Article

Journal of
Nanoscience and Nanotechnology
Vol. 19, 484–491, 2019
www.aspbs.com/jnn

Effect of Particle Restructuring During Reduction Processes Over Polydopamine-Supported Pd Nanoparticles

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The effect of catalyst restructuring on the polydopamine-supported Pd catalyzed transfer hydrogenation of ethyl 4-nitrobenzoate and the catalytic hydrogenation of (*E*)-2-methyl-2-butenoic acid is reported. Transmission electron microscopy investigation of different catalyst pre-treatment and reaction conditions revealed high catalytic activity in both reactions unless drastic aggregation of the active metal occurred. In the transfer hydrogenation reaction aggregation was primarily dependent on the H-source used, while in the catalytic hydrogenation additives in combination with the reductive environment led to extensive Pd aggregation and thus decreased catalytic activity. The enantioselective hydrogenation of (*E*)-2-methyl-2-butenoic acid showed increased enantioselectivity and decreased conversion with increased particle size.

Keywords: Polydopamine, Palladium, Heterogeneous Catalysis, Transfer-Hydrogenation, Enantioselective Hydrogenation, Transmission Electron Microscopy.

1. INTRODUCTION

Metal nanoparticles are increasingly becoming the catalysts of choice in many organic transformations.[1–3] Such systems are not only efficiently promoting a great variety of reactions but also part of the toolbox of green chemistry efforts.[4–6] Supported metal particles are robust, compatible with a range of reaction conditions (solvents, pressure and temperature, microwave and ultrasound) and, ideally, could be reused several times with preserved catalytic activity.

An important aspect of nanoparticle catalysis, both in colloidal[7–10] and supported[11–16] systems, is the restructuring (aggregation, shape and size alteration) of the active metal particles and its influence on the efficiency of the catalyst.[17–23] The catalytic nanoparticles are prone to sintering in order to minimize their surface energies which could be induced by high reaction temperature and the reactants can play a role as well.

Recently, among others,[24–35] we have reported on the application of mussel-inspired polydopamine as a support for Pd nanoparticles and its use in catalytic transfer-hydrogenation reactions.[36] Polydopamine,[37] a widely explored functional polymer,[38] can be easily prepared through the auto-polymerization of dopamine hydrochloride in basic aqueous medium (Fig. 1(a)). Pd nanoparticles of 1–3 nm could be obtained on the surface of polydopamine (Pd/PDA) by making use of its redox active interfacial catechol moieties (Fig. 1(b)).[36]

We have prepared core–shell Fe_3O_4/Pd/PDA magnetic particles also in order to facilitate the recycling of the catalyst in transfer hydrogenation of aromatic nitro groups. Compared to Pd/PDA, where particles between 1–3 nm

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 1533-4880/2019/19/484/008 doi:10.1166/jnn.2019.15770

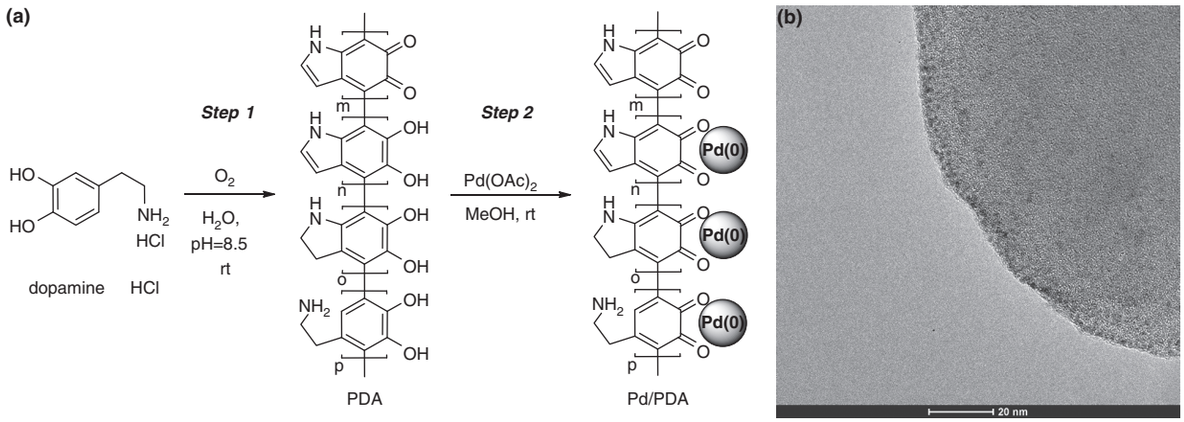


Figure 1. (a) Polymerization of dopamine hydrochloride to PDA (step 1) and Pd deposition onto the surface of PDA (step 2); (b) TEM image of Pd/PDA.

