

# Article (Special Issue for Excellent Research Work in Recognition of Scientists Who Are in Catalysis Field in China)

# Highly oxidized Pt species stabilized inside carbon nanotubes for asymmetric hydrogenation

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### 1. Introduction

# Due to the space confining effect provided by the well-defined one dimensional channel of carbon nanotubes (CNTs), catalysis inside CNTs has received attention. Several types of catalytic reactions in CNTs have been reported, including liquid phase hydrogenation reactions [1–3] and gas phase reactions [4–9]. In most cases, the activity and/or selectivity were enhanced when the catalytic reaction was confined in the channels of the CNTs. However, the origin of the enhanced catalytic performance still remains unknown for most cases. Only a few reports have focused on understanding the enhanced performance and the explanations were limited to a few reactions [10–13]. In order to understand the origin of the enhanced performance inside CNTs and the nano-space confinement effect, it is imperative to comprehensively investigate the factors that influence the reaction inside the CNTs.

Asymmetric hydrogenation of  $\alpha$ -ketoester on cinchonidine

ABSTRACT

The chemical state and its influence on Pt species in or outside of the channels of CNTs and the effect on the asymmetric hydrogenation of  $\alpha$ -ketoester were investigated. XPS analysis showed that 13% Pt species in a highly oxidized state (Pt<sup>4+</sup>) were stabilized inside the channels in the presence of Na<sup>+</sup>. There were more highly oxidized Pt species inside the CNTs than outside. The highly oxidized Pt species promoted the interaction between the nanoparticle and chiral modifier, which is crucial for high enantioselectivity. Hydrogen temperature programmed desorption showed that Pt nanoparticles confined in the channels can better activate hydrogen, which contributed to their high activity even at low hydrogen pressure.

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(CD) modified Pt catalysts has been regarded as one of the milestones in heterogeneous asymmetric catalysis. New findings and applications can still be seen in recent years [14–16]. CNTs have been used as the support to load metals for asymmetric hydrogenation [17,18]. But the initial research did not focus on introducing metal nanoparticles into the channels of the CNTs. Our previous study demonstrated heterogeneous asymmetric catalysis confined within the CNTs [19] (Scheme 1). It was found that the catalytic performance of Pt nanoparticles encapsulated in the channels (denoted as Pt/CNTs(in)) in the asymmetric hydrogenation of  $\alpha$ -ketoesters was much better than that of Pt nanoparticles outside the channels (denoted as Pt/CNTs(out)) [14] (Fig. 1). A trace amount of water in the solvent was found to further promote the performance of Pt/CNTs(in). For the reaction in an anhydrous solvent, Pt/CNTs(in) was still superior to Pt/CNTs(out) [20]. Using another widely studied asymmetric hydrogenation of  $\alpha$ , $\beta$ -unsaturated acid on CD modified Pd catalysts [21–23], we

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cinchonidine (CD) Scheme 1. Asymmetric hydrogenation of ethyl pyruvate (EtPy).



**Fig. 1.** TEM images of (a) Pt nanocatalyst confined inside the CNT nanochannels (Pt/CNTs(in)) and (b) Pt nanocatalyst loaded onto the outer surface of the CNTs (Pt/CNTs(out)).

also found that Pd nanoparticles inside CNTs delivered better performance than Pd nanoparticles outside the channels [24]. However, the main factors giving this significant difference are still not known. We previously suggested that the difference in catalytic performance is partly related to the enrichment of the chiral modifier CD and reactant in the channels [19,20,24]. Besides the enrichment effect, other possible factors such as the Pt nanoparticles and hydrogen pressure may also contribute to the enhanced performance of confined Pt nanoparticles. In this paper, we show that Pt species in a highly oxidized state can be stabilized inside the channels of CNTs in the presence of Na+, and that this benefits the interaction between the nanoparticles and chiral modifier, resulting in high enantioselectivity. Pt nanoparticles confined in the channels also had a stronger hydrogen adsorption, which may be further responsible for the high activity.

### 2. Experimental

### 2.1. Catalyst preparation

The loading of Pt for all the catalysts were 5 wt.% (weight percent). Pt/CNTs(in) and Pt/CNTs(out) were prepared according to our previous report [19]. The pristine CNTs were first oxidized by HNO<sub>3</sub> (68 wt.%) at 140 °C for 12 h, and then filtered and washed with deionized water, then dried at 60 °C for 18 h.

