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PVA-encapsulated Palladium Nanoparticles: Eco-friendly and Highly Selective Catalyst for Hydrogenation of Nitrobenzene in Aqueous Medium

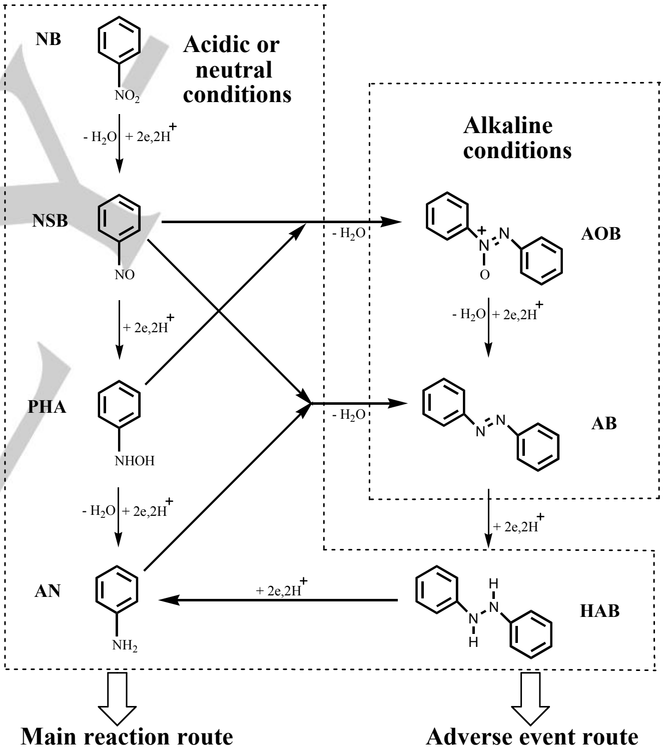
Xiaoyan Wang,[a] Changru Huang,[a] Xiaohao Li,[a] Congxia Xie,*[a] and Shitao Yu[b]

Abstract: In aqueous medium without any other additives, palladium (Pd) nanoparticles with water-soluble polyvinyl alcohol (PVA) as stabilizer were synthesized for the catalytic hydrogenation of nitrobenzene. Under the optimum experimental conditions, the nitrobenzene conversion and the selectivity for aniline were 99.3% and 100%, respectively. Comprehensive characterization methods, including TEM, UV-Vis, CLSM, XRD and XPS allowed a better understanding of the role of PVA aggregates and the properties of Pd nanoparticles. The nitrobenzene conversion exceeded 80% even after 6 cycles without any treatment of the catalyst. A mechanism about the hydrogenation of nitrobenzene catalyzed by Pd/PVA system was proposed. The Pd/PVA catalyst also exhibited excellent activity and selectivity particularly to ortho-fluoronitrobenzene and ortho-nitrotoluene.This research can provide a reference for the environmentally friendly catalysis for hydrogenation of nitrobenzene and other substituted nitrobenzene compounds.

Introduction

The production of aniline from the catalytic hydrogenation of nitrobenzene is a vital industrial reaction.[1-3] The major product is aniline together with some by-products such as azobenzene (AB) , hydrazobenzene (HAB) and azoxybenzene (AOB). Most published papers about the hydrogenation of nitrobenzene have tried to explain the reaction mechanism.[4-8] After sufficient supplement and correction, the following mechanism has gradually been accepted (Scheme 1). As indicated in Scheme 1, aniline can be produced through two different reaction paths. In acidic or neutral conditions, aniline tends to be formed via nitrosobenzene (NSB) and N-phenylhydroxylamine (PHA), which is also the main reaction route. The second path defined as adverse event route occurs only in alkaline conditions and two intermediates, AOB and AB, are formed from the condensation of NSB with PHA and the condensation of NSB with aniline, respectively.

The hydrogenation process is commercially conducted in vapor phase over copper-based catalysts or in liquid phase over Ni catalysts. It is well known that aromatic nitro-compounds are always thermally unstable and have high boiling points. In addition, hydrogenation in liquid phase has higher heat transfer coefficient and higher volume productivity compared with vapor phase.[4] Therefore, it is a better choice for the hydrogenation of nitrobenzene carrying out in liquid phase. Kinds of metals, such as Ni,[9] Co,[10] Ru,[11] Rh,[12] Pt,[13,14] Pd,[15] Au[16] as well as bi-metals,[17,18] can be used for nitrobenzene hydrogenation. However, one or more disadvantages for these reaction processes still exist, such as the complicated preparation method of catalyst, organic solvent as reaction medium, introducing toxic reductant, harsh reaction conditions and poor recyclability etc.