size were present, the size of the Pd nanoparticles on the surface of the magnetic system were somewhat bigger (5–6 nm), which had an influence on the catalytic activity especially in the early stages of the reaction. The conversion of ethyl 4-nitrobenzoate in 96% EtOH as solvent at 85 °C using HCOONa as a hydrogen source over Pd/PDA was found to be 10% to the corresponding amine after 10 min, while this value was about 30% over Fe_3O_4/Pd/PDA. The difference became smaller by time and after 40 min the conversion was complete in both cases. However, post-reaction TEM showed Pd particle aggregation in the case of Pd/PDA, while in the case of the magnetic catalyst no pronounced changes were observed.

Based on these findings we became interested in the effect of Pd particle size and morphology changes on the outcome of reduction processes over PDA supported Pd catalysts. We studied the effect of individual reactants on the aggregation behavior of the active Pd in order to gain deeper insights regarding the sensitivity of the system to certain reactants and reaction conditions. This study is aimed at better describing the applicability of Pd/PDA in both transfer hydrogenation and catalytic hydrogenation processes.

2. EXPERIMENTAL DETAILS

2.1. General

Commercial reagents and solvents (Aldrich, Fluorochem, VWR) were purchased as reagent-grade and used without further purification.

GC-MS analysis was performed on a Shimadzu GCMS-QP2010 Ultra System operated in Electron impact ionization mode. GC analysis was performed with a YL6100 gas chromatograph equipped with a flame ionization detector using a HP-Chiral capillary column (J & W Scientific Inc.)

For transmission electron microscopy (TEM) investigation the samples were dispersed in ethanol and deposited onto copper grids covered by carbon supporting films. TEM investigations were performed on a Morgagni 268D electron microscope at 100 kV accelerating voltage and a FEI TECNAI G2 20 X-Twin high-resolution transmission electron microscope operating at an accelerating voltage of 200 kV.

2.2. Catalyst Preparation

2.2.1. Polymerization of Dopamine

Tris base (484 mg, 4.0 mmol) was dissolved in deionised water (350 mL) and stirred for 30 min (pH = 8.5). A solution of dopamine hydrochloride (1.0 g, 5.27 mmol) in water (50 mL) was added and the solution was stirred at room temperature for 30 hours. The black suspension of polydopamine (PDA) was filtered, the residue was washed with deionised water and dried under air overnight.

2.2.2. Preparation of Pd/PDA

PDA (200 mg) was dispersed in a solution of $Pd(OAc)_2$ (21 mg, 0.094 mmol) in MeOH (50 mL) and stirred vigorously overnight. The suspension was filtered, washed with methanol (30 ml) and acetone (20 ml) and dried under ambient conditions.

2.2.3. Preparation of Pd/PDA(L)

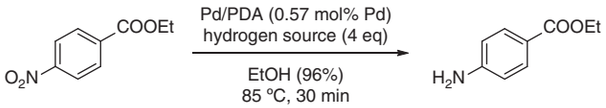
Pd/PDA(L), a catalyst bearing Pd particles that are larger in size (10–16 nm) were prepared based on a method reported in the literature:[39] a suspension of PDA (200 mg) in water (20 mL) was mixed with an acetone solution (5 mL) of $Pd(OAc)_2$ (70 mg) and stirred at 90 °C for 1 h. The solid was filtered, washed with acetone and methanol and dried on air overnight.

2.3. Catalytic Transfer Hydrogenation Reaction of Ethyl 4-Nitrobenzoate to Ethyl 4-Aminobenzoate

2.3.1. General Procedure for the Catalytic Transfer Hydrogenation (CTH) Reaction

Pd/PDA (10 mg, 0.57 mol% Pd), ethyl 4-nitrobenzoate (0.5 mmol), H-donor (2.0 mmol) and 96% EtOH (2 mL)

Table I. Effect of H-donors in the catalytic transfer hydrogenation reaction of ethyl 4-nitrobenzoate.



Entry	Hydrogen source	Yield (%)
1	HCOONa	59
2	THN	No conversion
3	Terpinene	12
4	HCOONa + THN	24
5	HCOONa + terpinene	30

were placed in a sealed vial and the mixture was stirred at 85 °C for 30 min. The reaction mixture was diluted with EtOAc, filtered through a pad of silica and concentrated under vacuum and analysed by GC-MS.

