparticles exhibits a 26% conversion in 16 h, while membrane-supported Pd nanoparticles have a 100% conversion in 16 h (entry 8, Table 1). While the reaction time was extended to 24 h, the conversion was increased to 84% with a slightly higher selectivity of 88% toward *cis*-stilbene (entry 9, Table 1). The above results suggest that the selectivity toward *cis*-stilbene is dominated by a kinetic mechanism since its ratio increases initially to a maximum, 72% for PANI membrane-supported Pd and 88% for PANI film-supported Pd, and then started to decrease as the ratio for bibenzyl started to increase. It is not entirely clear to us at this stage why the nanosized Pd on PANI displays a lower catalytic activity than Pd/C. However, similar results have been observed for other types of Pd nanoparticle catalysts, such as Pd EnCat.[29]

The catalytic properties of the PANI-supported Pd nanoparticles toward hydrogenation of ethyl phenylpropiolate were also examined in this study. In contrast to the hydrogenation of diphenylacetylene, hydrogenation reaction toward ethyl phenylpropiolate, an asymmetric alkyne, is less reactive mainly because of its electron deficiency nature. Three potential products could be produced from this reaction (Scheme 1).

The main results of our study on the hydrogenation of ethyl phenylpropiolate employing PANI membrane-supported Pd as the catalyst are summarized in Table 2. Under the catalyst loading of 5 mol %, ethyl phenylpropiolate was hydrogenated to the complete hydrogenation product ethyl hydrocinnamate within 24 h (entry 3, Table 2). The catalyst loading could go as low as 0.1 mmol % while maintaining decent catalytic activity (entries 4–6, Table 2). Compared with the commercially available Pd/C (entry 7, Table 2), the catalytic efficiency of the new supported catalyst is low. However, the PANI-supported Pd nanoparticles gave much better selectivity. For example, under the catalyst loading of 0.1 mol %, no selectivity was observed within 16 h for the commercial Pd/C (entry 7, Table 2). Under the similar conditions, ethyl phenylpropiolate was converted (23% conversion to product; entry 4, Table 2) to a mixture of 75% of *cis*-ethylcinnamate(I), 24% of ethyl hydrocinnamate(III), and a trace amount (<0.5%) of *trans*-ethylcinnamate(II) when PANI membrane-supported Pd was used. A series of NMR studies to analyze the yields of products at different times of the reaction suggest that the distribution of hydrogenation products could be controlled kinetically (entries 4–7, Table 2). An almost complete conversion (97%) of the starting material to ethyl hydrocinnamate (>93% selectivity) was achieved in 60 h.

Scheme 2



The catalytic activity of the PANI film-supported Pd nanoparticles has also been determined. With 5 mol % catalyst loading, the hydrogenation of ethyl phenylpropiolate reaches 100% conversion, which is similar to that of the PANI membrane-supported Pd (entries 2 and 9, Table 2). Meanwhile, a minimum selectivity of 17% toward *trans*-ethylcinnamate in the mixture product (entry 8, Table 2) is also observed. The overall catalytic activity of the PANI film-supported Pd for the hydrogenation of ethyl phenylpropiolate is comparable to that of the PANI membrane-supported Pd nanoparticles.

The high catalytic activity and selectivity of PANI membrane-supported Pd were manifested in our study of hydrogenation reaction toward cinnamaldehyde. The catalytic hydrogenation proceeded selectively to afford solely hydrocinnamaldehyde and 3-phenyl-1-propanol (Scheme 2).

The hydrogenation of cinnamaldehyde with a catalyst loading of 5 mol % exhibits a high selectivity toward hydrocinnamaldehyde. As summarized in Table 3, the catalytic hydrogenation apparently occurs first on the C=C double bond, and 3-phenyl-1-propanol is formed by the further hydrogenation of the aldehyde group in hydrocinnamaldehyde. Amazingly, a selectivity of around 80% toward hydrocinnamaldehyde was observed until a conversion 91% was reached in our system (entries 1–4, Table 3). Further extension of the reaction time resulted in the steady increase of 3-phenyl-1-propanol and the decrease of hydrocinnamaldehyde.

The PANI film-supported Pd nanoparticles exhibit an inferior catalytic activity compared with the membrane-supported Pd nanoparticles. In 24 h, membrane-supported Pd catalyst gives rise to 91% conversion and 81% selectivity toward hydrocinnamaldehyde. Meanwhile, it takes 48 h for the PANI film-supported Pd catalyst to reach 35% conversion with 75% selectivity toward hydrocinnamaldehyde (entries

Table 3. Catalytic Hydrogenation of Cinnamaldehyde as a Function of Reaction Time[a]

entry	catalyst	catalyst loading (% mol)	time (h)	conversion (%)	product I (%) Hydrocinnamaldehyde	product II (%) 3-phenyl-1-propanol
1	Pd/PANI membrane	5	8	7	84	16
2	Pd/PANI membrane	5	16	47	84	16
3	Pd/PANI membrane	5	20	67	83	17
4	Pd/PANI membrane	5	24	91	81	19
5	Pd/PANI membrane	5	28	100	72	28
6	Pd/PANI film	5	24	19	75	25
7	Pd/PANI film	5	48	35	75	25

[a] Reaction condition: *trans*-cinnamaldehyde 0.4 mmol, toluene 20 mL, pressure ~1 atm, room temperature.

