Journal of Catalysis 311 (2014) 1–5

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Research Note

Enantioselective hydrogenation of α,β-unsaturated carboxylic acid over cinchonidine-modified Pd nanoparticles confined in carbon nanotubes

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ARTICLE INFO

Article history:
Received 14 June 2013
Revised 10 October 2013
Accepted 12 October 2013
Available online 5 December 2013

Keywords:
Carbon nanotubes
Asymmetric hydrogenation
Heterogeneous
Palladium

ABSTRACT

We report the enantioselective hydrogenation of α,β-unsaturated acid catalyzed by Pd nanoparticles in carbon nanotubes (CNTs) taking the advantage of the channels as nanoreactors. The Pd nanocatalyst inside the channels of CNTs shows higher activity and enantioselectivity than that of Pd nanocatalyst outside the channels. As high as 92% enantioselectivity is achieved. The enhanced catalytic performance is attributed to the enrichment of reactant, chiral modifier, and additive in the channels of CNTs. This work demonstrates the unique feature of CNTs as nanoreactors for asymmetric catalytic reactions.

1. Introduction

Due to the unique properties of carbon nanotubes (CNTs), the improved catalytic performance has been reported when CNTs were used as supports to disperse the metal catalysts on the outer surface of the channels [1–3]. The well-defined one-dimensional channels of CNTs with the diameter ranging from less than 1–100 nm provide the opportunities to use the channels of CNTs as nanoreactors. The encapsulation of various substrates has been realized [4–8], making it possible to develop efficient catalytic systems inside the channels. However, only limited examples of gas-phase reactions [9–14] and liquid-phase hydrogenation reactions [15–17] inside the CNTs have been reported, and the application of CNTs in heterogeneous asymmetric catalysis was less explored. In 2011, this group reported the first study on enantioselective hydrogenation in the channels of CNTs as nanoreactors [18]. The results indicated that Pt nanoparticles encapsulated in the channels of CNTs showed excellent catalytic performance in the asymmetric hydrogenation of α-ketoesters, giving higher activity than the most efficient Pt/Al_2O_3 catalyst, which encourages us to further develop other heterogeneous asymmetric catalysis inside the channels of CNTs and explore the unique features of CNTs as nanoreactors in catalysis.

Asymmetric hydrogenation of α,β-unsaturated carboxylic acids is a convenient method for the synthesis of chiral carboxylic acid, which is an important intermediate for the production of pharmaceuticals, fragrances, and flavors [19–21]. The alkaloid-modified palladium catalyst is the most studied and used heterogeneous catalyst for this reaction. Different types of support such as TiO_2 [22], Al_2O_3 [23], and active carbon [24] were used to load palladium nanoparticles. Inspired by the special properties of the CNTs, we investigated the enantioselective hydrogenation of α,β-unsaturated acid (Scheme 1) on Pd nanoparticles inside CNTs and studied the essential role of CNTs as nanoreactors played in the chiral induction and hydrogenation. We found that the catalytic activity and enantioselectivity were greatly enhanced when the Pd nanoparticles were located inside the channels of CNTs.

2. Experimental

2.1. Catalyst preparation

Two catalyst samples with Pd nanoparticles confined inside the channels of CNTs (denoted as Pd/CNTs(in)) and loaded on the outer surface of CNTs (denoted as Pd/CNTs(out)) were prepared in this work. Preparation of 5 wt.% Pd/CNTs(in) and 5 wt.% Pd/CNTs(out) was according to our previous report [18] using an improved wet chemistry [25,26]. The pristine CNTs (denoted as CNTs(closed)) were first oxidized in concentrated HNO_3 (68 wt.%). The as-prepared oxidized CNTs (denoted as CNTs(open)) were used as support. For the synthesis of 5 wt.% Pd/CNTs(in), the Pd precursor was introduced into the channels of CNTs by ultrasonic treatment and prolonged stirring. After a slow drying process, the mixture was reduced in a sodium formate solution and then washed with deionized water and was dried to give Pd/CNTs(in). For the synthesis of 5 wt.% Pd/CNTs(out), the channels of CNTs were filled