Pt/CNTs(in) was prepared as follows. The oxidized CNTs (1.0 g) were immersed in an aqueous solution of  $H_2PtCl_6$  (25 mL, 10.25 mmol/L) followed by an ultrasonic treatment for 3 h. Then the mixture was stirred for 48 h at room temperature, slowly heated to 110 °C at the rate of 1 °C/min and held at 110 °C for 24 h. The slow drying method was beneficial to introducing the Pt precursor into the channels. The dried mixture was reduced in a sodium formate solution (42 mg/mL) at 90 °C for 1 h, filtrated, washed with deionized water and dried at 80 °C for 18 h.

For the preparation of Pt/CNTs(out), the oxidized CNTs (1.0 g) were immersed in xylene (25 mL) followed by an ultrasonic treatment for 3 h at room temperature. After the addition of  $H_2PtCl_6$  solution (2.72 mL, 94.21 mmol/L), the mixture was stirred for 0.5 h. Then the mixture was also reduced with sodium formate solution as described in the preparation of Pt/CNTs(in), filtered, and dispersed in ethanol (50 mL) for extraction of the residual xylene for 5 times. Finally the mixture was filtered and washed with deionized water and dried at 80 °C for 18 h.

Two reference catalysts were also prepared. After the introduction of the Pt precursor into the channels and the drying procedure, the catalyst was pre-reduced in a hydrogen stream at 90 °C for 1 h instead of in sodium formate solution (denoted as Pt/CNTs(in-H<sub>2</sub>)). The Pt nanoparticles of Pt/CNTs(in-H<sub>2</sub>) were well dispersed in the channels of CNTs. The catalyst with Pt nanoparticles randomly dispersed inside and outside the channels of CNTs (1.0 g) were immersed in an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> (25 mL, 10.25 mmol/L) and stirred



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for 6 h at room temperature. The mixture was heated to 110 °C at the rate of 5 °C/min and held at 110 °C for 24 h. The dried sample was reduced in H<sub>2</sub> stream at 90 °C for 1 h instead.

All the catalysts described above were stored in air.

### 2.2. Catalyst test

General procedure for hydrogenation: Take Pt/CNTs(in) as an example. 10 mg of Pt/CNTs(in) was pretreated for a set time in a H<sub>2</sub> stream at a set temperature. Under standard conditions, the reaction was carried out using 10 mg pretreated catalysts, 2 mL solvent and 2 mg cinchonidine in a 100 mL of stainless-steel autoclave. The substrate (0.1 mL) was added after magnetically stirring the mixture under H<sub>2</sub> for 2 min. Then the autoclave was purged with H<sub>2</sub> for 4 times to eliminate residual air, followed by setting the final H<sub>2</sub> pressure to 4–6 MPa. The reaction was carried out by magnetically stirring for a set time at room temperature. Then the catalyst was centrifuged, and the supernatant organic layer was diluted with ethanol. For EtPy, the conversion and enantiomeric excess were determined on a gas chromatograph (Agilent 6890) equipped with HP 19091G-B213 capillary column (30 m × 0.32  $\mu$ m × 0.25  $\mu$ m).

The activity of the hydrogenation was expressed as the average turnover frequency (TOF). TOF = ( $[M_0]$  × conversion)/( $[M_{Pt}]$  ×  $D_{Pt}$  × (reaction time)). [ $M_0$ ] is the initial molar concentration of the reactant. [ $M_{Pt}$ ] is the Pt molar concentration used in the reaction.  $D_{Pt}$  is the metal dispersion of Pt obtained by CO chemisorption. The ee (%) of the *R* isomer was expressed as ee (%) = ([R] - [S]) × 100/([S] + [R]).

