Heterogeneous hydroxylation catalyzed by multi-walled carbon nanotubes at low temperature

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Abstract

In this paper, multi-walled carbon nanotubes (MWCNTs) were directly used as catalysts for the hydroxylation of aromatic hydrocarbons at low temperature (50–70 °C). Without the assistance of any solvent or additive, high selectivity was still obtained. The catalysts were characterized by X-ray powder diffraction, infrared spectra, Raman spectra, and transmission electronic microscopy. These results prove that MWCNT was a highly-active, highly-selective, and well-reproductive heterogeneous catalyst. The curved sp2-hybridized carbon surfaces of MWCNT played an important role in these selective catalytic reactions. The reactions were proposed to occur via an oxene attacking process. The active oxygen species were generated through the interaction between the hydrogen peroxide and the MWCNTs and subsequently consumed by the aromatic hydrocarbons. This process was repeated in the catalytic reactions.

Keywords: Carbon nanotube; Heterogeneous catalysis; Hydroxylation; Aromatic hydrocarbon

1. Introduction

The discovery of fullerenes [1] and carbon nanotubes (CNTs) [2] initiated great interest in the study of non-planar sp2-hybridized carbon nanostructures. These carbon nanostructures can maintain their structural eccentricity and high stability at high temperatures, and even in severe environments, thus allowing them to have many novel electronic, adsorptive, mechanical, and thermal properties. Such characteristics make them more attractive as catalyst supports than activated carbons. Catalytic studies conducted in CNTs and graphite nanofibers (GNFs)-based systems have shown encouraging results in terms of activity and selectivity [3–5]. Furthermore, besides being used as catalyst support, carbon nanostructures can probably be directly used as active and stable catalysts for certain reactions. CNTs and GNFs have been successfully used to catalyze methane decomposition [6], and oxidative dehydrogenation of ethylbenzene to styrene at a high temperature (>500 °C) [7], respectively. Based on the results obtained in such studies, it is very reasonable to say that CNTs could be an excellent heterogeneous catalyst [8,9]. Detailed reasons are listed as below: (i) a specific mesoporous nature makes them have good adsorption properties; (ii) they are resistant to abrasion and acidic/basic environments; (iii) they have dimensional and thermal stability; (iv) they have high purity and can avoid self-poisoning. Exploring the possibility of using CNTs as heterogeneous catalysts in various reactions, and then understanding the reaction mechanisms in related selective catalytic reactions should be feasible and interesting.

In the present work, using H2O2 as oxidant, the catalytic functions of multi-walled carbon nanotubes (MWCNTs) were studied for the hydroxylation of aromatic hydrocarbons. Low-temperature (50–70 °C) interface reactions were successfully carried out without using any solvent or additives, and the high activity and selectivity of the catalysis functions of MWCNTs...
were proved in the efficient hydroxylation process. A possible mechanism was brought forward and the hydroxylation reactions were proposed to occur via an oxene attacking process.

2. Experimental section

All the reagents were purchased from Beijing Chemical Reagent Company (Beijing, China), and a fresh solution of H₂O₂ was prepared before each use. All other reagents were of analytical grade and were used as received. Multi-walled carbon nanotubes with diameters of 15–20 nm were purchased from Tsinghua_Nafine nano-powder Commercialization Engineering Center. The catalyst (support and metal particles) in the products was removed through sonicating the materials in 37 wt.% hydrochloric acid for 2 h. The obtained mixture was kept overnight and then diluted with de-ionized water, and finally filtered on a 0.1 µm Supor Membrane Disc Filter (Gelman). Other MWCNTs with various diameters were synthesized in our laboratory. MWCNTs with diameters between 30 and 50 nm were prepared using the one-step water-assisted method [10]. MWCNTs with diameters between 10 and 15 nm were prepared through AC arc-discharge (15–30 V and 20–40 A) in ethanol solution (70–90%). MWCNTs with diameter 15–20 nm were purchased from Tsinghua_Nafine nano-powder Commercialization Engineering Center. The catalyst (support and metal particles) in the products was removed through sonicating the materials in 37 wt.% hydrochloric acid for 2 h. The obtained mixture was kept overnight and then diluted with de-ionized water, and finally filtered on a 0.1 µm Supor Membrane Disc Filter (Gelman). Other MWCNTs with various diameters were synthesized in our laboratory. MWCNTs with diameters between 30 and 50 nm were prepared using the one-step water-assisted method [10]. MWCNTs with diameters between 10 and 15 nm were prepared through AC arc-discharge (15–30 V and 20–40 A) in ethanol solution (70–90%). MWCNTs with diameters about 10 nm (<10 nm) were prepared using the hydrogen-assisted AC arc-discharge (15–30 V and 20–40 A) method in water. The open-ended and functionalized MWCNTs were obtained through oxidizing MWCNTs in concentrated HNO₃ solution [11].

