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Synthesis of Co-N-C immobilized on carbon nanotubes for ethylbenzene oxidation

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ABSTRACT

The catalysts, namely noble-metal-free Co-N-C immobilized carbon nanotubes (CNTs), are synthesized via heating nitrogen-rich cobalt tetraphenyl porphyrin (CoTPP) supported on CNTs in N_2 atmosphere. The obtained catalysts have been characterized by BET, Raman, XRD, TEM, HRTEM and XPS. It is found that the synergistic effect between carrier and active sites plays an important role in the catalytic performance of Co-N-C/CNTs for ethylbenzene oxidation. When the mass ratio of CoTPP to CNTs is 0.15, the catalyst exhibits the highest catalytic performance for ethylbenzene oxidation (i.e. 19.9% for ethylbenzene conversion, 72.9% selectivity of acetophenone). It can be attributed to the well-dispersed Co-N-C species and the enhanced interaction chances between substrate and active sites with the introduction of CNTs.

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1. Introduction

Recently, carbon nanomaterials have attracted great attention in many fields, such as energy conversion, energy storage, drug delivery, catalysis, data storage, optoelectronic devices, etc [1–5]. The applications are attributed to the distinctive properties of nano-carbon material including the admirable conducting and semiconducting performance, quite large specific surface area, good chemical stability, biocompatibility as well as splendid photoelectric response [6,7]. In the field of catalysis, graphene, graphene nanoribbons, nano-diamond, nanotubes, nanofibers and other types of porous carbon are used as the supports or as the catalysts of metal-free oxygen reduction reaction (ORR) [8,9]. In most cases, the original carbon material has limited or even negligible ORR catalytic activity, the introduction of heteroatom into carbon seems to be a desirable alternative to solve the problem. The improved catalytic performance of heteroatom-doped carbon catalysts has been attributed to the charge redistribution adjacent to the dopants, which lower the activation energy, boost the stability of the transition state and weaken the O—O bond [10,11]. In general, nitrogen-doped carbon nanomaterials are proved to be high efficient catalysts in water splitting [12], water oxidation, selective oxidation of alcohols, heterogeneous hydrogenation and oxidation as well as electrocatalytic ORR [13–15]. In addition, the biomass derived nitrogen-containing carbon in styrene epoxidation [16], MOFs derived porous carbons in selective aerobic oxidations [17] and heteroatoms doped single-wall carbon nanohorns in nitrobenzene reduction [18] are realized. Morever, nitrogen-doped [19], sulfur-doped [20], phosphorus-doped [21] and boron-doped [22] carbon nanotubes are synthesized successfully and expressed outstanding ORR activity, which also shows considerable catalytic performance in selective oxidation of cycloalkanes and the degradation of organic compounds [23,24]. It is reported that the structural defects, surface modification and functionalization play significant roles in the carbon-catalyzed reactions [25,26]. For instance, carbonyl/quinone groups and surface acid properties have been proposed to be the active sites for the oxidative dehydrogenation of hydrocarbons and oxidation of alcohols [26,27].

Metal macrocyclic compounds are readily available carbon and nitrogen-rich precursors to synthesize metal-coordinating nitrogen-doped carbon materials (M-N-C) via a simple pyrolysis procedure. In addition, the M-N-C compounds are good substitute for the noble metal catalyst for its low-price, earth-abundant, environment-friendly and better leaching resistance in electrochemical ORR or organic redox [28–31]. Metalloporphyrin is a decent alternative precursor for the M-N-C owing to its nitrogen-rich macrocycle and the intrinsic metal-nitrogen bond which acts as the pivotal factor in the enhancement of catalytic performance in oxide reduction [31,32]. The importance of carbon support in the promotion of catalyst efficiency has been widely known. The intro-

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duction of carrier can not only increase the contact surface between the active sites and reactant, but provide a steady atmosphere for the active species which could delay the aggregation, slow the morphology change and keep its original properties [33,34].

The transformation of less expensive alkanes to high value-added chemicals remains a significant task in the current industrial and fine-chemical processes. For instance, the selectivity oxidation of alcohols to their corresponding aldehydes or ketones, the oxidative dehydrogenation of cyclohexane to cyclohexene, the aerobic oxidation of ethylbenzene and the like are still on the way for further optimization [35]. Acetophenone is an important intermediate in medicine, resin, flavouring agent, perfumes and esters, and also used as a solvent for cellulose esters and plasticizers in plastics [36–38]. Traditionally, the synthesis of acetophenone utilizes Friedel-Crafts acylation of benzene using acyl halides or acid anhydrides in the existence of Lewis acids, or utilizes the oxidation of alkylarenes with inorganic metal salt such as permanganate and dichromate [39,40]. There is no doubt that the traditional preparation process will cause a mass of wastes and pollution including toxic effluent, offscum, etc.

