Preparation of Pt/SWNTs for heterogeneous asymmetric hydrogenation of ethyl pyruvate

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Abstract

In order to be applied in heterogeneous asymmetric hydrogenation, a series of Single-Walled Carbon Nanotubes (SWNTs)-supported Pt nanoparticle catalysts with different controlled Pt loadings, i.e. 5%, 10% and 20%, were prepared, and characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). By modification with (−)-cinchonidine (Cd), these Pt/SWNTs catalysts were found to be efficient for the asymmetric hydrogenation of ethyl pyruvate, providing (*R*)-ethyl lactate in high activity and moderate enantioselectivity. Kinetic study showed that the Pt/SWNTs-catalyzed asymmetric hydrogenation of ethyl pyruvate was a "ligand-accelerated" reaction.
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1. Introduction

As an important strategy of heterogeneous asymmetric catalysis, supported metal catalysts which are easy to be separated and practical for reuse, have attracted broad research interests [1]. Among those examples, the asymmetric hydrogenation of α-ketoesters catalyzed by cinchona-modified Pt/Al₂O₃ catalyst has shown synthetic potential [2–4] and thus great strides have been made toward the improvement of the hydrogenation by preparing Pt catalysts with various supports [5–7]. Since the discovery in 1993 [8], Single-Walled Carbon Nanotubes (SWNTs) have been extensively studied and regarded as one of the most promising nanomaterials for various applications [9]. In the view of their curved aromatic surface, high surface area and ready electron-transfer capability, SWNTs have a feature totally different from other conventional heterogeneous supporting materials. With the support of SWNTs, metal catalyst can be dispersed into nanoparticles to exhibit high catalytic activity. These advantages have prompted many studies on the application of SWNTs as a support of heterogeneous metal cata-

lysts [10–14]. However, the application of metal-loaded SWNTs material (M/SWNTs) in asymmetric catalysis has not been well documented [15]. In this paper, we would like to report the results on the heterogeneous asymmetric hydrogenation of α-ketoesters catalyzed by SWNTs-supported Pt nanoparticles modified with (−)-cinchonidine (Cd). A series of Pt/SWNTs catalysts with different Pt loadings, i.e. 5%, 10% and 20%, were prepared and characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). After modified with Cd, these Pt/SWNTs catalysts can efficiently hydrogenate ethyl pyruvate in high activities and moderate enantioselectivities (Scheme 1).

2. Experimental

2.1. Materials and instruments

Single-Walled Carbon Nanotubes (SWNTs) were prepared by our modified arc-discharge method [16]. Ethyl pyruvate and solvents were distilled before use. Other reagents were purchased and used without further purification. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM2010FEF microscope at 300 kV, and the samples for TEM measurements were prepared by placing one drop of the catalyst dispersion (0.01 mg/mL in ethanol) on carbon-coated copper
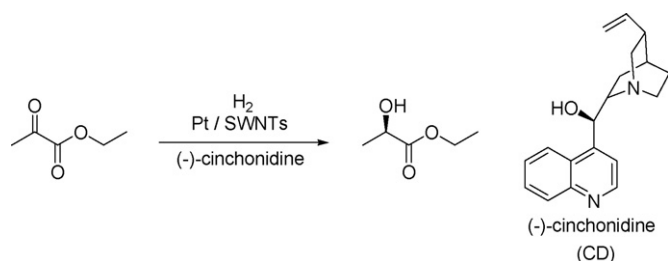
Scheme 1. Asymmetric hydrogenation of ethyl pyruvate catalyzed by Cd-modified Pt/SWNTs.

grids. The diameter distribution histogram was established from the data of particles in the TEM images. X-ray diffraction characterization was performed with a Bruker AXS D8 Advance spectrometer. Ultraviolet–visible (UV–vis) measurements were conducted on a JASCO V-570 UV–vis spectrophotometer. Centrifugation was conducted with an Eppendorf Centrifuge 5810R instrument. Gas chromatography (GC) analyses were performed using Hewlett Packard Model HP 6890 Series.

2.2. Catalyst preparation

SWNTs were purified using an acid-oxidation procedure in the literature [17]. The carboxylic group introduced in this process was used as the anchor site to immobilize Pt particles [11]. A typical manipulation was as follows. Pristine SWNTs (3.0 g) and HNO_3 (2.6 mol/L, 426 mL) were placed in a 1000 mL round-bottom glass flask. After ultrasonicated for 30 min, the mixture was refluxed for 12 h. SWNTs were then separated from the acid solution in a centrifugal machine (11000 rpm, 20 min). The solid was collected and washed with distilled water. The purified SWNTs (SWNTs-COOH) were dried in vacuum at 100 °C for 5 h.

