

## Short Communication

# Enhancing the catalytic activity of carbon nanotubes by filled iron nanowires for selective oxidation of ethylbenzene



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## ARTICLE INFO

## Article history:

Received 13 January 2014

Received in revised form 3 March 2014

Accepted 25 March 2014

Available online 2 April 2014

## Keywords:

Heterogeneous catalysis

Carbon nanotubes

Ethylbenzene

Aerobic oxidation

## ABSTRACT

Iron nanowire filled carbon nanotubes (Fe@CNTs) were synthesized by chemical vapor deposition method and employed as heterogeneous catalysts for selective oxidation of ethylbenzene to acetophenone with molecular oxygen. The results showed that filled iron nanowires efficiently enhanced the catalytic activity of CNTs, arising from improving electron transfer. Moreover, Fe@CNTs could be easily separated from the reaction mixtures by external magnet and displayed excellent stability with no significant loss of catalytic activity after six cycling reactions. The result presented herein paves the way for the development of novel carbon catalysts for the liquid phase oxidation of ethylbenzene.

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## 1. Introduction

Recently, the selective oxidation of ethylbenzene (EB) to higher-value added product acetophenone (AcPO) has received continuous growing interest, because AcPO is used as an important intermediate for the synthesis of pharmaceuticals, perfumes and resins [1,2]. Commercially, AcPO is produced by liquid phase cobalt-catalyzed oxidation of EB using molecular oxygen with acetic acid as solvent and manganese or bromide species as promoters [3,4]. However, not only is it unfriendly to the environment but it is also difficult to separate and recycle the catalysts from the reaction mixture. Fortunately, heterogeneous catalysis can overcome these problems. Especially, ferromagnetic metal filled carbon nanotubes (CNTs) have been widely studied in catalysis owing to their unique structures and significant magnetic properties [5–7]. On the one hand, the ferromagnetic metallic encapsulates are effectively protected by CNTs from oxidation and show long-term stability [8]. On the other hand, the well-defined nanosized channels of CNTs formed by graphene layers provide an intriguing confinement environment for nanocatalysts and catalytic reactions [9]. More importantly, the confined metal nanoparticles into CNTs have already proclaimed the ability to improve the catalytic activity in several important reactions such as syngas conversion [10,11], hydrogenation [12], ammonia decomposition [13] and oxidation [6,14]. The enhancement effect was caused by electron-deficiency, that is, the curvature of CNT walls causes the  $\pi$  electron density of the graphene layers to shift from the concave inner to the convex outer surface, leading to an electron-deficient interior

surface and an electron-enriched exterior surface [9,15]. In our previous work [14], we succeeded in using iron filled CNTs (Fe@CNTs) to catalyze the aerobic oxidation of cyclohexane in liquid phase, and demonstrated that the enhancement of activity was caused by the improved electron transfer from iron to CNTs.

Although the influence of the Fe-filling of CNTs on the catalytic properties has been described for the oxidation of cyclohexane (naphthenic hydrocarbon) for the first time, there is no report on other oxidation reaction systems [14]. Recently, we succeeded in using CNTs to catalyze the aerobic oxidation of ethylbenzene in liquid phase, and demonstrated that the electron transfer in graphene skeletons of CNTs played an important role [16]. Therefore, it is worth further proving our viewpoint in the liquid-phase selective oxidation of ethylbenzene (aromatic hydrocarbon) to acetophenone. Herein, we have further modified the electronic characteristics by filling iron nanowires into CNTs. The results showed that filled iron nanowires efficiently enhanced the catalytic activity of CNTs for aerobic oxidation of EB, arising from improving electron transfer. More importantly, Fe@CNTs could be easily separated from the reaction mixtures through applying an appropriate magnetic field, and exhibited excellent potential for industrial application of EB oxidation to AcPO. The present work clearly shows that it is generally practical to tailor the catalytic performance by tuning electronic property through filling the CNT channels with metallic iron.