Scheme 1. The different mechanisms of catalytic hydrogenation of nitrobenzene.[4-8]

In recent years, nano-catalysts have received more and more attention owing to their high catalytic activity and chemical selectivity.[19] Especially, the catalytic hydrogenation of nitrobenzene to aniline in an aqueous solution using transition or noble metals as catalysts, is one of the most extensive studies [13]. Metal nanoparticles have been prepared in water phase with surfactants as stabilizers, such as polyvinyl pyrrolidone (PVP),[20,21] polyoxyethylene-polyoxy-propylene-polyoxyethylene triblock copolymer,[22] et al. These surfactant molecules can be self-assembled into micelles. Micells with non-polar hydrophobic

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core feature in preventing aggregation of metal nanoparticles.[23] Furthermore, micellar non-polar micro-environment increases the solubility of organic substrates and accelerates organic reaction in water phase. Polyvinyl alcohol (PVA), a hydrophilic surfactant, is used as the stabilizer of metal nanoparticles as well. Different from PVP and some tri-block copolymers, PVA molecules can't form micelles, but can form aggregates due to the presence of hydroxyl groups in each PVA molecule. These hydroxyl groups can interact with metal nanoparticles, and control growth process of metal nanoparticles.[24] Nano-ruthenium confined in PVA solution has been synthesized for the selective hydrogenation of α-pinene by our group, exhibiting excellent activity and selectivity.[25] Unfortunately, poor catalytic performance was obtained for nitrobenzene hydrogenation. It has been found that Pd catalyst is highly efficient over hydrogenation of aromatic nitro functional group.[26] Bearing this in mind, PVA-stabilized Pd nanoparticles could be an alternative to improve the catalytic efficiency for hydrogenation of nitrobenzene.

Herein, we continue to report a new catalytic system, that is, Pd nanoparticles encapsulated in PVA aggregates (Pd/PVA) to explore a convenient, efficient and eco-friendly technology for the production of aniline. It is worth noting that no organic solvent was used during the preparation of Pd/PVA catalyst and hydrogenation of nitrobenzene. Not only preparation of catalysts but also the hydrogenation of nitrobenzene is in water medium under mild reaction conditions. The nitrobenzene hydrogenation is carried out under biphasic water/substrate conditions, which makes it much easier to separate the catalyst from products by simple extraction. The reaction system meets with the requirements of eco-friendliness due to the use of hydrogen (not toxic $NaBH_4$), water and nontoxic PVA. For a better understanding, a reasonable inference is made about the mechanism of the stabilization of Pd nanoparticles and nitrobenzene hydrogenation. Catalytic hydrogenation of other substituted nitrobenzenes by the Pd/PVA system was investigated as well.

Results and Discussion

The effects of PVA molecular weight on Pd/PVA system

Compared with $RuCl_3{\cdot}xH_2O$, $PdCl_2$, $NiCl_2$, $PtCl_4$ and $CoCl_2$, the best catalytic performance was obtained when $Pd(C_2H_3O_2)_2$ was used as the metal precursor under the same reaction conditions (Table S1). Therefore, $Pd(C_2H_3O_2)_2$ was selected as the metal precursor to do the following experiments. We further explored the effect of PVA molecular weight on the mean size and morphology of Pd nanocatalysts. Pd nanoparticles stabilized by PVA with different molecular weights (47000, 78000, 145000, 205000) are abbreviated as Pd-PVA_{47000}, Pd-PVA_{78000}, Pd-PVA_{145000} and Pd-PVA_{205000}, respectively.

TEM characterization was conducted with Pd nanoparticles pretreated with washing and centrifugal process (Figure 1). For Pd-PVA_{47000}, TEM characterization was not performed due to the obvious agglomeration of the sample during the pretreatment procedure. One of the possible reasons is that the shorter chain length of PVA_{47000} aggregates can't afford enough steric hindrance to stabilize Pd nanoparticles.