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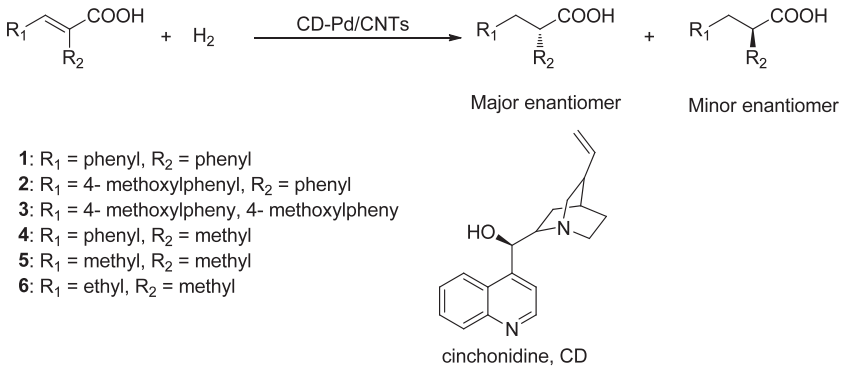
0021-9517/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcat.2013.10.010



Scheme 1. Asymmetric hydrogenation of α,β-unsaturated carboxylic acid.

with xylene by ultrasonic treatment. The Pd precursor was added into the mixture, followed by a controlled stirring and reduction in a sodium formate solution. Then, the mixture was extracted with ethanol, washed with deionized water, and dried to give Pd/CNTs(out). The detailed description of the preparation can be seen in the text below the transmission electron microscope (TEM) pictures of the catalysts shown in Fig. S1. The preparation of the oxidized multilayer graphene (GO) was similar to that of CNTs(open). The commercial 5 wt.% STD Pd/AC (AC = activated carbon) used for comparison is purchased from Alfa Aesar.

2.2. Catalyst characterization

Catalysts were usually pre-treated in H_2 stream for 0.5 h at 375 °C before characterization. The TEM measurements were obtained on TECNAI G^2 electron microscope operating at an accelerating voltage of 110 kV. The samples were outgassed at 120 °C for 6 h before N_2 sorption measurement tested on a Micromeritics ASAP 2020 volumetric adsorption analyzer and CO chemisorption measurement performed on a Quantachrome AUTOSORB-1-MS volumetric adsorption analyzer. X-ray photoelectron spectroscopy (XPS) analysis of the catalysts was performed on a VG ESCAB mk-2 instrument using Al Kα (1486.6 eV, 12.5 kV, 250 W) radiation. The samples were pressed into a sample holder and evacuated to $0.8–0.4 \times 10^{-6}$ Pa. The Pd loading was measured by inductively coupled plasma spectroscopy (Shimadzu ICPS-8100). The determined Pd loadings of Pd/CNTs(in) and Pd/CNTs(out) are 5.02 wt.% and 4.99 wt.%, respectively.

Adsorption of CD, BA, **1**, and **5** by the catalysts was measured in a similar method. Take CD as an example, the catalysts were pre-treated in H_2 stream at 375 °C for 0.5 h before the adsorption test. For the adsorption test of CD, the work solution was prepared by adding 5 mg CD in100 mL of 1,4-dioxane with H_2O content of 2.5% (v/v). After stirring, the mixture was centrifuged and 2 mL of the supernatant was taken out and analyzed on a SHIMADZU UV-2550 UV/Vis spectrophotometer with a 1,4-dioxane with H_2O content of 2.5% (v/v) as a comparison. The details for adsorption of BA, **1**, and **5** can be found in Figs. S5 and S6.