### 2.3. Catalyst characterization

TEM images were obtained on a TECNAI G<sup>2</sup> electron microscope with an accelerating voltage of 100 kV. For the TEM measurement, the powder sample was dispersed in ethanol and dripped onto a copper grid covered with a carbon film and then dried in air. N2 adsorption was performed on a Micromeritics ASAP 2020 volumetric adsorption analyzer after the sample was outgassed at 120 °C for 6 h. H<sub>2</sub>-TPD was carried out on a Micromeritics AutoChem 2910 analyzer after the sample was outgassed at 120 °C for 6 h before H<sub>2</sub> adsorption. After the adsorption reached equilibrium, the sample was heated at the rate of 10 °C/min to 900 °C. CO chemisorption was performed on a Quantachrome AUTOSORB-1-MS volumetric adsorption analyzer after the sample was outgassed at 120 °C for 6 h. X-ray photoelectron spectroscopic analysis of the catalysts was performed on a VG ESCAB mk-2 instrument using Al  $K_{\alpha}$ (1486.6 eV, 12.5 kV, 250 W) radiation. The sample was pressed into a sample holder and evacuated to  $0.4-0.8 \times 10^{-6}$  Pa for 12 h. Then the sample was in situ reduced in H<sub>2</sub> at a set temperature before the measurement.

Adsorption of CD and EtPy on the catalyst was carried out as follows. The catalyst was first pretreated in a  $H_2$  stream at 225 °C for 2 h before the adsorption. The working solution of CD was made by dissolving 5 mg CD in 100 mL of acetic acid. The mixture of catalyst (20 mg) and the working solution of CD (4 mL) was stirred at room temperature for a set time, followed by centrifuging. 2 mL of the supernatant was extracted and analyzed on a SHIMADZU UV-2550 UV/Vis spectrophotometer using acetic acid solution for reference. For the adsorption of EtPy, the working solution was made by dissolving 1.342 mmol of EtPy in 100 mL of acetic acid. 20 mg of catalyst was dispersed in 4 mL work solution and stirred for a set time. Then 2 mL of supernatant was taken out and analyzed by GC. The adsorption molar ratio of CD or EtPy was defined as Adsorption molar ratio = 1 – (Concentration in supernatant)/(Original concentration in working solution).

### 3. Results and discussion

### 3.1. Chemical state of the platinum species

Using X-ray photoelectron spectroscopy (XPS), we analyzed the composition of carbon and Pt species in Pt/CNTs(in) and Pt/CNTs(out). No obvious difference in the distribution of carbon species of Pt/CNTs(in) and Pt/CNTs(out), and little difference after the reduction treatment was found.

The deconvolution of the Pt 4f region illustrated that there were three Pt species in the Pt/CNTs. The doublet with the binding energy of 71.0 (Pt  $4f_{7/2}$ ) and 74.45 eV (Pt  $4f_{5/2}$ ) can be attributed to metallic Pt (Pt<sup>0</sup>), the doublet at 74.0 eV (Pt  $4f_{7/2}$ ) and 77.45 eV (Pt  $4f_{5/2}$ ) to PtO (Pt<sup>2+</sup>) species and the doublet at 75.0 eV (Pt  $4f_{7/2}$ ) and 78.45 eV (Pt  $4f_{5/2}$ ) to PtO<sub>2</sub> (Pt<sup>4+</sup>) species [25]. With increasing reduction, higher reduction temperature and longer reduction time, the amount of unreduced oxidized Pt species decreased while that of Pt<sup>0</sup> increased (Table 1, entries 1–4).

The catalytic activity of the Pt/CNTs catalysts was tested with the hydrogenation of EtPy. The results are listed in Table 1. For the hydrogenation of  $\alpha$ -ketoester, Pt<sup>0</sup> is the active site for the activation of hydrogen, adsorption of the chiral modifier, and hydrogenation of  $\alpha$ -ketoester [26,27]. The reference experiments indicated that the asymmetric hydrogenation of  $\alpha$ -ketoester did not proceed without the Pt<sup>0</sup> species (Table 2). So the Pt<sup>0</sup> species is the primary active site in the reaction. However, when the amounts of Pt<sup>0</sup> in Pt/CNTs(in) and Pt/CNTs(out) were further increased by a higher reduction temperature, the enantioselectivity was decreased (Table 1,

Table 1

XPS spectra data and activity of Pt catalysts in the asymmetric hydrogenation of EtPy.