Herein, considering the low catalytic activity of original CNTs, the combination of the advantages of CNTs and metal macrocyclic compound is adopted. Besides, the complex and tedious covalently bonded procedure is successfully replaced by a facile impregnation method in which the loading amount of M-N-C is easily controllable [41]. After that, a high-performance catalyst is obtained by pyrolyzing cobalt tetraphenyl porphyrin coated multi-walled carbon nanotubes in N_2 atmosphere and the catalytic activity of Co-N-C is greatly improved (Scheme 1).

2. Experimental

2.1. Preparation of catalysts

2.1.1. Synthesis of cobalt (II) tetraphenyl porphyrin (CoTPP)

Cobalt tetraphenyl porphyrin was synthesized as the literature reported previously [42]. During a typical synthesis process, 0.1 mol benzaldehyde was added into a three-neck flask containing 250 mL propanoic acid. Then the mixture was heated to the target temperature (130 °C) slowly and 0.1 mol freshly distilled pyrrole was added dropwise. After stirring for another 1 h, the obtained product was refrigerated overnight, then filtered and purified. 1.6 mmol pure trtraphenyl porphyrin was transferred into 100 mL N,N-dimethylformamide (DMF) solution, heating to reflux subsequently. 0.01 mol cobalt chloride hexahydrate was added to

the mixture in batches and kept for 1 h. After refrigerated overnight, the resulting product was filtered and washed with deionized water for several times. The end product was obtained and denoted as CoTPP after drying.

2.1.2. Synthesis of Co-N-C/CNTs

Commercial carboxylated multi-walled carbon nanotubes (CNTs) were dried in a vacuum oven overnight without any other purification. Accordingly, 0.01 g CoTPP (0.0149 mmol) was dissolved with 2 mL dichloromethane, then 0.1 g CNTs was added to the solution and sonicated for 30 min to disperse them. Following that, the paste was placed in vacuum oven overnight. The obtained product was transferred to a quartz boat and heated to 500 °C with heating rate 10 °C per minute in nitrogen atmosphere and kept at 500 °C for 3 h. The final products were named as Co-N-C/CNTs$_x$ in which "x" represented the mass ratio of CoTPP to CNTs.

2.2. Characterization of catalysts

The surface area and pore volume of the samples were characterized by nitrogen adsorption/desorption analysis instrument at liquid nitrogen temperature on Novav1000e apparatus from Quantachrome Instrument. The Brunauer-Emmett-Teller (BET), Barret-Joyner-Halenda (BJH) and Dubinin-Astakhov (DA) equation were applied to calculate the surface area, pore size distribution and total/meso/micropore volume. Raman spectra were obtained in a Labram–010 micro Raman spectrometer with an excitation wavelength at 632 nm with 3 cm^{-1} spectral resolution. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were collected on JEM-3010 ultra-high resolution transmission electron microscopy. X-ray diffraction (XRD) patterns were conducted on X-ray powder diffractometer XRD-6100 (Shimadzu). The X-ray photoelectron spectroscopy (XPS) was performed on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation (hν = 1253.6 eV) or Al Kα radiation (hν = 1486.6 eV). Binding energies were calibrated with the reference of C 1s peak at 284.5 ev.

2.3. Catalytic performance

The selective oxidation of ethylbenzene was carried out at a 50 mL Teflon-lined stainless steel autoclave. Typically, 10 mL of ethylbenzene (81.7 mmol) and 30 mg of catalyst was added to the reactor and then sealed with the O_2 pressure raised to 0.8 MPa. Sub-
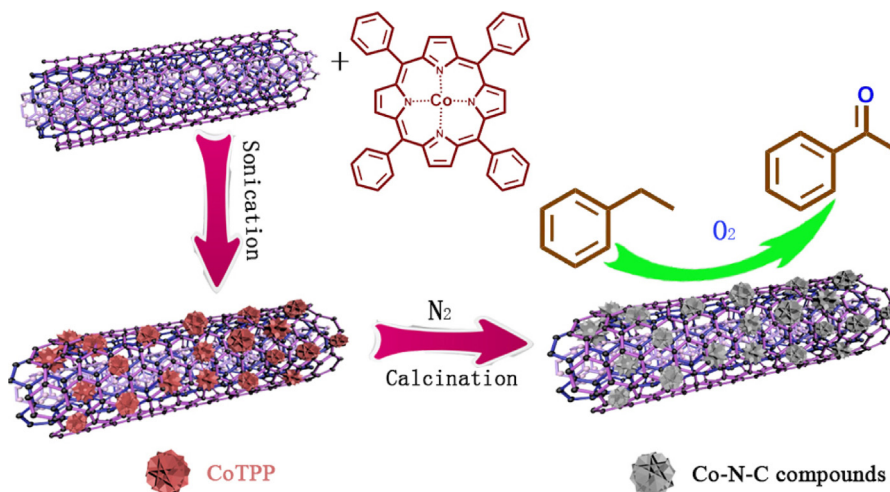
Scheme 1. Schematic diagram showing the preparation procedure of Co-N-C decorated CNTs by thermal treatment using CoTPP and commercial available CNTs.