The deposition of Pt nanoparticles on SWNTs was performed by literature procedure [18]. SWNTs-COOH (2.0 g) was ultrasonicated with 100 mL of ethanol/toluene (1:4 in volume) in a 250 mL round-bottom flask for 1 h to disperse the SWNT bundles. The solution of H_2PtCl_6 (0.18 g, 0.44 mmol) in ethanol (10 mL) was added to the flask, and the resulting mixture was magnetically stirred for 25 h at room temperature. After evaporating the solvent, the solid was dried in vacuum at 90 °C for 16 h to yield 2.2 g powder. The reduction of platinum salt was performed in a H_2 flow (40 mL/min) at 200 °C for 4 h and at 400 °C for 6 h. With ∼20% weight loss of the purified SWNTs observed after the reduction, the resulting Pt/SWNTs catalyst (1.7 g, 5% Pt) was preserved in Ar atmosphere. The same method was used for the preparation of the catalysts with 10% and 20% loadings of Pt.

2.3. Asymmetric hydrogenation of ethyl pyruvate using Pt/SWNTs catalysts

As a typical example, the asymmetric hydrogenation of ethyl pyruvate with 20% Pt/SWNTs was carried out in a 20 mL autoclave equipped with a glass tube. The modifier Cd (8 mg, 0.027 mmol), catalyst Pt/SWNTs (20% Pt, 10 mg, 0.01 mmol Pt)

and toluene (2 mL) were added to the glass tube, and the tube was put in an ultrasonic bath for 30 min to disperse the catalyst into solvent. After ethyl pyruvate (250 μL, 2.3 mmol) was added, the tube was put into an autoclave. The autoclave was filled and flushed with hydrogen three times and was finally charged with hydrogen to 50 atm. The reaction mixture was magnetically stirred (1200 rpm) under hydrogen at room temperature for a proper time. The pressure was released and the reaction mixture was filtered through a short silica column and submitted to the analyses of the conversion and enantioselectivity of the hydrogenation product ethyl lactate by GC (β-dex-225 column, 30 m, 0.25 mm).

2.4. Kinetic studies

The modifier Cd (40 mg, 0.14 mmol), catalyst 20% Pt/SWNTs (50 mg, 0.051 mmol Pt) and toluene (10 mL) were added to a glass tube. The tube was put in an ultrasonic bath for 30 min to disperse the catalyst into solvent. After ethyl pyruvate (1.25 mL, 11.4 mmol) was added, the tube was put into an autoclave. The autoclave was filled and flushed with hydrogen three times and was finally charged with hydrogen to 50 atm. The reaction mixture was then magnetically stirred (1200 rpm) under hydrogen at room temperature. The samples for GC analysis were withdrawn by means of the sampling tube every 10 min. The conversion and enantioselectivity of hydrogenation product were analyzed by GC.

3. Results and discussion

3.1. Pt/SWNTs catalysts preparation and characterization

Fig. 1 shows typical TEM images of the purified SWNTs (SWNTs-COOH) and three Pt/SWNTs catalysts with different Pt loadings. There was no metal particle found on the surface of SWNTs in Fig. 1a, which implied that most of metal (Ni/Y) particles used for the synthesis of SWNTs were removed during the purification of SWNTs. This was also confirmed by Energy Dispersive X-ray analysis (not shown). The Pt particles can be clearly seen on the surface of SWNT bundles in all three Pt/SWNTs catalysts and a clear trend for the density of Pt particles to increase was observed as the loading of Pt raised from 5% to 20% (Fig. 1b–d). Moreover, for all three catalysts, the Pt nanoparticles were rather uniformly distributed on the surface of the SWNT bundles. The Pt nanoparticle size distributions of catalysts obtained by TEM image analysis were relatively narrow as shown in Fig. 2. The mean nanoparticle sizes (diameters) were found to be about 1.17 nm, 1.24 nm, and 2.29 nm for the catalysts with 5%, 10%, and 20% Pt, respectively. It was worth pointing out that the size of Pt particles increased when the loading of Pt raised. This phenomenon was also reported in the preparation of Pt nanoparticles on multiwalled carbon nanotubes [19].