## 2. Experimental

Fe@CNTs were prepared by chemical vapor deposition using ferrocene as catalyst and a mixture of xylene and orthodichlorobenzene (DCB) as carbon sources in a horizontal tubular quartz furnace of 8 cm

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inner diameter [8,14]. Typically, the concentration of DCB in the mixture was varied from 0, 2.5, 5, 10 to 20 vol.%. Ferrocene was dissolved in the DCB/xylene mixture to form solutions with concentration of 0.1 g/mL. A quartz slide was placed in the middle of the furnace to collect CNTs. When the temperature of the reaction region reached 800 °C, the solutions were injected by a syringe pump at a rate of 5 mL/h for 3 h, accompanied with 150 sccm H<sub>2</sub> and 1000 sccm Ar, respectively. Cooled under Ar to room temperature prior to exposure to air, the corresponding materials were denoted as Fe@CNTs-0, Fe@CNTs-2.5, Fe@CNTs-5, Fe@CNTs-10 and Fe@CNTs-20, respectively.

To test the role of confined Fe, the unfilled CNTs were prepared by chemical vapor deposition of xylene with Fe–Mo/Al<sub>2</sub>O<sub>3</sub> as a catalyst according to our previous work [17]. To remove residual Fe–Mo/Al<sub>2</sub>O<sub>3</sub> catalyst, as-grown catalysts were stirred in concentrated HCl for 6 h then washed with deionized water to pH = 6–7, and dried in air at 383 K overnight, denoted as CNTs–W. The iron content of CNTs–W was 3.4% by thermal gravimetric analysis (TGA). We also loaded FeO<sub>x</sub> on the CNTs–W to prepare Fe/CNTs–W with 7.8% Fe.

The BET specific surface areas of the prepared samples were measured by N<sub>2</sub> adsorption at liquid N<sub>2</sub> temperature in an ASAP 2010 analyzer. Fe content was measured by thermo gravimetric analysis (Netzsch, STA449C) in air from 30 to 800 °C at a ramping rate of 10 °C/min. Raman spectra were obtained in a LabRAM Aramis micro Raman spectrometer excited at 633 nm with 2 μm spot size. XRD patterns were recorded on a Bruker D8 ADVANCE diffractometer which was equipped with a rotating anode using Cu Kα radiation (40 kV, 40 mA). SEM images were obtained in a LEO 1530VP scanning electron microscope. TEM images were obtained in a JEM-2010 microscope operating at 200 kV. XPS analysis was performed with a Kratos Axis ultra (DLD) spectrometer equipped with an Al Kα X-ray source, the binding energies (±0.2 eV) were referenced to the C<sub>1s</sub> peak at 284.6 eV.

The catalytic aerobic oxidation of EB was carried out according to our previous work [16]. Typically, the oxidation reactions were conducted in a Teflon-lined 100 mL stainless-steel autoclave equipped with a magnetic stirrer at 1100 rpm. EB (5 mL) and CH<sub>3</sub>CN (30 mL) as the solvent,

and anisole (1 mL) as an internal standard were added into the autoclave, and the reactor was flushed with argon to remove air. Then, the reactor was heated to a stable operational temperature; subsequently, pure O<sub>2</sub> was fed into the reactor, and the pressure was kept constant by supplying pure O<sub>2</sub> during the reaction. The products were identified by a Shimadzu GCMS-QP2010 detector and quantitated by Agilent GC-6820 equipped with a 30 m × 0.25 mm × 0.25 μm HP-5 capillary column and a flame ionization detector. It is worth noting that the yield of 1-phenyl-ethyl-hydroperoxide (PEHP) could not be directly measured by GC because of its thermal stability. According to literature [18,19], PEHP can be converted quantitatively to 1-phenyl-ethyl alcohol (PEA) with excessive Ph<sub>3</sub>P at room temperature. Furthermore, for the test of reusability, the used catalyst was recovered from the reaction mixture by an external magnetic force, washed orderly with deionized water, ethanol and acetone, and dried in air. The experimental results of oxidation reaction were repeated two times, the mean data were shown. The range of experimental errors was about ±5%.

