



Filled cobalt nanoparticles into carbon nanotubes as a rapid and high-efficiency catalyst for selective epoxidation of styrene with molecular oxygen



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HIGHLIGHTS

- Cobalt nanoparticles uniformly dispersed in carbon nanotubes with wet chemistry method.
- Our reaction time is the shortest and yield is the highest at appropriate temperature.
- The catalysts were recycled three times without significant loss activity.

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ABSTRACT

A new nanocatalyst has been synthesized by a simple and effective wet chemical method confined magnetic cobalt nanoparticles within carbon nanotubes (CNTs). We characterized the catalysts by transmission electron microscopy (TEM), X-ray powder diffraction (XRD) and vibrating sample magnetometer (VSM). The TEM results demonstrated that the cobalt nanoparticles were filled into the CNTs successfully. In the meantime, the CNTs mesostructure were not destroyed in multistep synthetic procedure. In the catalytic activity test, liquid phase epoxidation of styrene by molecular oxygen was carried out at atmospheric pressure employed Co/CNTs (in) catalysts. The results showed that styrene conversion over 99% and epoxide selectivity of 93% for 1 h reaction. The catalysts can be easily separated from the reaction mixtures by external magnet, and reused three times without significant loss in catalytic activity.

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1. Introduction

Carbon nanotubes (CNTs), which were discovered in 1991 [1], have attracted intensive interests in many important research fields [2–4]. Carbon nanotubes can be regarded as graphite with cylindrical hollow micro-crystals having their own unique properties [5,6]. Such as excellent electronic conductivity [7], good resistance to acidic/basic chemicals at high temperature, tunable surface properties [8], mechanical strength and thermal stability. All carbons form a seamless shell and each carbon is completely bonded to three neighboring carbon atoms by sp^2 hybridization. These structures can be used as nanoreactors and to create novel composites through the encapsulation of guest materials in their well-defined channels. The unique structures restrict the size of the encapsulated materials down to the nanometer and even the subnanometer scale. In the last decade, studies have shown the

benefits of CNTs, which as supports to disperse transition metal (such as cobalt oxide, nickel oxide, copper oxide and iron oxide, and so on) on their surface for hydrogenation reactions and electro-catalysis reactions [2,9–12].

CNTs distinguish themselves from other support materials, e.g., Al_2O_3 , SSZ-51, SBA-15, MSM-41 and even activated carbon support catalysts [12–15], in that they have rolled graphene sheets framework and properties of sp^2 hybridized carbon atoms [8], such as originality materials for electronics, catalysis and polymer reinforcements for composites. CNTs supported nanoparticles for catalysis have been reported in many literatures, and for reactions have resulted in an improved conversion and/or product selectivity [16,17]. Nevertheless, transition metal catalysts located CNTs outer surface versus on the inside is less efforts to carry out some reactions [18–20]. Metal nanoparticles in CNTs can give birth to a surprising and exciting catalytic capability [21], because of the curvature of CNT walls causes the π 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

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electron-enriched exterior surface [22]. As a result, the interaction between the reactants and the CNT surface can lead to enriched reactants inside the CNT channels, which create more opportunities to modulate the catalytic performance and can also modify the diffusion behavior. In addition, different properties and chemical reactivities are displayed between the reactants and nanoparticles on the exterior walls of CNTs and those confined within lumen of CNTs. The well-defined nanosized channels of CNTs formed by graphene layers provide an intriguing confinement environment for catalysis [10]. On one hand, they exert a spatial restriction on metal particles hampering their sintering. On the other hand, they make it possible to tune the particle size simply by changing the channel diameters. However, the exterior walls of CNTs do not provide spatial restriction on metal particles, which cannot hamper their aggregation under reaction conditions. This is important because aggregation of nanoparticles frequently results in deactivation of catalysts. Bao et al. reported the effect of catalysts that metal nanoparticles were confined inside the CNT channels on the different reactions [23–25]. They used wet chemistry method so that many metal nanoparticles can be uniformly dispersed inside CNTs [22,26,27]. The filling depends on the liquid surface tension and the contact angle between the liquid and the pore walls [28].

The epoxidation of styrene is becoming increasingly attractive, because the epoxide is useful intermediate in the production of many pharmaceuticals and fine chemicals [29]. Recently many studies about the epoxidation of styrene have been reported [30–34]. However, low catalytic activity, more byproducts and high reaction temperature are still serious problem. Researchers exploited easily separable solid catalysts, containing Co [13,14], Ti [35–37], Pd [29], V [38], nanosize-gold [39] and employed normal oxidizing agent (e.g.: tertiary butylhydroperoxide (TBHP) [40], O_2 [41] or H_2O_2 [42]) to overcome these limitations. However, those did not markedly change conversion and/or selectivity of styrene oxide.