The X-ray diffraction (XRD) patterns of three Pt/SWNTs catalysts are shown in Fig. 3. The Pt nanoparticles in three Pt/SWNTs catalysts are crystalline as indicated by the characteristic peaks at $2\theta = 39.7°$, $46.4°$ and $67.5°$. The lower intensity peaks at about $2\theta = 26°$ and $44°$ were attributed to the graphite
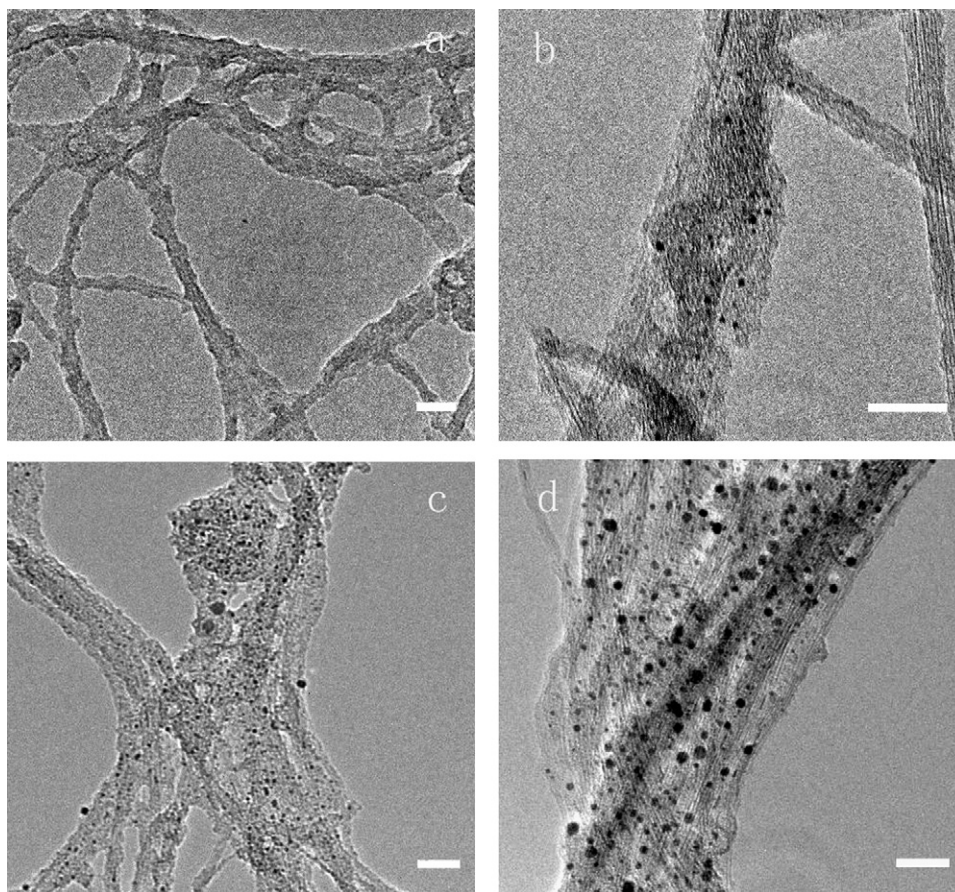
Fig. 1. TEM figures for the purified SWNTs and Pt/SWNTs catalysts: (a) purified SWNTs, (b) 5% Pt/SWNTs, (c) 10% Pt/SWNTs, (d) 20% Pt/SWNTs. The scale bars are all 20 nm.

structure of SWNTs and no peak for other metals were observed in all cases. With the increase in the Pt loading, the graphite peaks became relatively weak.

3.2. Asymmetric hydrogenation

All three Cd modified Pt/SWNTs catalysts showed good catalytic activities in the asymmetric hydrogenation of ethyl
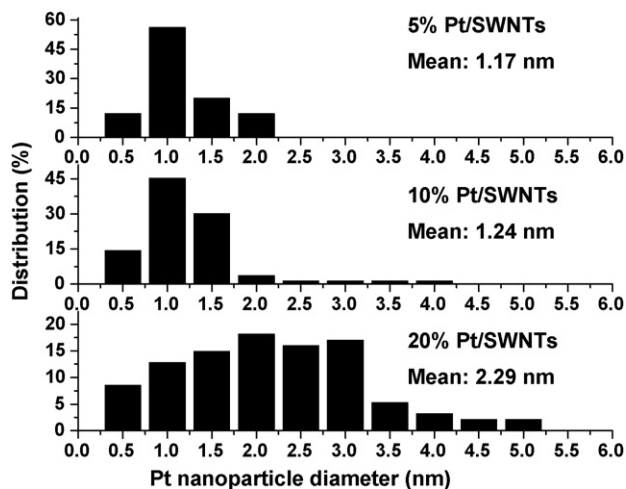