2.4. Catalytic Hydrogenation of TA to 2-Methylbutyric Acid

2.4.1. Racemic Hydrogenation

Pd/PDA (15 mg) and toluene (10 mL) was placed in a glass tube, which was placed in a stainless steel autoclave and one of the following pre-treatments were applied (for details see text): (1) no pre-treatment, (2) stirring the catalyst in toluene for 30 min or (3) stirring the catalyst in toluene under a H_2 atmosphere (50 bar) for 30 min. Following the pre-treatment TA (1 mmol) was added to the mixture and the reaction was stirred under a H_2 atmosphere (50 bar) at rt for 90 min. Subsequently, the catalyst was filtered, washed with toluene and MeOH then dried. The filtrate was concentrated under reduced pressure and analyzed by GC-FID on a HP-Chiral capillary column.

2.4.2. Enantioselective Hydrogenation

Pd/PDA (15 mg), cinchonidine (CD) (0.05 mmol), benzylamine (BA) (1 mmol) and toluene (10 mL) were placed in a glass tube, which was placed in a stainless steel autoclave and one of the following pre-treatments were applied (for details see text): (1) no pre-treatment, (2) stirring the catalyst in toluene for 30 min or (3) stirring the catalyst in toluene under a H_2 atmosphere (50 bar) for 30 min. Following the pre-treatment TA (1 mmol) was added to the mixture and the reaction was stirred under a H_2 atmosphere (50 bar) at rt for 90 min. Subsequently, the catalyst was filtered, washed with toluene and MeOH then dried. The filtrate was concentrated under reduced pressure and analyzed by GC-FID on a HP-Chiral capillary column. Analysis conditions: head pressure—140 kPa, column temperature—85 °C. Retention times: (*S*)-2-methylbutyric acid—13.2 min, (*R*)-2-methylbutyric acid 14.1 min, (*E*)-2-methyl-2-butenoic acid 22.0 min.

3. RESULTS AND DISCUSSION

3.1. Transfer Hydrogenation of Ethyl 4-Nitrobenzoate

We have investigated the reduction of ethyl 4-nitrobenzoate to ethyl 4-aminobenzoate (Table I), also known as benzocaine, which is a compound of pharmaceutical interest due to its use as a local anesthetic.

Among the tested H-donors, HCOONa was found to be the best reagent as after 30 min reaction, the product aniline derivative was isolated in 59% yield while the conversion reached completion after 40 min (Table I, entry 1). 1,2,3,4-Tetrahydronaphthalene (THN) was an inactive H-donor under the reaction conditions (Table I entry 2) which is in agreement with previous literature reports,[40,41] while γ-terpinene, although in a similar

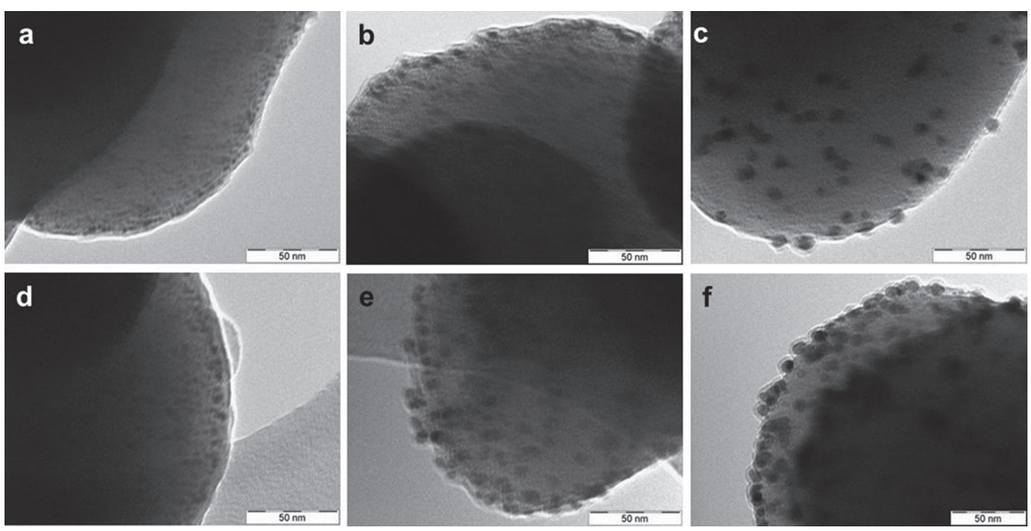


Figure 2. TEM images of Pd/PDA catalysts under different CTH conditions. Effect of the H-donors HCOONa (a), THN (b) and terpinene (c) on the aggregation of the Pd particles in the absence of the nitro compound and images following the reduction of ethyl 4-nitrobenzoate in the presence of HCOONa (d), THN (e) and terpinene (f).