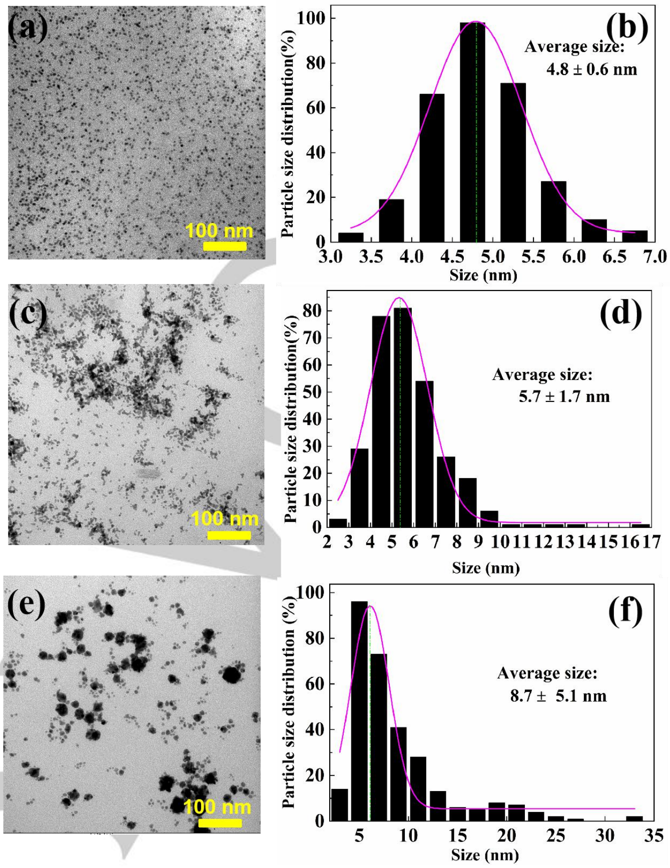

Figure 1. TEM images and distribution histograms of Pd nanoparticles. (a) and (b): Pd-PVA_{78000}, (c) and (d): Pd-PVA_{145000} , (e) and (f): Pd-PVA_{205000}.

As exhibited in Figure 1a and Figure 1b, Pd-PVA_{78000} has the best dispersion and the smallest average particle size. In contrast, Pd-PVA_{145000} forms larger particles and some of them link together (Figure 1c and Figure 1d). For Pd-PVA_{205000}, obvious agglomeration and particle sizes in a wider range can be observed (Figure 1e and Figure 1f). With an increase in PVA molecular weight from 78,000 to 205,000, the average particle sizes of Pd nanoparticles increased from 4.8 nm to 8.7 nm. Similar to Oh and coworkers' reports, the kinetic behavior of longer PVA carbon chains in water phase is more complex, which causes that the closer capped Pd^{2+} within PVA aggregates can aggregate more easily once Pd^{2+} is reduced and grown.[27] Therefore, Pd-PVA_{205000} has a largest average size and a poorest dispersion.

Previously, Dai et al. demonstrated that the average size and particle distribution of nano-Pd were consistent with their catalytic performance.[28] Such a relation in our work was completely observed as shown in Table 1. It indicates that the molecular weight of PVA is a key factor for the formation and catalytic activity of Pd nanoparticles.

Table 1. The catalytic performance of 4 different nano-Pd catalysts for nitrobenzene hydrogenation.

Entry	Mw. of PVA (g/mol)	The average size of PVA-stabilized Pd nanoparticles(nm)	Conversion of nitro-benzene(%)	Selectivity for aniline(%)
1	47,000	-	45.5	100
2	78,000	4.8 ± 0.6	84.8	100
3	145,000	5.7 ± 1.7	61.3	100
4	205,000	8.7 ± 5.1	55.6	100

Reaction conditions for the preparation of Pd nanoparticles: 15 mg PVA, 1.0×10^{-5} mol $Pd(C_2H_3O_2)_2$, 3 mL H_2O, 1.0 MPa H_2, 50 °C, 1 h. Reaction conditions for the hydrogenation of nitrobenzene: the molar ratio of catalyst to substrate is 1:500 (0.62 g nitrobenzene, 3.02 g Pd/PVA catalyst (9.1×10^{-6} mol Pd)), 1.0 MPa H_2, 45 °C, 2 h.

According to the above results, PVA (Mw.: 78,000) was selected as the stabilizer of Pd nanoparticles.

Catalyst characterization

PVA concentration also had a remarkable effect on PVA-encapsulated Pd nanoparticles. Accoring to their catalytic performance for the hydrogenation of nitrobenzene, the optimal PVA concentration was determined as 5.0 $g \cdot L^{-1}$ (Figure S1). The original $Pd(C_2H_3O_2)_2$-PVA solution was pale yellow and translucent, and it changed to be dark brown and opaque after reduction (Figure 2a). The UV-Vis spectra for the original solution and hydrogenated solution (Figure S2) suggest that most of Pd^{2+} ions have been reduced to Pd^0 nanoparticles, which can be confirmed by the subsequent XRD and XPS characterization.