Fig. 2. Diameter distribution of Pt nanoparticles on SWNTs.

pyruvate. Complete conversions of ethyl pyruvate were achieved within 12 h. The heterogeneous asymmetric hydrogenation of ethyl pyruvate with 10% Pt/SWNTs was carried out for optimizing reaction conditions, and the results are summarized in Table 1. Solvent screening found that toluene was the best choice of solvent to give highest enantioselectivity, albeit the hydrogenation reaction could also be performed in CH_2Cl_2, THF, ethyl acetate and ethanol. However, a very poor activity was observed and a nearly racemic product was obtained in acetic acid, which was widely used in the enantioselective hydrogenation using Pt/Al_2O_3 catalyst [2]. We suspected that the great differences in the surface structure and electron property between SWNTs and Al_2O_3 may play a crucial role in making different activity and enantioselectivity. Within the testing pressure range and the reaction temperature, the medium pressure of hydrogen (50 atm) at room temperature gave better enantioselectivity. Neither reducing the H_2 pressure nor lowering the temperature improved the enantioselectivity of reaction (Table 1, entries 1–5). Comparison of catalysts indicated that the catalysts with higher Pt loading have higher catalytic activity and higher enantioselectivity. 20% Pt/SWNTs giving the best catalytic result. Complete conversion of ethyl pyruvate can be achieved within 2 h, with 50% ee of enantioselectivity (Table 1, entry 14), which was better than the result obtained by using Pt/C catalyst [7].
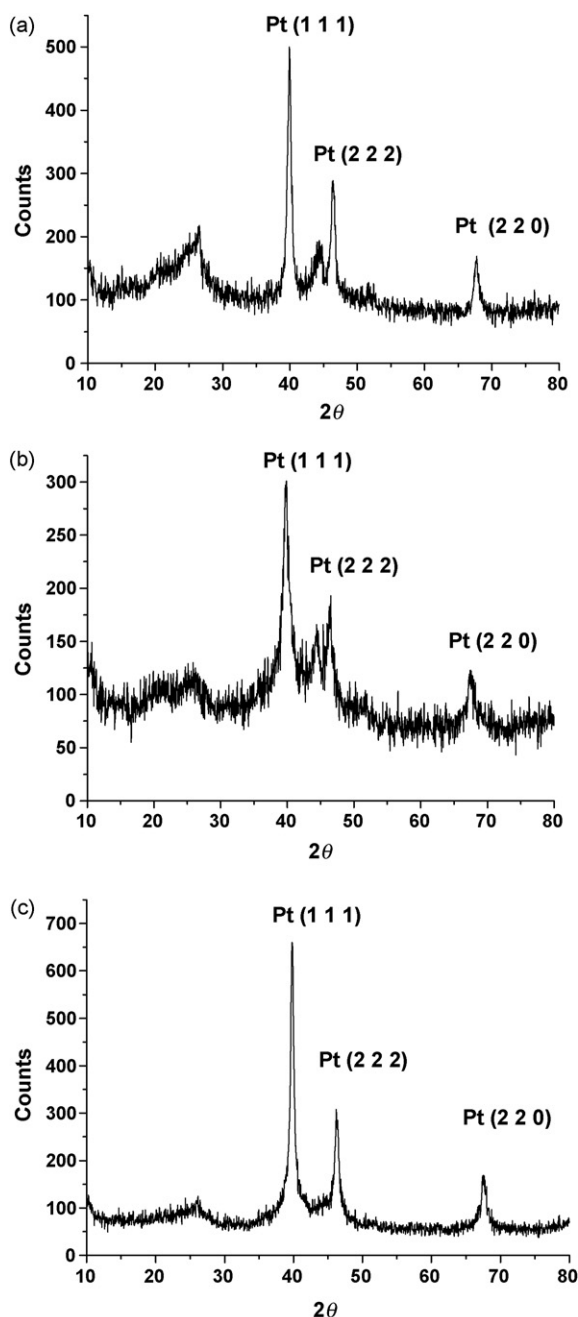
Fig. 3. X-ray diffraction images of: (a) 5% Pt/SWNTs, (b) 10% Pt/SWNTs and (c) 20% Pt/SWNTs.