Entry	Catalyst	Method	Pt <sup>0</sup>	Pt <sup>2+</sup>	Pt4+	TOF	ee
						(10 <sup>4</sup> h <sup>-1</sup> )	(%)
1	Pt/CNTs(in)	А	63.7	22.9	13.4	9.6	95
2	Pt/CNTs(in)	В	79.5	13.4	7.1	7.7	90
3	Pt/CNTs(out)	А	67.3	32.7	0	1.6	74
4	Pt/CNTs(out)	В	79.6	20.4	0	0.2	62
5	Pt/AC	А	60.3	39.7	0	0.7	61
6	Pt/Al <sub>2</sub> O <sub>3</sub>	А	81.7	5.0	13.3	1.0	90

Conditions: 10 mg of Pt/CNTs, 2.0 mg cinchonidine (6.725  $\mu$ mol), 0.2 mL of substrate, 2 mL acetic acid (containing 0.96 wt.% water), H<sub>2</sub> pressure of 6.5 MPa, 20 °C. Reaction time: 1 min for Pt/CNTs(in) and 3 min for the others.

A—H $_2$  reduction at 225 °C for 2 h before test.

B-H<sub>2</sub> reduction at 400 °C for 2 h before test.

Table 2 Catalytic activity of Pt/CNTs and Pt precursor species in the asymmetric hydrogenation of EtPy.

Entry	Catalyst	Conversion (%)	ee (%)
1	K <sub>2</sub> PtCl <sub>4</sub> <sup>a</sup>	0	0
2	$H_2PtCl_6a$	0	0
3	PtO <sub>2</sub> <sup>a</sup>	0	0
4	Pt/CNTs(in) <sup>a</sup>	>95	95
5	Pt/CNTs(out) <sup>a</sup>	>95	75
6	Pt/CNTs(in-H <sub>2</sub> ) <sup>b</sup>	56	60

Conditions: 0.5 mg Pt, 2.0 mg cinchonidine (6.725 µmol), 0.2 mL of substrate, 2 mL acetic acid, H<sub>2</sub> pressure of 6.5 MPa, 25 °C. Reaction time: <sup>a</sup> 10 min; <sup>b</sup> 1 min.

entries 1-4). Thus, we considered that for Pt/CNTs(in) and Pt/CNTs(out), besides Pt<sup>0</sup> as the primary active site, another component of the Pt nanoparticles, possibly some unreduced oxidized Pt species played a role in the reactions.

As listed in Table 1, the major difference between Pt/CNTs(in) and Pt/CNTs(out) was the composition of the oxidized Pt species. For Pt/CNTs(out), no highly oxidized Pt species (Pt<sup>4+</sup>) were detected when it was reduced at 225 °C for 2 h (Method A, Table 1, entry 3). As for Pt/CNTs(in), the Pt<sup>4+</sup> species still remained at 13% (Table 1, entry 1). It is noteworthy that the Pt4+ species in Pt/CNTs(in) even remained at 7% after it was reduced at 400 °C for 2 h (Method B, Table 1, entry 2). Two representative commercial Pt catalysts, Pt/AC and Pt/Al<sub>2</sub>O<sub>3</sub> were also investigated (Table 1, entries 5, 6). The XPS results showed that no Pt4+ species existed in commercial Pt/AC after reduction in a  $H_2$  stream at 225 °C for 2 h (Method A) and only moderate enantioselectivity (61% ee) was obtained (Table 1, entry 5). For the commercial Pt/Al<sub>2</sub>O<sub>3</sub>, 13% Pt4+ species remained after reduction in a H<sub>2</sub> stream at 225 °C for 2 h (Method A, Table 1, entry 6) and 90% enantioselectivity was achieved (Table 1, entry 6). The binding energy of Al 2p in Al<sub>2</sub>O<sub>3</sub> is centered at 74.7 eV, which was enveloped by the Pt 4f region from 71-77 eV [28], making it difficult to accurately analyze the composition of the Pt species. Only a few studies on the XPS analysis of Pt species in Pt/Al<sub>2</sub>O<sub>3</sub> have been reported [29-32]. However, the promotion effect of oxidized Pt species in Pt/Al<sub>2</sub>O<sub>3</sub> on a reaction such as propane oxidation was observed [32]. So the important role of the oxidized Pt species, especially the highly oxidized Pt species (Pt4+), in the asymmetric hydrogenation of  $\alpha$ -ketoester may have been missed in the previous study. The XPS analysis showed that more highly oxidized Pt species can be stabilized within the channels of the CNTs.