The XRD pattern provides more accurate evidence for the generation of Pd^0 nanoparticles (Figure 2b). Four diffraction peaks at 40.15°, 46.40°, 68.10°, and 81.93°, can be ascribed to four crystal faces that are Pd (111), Pd (200), Pd (220) and Pd (311). The spectrum is coincident with the standard XRD patterns of metallic palladium (JCPDS: No.46-1043).[29, 30] The XRD results also imply that nano-Pd has face-centered cubic structure.[31]

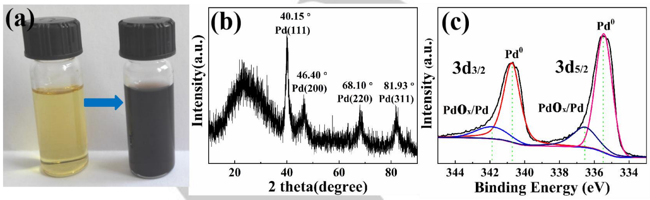

Figure 2. (a) Reduction process, (b) XRD spectrum and (c) XPS patterns of PVA-encapsulated Pd nanoparticles.

The XPS spectra give the proportional relationship of different valence of Pd species in samples (Figure 2c). According to XPS standard library, the standard binding energy of Pd 3d5/2 is 335.00-335.80 eV and that of PdO_x/Pd 3d5/2 is 336.40-336.60 eV. As indicated in Figure 2c, two peaks at 335.49 eV and 336.69 eV are assigned to Pd 3d5/2 and PdO_x/Pd 3d5/2. The standard binding energies for Pd 3d3/2 and PdO_x/Pd 3d3/2 are 340.30-340.50 eV and 340.40-341.60 eV, respectively. In Figure 2c, two peaks located at 340.78 eV and 341.92 eV are assigned to Pd 3d3/2 and PdO_x/Pd 3d3/2. These measured binding energies are slightly higher than the standard values, which might result from the highly dispersion of Pd nano-catalysts.[32] All results can match with the standard spectrum library perfectly, and the molar ratio of PdO_x to Pd^0 is calculated to be 1:11.

The CLSM technique was applied in the morphological analysis of Pd/PVA system in depth. Two specimens were measured by CLSM, including PVA_{78000} aggregates (Figure 3a) and Pd-PVA_{78000} (Figure 3b). In Figure 3a, the majority of PVA aggregates can be seen clearly with transparent cavity-like structure, while a small amount of them is black. Additionally, most of PVA aggregates present spherical shape. The formation of PVA aggregates is the self-assembly of PVA molecules in water attributed to their hydroxyl functional groups.

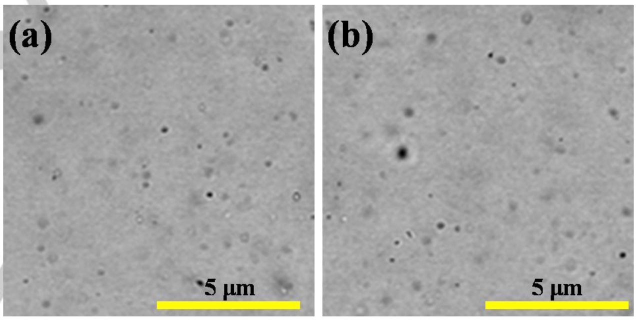

Figure 3. The CLSM images of (a) PVA_{78000} aggregates, (b) Pd-PVA_{78000}.

Figure 3b is the CLSM image of PVA aggregates containing Pd nanoparticles. Compared with PVA aggregates, there is no obvious difference for the two samples in the size and morphology. It suggests that Pd nanoparticles have little influence in the morphology of Pd-PVA_{78000}. Figure 3 also underlines the ability of PVA to both stabilize and disperse Pd nanoparticles. It indicates that the dispersion of PVA aggregates plays a crucial role in formation and distribution of Pd nanoparticles.[33]

The influence of reaction conditions in nitrobenzene hydrogenation

As indicated in Figure 4a, the catalytic activity decreases with an increase in the amount of substrate. When the nitrobenzene amount exceeds a certain value (1:550), the ntro-