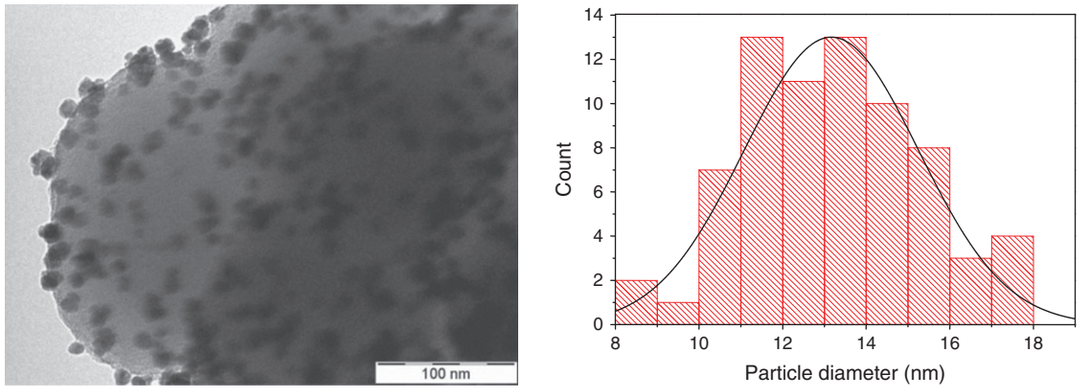


Figure 3. TEM image and particle size distribution of Pd/PDA(L).

system was found to be an efficient H-donor,[42] delivered only 12% conversion after 30 min reaction (Table I, entry 3).

First, we examined the effect of the H-donors in the absence of the nitro compound on the aggregation behavior of the Pd particles. TEM imaging of the samples after stirring Pd/PDA in EtOH at 85 °C for 30 min in the presence of each H-donor, revealed different effects on Pd aggregation. Although aggregation was clearly induced in the presence of HCOONa as particle sizes up to 5 nm were observed (Fig. 2(a)), it occurred to a lesser extent compared to THN (Fig. 2(b)) and terpinene (Fig. 2(c)) where particles sizes up to 9 nm were measured. Similar trend was observed upon post-reaction imaging of the catalyst after the reduction of the nitro compound was carried out. In the reduction performed using HCOONa the aggregation was comparable to that occurred in the absence of the nitro compound (Fig. 2(d)). When both the nitro