All solid samples were dried under vacuum at 60 °C for 8–10 h before measurement. The XRD patterns were obtained on a Rigaku D/max 2500V PC diffractometer with Cu Kα radiation. A JEM-2010 transmission electron microscope was used to examine the morphology of the MWCNTs. For the electron microscopy study, the powder was dispersed in absolute alcohol assisted by an ultrasonic vibrator for 20 min, and then deposited on a copper grid covered with a perforated carbon film. Raman spectra were recorded at ambient temperature on a Spex 1403 Raman spectrometer with an argon-ion laser at an excitation wavelength of 514.5 nm. IR spectra (KBr pellet; 4000–400 cm⁻¹) were recorded on a Mafna FT-IR 560 spectrophotometer. Electrochemical measurements were carried out in a conventional three-electrode electrochemical cell. Typically, the working electrode was a modified carbon paste electrode. The auxiliary electrode was a platinum wire and the reference electrode was a Ag/AgCl (saturated KCl) electrode. Cyclic voltammetry measurements were performed with a CHI 832 electrochemical instrument (CHI Inc., USA). Electrolyte solutions were purged with high-purity nitrogen prior to and blanketed with nitrogen during electrochemical experiments. The products of the hydroxylation reactions were analyzed using a gas chromatograph. The gas chromatography were performed in a Varian 3400 GC column with a cross-linked 5% PhMe silicone column (25 m × 0.20 mm × 0.33 µm) and a FID detector under the following conditions: carrier gas (N₂) at 140 K; temperature program 60 °C; 1 min, 15 °C/min, 200 °C; 15 min; split ratio, 10:1; injector, 300 °C; detector, 300 °C.

The typical hydroxylation reactions were performed in a stirred round-bottom flask fitted with a water-cooled condenser. Reactions were carried out in the air at 50–70 °C for 10 h. A 5 mg of MWCNTs (with diameters 15–20 nm) and 45 ml of benzene were put into a flask. Then the flask was placed in an ultrasonic bath and kept for 20 min. Subsequently, 10 ml H₂O₂ aqueous solution (30%) was added stepwise (drop by drop) to the above benzene solution. The mixture was kept under stirring at 50–70 °C for 10 h. At the end of the reaction, the solution was cooled to room temperature, and the aqueous and organic phases were separated. Benzene conversion was 5.5%. The selectivity to phenol is about 98% based on benzene. The product was analyzed using a gas chromatograph. The molar product distribution was: phenol about 98.2, hydroquinone about 0.5, catechol about 0.6, 1,4-nenzoquinone about 0.3, and biphenol about 0.4%.

3. Results and discussion

In our experiments, benzene, toluene, chlorobenzene (or bromobenzene), and nitrobenzene were selected as substrates. The hydroxylation reactions of these substrates were carried out under the same condition. Fig. 1 shows the relationship between the reaction time and the benzene conversion. Curves a–e shows the relationship between the reaction time and the benzene conversion when using different amount of CNTs: 2, 4, 6, 8, and 10 mg respectively. The relationship indicates that benzene conversion becomes higher with the increase of the amount of CNTs. A series of experiments show that the selectivity maintained at about 98% and did not vary with the reaction time. On the other hand, many experimental results also show that the amount of CNTs has nothing to do with the selectivity of phenol. A series of experiments were carried out to explore the relationship between the times of using CNTs and the conversion or the selectivity. It is found that there is no obvious activity-decrease of the catalyst after 10 times recycling. This may be due to the excellent dimensional and thermal stability of CNTs.