3.3. Kinetic studies

We performed a kinetic study on the activity of catalysts. The results are illustrated in Fig. 4. The initial rate of the reaction with Cd was about 3.78 mmol/min per gram of the 20% Pt/SWNTs catalyst within the first 20 min, while the initial rate of the reaction without Cd was only 0.61 mmol/min per gram of the Pt/SWNTs catalyst (Fig. 4A). This result clearly showed that there was a "ligand-acceleration" phenomenon in the heterogeneous hydrogenation with Pt/SWNTs catalysts, which provided a potential for obtaining a high enantioselectivity in the reactions. It should be noted that the "ligand-acceleration" phenomenon
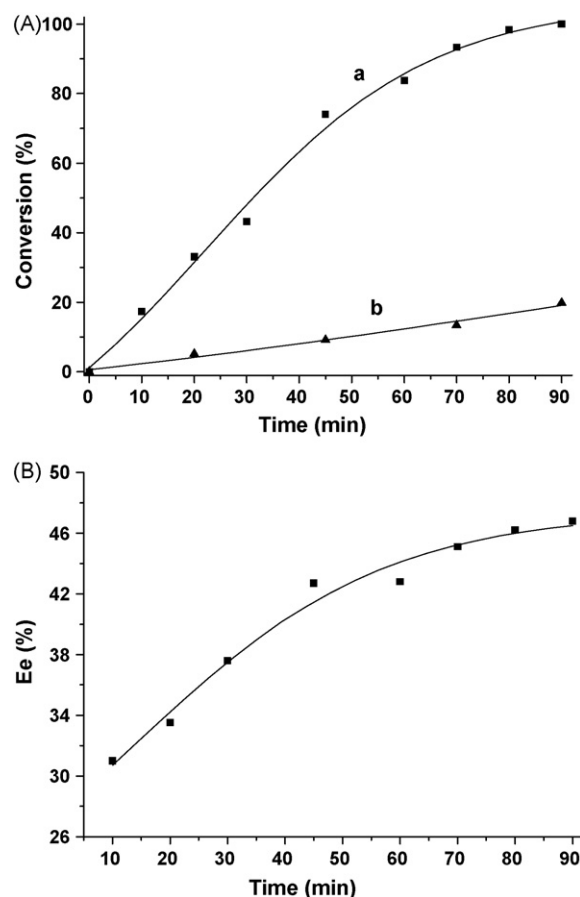

Fig. 4. Kinetic study. (A) The relationship between conversion and time. Line a: the reaction with Cd modifier. Line b: the reaction without Cd modifier. (B) The relationship between Ee value and time for the reaction with Cd.

was also observed in the hydrogenation with Pt/Al$_2$O$_3$ catalysts [20–22]. The ee value was not constant, but increased along with the reaction process, and leveled off at the end of reaction as in the Pt/Al$_2$O$_3$ system (Fig. 4B) [23].

3.4. Absorption of Cd on the surfaces of Pt/SWNTs catalysts

Based on the "ligand-acceleration" phenomenon in our system, there should be two types of Pt metal sites on the surface of SWNTs in the catalysts, namely unmodified and modified metal sites. It was obvious that the Cd-modified Pt particles gave an optically active product and that the unmodified Pt particles gave a racemic product. In other words, only the Cd absorbed on the surface of Pt particles could act as modifier in the asymmetric hydrogenation. Fig. 4 has demonstrated that the Pt particles modified by Cd show a faster reaction rate and give an optically active product.