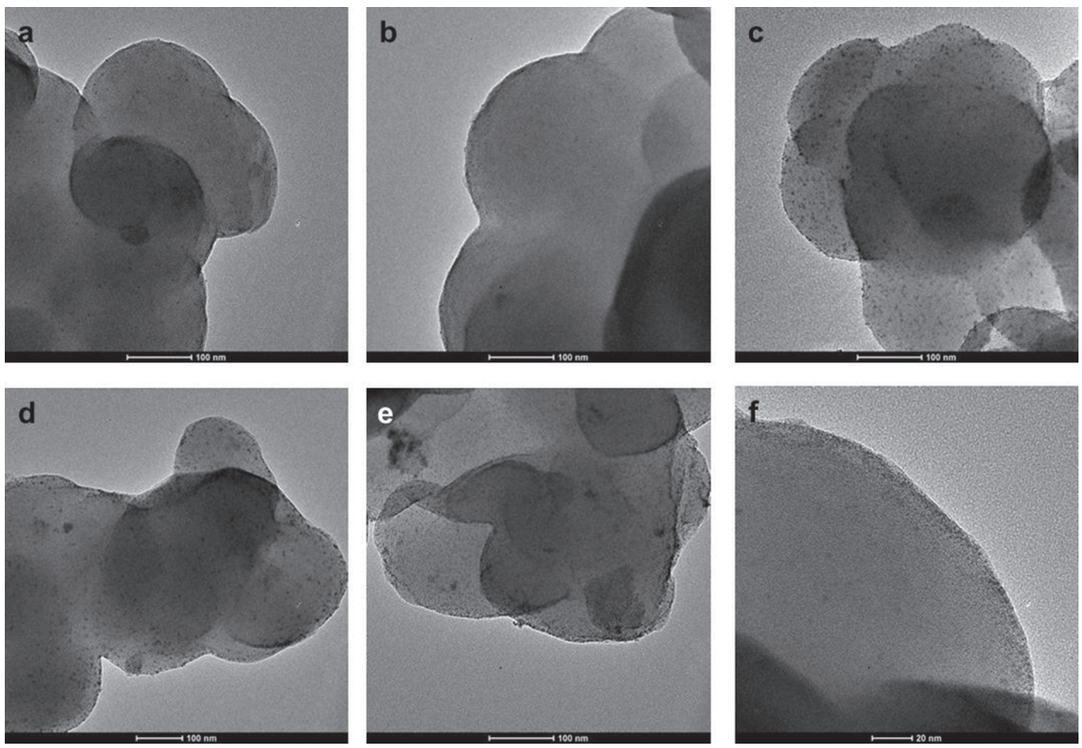


Figure 4. TEM images of Pd/PDA catalysts after different pre-treatment and catalytic hydrogenation conditions of TA. Effect of pre-treatment on the aggregation of the Pd particles: (a) After stirring the catalyst in toluene for 30 min and (b) after pre-hydrogenation of the catalyst (50 bar H_2) in toluene for 30 min. TEM images of differently pre-treated catalysts following the hydrogenation of TA: (c) No pre-treatment, (d) stirring the catalyst in toluene for 30 min and (e) pre-hydrogenation of the catalyst (50 bar H_2) in toluene for 30 min. (f) TEM image after stirring the catalyst in the presence of TA (1 mmol) in toluene at rt for 30 min.

compound and THN (Fig. 2(e)) or terpinene (Fig. 2(f)) H-donor was present in the reaction mixture, the Pd aggregation was more pronounced. These results point towards the contribution of the H-donors to the aggregation of the Pd particles, furthermore, suggest the effect of particle size on the reaction efficiency.

To further test this possibility we performed control experiments where HCOONa/THN (Table I, entry 4) and HCOONa/terpinene (Table I, entry 5) mixed H-sources were used. In the former case, 24%, while in the latter case 30% conversion of the nitro compound was detected under otherwise identical reaction conditions (85 °C, 30 min). Both are lower than using HCOONa alone (59%). When the catalyst was stirred at 85 °C for 30 min in the presence of THN or terpinene prior to the addition of the nitro compound and HCOONa as H-donor the difference increased. The THN treated catalyst provided 17% conversion while the one treated with terpinene led to only 12% conversion of the nitro compound to the corresponding aniline. These results could be explained by the poisoning of the Pd by the THN and terpinene H-sources, however, could also point towards the size dependent catalytic activity of the Pd in the reaction. The catalysts that were treated with THN and terpinene contained larger Pd particles, which could be less active in the nitro reduction catalyzed by HCOONa. To test this latter speculation, we prepared Pd/PDA catalyst (Pd/PDA(L)) with larger Pd particle sizes[39] in the 10–16 nm range (Fig. 3). Performing the reaction in the presence of this catalyst using HCOONa as H-source the conversion was only 9% after 30 min reaction indicating a clear size dependent catalytic activity.

3.2. Hydrogenation of Tiglic Acid Over Pd/PDA

We also aimed at extending the Pd/PDA catalyzed reduction processes to catalytic hydrogenation of C═C double bonds and studied the hydrogenation of (*E*)-2-methyl-2-butenoic acid (tiglic acid, TA) (Table II).

Initially, we examined the effect of pre-treatments on the aggregation behavior of the catalyst. Two different room temperature pre-treatments were applied: (A) stirring the catalyst in toluene for 30 min prior to adding the substrate (Fig. 4(a)) and (B) pre-hydrogenation of the catalyst (50 bar H_2) in toluene for 30 min prior to adding the substrate (Fig. 4(b)). None of the pre-treatments had a pronounced effect on the Pd morphology, apart from the appearance of few somewhat larger particles on the PDA surface.

Following the different pre-treatments the hydrogenation was complete in 90 min (Table II, entry 1 and 2). Similar result was obtained when no pre-treatment was applied

