

# Purified oxygen- and nitrogen-modified multi-walled carbon nanotubes as metal-free catalysts for selective olefin hydrogenation

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## Abstract

Oxygen- and nitrogen-functionalized carbon nanotubes (OCNTs and NCNTs) were applied as metal-free catalysts in selective olefin hydrogenation. A series of NCNTs was synthesized by NH<sub>3</sub> post-treatment of OCNTs. Temperature-programmed desorption, N<sub>2</sub> physisorption, Raman spectroscopy, high-resolution transmission electron microscopy and X-ray photoelectron spectroscopy were employed to characterize the surface properties of OCNTs and NCNTs, aiming at a detailed analysis of the type and amount of oxygen- and nitrogen-containing groups as well as surface defects. The gas-phase treatments applied for oxygen and nitrogen functionalization at elevated temperatures up to 600 °C led to the increase of surface defects, but did not cause structural damages in the bulk. NCNTs showed a clearly higher activity than the pristine CNTs and OCNTs in the hydrogenation of 1,5-cyclooctadiene, and also the selectivity to cyclooctene was higher. The favorable catalytic properties are ascribed to the nitrogen-containing surface functional groups as well as surface defects related to nitrogen species. In contrast, oxygen-containing surface groups and the surface defects caused by oxygen species did not show clear contribution to the hydrogenation catalysis.

## Key words

multi-walled carbon nanotubes; nitrogen-containing functional groups; oxygen-containing functional groups; metal-free catalyst; selective olefin hydrogenation

## 1. Introduction

Carbon nanotubes (CNTs) are considered promising for various applications due to their unique structural and electronic properties. For example, CNTs can be used as metal-free catalyst, where the active sites are created by the surface modification with heteroatoms [1,2]. Nitrogen, as one of the most commonly used heteroatoms, can be incorporated into CNTs either by feeding nitrogen-containing precursors during the CNTs synthesis, or by the post-treatment of CNTs with nitrogen-containing molecules [3,4]. The presence of electron-rich nitrogen atoms in the graphite sheet induces metal-like properties, and in turn, catalytic activity [5]. Therefore, nitrogen-functionalized CNTs (NCNTs) can be used as metal-free catalyst, which is of great interest in the production of pharmaceuticals, health care and fine chemicals. Avoiding precious metals not only reduces the production cost greatly, but also allows obtaining high-purity products more easily by excluding tedious separation processes.

NCNTs-based metal-free catalysts have been intensively studied especially in the field of electrocatalysis. NCNTs synthesized by pyrolysis of N-containing precursors were successfully used as metal-free catalyst for oxygen reduction reaction (ORR) in alkaline electrolytes [1]. In our group, several methods have been explored to synthesize NCNTs and to apply them as metal-free catalyst for ORR including the growth from N-containing precursors such as acetonitrile using cobalt as catalyst [6], polyaniline coating and subsequent carbonization [7], and the post-treatment of partially oxidized CNTs (OCNTs) in NH<sub>3</sub> atmosphere [8]. The structural properties and the intrinsic electrocatalytic performance of the obtained NCNTs were systematically investigated by a series of techniques. Under optimized conditions, the activity was found to be comparable to that of a commercial Pt/C catalyst [8]. Recently, NCNTs grown on a plasma-etched substrate or obtained by nitrogen-promoted self-assembly have been applied as electrocatalyst which showed superior performance in ORR in terms of activity and long-term stability [9,10]. It has to be

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noted that CNTs used in these studies were grown using transition metal catalysts, which were subsequently removed by being washed with acid and/or base before the catalytic applications. Nevertheless, traces of metal residuals cannot be fully excluded [11], which may promote the ORR by catalyzing the chemical disproportionation of reaction intermediate such as  $\text{HO}_2^-$  [12].

The electronic properties of NCNTs are also advantageous in other reactions such as selective oxidation and hydrocarbon activation [2,4,13]. Very recently, NCNTs as metal-free catalyst were found to be highly active and stable in the selective oxidation of harmful  $\text{H}_2\text{S}$  to elemental sulfur [4]. In liquid-phase selective oxidation of cyclohexane, NCNTs exhibited a higher activity than CNTs without nitrogen modification and also than most of the reported solid catalysts and were of high selectivity to adipic acid [2]. Studies on the origin of the activity revealed that the N-C species of NCNTs can act as centers for the activation of C–H bond in methane. Thus, NCNTs as metal-free catalyst have a comparable activity to noble metal catalysts in the selective oxidation of methane [14]. Furthermore, with NCNTs as catalyst both the oxygen atoms of  $\text{O}_2$  molecule can be effectively used as oxidant in the catalytic cycle of methane oxidation reactions [14].