In heterogeneous asymmetric catalytic reactions, the enantioselectivity was very sensitive to the amount of added modifier. The correlation between ee value of the product and the amount of Cd in the asymmetric hydrogenation of ethyl pyruvate using a 20% Pt/SWNTs catalyst was shown in Fig. 5. A rapid increase in ee was found with the addition of Cd. A maximum appeared

Table 1
Asymmetric hydrogenation of ethyl pyruvate catalyzed by Pt/SWNTs[a]

Entry	Catalyst	Cd (mg)	P_{H_2} (atm)	Temperature (°C)	Time (h)[b]	Ee (%)[c]
1	10% Pt/SWNTs	2	100	25	3	26
2	10% Pt/SWNTs	2	50	25	4	34
3	10% Pt/SWNTs	2	30	25	5	23
4	10% Pt/SWNTs	2	15	25	8	13
5	10% Pt/SWNTs	2	50	0	5	28
6	10% Pt/SWNTs	2	50	50	3	20
7	10% Pt/SWNTs	1	50	25	5	33
8	10% Pt/SWNTs	4	50	25	3	32
9	5% Pt/SWNTs	1	50	25	12	27
10	5% Pt/SWNTs	2	50	25	12	23
11	5% Pt/SWNTs	4	50	25	12	29
12	20% Pt/SWNTs	2	50	25	2	32
13	20% Pt/SWNTs	4	50	25	2	33
14	20% Pt/SWNTs	8	50	25	1.5	50

[a] Reaction conditions: 250 μL ethyl pyruvate, 10 mg Pt/SWNTs, and 2 mL toluene.
[b] Time for 100% conversion.
[c] Determined by chiral GC using a Supelco β-dex-225 column (30 m, 0.25 mm).

when 8 mg of Cd was used. The ee value of product was decreased as the amount of Cd was further increased to 10 mg and 12 mg (Fig. 5, line a). To understand the implication of the maximum of ee at the point where 8 mg of Cd was used, we studied the behavior of absorption of Cd on the surface of Pt/SWNTs. The mixture of 10 mg of 20% Pt/SWNTs nanocatalyst and different amounts of Cd in toluene (2.0 mL) was ultrasonically treated for 30 min, and then 250 μL ethyl pyruvate was added to the mixture. The system was then stirred wildly for 15 min to be mixed uniformly and then allowed to stand for 30 min to deposit the solid particles. A portion of clear solution (100 μL) was taken from the top layer of the system, and diluted with 2.0 mL toluene. Then the concentration of Cd in this sample was measured by a UV–vis spectrophotometer to determine the amount of Cd dissolved in the solution, which is the amount of unabsorbed Cd. The amount of Cd absorbed on the Pt/SWNTs surface was obtained by subtraction of dissolved Cd from total amount of Cd. The line b in Fig. 5 clearly shows that the absorption of Cd on the Pt/SWNTs surface was saturated when ∼8 mg Cd was added.
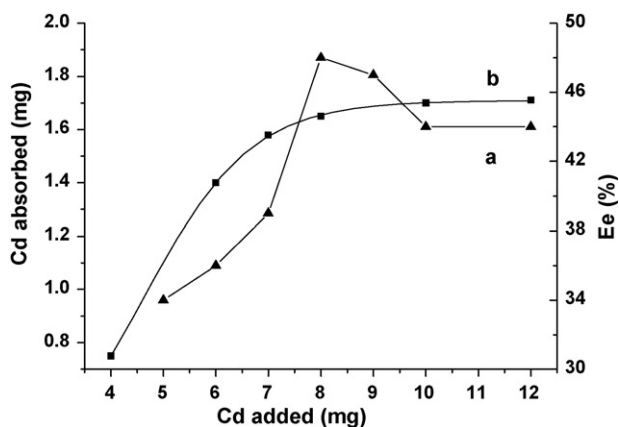

Fig. 5. Line a: the correlation between Ee value of product and the amount of added Cd in the reaction using 20% Pt/SWNTs catalyst. Reaction conditions: 250 μL ethyl pyruvate, 10 mg 20% Pt/SWNTs, 2 mL toluene, 50 atm H_2, 25 °C. Line b: the absorbed amount of Cd.

Thus we could conclude that the highest enantioselectivity was achieved at the point of saturated absorption and using more Cd beyond this point caused a decrease in the enantioselectivity.

4. Conclusion

SWNTs-supported Pt nanoparticle catalysts with controlled Pt loadings have been prepared by a simple method and were characterized by TEM and XRD. Modified by (−)-cinchonidine these Pt/SWNTs catalysts showed high catalytic activities in the heterogeneous asymmetric hydrogenation of ethyl pyruvate with moderate enantioselectivities, providing a good application of SWNTs-supported metal catalyst in asymmetric synthesis. The high catalytic activity along with a "ligand-acceleration" effect and a unique absorption feature of the surface of SWNTs indicated a potential for wide application of SWNTs-supported metal catalysts in heterogeneous asymmetric synthesis.

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