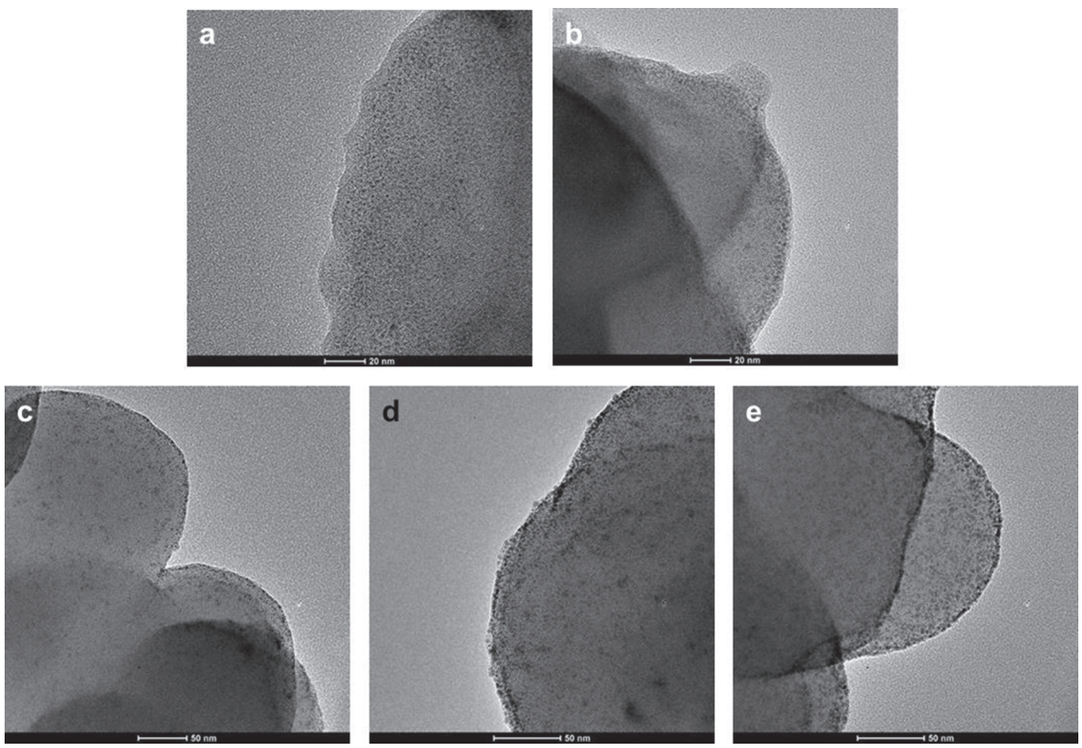
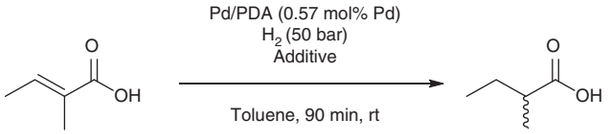


Figure 5. TEM images of Pd/PDA catalysts after different pre-treatment and catalytic enantioselective hydrogenation conditions of TA in the presence of CD. Effect of pre-treatment on the aggregation of the Pd particles: (a) After stirring the catalyst and CD (0.05 mmol) in toluene for 30 min and (b) after pre-hydrogenation of the catalyst and CD (0.05 mmol) (50 bar H_2) in toluene for 30 min. TEM images of differently pre-treated catalysts following the enantioselective hydrogenation of TA: (c) No pre-treatment, (d) stirring the catalyst and CD (0.05 mmol) in toluene for 30 min and (e) pre-hydrogenation of the catalyst (50 bar H_2) in toluene for 30 min.

Table II. Catalytic hydrogenation of tiglic acid over Pd/PDA catalyst.



Entry	Pre-treatment	Additive	Conversion (%)	Ee (%, S)
1	A	–	100	–
2	B	–	100	–
3	–	–	100	–
4	A	CD (0.05 mmol)	95	12
5	B	CD (0.05 mmol)	97	32
6	–	CD (0.05 mmol)	100	19
7	–	CD (0.05 mmol) BA (1 mmol)	53	33
8	A	CD (0.05 mmol) BA (1 mmol)	39	27
9	B	CD (0.05 mmol) BA (1 mmol)	11	34

Notes: A: Stirring the catalyst in toluene for 30 min prior to adding the substrate and additives. B: Pre-hydrogenation of the catalyst (50 bar H_2) in toluene prior to adding the substrate and additives.

(Table II, entry 3). Compared to the pre-treated catalyst, post-reaction imaging revealed stronger aggregation of the active metal upon contact with TA (Figs. 4(c–e)), although TA itself had no pronounced effect on the catalyst (Fig. 4(f)).

We also examined the possibility of the enantioselective hydrogenation of TA[43–51] over cinchonidine (CD) modified Pd/PDA as chiral short-chain carboxylic acids and esters[52] are industrially relevant as building blocks in the synthesis of pharmaceuticals and fragrances.[53–57]

Pre-treatment of the catalyst in the presence of CD had no particular effect on the Pd particles (Figs. 5(a, b)) compared to the as-prepared Pd/PDA.