2.3. Catalyst testing

General procedure for hydrogenation: Hydrogenation was carried out in a magnetically stirred autoclave in 1,4-dioxane containing 2.5% (v/v) of water under an atmospheric pressure of hydrogen at room temperature. The catalyst (20 mg) was pre-treated in a H_2 flow at 375 °C for 30 min. After cooling down and transferred to the autoclave, the catalyst was pre-treated with modifier CD (0.02 mmol) in 4 mL solvent for an additional 30 min. Then, certain amount of substrate and BA, as an effective additive, in 2 mL solvent were added to the mixture. After adjusting the hydrogen pressure to the desired H_2 pressure, the stirring was started. For substrates **1–4**, the mixture after reaction was first neutralized with a diluted HCl solution, extracted with ethyl ether and analyzed by hydrogen nuclear magnetic resonance (^{1}H NMR, Bruker DRX 400 MHz type spectrometer) for conversion and a high performance liquid chromatography (HPLC, 6890 Agilent Co.) equipped with a chiral column (Daicel Chiralcel OJ-H) for enantiomeric excess (ee). For substrates **5** and **6**, the mixture after reaction was first neutralized with a diluted HCl solution. Then, the catalyst and liquid were separated by centrifugation. After passing the liquid phase through a short silica column and drying, the conversion and enantioselectivity of **5** or **6** were determined on a gas chromatograph (Agilent 6890, 30 m × 0.32 mm × 0.25 μm HP19091G-B213 capillary column).

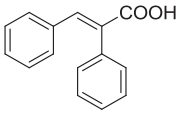
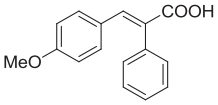
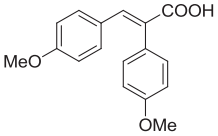
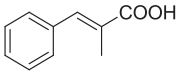
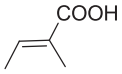
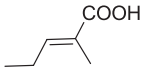
The activity of the hydrogenation was expressed by the average turnover frequency (TOF). TOF = ($[M_0]$ × conversion)/($[M_{Pd}]$ × D_{Pd} - × (reaction time)). $[M_0]$ stands for the initial molar concentration of the reactant. M_{Pd} stands for the Pd molar concentration used in the reaction. D_{Pd} stands for the metal dispersion of Pd obtained by CO chemisorptions. The conversion used to calculate the TOF was lower than 30%. The ee (%) of the S isomers was expressed according to ee (%) = ($[S] - [R]$) × 100/($[S] + [R]$).

3. Results and discussion

The TEM characterization shows that the Pd nanoparticles of Pd/CNTs(in) are uniformly distributed inside the channels of CNT (Fig. S1(a)) and that the Pd nanoparticles of Pd/CNTs(out) were almost exclusively dispersed on the outer surface of CNTs (Fig. S1(b)). Table 1 gives the catalytic performance of Pd/CNTs and the commercial STD Pd/AC in the hydrogenation of α-phenylcinnamic acid analogues (**1–4**) and aliphatic analogues (**5** and **6**) using CD as the chiral modifier and BA as additive. The TOF of Pd/CNTs(in) in racemic hydrogenation of **1–6** is higher than that of Pd/CNTs(out) and STD Pd/AC. In particular, the highest TOF of Pd/CNTs(in) for α-phenylcinnamic acid analogues reaches over 260 h^{-1} (Table 1, entry 3), about 1.5 times of that Pd/CNTs(out) and about 2 times of that of STD Pd/AC. For the aliphatic analogues (**5** and **6**), the Pd/CNTs(in) also shows the highest TOF value of 1089 h^{-1} (Table 1, entry 16). It is noteworthy that the addition of BA decreases the activity of racemic hydrogenation by half (Table 1, entries 4 and 17).

Modified by CD, the activity for these three catalysts is decreased. This is unlike the "ligand acceleration" for CD-modified Pt system [27]. The TOF of Pd/CNTs(in) in chiral hydrogenation of **1–6** is also much higher than that of Pd/CNTs(out) and STD Pd/AC. The addition of benzyl amine as additive promotes not only the activity but also the enantioselectivity of **1–6**. Modified by

Table 1
The catalytic performance of Pd/CNTs(in), Pd/CNTs(out), and STD Pd/AC on hydrogenation of α,β-unsaturated carboxylic acid.