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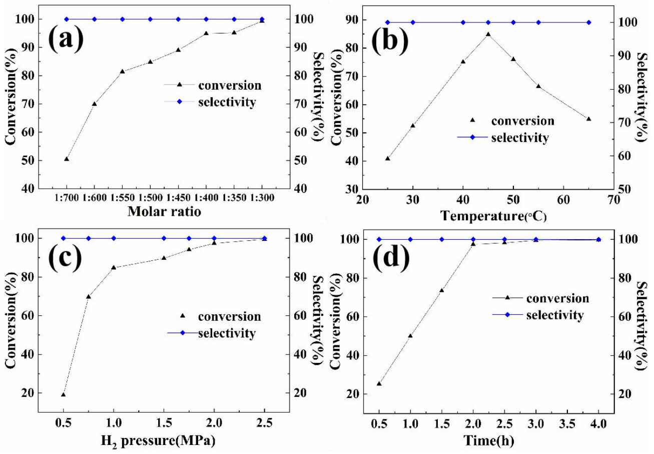

Figure 4. The influence of reaction conditions in nitrobenzene hydrogenation. (a) the molar ratio of Pd nanoparticles to nitrobenzene (1.0 MPa H_2, 45 °C, 2 h), (b) temperature (the molar ratio of catalyst to substrate is 1:500 (0.62 g nitrobenzene, 3.02 g Pd/PVA catalyst (9.1×10^{-6} mol Pd)), 1.0 MPa H_2, 2 h), (c) hydrogen pressure (the molar ratio of catalyst to substrate is 1:500, 45 °C, 2 h), (d) reaction time (the molar ratio of catalyst to substrate is 1:500, 45 °C, 2.0 MPa H_2).

benzene conversion sharply decreases. Meanwhile, obvious aggregation of Pd nanoparticles was observed after the reaction. It suggests that the structure of PVA aggregates might have been broken. Therefore, the molar ratio of 1:500 is selected for the following experiments. It should be noted that the blank experiment was carried out to better understand the reaction route. When no catalyst was added, aniline was not detected. We also did another control experiment. All the steps for both the preparation of catalyst and hydrogenation of nitrobenzene were the same as the experimental section described except that palladium acetate was not added. This experiment (without Pd) gave no activity as well. These results indicate that Pd nanoparticles in PVA matrix show an excellent catalytic performance for the hydrogenation of nitrobenzene. From 25 °C to 45 °C, nitrobenzene conversion significantly increases with the rising temperature (Figure 4b). At 45 °C, the highest nitrobenzene conversion is obtained. Further increasing the temperature, the conversion of nitrobenzene obviously decreases. It indicates that in the high-temperature environment, Pd/PVA system easily denatures and inactivates. A narrower range of temperature (40-50 °C) is suitable for nitrobenzene hydrogenation. Gradually increasing H_2 pressure or prolonging the reaction time (Figure 4c and Figure 4d), nitrobenzene conversion rises correspondingly. The higher hydrogen pressure results in larger hydrogen solubility, which is in favor of the hydrogenation of nitrobenzene.[34] The increasing nitrobenzene conversion with reaction time also demonstrates that Pd nanoparticles are well stabilized by PVA aggregates.[35] Catalytic activity maintains the same when reaction time is prolonged to 3 h under 2.0 MPa H_2.

To sum up, the optimized reaction conditions are as follows. Pd nanoparticles are confined in PVA (M_W: 78,000) solution with a dosage of 5.0 g·L^{-1}. The hydrogenation of nitrobenzene proceeds with a molar ratio of 1:500 at 45 °C with 2.0 MPa H_2 for 3 h. 99.3% nitrobenzene conver-sion and 100% selectivity for aniline have been achieved.

Under the optimal conditions, several different catalysts were chosen to compare their catalytic performance with the Pd/PVA catalyst, including commercially available Pd/C, Ru/C, and Pd nanoparticles stabilized by other common polymers such as polyvinyl pyrrolidone (Mw.: 58000) and polyethylene glycol (Mw.: 70000).

Table 2. The catalytic performance of different catalysts for nitrobenzene hydrogenation.

Entry	Catalyst	Conversion of nitrobenzene(%)	Selectivity for aniline(%)
1	Pd/C (10 wt%)	100.0	100
2	Ru/C (5 wt%)	93.5	100
3	Pd-PVA$_{78000}$	99.3	100
4	Pd/PEG	91.7	100
5	Pd/PVP	96.0	100

Reaction conditions for the hydrogenation of nitrobenzene: the molar ratio of catalyst to substrate is 1:500, 2.0 MPa H_2, 45 °C, 3 h.