When TA was added to the reaction mixture, stronger aggregation was observed, regardless of the pre-treatment (Figs. 5(c–e)), however, it was only slightly affecting the conversion, which was virtually complete in each case (Table II, entries 4–6). Particle sizes in the range of 6–8 nm, regardless of their shape, were previously found to be ideal in this transformation.[46,58] On the other hand, the pre-treatment was influencing the obtained enantioselectivity of the reaction. While no pre-treatment or stirring the catalyst in toluene resulted in 12% and 19% ee, respectively, pre-hydrogenation was more beneficial, as an ee of 32% was obtained in this case.

As it has been reported in the literature that the presence of benzylamine (BA) is beneficial in enantioselective hydrogenations over CD modified Pd catalyst,[48–51,59,60] we tested the effect of the added amine (Table II, entries 2–9). Interestingly, in this case, already the pre-treatments showed pronounced differences in the catalyst

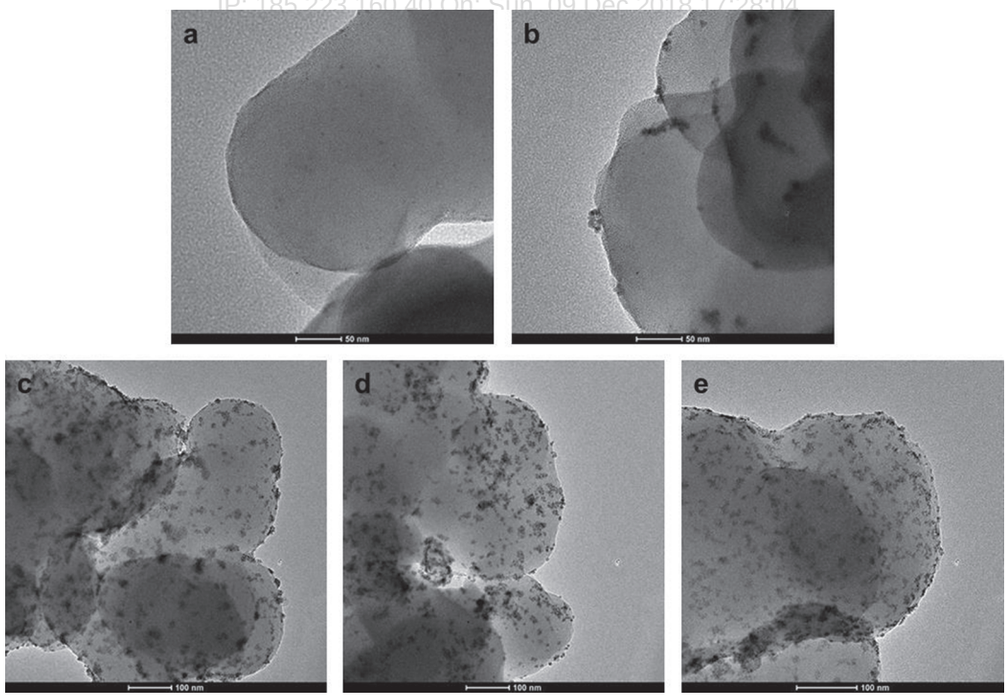


Figure 6. TEM images of Pd/PDA catalysts after different pre-treatment and catalytic enantioselective hydrogenation conditions of TA in the presence of CD and BA. Effect of pre-treatment on the aggregation of the Pd particles: (a) After stirring the catalyst, CD (0.05 mmol) and BA (1 mmol) in toluene for 30 min and (b) after pre-hydrogenation the mixture of the catalyst, CD (0.05 mmol) and BA (1 mmol) (50 bar H_2) in toluene for 30 min. TEM images of differently pre-treated catalysts following the enantioselective hydrogenation of TA in the presence of CD and BA: (c) No pre-treatment, (d) stirring the catalyst, CD (0.05 mmol) and BA (1 mmol) in toluene for 30 min and (e) pre-hydrogenation (50 bar H_2) of the catalyst, CD (0.5 mmol) and BA (1 mmol) in toluene for 30 min.