Entry	Substrate		Pd/CNTs(in)		Pd/CNTs(out)		STD Pd/AC	
			TOF (h^{-1})	Ee (%)	TOF (h^{-1})	Ee (%)	TOF (h^{-1})	Ee (%)
1		1[a]	62	75	36	61	42	64
2		1[b]	29	65	24	51	19	52
3		1[c]	261	–	175	–	140	–
4		1[d]	119	–	94	–	77	–
5		2[a]	33	84	20	68	29	69
6		2[b]	22	75	17	64	16	58
7		2[c]	101	–	90	–	84	–
8		3[a]	29	92	20	80	21	79
9		3[b]	20	74	12	64	13	68
10		3[c]	84	–	56	–	52	–
11		4[a]	60	36	32	31	24	30
12		4[b]	26	30	14	20	10	20
13		4[c]	237	–	118	–	96	–
14		5[a]	248	37	123	31	106	30
15		5[b]	176	30	140	26	120	26
16		5[c]	1089	–	743	–	265	–
17		5[d]	746	–	502	–	174	–
18		6[a]	381	42	204	37	176	35
19		6[b]	229	38	172	33	148	32
20		6[c]	1006	–	681	–	240	–

Reaction conditions: 20 mg catalyst (pre-treated in H_2 stream at 375 °C for 0.5 h before reaction), 6 mg (0.02 mmol) CD, BA/reactant = 0.6 (molar ratio). For substrate **1**–**4**: 0.34 mmol reactant, 6 mL 1,4-dioxane containing 2.5% (v/v) of water, 0.1 MPa H_2 pressure. For substrate **5** and **6**: 1.5 mmol reactant, 6 mL toluene, 5.0 MPa H_2 pressure. The preparation of substrates 2 and 3 is described in Supplementary material.

[a] With BA as additive (BA/substrate molar ratio of 0.6).
[b] Without BA.
[c] Without CD and BA.
[d] With BA and without CD.

CD, Pd/CNTs(in) obtains 65% ee and TOF of 29 h^{-1} for **1** (Table 1, entry 2). While in the presence of benzyl amine, Pd/CNTs(in) delivers 75% ee and TOF of 62 h^{-1} for **1** (Table 1, entry 1). Compared with **1**, the *p*-methoxyl substitutions at the benzene rings (**2** and **3**) further improve the enantioselectivity. Pd/CNTs(in) delivers as high as 92% ee for **3** (Table 1, entry 8), which is equivalent to the highest ee obtained on the commercial STD Pd/AC (N.E. Chemcat) reported by Sugimura [24]. While for the methylcinnamic acid (**4**) and aliphatic analogues (**5** and **6**), Pd/CNTs(in) delivers relatively high activity but only achieves middle or relatively low enantioselectivity even in the presence of BA. From the catalytic performance demonstrated in Table 1, it can be concluded that the catalytic activity and enantioselectivity are greatly enhanced when the Pd nanoparticles are located inside the channels of CNTs.

The average sizes of Pd nanoparticles in Pd/CNTs(in) and Pd/CNTs(out) estimated by CO chemisorption are 4.9 nm and 5.1 nm, respectively (Table S1). The small difference in particle size cannot explain the enhanced catalytic performance of Pd/CNTs(in). Besides, the XPS analysis shows that no obvious difference in the distributions of Pd species in Pd/CNTs(in) and Pd/CNTs(out) is observed (Details in Supplementary material).

In our previous work [18], it is found that the high activity and enantioselectivity are ascribed mainly to the enrichment of the chiral modifier and reactant in channels of CNTs. Therefore, the adsorption of the chiral modifier, additive, and reactant by the catalysts is investigated. The chiral modifier, CD, has relatively larger molecular size than the others. Based on the previous theoretical calculation results [28], the size of CD is estimated to be around 1 nm^2. The inner diameter of channels is about 5–10 nm (Fig. S1). So the pores are large enough for the substrates related to the reaction to diffuse into the inner surface of the channels. Since the adsorbents have the similar morphology and surface areas (Table S3), the adsorption molar ratio is used to directly and clearly demonstrate the adsorption behaviors of the catalysts and the supports. Fig. 1 shows the adsorption of the chiral modifier (CD) by Pd/CNTs, CNTs(open), CNTs(closed), and GO. Pd/CNTs(in) exhibits the highest CD adsorption molar ratio (85%). Pd/CNTs(out) and CNTs(open) show a slightly lower adsorption molar ratio, while CNTs(close) shows a much lower adsorption molar ratio. The adsorption measurement is unable to discriminate the adsorption on the outer surface and in the channels. However, due to the cap-