![Fig. 1. The relationship between the reaction time and the benzene conversions.](image_url)
When the substrate was toluene, a mixture of cresols (o-:m-:p-isomer ratio = 3.2:1.0:4.9) was produced with high selectivity (>85%). When the substrate was chlorobenzene (or bromobenzene), ortho and para substitution products were obtained with high selectivity. No other isomers were present, as identified by GC–MS. When the substrate was nitrobenzene, a mixture of nitrophenol (o-:m-:p-isomer ratio = 11.8:2.8:1) was produced with high selectivity (nearly no other isomers were identified by GC–MS). The substituent functional groups on a benzene ring can greatly influence its reactivity, because the substituent functional groups that bear electron-donating or electron-withdrawing characteristics can activate or deactivate a benzene ring towards electrophilic attack. Although the yield of the nitrophenol is low in our experiments, this result still demonstrated that the activity of the oxygen species created on MWCNTs surfaces was very high.

The XRD patterns, TEM images and the Raman spectra analyses show that the structure of the MWCNTs remains intact in the hydroxylation reactions. The XRD patterns demonstrate that the products obtained on the cathode are made up of carbon; the three peaks correspond to (0 0 2), (1 0 0), and (1 0 1), respectively. Fig. 2 (curve a) gives the XRD patterns of pristine MWCNTs before hydroxylation reactions. Fig. 2 (curve b) exhibits the XRD patterns of MWCNTs after 10 times recycling. There is no obvious difference in the XRD patterns before and after hydroxylation reaction, even after 10 times recycle. These phenomena show that the structures of the MWCNTs are not changed during the hydroxylation reaction. TEM studies were carried out before and after 10 repetitions of the hydroxylation reaction cycle. Fig. 3 shows the typical high-resolution TEM image for the wall structure of MWCNTs before (a) and after (b) benzene hydroxylation reactions (after 10 times recycling). The walls are composed of graphite sheets aligned to the tube axis. The interlayer spacing in the walls, about 0.34 nm, corresponds to the (0 0 2) distance of graphitic lattice [12]. The observations reveal that the structures of the MWCNTs used as heterogeneous catalyst are kept very good.

Fig. 4 gives the Raman spectra of the MWCNTs before (curve a) and after (curve b) benzene hydroxylation reactions (after 10 times recycling). The peak at 1580 cm⁻¹ (G-band) corresponds to an E₂g mode of the graphite and is related to the vibration of sp²-bonded carbon atoms in a two-dimensional hexagonal lattice, such as in a graphite layer. Nanotubes with concentric multi-walled layers of hexagonal carbon lattice display the same vibrations. The D-band at around 1360 cm⁻¹ is associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite or glassy carbons [13–16]. The two Raman spectra have almost the same pattern, implying that the reduction reaction does not affect the graphite structure of the MWCNTs. This can also be proved by TEM images.

IR analyses proved that carbon-based surface functional groups could also be created on MWCNTs surfaces after benzene hydroxylation reactions. Fig. 5 (curve a) shows the IR spectra of...
functionalized MWCNTs. Pristine MWCNTs were refluxed in concentrated nitric acid, then washed thoroughly with de-ionized water and dried completely. The samples were prepared through pressing samples in alkali metals halides (KBR). The peaks indicate the existence of carboxylic groups on the tubes [17,18]. Curve b in Fig. 5 shows the IR spectra of MWCNTs after benzene hydroxylation (after 10 times recycling). It is obvious that various functional groups can be created on the MWCNTs surfaces during benzene hydroxylation.