Theoretical studies using universal force field and density functional theory revealed that nitrogen as heteroatom in CNT network could be the active sites for hydrogen adsorption and activation [15]. More interestingly, dissociative adsorption of  $\text{H}_2$  can occur on NCNTs with a smaller energy barrier than on pristine CNTs [16], which is essential for the catalytic application of NCNTs in hydrogenation reactions. In addition, experimental evidence on the intrinsic activity for CNTs in the

activation of hydrocarbons has been found [14,17]. The theoretical and experimental evidence suggests that NCNTs can be used as catalyst in hydrogenation reactions.

In this work, purified OCNTs and NCNTs were tested as metal-free catalysts in selective olefin hydrogenation. The catalytic performance of NCNTs prepared under different conditions was examined using the hydrogenation of 1,5-cyclooctadiene (COD) as a model reaction. Kinetic data were obtained in a batch reactor and were simulated using Athena Visual Studio software.

## 2. Experimental

### 2.1. NCNT preparation

CNTs (Baytubes<sup>®</sup> C 150 P, outer mean diameter 13–16 nm, inner mean diameter 4 nm, loose agglomerate size 0.1–1 mm) supplied by Bayer Material Science (Leverkusen, Germany) were purified before any further use by being washed in diluted nitric acid in order to remove residual growth catalysts from CNT synthesis. Surface functionalization of the purified CNTs was carried out in the gas phase as described in literature [3,18]. Briefly, oxygen functionalization was achieved by treating the purified CNTs in  $\text{HNO}_3$  vapor at 200 °C to create oxygen-containing groups on CNT surface [18]. The obtained OCNTs were subsequently converted to NCNTs in flowing  $\text{NH}_3$  (10%  $\text{NH}_3$  in He, 50 mL·min<sup>-1</sup>) atmosphere at elevated temperatures [3]. A series of NCNTs was prepared by varying the oxygen functionalization time and  $\text{NH}_3$  post-treatment temperature as summarized in Table 1.

Table 1. Preparation conditions and physical properties of OCNT and NCNT samples

Samples	Preparation conditions		$\text{N}_2$ physisorption	
	time in $\text{HNO}_3$ vapor (h)	temperature of $\text{NH}_3$ treatment (°C)	surface area ( $\text{m}^2\cdot\text{g}^{-1}$ )	pore volume ( $\text{cm}^3\cdot\text{g}^{-1}$ )
OCNT24	24	–	313	0.49
OCNT48	48	–	442	0.71
OCNT120	120	–	424	0.64
NCNT24-400	24	400	304	0.53
NCNT48-400	48	400	324	0.56
NCNT120-400	120	400	276	0.41
NCNT48-200	48	200	204	0.33
NCNT48-600	48	600	328	0.52

### 2.2. Characterization

Temperature-programmed desorption (TPD) experiments were carried out in a horizontal quartz tube reactor with an inner diameter of 4 mm. Helium (99.9999%, 30 mL·min<sup>-1</sup>) was used as carrier gas. Typically, about 50 mg OCNTs were used for each measurement. For a TPD experiment, the reactor was heated from room temperature to 1000 °C at a heating ramp of 2 K·min<sup>-1</sup>. An on-line infrared detector (ABB, Germany) was used for quantitative analysis of CO and  $\text{CO}_2$  released during the decomposition of surface oxygen groups. The infrared detector was calibrated in the range of 0 to 4000 ppm

with reference gas mixtures prior to each measurement. Quantitative analysis of TPD results was performed by integrating CO and  $\text{CO}_2$  desorption peaks.

Static  $\text{N}_2$  physisorption measurements were carried out at 77 K using an Autosorb-1 MP Quantachrome system. Samples were degassed at 200 °C for 2 h before the measurements. Raman spectra were taken on a Horiba Jobin Yvon LabRam 2 confocal Raman Microscope with a HeNe Laser excitation at 633 nm (1.96 eV) with a power of 3.5 mW. The intensity ratios of D-band and G-band ( $I_D/I_G$ ) were calculated based on the spectra after background subtraction. The structure of OCNTs and NCNTs were studied by high-resolution transmission

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