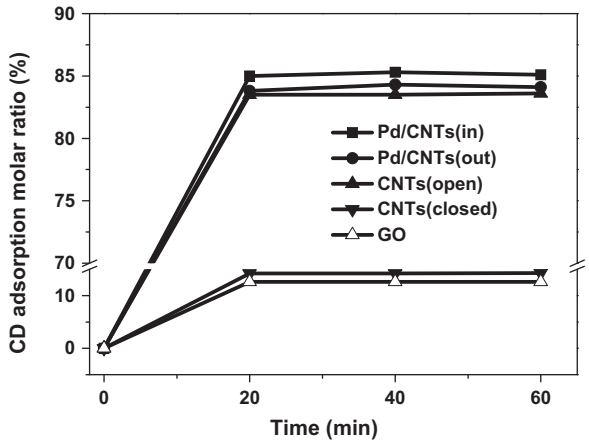


Fig. 1. Comparison of the adsorption molar ratio of CD as a function of adsorption time for Pd/CNTs(in) (■), Pd/CNTs(out) (●), CNTs(open) (▲), CNTs(closed) (▼), and GO (△).

illarity of the channels, the adsorption in the channels may take up the major part. The adsorption of CD on the GO is test and used to estimate the adsorption on the outer surface of CNTs. Take CD as an example, the GO adsorbs about 13% of CD (Fig. 1). So the channels take up major part of the adsorption (72%). In other words, the adsorption amount in the channels is 6 times as that on the outer surface of CNTs. The enrichment of BA and the reactants in the channels are also estimated: 4 times for BA, 6 times for substrate **1**, and 2 times for substrate **5** (Details in Supplementary material).

The influence of CD/BA concentration on the catalytic performance of Pd/CNTs(in), Pd/CNTs(out), and STD Pd/AC is investigated. Generally speaking, the TOFs of the three catalysts decrease with the increase in CD concentration (Fig. 2), and the enantioselectivity of gradually increases with the increase in CD concentration (Fig. 2). While it is worth to point out that due to the enrichment of CD in the channels of CNTs, Pd/CNTs(in) is more sensitive to the change in CD concentration in the beginning. After addition of only 1 mg CD, the activity and enantioselectivity of Pd/CNTs(in) decrease and increase more rapidly than Pd/CNTs(out) and STD Pd/AC (Fig. 2). As for the influence of BA concentration, similar to the circumstances of CD, the activity and enantioselectivity of Pd/CNTs(in) increase more rapidly than Pd/CNTs(out) and STD Pd/AC in the beginning due to the enrichment of BA in the channels (Fig. S7). These results suggest that the enrichment of CD/BA obviously influences the reaction inside the channels of CNTs.

