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Trace iron impurities deactivate palladium supported on nitrogen-doped carbon nanotubes for nitrobenzene hydrogenation

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ABSTRACT

Nitrogen-doped carbons can effectively stabilize noble metal particles to achieve high catalytic performances. However, the metallic impurities in carbon nanomaterials, e.g. the residual growth catalysts of carbon nanotubes (CNTs), have some unforeseen effects on the catalysis involving nanocarbons. Herein, we demonstrate that the residual growth catalysts of N-doped CNTs (NCNTs) may significantly deactivate Pd catalysts for the hydrogenation of nitrobenzene. Through high-resolution transmission electron microscopy and CO-stripping, it was determined that the N dopants improved the dispersion of Pd nanoparticles. However, the iron, at ppm level, in residual catalysts encapsulated inside NCNTs can transfer onto the surface of Pd to block active sites so that the activity of Pd/NCNTs was much lower than that of Pd/CNTs. The similar effect was observed for most of the common metallic impurities in carbon materials, including Co, Ni, Mn, Cr, Cu, Zn, Mo, Al and Mg. To exploit the N-doped carbons, we deposited N-doped carbon layers on purified CNTs through pyridine pyrolysis and then supported Pd nanoparticles. By this means, the activity of Pd for nitrobenzene hydrogenation was improved by 3.85 folds compared to conventional CNTs, emphasizing the importance of controlling impurities in N-doped carbon materials for high performance catalysts.

1. Introduction

Noble metals, Pd, Pt, Ru, Rh etc., play vital roles in petroleum refinery, chemical synthesis and environment protection. For practical applications, the noble metals are dispersed on supporting materials to maximize the number of active sites on surfaces, due to the high cost and limited resources. Carbon is one of the most popular supports. In recent two decades, carbon nanomaterials are emerging as excellent supports for noble metal catalysts, due to the tunable structure, surface chemistry and excellent electronic and conductive properties [1]. Carbon nanotubes (CNTs) have been firstly used to immobilize Ru nanoparticles (NPs) for catalyzing the hydrogenation of cinnamaldehyde in 1994 [2]. So far, CNTs have been widely adopted as supports for a wide spectrum of catalytic reactions, including hydrogenation [3], oxidation [4], dehydrogenation [5], ammonia synthesis [6] and decomposition [7] and various electrochemical processes [8,9]. (see the review article [10] for more examples)

Doping carbons with nitrogen has been demonstrated promotional to the effective immobilization of noble metal NPs by strengthening the metal-support interaction (MSI) [11]. Superior catalytic activity was achieved over Pt on nitrogen-doped CNTs (NCNTs) in the oxidation of

glycerol and electro-oxidation of CO, compared with conventional CNTs as support [12]. Pt-Ni NPs can be highly dispersed on NCNTs and the electro-oxidation activity of methanol and the tolerance to CO poisoning can be improved effectively, in comparison with the commercial Pt/C catalyst [13]. Chen et al. have shown that the Pd supported on polyaniline-functionalized CNTs was more active in the selective hydrogenation of phenol and derivatives [14]. Zhang et al. recently demonstrated that the NCNTs more strongly anchor Pt NPs during the hydrogenation reaction of nitrobenzene than the CNTs with oxygen-containing groups do through a sophisticated TEM technique [15].

Although many methods have been developed to synthesize N-doped CNTs, the catalytic chemical vapor deposition (CVD) method is regarded as the most feasible for a large scale production [16]. Transition metal catalysts [17,18] are used for the CVD growth of CNTs, and may be encapsulated inside the cavity of CNTs or wrapped by graphite sheets. Because nitrogen heteroatoms interrupt the formation of graphitic layers, the NCNTs by CVD methods usually contains more residual catalysts. These residual catalysts can survive even after thoroughly acid- or base-washing [19,20], resulting in some unforeseen effects on the catalysis of CNTs and other types of carbon materials.

Compton et al. [21,22] discovered that the residual metal NPs are responsible for the electro-catalysis of hydrogen peroxide and hydrazine on CNT-modified electrodes. The effect of impurities on the "metal-free" carbon-catalyzed electrochemical processes is continuously under debate, since the ground-breaking work on the oxygen reduction reaction (ORR) by Dai's group in 2009 [23]. Pumera et al. [24,25] proposed that trace levels of metallic, especially manganese, impurities in graphene and CNTs have profound influences on the ORR activity. They also revealed that metal impurities higher than 100 ppm can dominate the electrocatalytic performance of CNTs in the reduction of hydrogen peroxide [26]. Jin et al. [27] showed that residual metals (Fe, Co, Ni) were inevitably present in N-doped carbons prepared by pyrolyzing EDTA and melamine. The trace metals contributed to the main active sites for the hydrogen evolution reaction (HER). Recently, Lum et al. [28] confirmed that the observed high activity of carbon materials for CO_2 electro-reduction may be originated from the copper impurities of trace level. In the case of supported noble metal catalysts, Xia et al. have noticed that the residual growth catalyst significantly influenced the oxygen and nitrogen functionalization of CNTs, which consequently altered the reducibility of the supported Pt NPs for olefin hydrogenation [29].