To understand the role of the oxidized Pt species, the mechanism of this reaction has to be considered. The reaction mechanism of the asymmetric hydrogenation of  $\alpha$ -ketoester has been extensively studied since its discovery by Orito et al. [33,34]. There is much discussion of this in several recent reviews [35-38]. The widely accepted conclusions about the mechanism can be summarized as follows. Hydrogen is dissociatively adsorbed on the Pt surface. In the situation that most favor the enantioselectivity, the cinchona modifier is anchored on the Pt surface through its quinoline ring using the SO3 configuration. The quinuclidine N of the cinchona modifier is protonated by either the dissociated H or the proton from the protic solvent, such as acetic acid, and it then interacts with the  $\alpha$ -ketoester through the N–H–O bond, which was confirmed by theoretical calculations [39] and in situ IR spectroscopy results[27,40]. Based on our results, we propose that the role of the oxidized Pt species is also important in the reaction. As shown in Fig. 2, the existence of the oxidized Pt species, especially the highly oxidized Pt species, increase the electrophilicity of Pt nanoparticles, which enhances the interaction between the CD/reactant and Pt nanoparticles. This results in a better chiral environment on the surface of the Pt nanoparticles for high enantioselectivity.

Figure 3 shows the adsorption of CD by Pt/CNTs(in), Pt/CNTs(out) and oxidized CNTs (denoted as ox-CNTs, used as the support). The adsorption fraction on Pt/CNTs(in) reached 90%, which is higher than that on Pt/CNTs(out) and ox-CNTs. We suggest that this high CD adsorption fraction on Pt/CNTs(in) was due to there being more electrophilic Pt nanoparticles confined in the channels. For Pt/CNTs(out), the Pt nanoparticles were less electrophilic, which led to almost the same CD adsorption fraction as ox-CNTs.

For the reactant EtPy, the adsorption fraction on Pt/CNTs(in) was also higher than that on Pt/CNTs(out) or ox-CNTs (Fig. 4). The more electrophilic Pt nanoparticles in the channels "entrap" more EtPy through the interaction with the



Fig. 2. Role of oxidized Pt species in CD and EtPy adsorption on Pt nanoparticles inside CNTs.



Fig. 3. Adsorption kinetics of CD versus adsorption time on (1) Pt/CNTs(in), (2) Pt/CNTs(out), and (3) ox-CNTs.



**Fig. 4.** Adsorption kinetics of EtPy versus adsorption time on (1) Pt/CNTs(in), (2) Pt/CNTs(out), and (3) ox-CNTs.

oxygen containing groups of EtPy. From the adsorption results, it can be concluded that ox-CNTs first enrich the CD and EtPy reactants in the channels and then the more electrophilic Pt nanoparticles confined in the channels promote the interaction between CD/EtPy and the Pt nanoparticles.

Besides the role of the oxidized Pt species in the adsorption of the chiral modifier, CD, and reactant, the more fundamental issue is what caused the different distribution of the oxidized Pt species between Pt/CNTs(in) and Pt/CNTs(out). Recently it was reported that residual alkali metal ions (such as Na+, K+) in the catalyst enhanced the catalytic performance of Pt/TiO<sub>2</sub> in formaldehyde oxidation [41] and Pt/SiO<sub>2</sub> in the water-gas shift reaction [42]. One important role of alkali metal ions is to enhance the stability of the Pt species in a highly oxidized state due to the formation of Pt-(ONa)<sub>x</sub> moieties [41–43]. In the preparation of Pt/CNTs(in) and Pt/CNTs(out), sodium formate was used to reduce the Pt precursor. Even after the samples were fully washed with deionized water, the Na+ concentration in Pt/CNTs(in) measured by inductively coupled plasma (ICP) optical emission spectrometry was still as high as 1.7 wt.%, and higher than the 0.6 wt.% in Pt/CNTs(out). In the absence of Pt, only 0.3 wt.% Na+ exist in both ox-CNTs-in and ox-CNTs-out.