As chiral modifier, CD can adsorb nearly parallel to the Pd surface via the quinoline ring (denoted as "π-bonded CD") [27,29] or with quinoline ring perpendicular to the Pd surface (denoted as "N-lone pair bonded CD") [30]. It is generally accepted that the π-bonded CD plays an important role in the enantiodifferentiation [27,29]. The carboxyl group of the α,β-unsaturated acid interacts with the basic quinuclidine N of the π-bonded CD [30] and is hydrogenated to give the product. Due to the acid–base interaction between the product and CD, product desorption is found to be the rate-determining step [31]. Recently, the study by in situ attenuated total reflection infrared spectroscopy shows that the addition of BA not only improves the desorption of product by competing with CD through the acid–base interaction, which improves the activity of the chiral hydrogenation, but also facilitates a gradual transformation from the N-lone pair bonded CD to the π-bonded CD forming a better defined surface for the enantiodifferentiation [30]. Therefore, as a non-chiral molecule, BA improves both the activity and the enantioselectivity of the chiral hydrogenation of α,β-unsaturated acid (Table 1). For the racemic hydrogenation of α,β-unsaturated acid, the high activity of Pd/CNTs(in) is mainly attributed to the enrichment of reactant in channels of CNTs. For the chiral hydrogenation, the CD modification decreases the activity. Modified by CD, we suggest the higher activity of Pd/CNTs(in) is the outcome of the enrichment of reactant and CD in the channels. Besides, another benefit of the enrichment effect is that the enriched CD and BA within the channels may facilitate the interaction with each other, thus resulting into a better chiral environment for enantiodifferentiation on the Pd surface. So Pd/CNTs(in) delivers relatively higher enantioselectivity than that of Pd/CNTs(out). Based on the above results, we suggest that in the limited space of the channels of CNTS, the enrichment of the substrates related to the reaction facilitates the chiral hydrogenation of α,β unsaturated carboxylic acid, resulting into the relatively higher activity and enantioselectivity of Pd/CNTs(in) than those of Pd/CNTs(out).

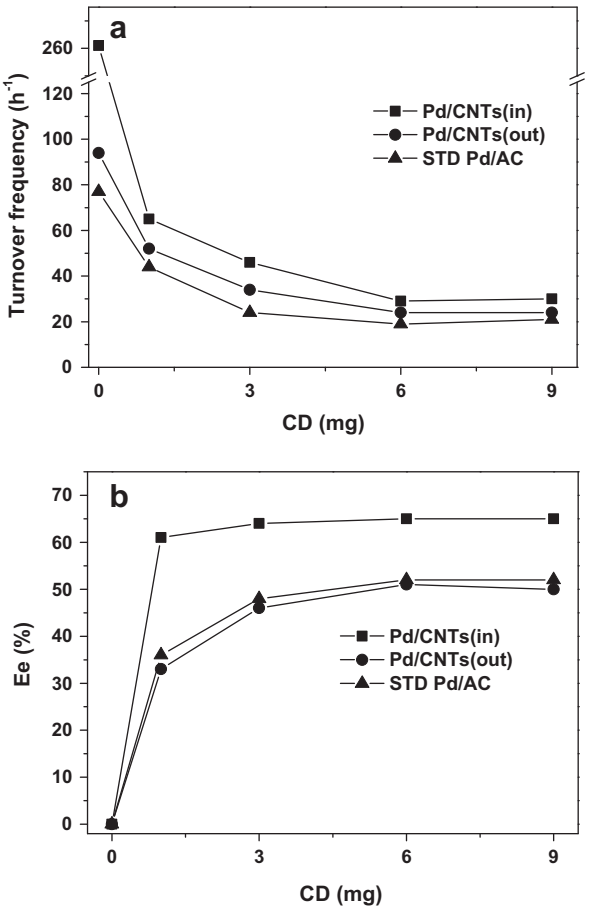


Fig. 2. Influence of CD concentration on the (a) activity and (b) enantioselectivity of Pd/CNTs(in) (■), Pd/CNTs(out) (●), STD Pd/AC (▲) in the asymmetric hydrogenation of 1.

4. Conclusions

In summary, we demonstrate CNTs as nanoreactors for the Pd nanoparticle-catalyzed enantioselective hydrogenation of α,β-unsaturated acid. Due to the enrichment of reactant, CD and BA in the channels, the Pd nanocatalyst inside the channels of CNTs achieves higher activity and enantioselectivity than those of Pd nanocatalyst outside the channels and the commercial STD Pd/AC. This work further demonstrates the unique adsorption property of CNTs as nanoreactors and the importance of this feature in a wide range of catalytic reactions.

Acknowledgment

This work was financially supported by the National Natural Science Foundation of China (NSFC Grant Nos. 20921092 and 20902032).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2013.10.010.

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