### 3. Results and discussion

#### 3.1. Characterization of catalysts

Fig. 1 shows the SEM and TEM images of the synthesized catalysts. Without DCB, a well-aligned CNT array was obtained, while added DCB resulted in random orientation of CNTs. TEM images reveal that some CNTs were partially filled with long continuous Fe nanowires and the filling ratio of Fe dramatically increased with the content of DCB in the precursors increasing. Surprisingly, almost no Fe nanoparticles were attached on the outer surface of CNTs.

Fig. 2(a) depicts the XRD patterns of the synthesized catalysts. The main diffraction peaks in the 10° < θ < 70° can be assigned to α-Fe, γ-Fe and graphite structure of CNTs [20,21]. It indicates that Fe nanowires in synthesized samples are composed of α-Fe and γ-Fe phases. Fig. 2(b) shows the TGA profiles of the synthesized catalysts. No remarkable weight loss occurs before 500 °C in air, demonstrating that they possess high thermal stability and the content of amorphous

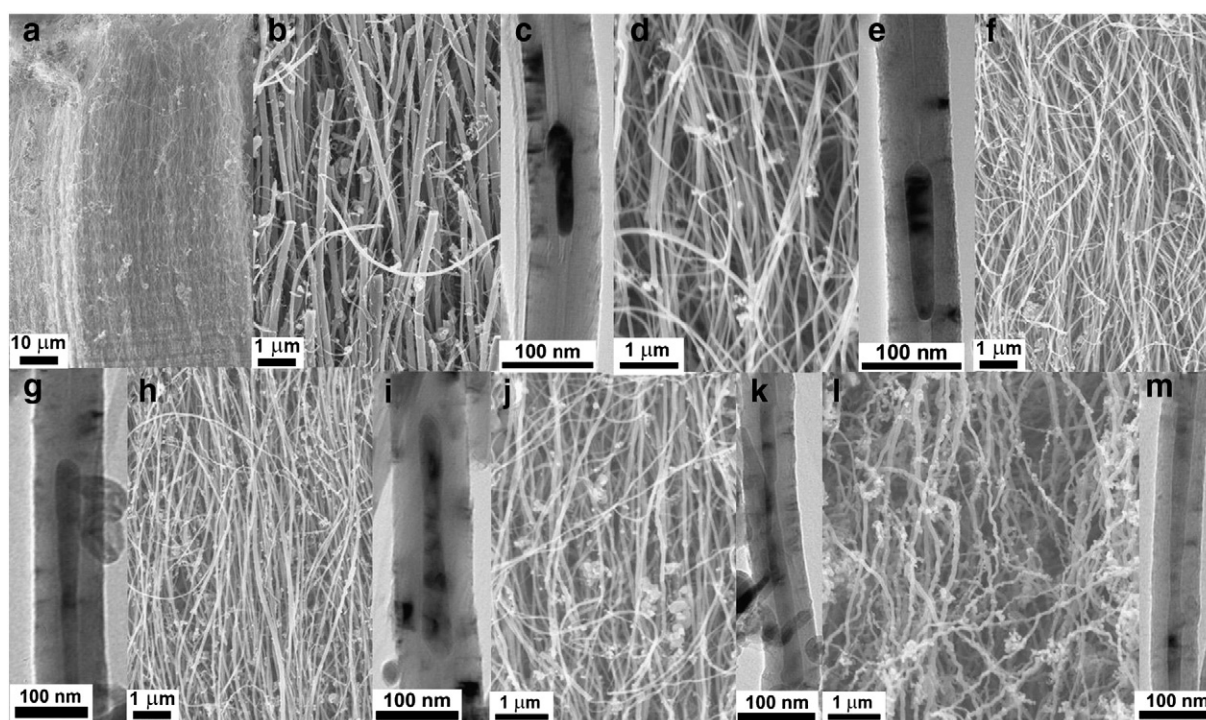


Fig. 1. SEM (a, b, d, f, h, j and l) and TEM (c, e, g, i, k and m) images of the Fe@CNTs (a, b and c), Fe@CNTs-2.5 (d and e), Fe@CNTs-5 (f and g), used Fe@CNTs-5 for 6th cycle (h and i), Fe@CNTs-10 (j and k) and Fe@CNTs-20 (l and m).

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