To investigate the influence of the residual Na<sup>+</sup> on the distribution of the oxidized Pt species, another two reference catalysts were prepared similar to the preparation of Pt/CNTs(in). The corresponding XPS analysis was carried out. One was denoted as Pt/CNTs(in-H<sub>2</sub>). It was pre-reduced in a hydrogen stream at 90 °C for 1 h instead of in sodium formate solution after the introduction of Pt precursor into the channels and the drying procedure. The Pt nanoparticles of Pt/CNTs(in-H<sub>2</sub>) were well dispersed in the channels of CNTs (Fig. 5(a)). The other reference catalyst was denoted as Pt/CNTs(H<sub>2</sub>), which was prepared similarly to Pt/CNTs(in-H<sub>2</sub>), with Pt nanoparticles randomly dispersed inside and outside the channels of the CNTs (Figure 5(b)). The size of the Pt nanoparticles in Pt/CNTs(in-H<sub>2</sub>) and Pt/CNTs(H<sub>2</sub>) were almost identical to those in Pt/CNTs(in) or Pt/CNTs(out) (Table 3).

Table 4 displays the distribution of the oxidized Pt species in Pt/CNTs(in), Pt/CNTs(in-H<sub>2</sub>), Pt/CNTs(H<sub>2</sub>) and Pt/CNTs(out), and their catalytic activity in the asymmetric hydrogenation of



Fig. 5. TEM images of (a)Pt/CNTs(in-H<sub>2</sub>) and (b) Pt/CNTs(H<sub>2</sub>).

EtPy. The residual Na<sup>+</sup> influenced the distribution of the oxidized Pt species. For Pt/CNTs(in-H<sub>2</sub>) with no Na<sup>+</sup> residual, although the oxidized Pt species was 35% of the Pt species, no highly oxidized Pt species existed after it was reduced in a hydrogen stream at 225 °C for 2 h (Method A, Table 4, entry 3). Pt/CNTs(in-H<sub>2</sub>) as the catalyst gave only 72% enantioselectivity. Due to the absence of residual Na<sup>+</sup>, Pt/CNTs(H<sub>2</sub>) showed a

### Table 3

Metal dispersion and Pt nanoparticle size of Pt/CNTs determined by CO chemisorption.

Catalyst	Active metal surface aera	Metal dispersion	Average Pt particles size
	(m²/g)	(%)	(nm)
Pt/CNTs(in) <sup>A</sup>	3.8	31	3.7
Pt/CNTs(in) <sup>B</sup>	3.6	29	3.9
Pt/CNTs(in) <sup>c</sup>	3.4	28	4.1
Pt/CNTs(out) <sup>A</sup>	3.8	31	3.7
Pt/CNTs(out) <sup>B</sup>	3.4	28	4.1
Pt/CNTs(out) <sup>c</sup>	3.4	27	4.2
Pt/CNTs(in-H <sub>2</sub> ) <sup>A</sup>	3.7	30	3.7
Pt/CNTs(H <sub>2</sub> ) <sup>A</sup>	3.4	28	4.1

A—Catalyst treated in 225  $^{\circ}C$  H\_{2} stream for 2 h after the sample was outgassed at 120  $^{\circ}C$  for 6 h.

B—Catalyst treated in 300  $^\circ C$  H\_2 stream for 2 h after the sample was outgassed at 120  $^\circ C$  for 6 h.

C—Catalyst treated in 400  $^\circ C$  H\_2 stream for 2 h after the sample was outgassed at 120  $^\circ C$  for 6 h.

### Table 4

XPS data and catalytic activity of Pt/CNTs(in), Pt/CNTs(out) and the reference catalysts in the asymmetric hydrogenation of EtPy.