As shown in Table 2, Pd/C catalyst gave the highest activity. However, Pd/C was seriously stuck on the inner wall of the autoclave after the reaction and could not be recycled. For Pd/PEG and Pd/PVP catalyst, aggregation of Pd nanoparticles was observed after the catalytic hydrogenation. It indicates that PVA can provide better stabilization for Pd nanoparticles. These results have shown the advantages of PVA as the stabilizer.

The reusability of Pd/PVA catalyst on nitrobenzene hydrogenation

The reusability for this catalytic system was explored as well. Under the optimized conditions, Pd-PVA$_{78000}$ catalyst was recycled without any reactivation treatments. Figure 5a displays that the conversion of nitrobenzene decreases gradually during the recycling process. The probable reason is the mass transfer limitation between PVA-stabilized nano-Pd in water phase and substrates in organic phase during the hydrogenation reaction (Scheme 2). During mass transfer process, the loss of Pd nanoparticles is inevitable. When the lost Pd nanoparticles enter into the organic phase, the PVA aggregates can not stabilize them again. The aggregation of Pd nanoparticles is also observed (Figure 5b). Nevertheless, nitrobenzene conversion still exceeds 80% even after 6 cycles. It is worth mentioning that these experimental results are gained without any additional stabilizer. In addition, the selectivity for aniline remains 100% for each cycle. It suggests that the backbone of PVA aggregates has not changed, and it may still play a valuable role in controlling the selectivity for aniline.[36, 37]

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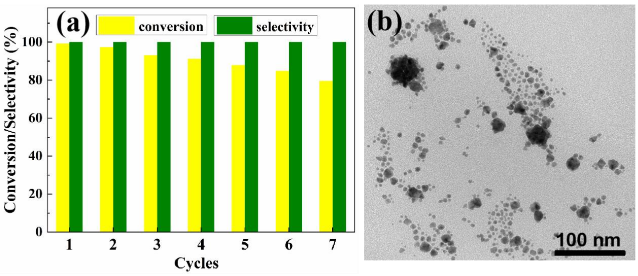


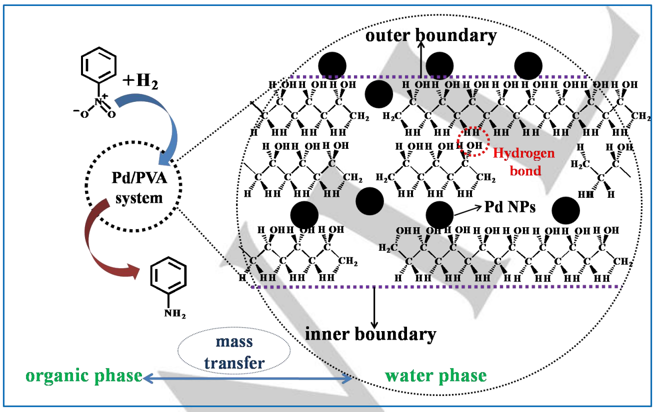
Figure 5. (a) Reusability of Pd/PVA system, (b) TEM characterization for the recycled catalyst after 3 runs.

The catalytic activity of Pd/PVA in hydrogenation of nitrobenzene to aniline were compared in detail with some catalysts reported previously (Table S2).

As shown in Table S2, our Pd/PVA catalyst exhibits excellent catalytic performance. It is worth noting that no organic solvent is used during the preparation of Pd/PVA catalyst and hydrogenation of nitrobenzene. Not only preparation of catalysts but also the hydrogenation of nitrobenzene is in water medium under mild reaction conditions. It is much easier to separate the catalyst from products by simple extraction.The preparation of previously reported catalysts always required toxic $NaBH_4$ as reductant and organic solvents. These comparison results confirm that Pd/PVA catalyst is effective and eco-friendly for hydrogenation of nitrobenzene.