Herein, we highlight that the metallic impurities from residual growth catalysts in NCNTs may seriously deteriorate the catalytic activity of supported Pd NPs for the hydrogenation of nitrobenzene (NB). It is surprising that the existence of iron impurities of ppm level dramatically deactivated Pd/NCNTs so much that the promoting effect of N-doping cannot be observed in the NB hydrogenation reaction. This finding is unexpected because iron has frequently been documented as an effective promoter of Pd catalysts. Du Pont has claimed that iron-promoted Pt or Pd catalysts supported on carbon blacks have improved activity for the hydrogenation of aromatic nitrocompounds [30,31]. Pd-Fe/SiO_2 bimetallic catalysts showed the facilitated hydrogen transfer step and higher catalytic activity in the hydrogenation of 2,4-dinitrotoluene [32]. The promoting effect of iron (oxides) has also been discovered on hydrodechlorination [33], hydrolysis of phenethyl phenyl ether to aromatics [34], hydrogenation of succinic acid [35] and hydrodeoxygenation of furans [36]. In this work, we demonstrated that: i) the iron encapsulated in NCNTs survives from acid-washing and transfers to the surface of Pd NPs, and ii) the iron suppresses the activity as active site blockers through a geometrical effect; in addition, iii) similar effect can be observed with other metals frequently detected in carbon materials. To overcome this, a post N-doping treatment of purified CNTs was proposed to yield N-doped CNTs, by which the unique MSI between Pd NPs and N-dopants can be exploited to achieve a high-performance Pd catalyst for the hydrogenation reaction of NB. The mechanism of trace iron poisoning the Pd catalysts is discussed based on XPS, electrochemical CO-stripping and DFT calculations.

2. Experimental

2.1. Materials

CNTs were provided by Shenzhen Nanotech Port Co., Ltd. The as-received CNTs were purified to remove residual growth catalysts by refluxing in concentrated HCl (12 M) at room temperature for 12 h and then thoroughly washed with de-ionized water to neutral pH. The resulting solids were dried in vacuum overnight and designated as purified CNTs. All other reagents were of analytical grade and used as purchased without further purification.

2.2. Synthesis of NCNTs

NCNTs were synthesized by CVD of xylene over a FeMo/Al_2O_3 catalyst in a horizontal tubular quartz furnace with 4 cm inner diameter [37]. The details of the FeMo/Al_2O_3 catalyst can be found in Ref [38]. 15 ml xylene was injected by a syringe pump at a rate of 3 ml h^{-1} and

was vaporized in the quartz tube at 453 K. The growth of NCNTs was carried out at 1073 K in NH_3 at 500 Ncm^3 min^{-1}. The obtained NCNTs was refluxed in concentrated HCl (12 M) at room temperature for 12 h and then thoroughly washed with de-ionized water to neutral pH to remove residual catalysts as possible.

2.3. Synthesis of surface-nitrogen-enriched CNTs (N@CNTs)

N@CNTs were prepared by a post-thermal-deposition of pyridine on the surfaces of purified CNTs following a literature method [39]. Briefly, 100 mg purified CNTs were firstly placed on a quartz tube at the center of a horizontal quartz tube. The quartz tube was heated to 1033 K in a tube furnace at atmosphere pressure under flowing Ar (200 Ncm^3 min^{-1}). 4.5 ml pyridine was fed into the reactor by a syringe pump at 1.5 ml h^{-1} to conduct the deposition reaction. After the reaction for an anticipated duration, the furnace was cooled down to room temperature in Ar atmosphere. The as-prepared products are denoted as N@CNTs.

2.4. Immobilization of Pd NPs

An aqueous solution of H_2PdCl_4 was initially prepared by mixing 1 g of $PdCl_2$ into 100 ml 5% v/v HCl aqueous solution by stirring at room temperature until the salt was completely dissolved. 0.2 g carbon materials (CNTs, NCNTs or N@CNTs) were suspended in 20 ml deionized water, and sonicated until a uniform suspension was obtained. Then, a certain amount of the H_2PdCl_4 solution, corresponding to a nominal Pd content of 4.3w%, was added into the suspension with stirring. KOH or NaOH aqueous solution (1 M) was added to adjust pH to 8.5. Then excess $NaBH_4$ aqueous solution was added drop wise to the suspension in ice bath. Finally, the slurry was filtered, washed with deionized water and absolute ethanol for several times, and dried at 343 K overnight in vacuum.

2.5. Preparation of M-Pd/N@CNTs catalysts

M-Pd/N@CNTs (M = Fe, Co, Ni, Mn, Cr, Cu, Zn, Mo, Al, Mg) catalysts were prepared with the incipient-wetness impregnation method. In the case of Fe-Pd/N@CNTs, about 300 μl Fe(NO_3)$_3$ aqueous solution was used for impregnating 50 mg Pd/N@CNTs. The amount of Fe in final catalyst was controlled by varying the concentration of Fe(NO_3)$_3$. The mixture was dried at 333 K and then heated in a quartz tube in Ar gas flow (200 Ncm^3 min^{-1}) at 673 K for 3 h. The catalysts are denoted as Fe$_x$-Pd/N@CNT, where x is the nominal Fe content in ppm in the catalyst. A reference catalyst without secondary metal is denoted as Pd/N@CNTs-673, where 673 means that the Pd/N@CNTs was annealed at 673 K for 3 h. For other metals, the same procedure was applied but with different amounts of corresponding nitrate solution.

2.6. Catalyst characterizations

Atomic absorption spectrometer (AAS, Hitachi Z-5000) was used to detect Fe and Pd content in solution. The residual growth catalysts in CNTs and NCNTs were detected by inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer ICP8300). Before measurements, the samples were fully combusted at 1073 K and the residuals were dissolved in aqua regia. The Brunauer–Emmett–Teller (BET) specific surface areas (S_{BET}) were measured by N_2 adsorption at liquid N_2 temperature in an ASAP 2010 analyzer. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 CEVANCE diffractometer equipped with a rotating anode using Cu Kα radiation (40 kV, 40 mA). The average crystallite size of Pd NPs was calculated by the Scherrer–Warren equation. Raman spectra were measured in a LabRAM Aramis micro Raman spectrometer excitated at 632.8 nm with 2 μm spot size. X-ray photoelectron spectroscopy (XPS) was performed in a Kratos Axis ultra (DLD) spectrometer equipped with an Al Kα X-ray