Entry	Catalyst	Method	Pt <sup>0</sup>	Pt <sup>2+</sup>	Pt <sup>4+</sup>	[Na+]	TOF	ee
						(wt.%)	$(10^4 h^{-1})$	(%)
1	Pt/CNTs(in)	А	63.7	22.9	13.4	1.7	9.6	95
2	Pt/CNTs(in)	В	79.5	13.4	7.1	1.7	7.4	90
3	Pt/CNTs(in-H <sub>2</sub> )	А	64.6	35.4	0	0	8.1	72
4	Pt/CNTs(in-H <sub>2</sub> )	В	80.4	19.6	0	0	5.9	60
5	Pt/CNTs(H <sub>2</sub> )	А	61.7	38.3	0	0	3.9	71
6	Pt/CNTs(H <sub>2</sub> )	В	80.6	19.4	0	0	2.1	62
7	Pt/CNTs(out)	А	67.3	32.7	0	0.6	1.3	74
8	Pt/CNTs(out)	В	79.6	20.4	0	0.6	0.2	62

Reaction conditions: 10 mg of Pt/CNTs, 2.0 mg cinchonidine (6.725  $\mu$ mol), 0.2 mL of substrate, 2 mL acetic acid (containing 0.96 wt.% water), H<sub>2</sub> pressure of 6.5 MPa, 20 °C. Reaction time: 3 min for Pt/CNTs(out) and 1 min for others.

A—H<sub>2</sub> reduction at 225 °C for 2 h before test.

B-H<sub>2</sub> reduction at 400 °C for 2 h before test.

similar distribution of the oxidized Pt species as  $Pt/CNTs(in-H_2)$  and gave 71% enantioselectivity (Table 4, entry 5). By comparing the distribution of the oxidized Pt species of these four catalysts, we concluded that residual  $Na^+$  in the catalyst played an important role in stabilizing the oxidized Pt species, especially the highly oxidized Pt species, which are crucial for high enantioselectivity in the asymmetric hydrogenation of EtPy.

The adsorption of CD and EtPy on Pt/CNTs(in-H<sub>2</sub>) showed that the CD and EtPy adsorption molar fraction on Pt/CNTs(in-H<sub>2</sub>) with no residual Na<sup>+</sup> was lower than that on Pt/CNTs(in) with more highly oxidized Pt species (Figs. 6 and 7).

The results above showed that the difference in the distribution of the oxidized Pt species between Pt/CNTs(in) and Pt/CNTs(out) was dependent on the Na<sup>+</sup> residual amounts. More highly oxidized Pt species were stabilized when there is Na<sup>+</sup> in the channels of the CNTs. The highly oxidized Pt species promoted the interaction between CD/EtPy and the Pt nanoparticles, which is crucial for high enantioselectivity in the asymmetric hydrogenation of EtPy. However, the influence of the oxidized Pt species on the activity was not obvious.

### 3.2. Hydrogen adsorption activity of the catalysts

Hydrogen temperature programmed desorption ( $H_2$ -TPD) data are displayed in Fig. 8, which showed that no hydrogen desorption was detected below 500 °C for the pristine CNTs



**Fig. 6.** Adsorption of CD versus adsorption time on (1) Pt/CNTs(in) and (2) Pt/CNTs(in-H<sub>2</sub>).



**Fig. 7.** Adsorption of EtPy versus adsorption time on (1) Pt/CNTs(in) and (2) Pt/CNTs(in-H<sub>2</sub>).



**Fig. 8.** H<sub>2</sub>-TPD profiles of (1) pristine CNTs, (2) ox-CNTs, (3) Pt/CNTs (in), and (4) Pt/CNTs(out).

and oxidized CNTs (denoted as ox-CNTs, used as the support). The hydrogen desorption above 600 °C can be attributed to the decomposition of CH• in CNTs-pristine and CNTs-oxide [44]. Both Pt/CNTs(in) and Pt/CNTs(out) have a wide desorption peak from 200 to 400 °C and a small desorption peak at 120 °C. For Pt/CNTs(in), the hydrogen desorption peaks at 120 °C and 330 °C were much larger than those of Pt/CNTs(in-H<sub>2</sub>) and Pt/CNTs(out).

The hydrogen desorption peaks in the range of 400 °C to 600 °C can be ascribed to the desorption of chemisorbed hydrogen on Pt [45,46]. The desorption peaks at 300 °C and even lower temperatures indicated a weaker interaction between hydrogen and Pt. This weak interaction can be ascribed to weakly bonded hydrogen on Pt that has a higher hydrogenation activity [47]. The H<sub>2</sub>-TPD result clearly showed that Pt/CNTs(in) has more more active hydrogen than Pt/CNTs(out) as the amount of hydrogen in the lower temperature region was more for Pt/CNTs(in) than Pt/CNTs(out).