Herein, we filled cobalt nanoparticles in lumen wall of CNTs with wet chemistry methods (denoted as Co/CNTs (in); Fig. 1), and used them as nanoreactors. Co/CNTs (in) as catalysts were employed in the epoxidation of styrene. In addition, we contrasted nanoparticles on the inside and outer surface catalytic behavior (denoted as Co/CNTs (out)).

2. Experiment

2.1. Materials

Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, >99%) as a single cobalt source, CNTs were purchased from Shenzhen Nanotech Port

Co. Ltd., China. nitric acid (68 wt.% and 33 wt.%), anhydrous sodium carbonate, N,N-dimethylformamide ($\geq 99.5\%$, DMF), styrene ($\geq 99\%$). All chemicals were of analytical grade and used as received without further purification. Deionized water was used throughout the experiments.

2.2. Preparation of CNTs with open ends and shorten

The CNTs used in this work were shortened, functionalized, and the ends were opened. 1.0 g raw CNTs were refluxed in 50 mL concentrated nitric acid (68 wt.%, analysis grade) for 14 h at 140 °C in an oil bath. After the mixture cooled to room temperature, it was filtered and washed with distilled water until the pH reached 7. The sample was dried for 12 h in an oven at 60 °C, to obtain clean opened CNTs.

2.3. Preparation of Co/CNTs (in) catalyst

The CNTs (1.0 g) with open ends were first immersed into $Co(NO_3)_2 \cdot 6H_2O$ /aqueous solution (50 wt.%, 50 mL), which ultrasonic treatment for 1 h, then was stirred for 24 h under ambient conditions, at last the mixture was slowly rotary steaming. By this slow drying method, the catalyst precursor was introduced into the CNTs channels. Owing to the capillary force and temperature difference, cobaltous liquid can be sucked into the channels of CNT easily and a paste-like mixture was obtained. Subsequently it was dried slowly at 60 °C for 10 h under vacuum condition. Then the dried matter was calcinated at 350 °C in muffle furnace for 5 h. Finally obtained catalyst was denoted as Co/CNTs (in).

2.4. Preparation of Co/CNTs (out) catalyst

As compared sample, the pristine CNTs were purified by refluxing in dilute HNO_3 solution (37 wt.%) at 60 °C for 6 h to remove impurities. Then these unopened same amount CNTs were immersed into cobalt nitrate solution (50 wt.%, 50 mL), then complete similarity method with the above were used.

2.5. Catalytic reaction

The epoxidation of styrene with O_2 was performed in a 25 mL two-necked round bottom flask equipped with a reflux condenser. Typically, 5 mL N,N'-Dimethylformamide (DMF) solution containing a given substrate (0.1 mL) and 30 mg catalyst was taken, which ultrasonic treatment for 15 min, the reaction was kept at 100 °C with vigorously stirring. After O_2 at a certain stable flow rate controlled by a mass flow controller was introduced into the liquid by bubbling at atmospheric pressure. The reaction was stirred vigorously for a specified period of time. Samples were withdrawn by

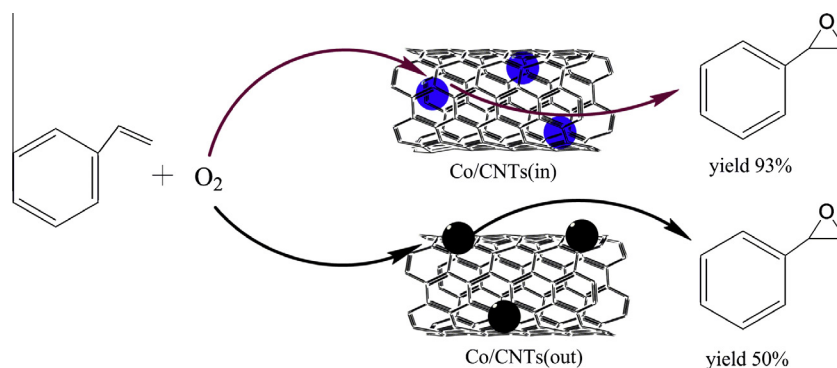


Fig. 1. The epoxidation of styrene on the Co nanoparticles encapsulated within the CNTs (Co/CNTs (in)) and adsorbed onto CNTs (Co/CNTs (out)).

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