Mechanism of catalytic hydrogenation of nitrobenzene

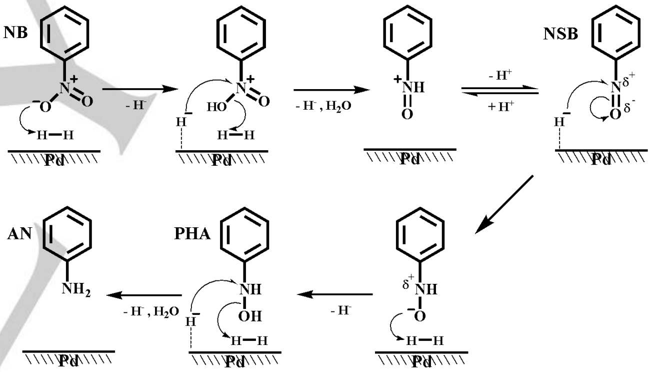
According to the comprehensive analysis of these obtained experimental data, a mechanism about the preparation of Pd nanoparticles (Scheme 2) and catalytic hydrogenation of nitrobenzene (Scheme 3) can be reasonably inferred.



Scheme 2. The scheme for catalytic hydrogenation of nitrobenzene by Pd/PVA system.

Initially, the Pd(Ⅱ) precursor is in situ converted into Pd^0 nanoparticles that are the catalytically active species (Scheme 2). Prior to being reduced, Pd^{II} dispersed in the aqueous PVA matrix via coordination bonds between Pd^{2+} and hydroxyl groups of PVA.[38] During the reduction process with H_2 as the reductant, a large amount of Pd nanocrystals will be gradually formed in the water phase. As exhibited in Scheme 2, Pd nanoparticles can also be adsorbed on the PVA aggregates by interacting with their hydroxyl groups.[28] Meanwhile, Pd nanoparticles tend to be gradually confined into the PVA aggregates due to their nonpolar micro-environment. Therefore, both the hydroxyl groups of the PVA aggregates and the nonpolar micro-environment have a strong adsorbability to Pd^0 nanoparticles, which give enough protection to Pd nanoparticles through steric hindrance.[39]

It has been widely accepted that aniline can be formed directly without other by-products via the main reaction route under acidic or neutral conditions (Scheme 1). The pH value of Pd/PVA system is about 6.0, which facilitates the main reaction route for nitrobenzene hydrogenation. Herein, we propose a reaction mechanism about hydrogenation of nitrobenzene (Scheme 3).



Scheme 3. The mechanism of nitrobenzene hydrogenation catalyzed by Pd/PVA system.

Nitrobenzene hydrogenation occurs on the surface of Pd nanoparticles, and hydrogen transfers from metal-hydride complex on metal surface to nitrobenzene.[40] Metal-hydrogen bonds can be formed between Pd nanoparticles and hydrogen.[41] Therefore, PHA (C_6H_5-NHOH) is still an intermediate. The electronegative hydrogen atom will be enriched with electrons provided by metallic Pd nanoparticles. It might be vital for the selection of the reaction route for the reason that it is more conducive to nucleophilic reaction. In addition, temperature is also an important factor for the reaction route. 40-50 °C is the suitable temperature range for this catalyst system. The mild reaction temperature also inhibits the occurrence of side reactions such as polycondensation reaction and deep hydrogenation of aniline. Therefore, a synergistic effect causes the high selectivity for aniline.

We further investigated the catalytic performance of the Pd/PVA catalyst for hydrogenation of other substituted nitrobenzenes (Table S3). To our delight, the Pd/PVA catalyst also exhibited excellent activity and selectivity particularly to ortho-fluoronitrobenzene and ortho-nitrotoluene. It indicates that the catalyst is also suitable for the hydrogenation of other substituted nitrobenzene compounds, not just nitrobenzene.

Conclusions

In summary, Pd nanoparticles confined in PVA aggregates were prepared by the reduction of Pd^{2+} ion with H_2. The particle size, morphology and chemical states of Pd nanoparticles were estimated by TEM, UV-Vis, CLSM, XRD and XPS, respectively. Judging from the CLSM and TEM measurements, the particle size and distribution of Pd nanoparticles can be controlled by PVA aggregates. The Pd/PVA system exhibits excellent catalytic performance. 99.3% nitrobenzene conversion have been achieved together with 100% selectivity for aniline. The unique selectivity for aniline is possibly dependent on a synergistic effect of metal-hydrogen bonds and mild reaction temperature. It is worth noting that the reaction system is environment-friendly, which can be especially attributed to the good biological compatibility of PVA, hydrogen as reductant, the mild reaction conditions and no use of any solvent except water. In addition, it is easy to separate the products from the catalysts by simple extraction. The nitrobenzene conversion exceeded 80% even after 6 cycles. The Pd/PVA catalyst also exhibited excellent performance for the hydrogenation of other substituted nitrobenzene compounds.