4 and 7, Table 3). The lower conversion rate did not result in an increase in selectivity as one might have expected. The selectivity toward hydrocinnamaldehyde is at 75% throughout the 48 h reaction time period (entries 6 and 7, Table 3).

The formation of hydrocinnamaldehyde with high selectivity is significant because it is an essential raw material in the production of cinnamic acid for the preparation of certain drugs, including protease inhibitors used in the treatment of HIV.[34] Hydrocinnamaldehyde and its derivatives are also used as light penetration inhibitors in sunscreen formulations, as an ingredient for herbicidal compositions, and as raw materials in the synthesis of heterocyclic color complexes and in the electroplating process for zinc.[35]

Chemical and Thermal Stability of PANI Membrane-Supported Pd Nanoparticles. PANI membranes are thermally and chemically stable under the reactions conditions that involve usage of organic solvent, reducing agent (H_2), and elevated temperature (up to 60 °C). The stability of the PANI membrane is mainly determined by using infrared spectroscopy. Infrared spectroscopy has been used as one of the main spectroscopy tools to probe the molecular structure and redox state of PANI.[36,37] The IR spectra of PANI membrane before and after the hydrogenation reactions are essentially the same (see Figure 4). This result suggests that the molecular structure of the PANI membrane is unchanged, and the redox state of PANI is not influenced by the presence of H_2 as well as the chemicals involved before and after the reaction. The nanoparticles before and after the reaction are also examined by using SEM and XRD spectroscopy. The SEM micrographs and XRD spectra of the nanoparticles before and after the reactions are basically identical. The stability of the membrane support along with the Pd nanoparticles immobilized onto the membrane surfaces insinuates very stable catalytic membrane reactors.

Conclusion

We have demonstrated synthesis of PANI-supported Pd nanoparticles (Pd/PANI) by way of in situ reduction of Pd^{2+} ions in aqueous solutions. Pd nanoparticles on the PANI substrate display a unique morphology and a high catalytic efficiency toward selective hydrogenation of alkyne and cinnamaldehyde. The catalytic activity of Pd nanoparticles is morphology dependent presumably because of the difference in the surface area. Pd/PANI can be easily recycled and repeatedly used many times (>seven times) without significant loss of catalytic activity and selectivity. The catalytic efficiency and high selectivity of our Pd/PANI are at least comparable to the commercial Pd nanocatalyst Pd EnCat (Aldrich). The PANI membrane support is chemically stable under experimental conditions involving organic solvents and reducing agents for more than a week. This conducting polymer-mediated electrodeless deposition represents probably the most inexpensive and simple method of making catalytic membrane reactors. Therefore, it makes our Pd/PANI membrane reactor an ideal candidate for the further development of heterogeneous catalysts and novel fuel cell devices.

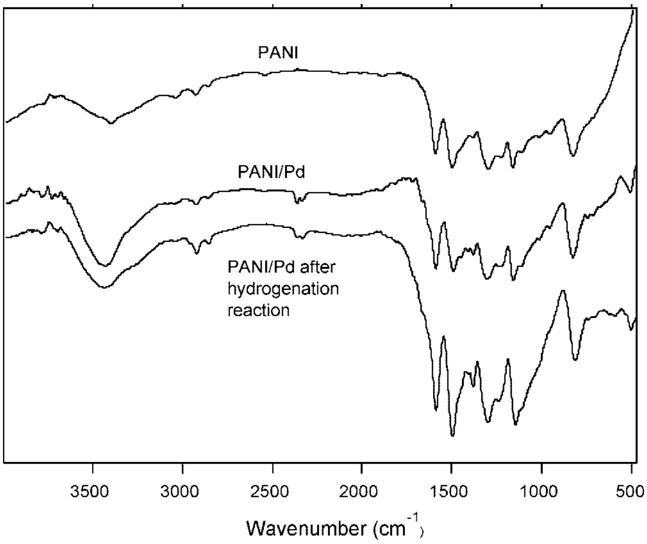


Figure 4. FTIR spectra of the PANI membrane, the PANI membrane with Pd nanoparticles, and the same PANI membrane after hydrogenation reaction.

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