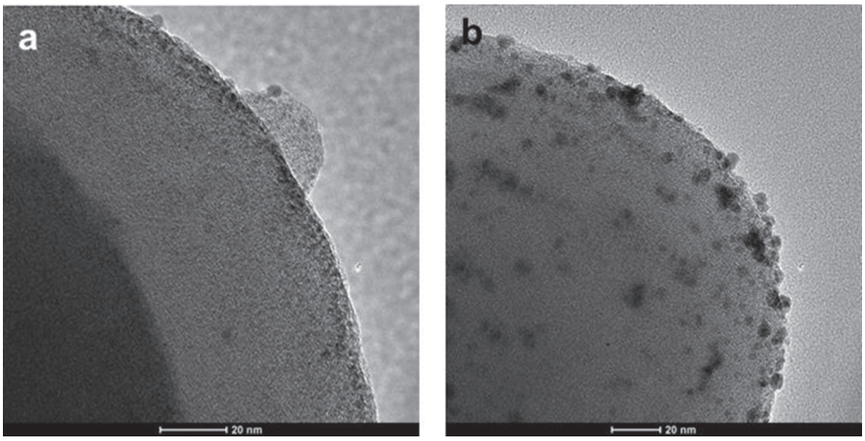


Figure 7. The effect of BA under different conditions on the catalyst morphology. (a) After stirring the catalyst in the presence of BA in toluene at rt for 30 min and (b) after stirring the catalyst in the presence of BA and H_2 (50 bar) in toluene at rt for 30 min.

morphology (Figs. 6(a, b)). When the Pd/PDA was stirred in toluene for 30 min in the presence of both CD and BA, no extensive aggregation was observed. However, when reductive pretreatment was applied (50 bar H_2) TEM imaging of the catalyst showed stronger aggregation of the Pd particles. Such H_2-induced aggregation of Pd nanoparticles has been mentioned in the literature.[59, 61, 62] To further support the effect of reductive pre-treatment on the catalyst morphology, we compared the effect of BA with and without H_2 atmosphere (Figs. 7(a, b)). The images reveal the large impact of the H_2 atmosphere on the metal aggregation in the presence with BA. However, it has to be noted that the reductive atmosphere in the presence of CD influenced Pd aggregation much less (Fig. 5(b)). It could be due to the adsorption of CD on the surface of Pd which hinders the restructuring of the metal.

The pre-treatment in the case of the CD + BA system strongly influenced the outcome of the catalytic hydrogenation also (Table II, entries 2–9). The reduction of TA in the presence of CD and BA, when no catalyst pretreatment was applied, resulted in a moderate 53% conversion and 33% ee. When the pre-treatment involved stirring the catalyst in toluene, a decreased conversion of 39% and ee of 27% was obtained. Strikingly, when reductive pretreatment was applied, the conversion was diminished to 11% and an ee of 34% was obtained. Additionally, all these decreased conversions were associated with considerable Pd aggregation (Figs. 6(c–e)). Although the poisoning effect of BA on the catalytic hydrogenation of TA has been considered in the literature,[59] furthermore the reaction rate lowering effect of the CD has been described;[47] the observed decreasing tendency of the conversion cannot be solely attributed to these effect. In all three reactions both TA, CD and BA are present and they only differ in the pre-treatment method. Thus, it is suggested that these features together with the contribution of the reagents to strong Pd aggregation, which is also facilitated by the reductive pre-treatment[59] has an overall hindering effect on the hydrogenation reaction. This is also supported by literature data where decreased conversions and increased ees were reported with increasing Pd particle sizes in the catalytic enantioselective hydrogenation of TA over CD modified Pd nanocube catalysts.[58]

4. CONCLUSIONS

In summary, we have shown that both transfer hydrogenation and catalytic hydrogenation type reduction processes over polydopamine supported Pd catalyst are sensitive to the aggregation of Pd. In both cases decreased catalytic activity was associated with pronounced Pd particle aggregation. For transfer hydrogenation, the aggregation was found to be dependent on the nature of the H-source, for catalytic hydrogenation of a C=C double bond the H_2 atmosphere in combination with the substrate and different additives (CD, BA) played a crucial role. In the latter case the contribution of H_2 induced structural changes of PDA to particle aggregation cannot be ruled out.

Acknowledgments: Financial support by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences (AS, GL), the ÚNKP-ÚNKP-16-4 New National Excellence Program of the Ministry of Human Capacities (AS) and the National Research, Development and Innovation Office, Hungary (NKFIH OTKA Grants PD 120877 (AS), PD 115436 (GL) and K 109278 (KS)) is gratefully acknowledged. This collaborative research was partially supported by the "Széchenyi 2020" program in the framework of GINOP-2.3.2-15-2016-00013 "Intelligent materials based on functional surfaces—from syntheses to applications" project and the NKFIH (OTKA) K112531 grant. The Chemical Biology Research Group and the Organocatalysis Research Group (both at the Institute of Organic Chemistry Research Centre for Natural Sciences, Hungarian Academy of Sciences) are acknowledged for support.

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Received: 6 September 2017. Accepted: 9 November 2017.