Experimental Section

Materials

Nitrobenzene (≥99%) was obtained from Chinasun Specialty Products Co., Ltd. $Pd(C_2H_3O_2)_2$ (≥98.0%) and $RuCl_3{\cdot}xH_2O$ (35.0%~42.0%) were obtained from Shanghai Civi Chemical Technology Co., Ltd. $PdCl_2$ (>99%) was obtained from Shanghai Macklin Biochemical Co., Ltd. $NiCl_2$ (≥98%), $PtCl_4$ (≥99%) and $CoCl_2$ (≥99%) were purchased from Beijing lark technology Co., Ltd. Pd/C (10wt%), Ru/C (5wt%) and polyvinyl pyrrolidone (PVP, Mw: 58000) were purchased from Aladdin Industrial Corporation. PVA with different molecular weights (47000, 78000, 145000, 205000) were supplied by Sigma-Aldrich Co., Ltd. Polyethylene glycol (PEG, Mw: 70000) and CH_2Cl_2 (≥99.5%) were purchased from Shanghai Macklin Biochemical Co., Ltd. H_2 (≥99.9%) was purchased from Qingdao Heli Co., Ltd.

Preparation of Pd nano-catalyst

A certain amount of $Pd(C_2H_3O_2)_2$, PVA with different molecular weights (47000, 78000, 145000, 205000) and ultrapure water were added into a 75 mL stainless steel autoclave, and vigorously stirred at ambient temperature for 1 h. Afterwards, the reduction of Pd(Ⅱ) acetate was performed under 1.0 MPa H_2 at 50 °C with stirring for 1 h. The dark brown colloids was achieved, showing the formation of Pd nanoparticles. The Pd/PVA catalyst can be directly applied in hydrogenation of nitrobenzene.

Hydrogenation of nitrobenzene

The Pd/PVA catalyst and nitrobenzene in certain proportion were put into a 75 mL stainless-steel autoclave. The autoclave was then sealed and flushed with 1.0 MPa H_2 3 times. Subsequently, the hydrogenation of nitrobenzene was carried out at desired temperature under required H_2 pressure with continuous stirring. After the reaction, the mixture was extracted by dichloromethane, and the organic phase was determined by Gas Chromatography (GC, Fuli GC-9790) with a capillary column (OV-1701, 50 m × 0.25 mm × 0.25 μm) and a FID detector. The catalytic performance of Pd/PVA system was evaluated according to nitrobenzene conversion and selectivity for aniline. For the recycling experiments, the organic layer was collected with a pipette for GC analysis. The aqueous Pd/PVA phase remained in the autoclave for the next cycle.

Characterization

Particle size and shape of Pd nano-catalysts were tested by transmission electron microscopy (TEM, Hitachi-7650). Before TEM characterization, the prepared Pd/PVA catalyst was centrifuged and the solid residue was first washed with ultrapure water three times and then with ethanol twice to remove any traces of PVA. After that, the pretreated Pd nanoparticles were dispersed in ethanol for the following TEM characterization. A drop of Pd/PVA suspension was added onto the copper grid. More than 300 particles were counted to obtain each size distribution histogram of Pd nanoparticles.

The reduction degree of Pd (Ⅱ) was determined by ultraviolet-visible absorption spectra (UV-Vis). Freshly prepared Pd/PVA system was diluted 20 times before determination.

The phase structure of nano-Pd were recorded through X-ray diffraction (XRD, Rigaku multiflex diffractometer) with Ni filtered Cu Kα radiation. The valence of nano-Pd was tested by using X-ray photoelectron spectroscopy (XPS, Kratos-Axis 165). The measured binding energies were calibrated by C1s peak at 284.60 eV. Before determination, ethanol was evaporated under vacuum.

The photographs of PVA aggregates and Pd/PVA system were taken by a confocal laser scanning microscope (CLSM, Leica, TCS-SP5-II) with an ultraviolet source.

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Keywords: PVA aggregates • Pd nanoparticles • Water • Hydrogenation of nitrobenzene

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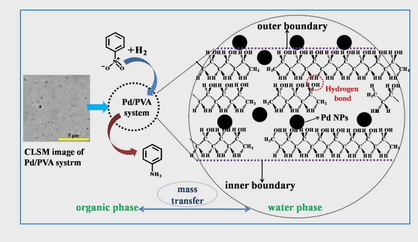

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