Considering the limited space in the channels, the hydrogen concentration around the Pt nanoparticles confined in the channels was much higher than that around the Pt nanoparticles outside the channels. Recent theoretical simulations also indicated that hydrogen is enriched in the channels of CNTs [48]. Inspired by the H<sub>2</sub>-TPD results, the asymmetric hydrogenation of EtPy under different hydrogen pressure was conducted to investigate the influence of hydrogen adsorption activity on the catalytic activity of Pt/CNTs(in) and Pt/CNTs(out) (Table 5). With the decrease of hydrogen pressure from 6.5 to 0.1 MPa, the TOF of Pt/CNTs(out) decreased significantly from  $1.6 \times 10^4$  to  $140 h^{-1}$  (Table 5, entries 4 and 6). However, Pt/CNTs(in) could still maintain a high TOF at a hydrogen pressure of 0.1 MPa (Pt/CNTs(in): 0.6 × 10<sup>4</sup> h<sup>-1</sup>, Table 5, entry 3). From the reaction conditions in Table 5, it can be proposed that the reaction rate can be expressed by the following kinetic equations:

$$R_{\rm out} = k P_{\rm out}^n \tag{1}$$

$$P_{\rm in} = K_{\rm P} P_{\rm out} \tag{2}$$

$$R_{\rm in} = k P_{\rm in}{}^n = k (K_{\rm P} P_{\rm out})^n \tag{3}$$

*R* stands for the reaction rate of the asymmetric hydrogenation of EtPy, *k* stands for the rate constant, *P* stands for the hy-

Table 5	
Catalytic activity of Pt/CNTs(in) and Pt/CNTs(out) under different	H <sub>2</sub>
pressures in the asymmetric hydrogenation of EtPy.	

Entry	Catalyst	H <sub>2</sub> (MPa)	TOF (h <sup>-1</sup> )	ee (%)
1	Pt/CNTs(in)	6.5	$9.6 \times 10^{4}$	95
2	Pt/CNTs(in)	1.0	$1.5 \times 10^{4}$	88
3	Pt/CNTs(in)	0.1	$0.6 \times 10^{4}$	86
4	Pt/CNTs(out)	6.5	$1.6 \times 10^{4}$	74
5	Pt/CNTs(out)	1.0	210	62
6	Pt/CNTs(out)	0.1	140	60

Reaction conditions: 10 mg of Pt/CNTs, 2.0 mg cinchonidine (6.725  $\mu$ mol), 0.1 mL of substrate, 2 mL acetic acid (containing 0.96 wt.% water), 25 °C. Reaction time: 1 min for Pt/CNTs(in) and 3 min for Pt/CNTs(out).

drogen pressure and  $K_P$  is defined as the enrichment factor of Pt/CNTs(in) under a hydrogen pressure of *P*. From the results in Table 5 (entry 4 and 5), the index n in Eq. (1) was estimated to be 2.3. Therefore, the enrichment factor  $K_P$  under different hydrogen pressures can be calculated. For Pt/CNTs(in),  $K_{6.5 \text{ MPa}} = 2.3$ ;  $K_{1.0 \text{ MPa}} = 6.3$ ;  $K_{0.1 \text{ MPa}} = 5.2$ . From the kinetic point of view, hydrogen was enriched in the channels, which led to the much higher activity of Pt/CNTs(in) than that of Pt/CNTs(out) at low hydrogen pressure. These results clearly demonstrated that the enrichment of hydrogen in the channels also contributed to the high activity.

### 4. Conclusions

Highly oxidized Pt species can be stabilized inside the channels of CNTs when Na<sup>+</sup> is present. The more electrophilic Pt species in the highly oxidized state promoted the interaction between the chiral modifier/reactant with the Pt nanoparticles, which is crucial for high enantioselectivity in the asymmetric hydrogenation of EtPy. The enrichment of hydrogen in the channels also contributed to the high activity. These results provide information for understanding why the catalytic performance of Pt located inside the channels of CNTs is much higher than that outside the channels. This work also revealed that the function of the CNTs as a nano-reactor is not only to enrich the molecules inside the channels but also to stabilize the chemical state of Pt in the higher oxidative state.

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