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Highly oxidized Pt species stabilized inside carbon nanotubes for asymmetric hydrogenation

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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 α-ketoester were investigated. XPS analysis showed that 13% Pt species in a highly oxidized state (Pt^{4+}) were stabilized inside the channels in the presence of Na^{+}. 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.

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 α-ketoester on cinchonidine (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 α-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 α,β-unsaturated acid on CD modified Pd catalysts [21–23], we

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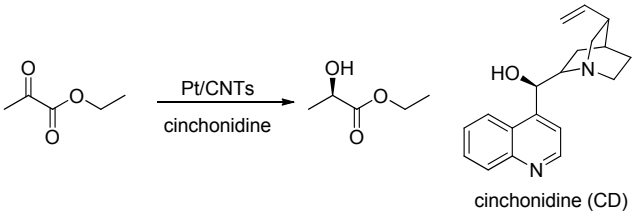

Scheme 1. Asymmetric hydrogenation of ethyl pyruvate (EtPy).

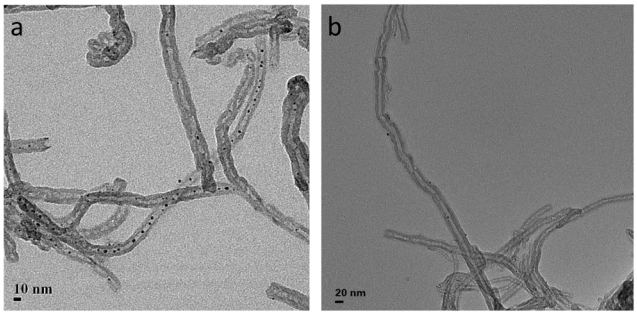

Fig. 1. TEM images of (a) Pt nanocatalyst confined inside the CNT nanochannels (Pt/CNTs(in)) and (b) Pt nanocatalyst loaded onto the outer surface of the CNTs (Pt/CNTs(out)).

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_3 (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_2)). The Pt nanoparticles of Pt/CNTs(in-H_2) were well dispersed in the channels of CNTs. The catalyst with Pt nanoparticles randomly dispersed inside and outside the channels of CNTs was prepared (denoted as Pt/CNTs(H_2)). The oxidized CNTs (1.0 g) were immersed in an aqueous solution of H_2PtCl_6 (25 mL, 10.25 mmol/L) and stirred

Can Li *(Dalian Institute of Chemical Physics, Chinese Academy of Science)* ***received the Catalysis Achievement Award (the Dayu Zhang Award) in 2014****, which was presented by The Catalysis Society of China. Professor Can Li received his Ph.D. degree in Physical Chemistry from Dalian Institute of Chemical Physics, Chinese Academy of Sciences, in 1989, and he joined the same institute and was promoted to full professor in 1993. He did postdoctoral research on catalysis and UV Raman spectroscopy at Northwestern University and was visiting professor at Lehigh University, the University of Liverpool, and The Queensland University, and he was awarded the JSPS Professor at Waseda University, Tokyo University of Technology, and Hokkaido University. He was an invited professor at Université Pierre et Marie Curie, Paris VI. He was the President of the International Association of Catalysis Societies (2008–2012). Currently, he is the director of the State Key Laboratory of Catalysis, and the director of the Dalian National Laboratory for Clean Energy (DNL). His research interests include (1) UV Raman spectroscopy and ultrafast spectroscopy; (2) environmental catalysis and green catalysis; (3) heterogeneous asymmetric catalysis; and (4) solar energy utilization based on photocatalysis, photoelectrocatalysis and photovoltaic cells. He has published more than 500 peer-reviewed papers with over 10 000 citations.*