However, a series of control experiments provide powerful evidence showing that the existence of functional groups is not the key factor for these selective catalytic reactions. Control experiments were carried out using MWCNTs with few (close ends) or abundant functional groups (open ends) as catalyst, respectively. The results indicated that there were no obvious changes on benzene conversions whether closed or open-ended MWCNTs (both have diameters within 15–20 nm) were used as catalyst. Furthermore, there was no obvious activity-decrease or -increase of the both kind of catalysts after10 times recycling. Therefore, functional groups of the carbon nanotubes are not the key factors for these heterogeneous hydroxylation reactions.

The chemical reactivity of CNTs is, compared with that of a graphite sheet, enhanced as a direct result of the pi-orbital mismatch caused by an increased curvature of the CNTs surface. Therefore, the chemical reactivity in sidewall and the end caps of a nanotube should be different. Similarly, a smaller nanotube diameter will result in increased reactivity [5,6,8,19]. Then MWCNTs with various curvatures deserve more attention. A serious of control experiments were carried out under the same condition with benzene as substrate. When graphite powders were used as catalyst, almost no phenol was obtained. When amorphous carbon powders were used as catalyst, more by-products were obtained (the selectivity of phenol, <80%). The MWCNTs with various diameters (about 10, 15–20, and 30–50 nm) were also used as catalysts in the control experiments. Under these conditions, phenol was produced in high selectivity (about 98%) with benzene conversion in the range from 2 to about 6% (reaction time: 10 h, MWCNTs 5 mg, 50–70 °C, the catalyst was recycled 1–10 times). The benzene conversions in these control experiments are shown in Fig. 6. It can be seen that smaller MWCNTs diameters indeed led to an increased catalytic activity. However, too small diameters, about 10 nm for MWCNTs, for example, still led to the decrease of the catalytic activity. Hence the curved sp2-hybridized carbon surface of MWCNTs should be the key factor in these catalytic reactions, and provided a suitable reaction field for these hydroxylation reactions.

Generally speaking, the methyl group oxygenation requires abstraction of an H+ radical using active oxygen species, while ring oxygenation is initiated by the attack of active oxygen species on the ring. Active oxygen species that are electrophilic tend to attack the ring, and oxygen species that have a radical character tend to attack the methyl group [20,21]. In the present work, when the substrate was toluene, a mixture of cresols (o-:m-:p-isomer ratio = 3.2:1.0:4.9) was produced with high selectivity (>85%). The ring oxygenation to methyl group oxygenation ratio was about 8.0. It then can be concluded that active oxygen species generated in the present process should bear electrophilic characteristics. Among various active oxygen species considered [for example, O (atomic oxygen at the ground state: 3P), oxene, HOO*, HO*, O2-, O-, OH-, etc.], negatively charged species are unlikely to be the active species because they are nucleophilic. If the HO* (or HOO*) radicals are the main active species, as previously reported [20–22], more benzylic alcohol and benzaldehyde rather than cresols should be produced in the toluene hydroxylation, similar to the reactions occurring in the system with EuX3–TiO(acac)2–Pt oxide/SiO2 (X = Cl and ClO4) as catalysts [20,21]. Oxene, one of the active oxygen species produced by the decomposition of hydrogen peroxide, can easily add to carbon–carbon double bonds including conjugated ones such as benzene. This type of addition is 103 times faster in rate than the hydrogen abstraction from the methyl group [20,23–25]. In order to further confirm the oxene character of the active oxygen species, cyclohexene and styrene were selected as substrates. When styrene was used as substrate, polyreaction occurred and a large amount of resinous product...
was obtained. Under the same condition, a large amount of 3-hydroxyl-cyclohexene, and a small amount of 7-oxa-bicyclo[4.1.0]heptane and 4-hydroxyl-cyclohexene were produced when cyclohexene was used as substrate. As reported, the oxene species can add to conjugated carbon–carbon unsaturated bond, but the intermediate of the reaction can easily polymerize and yield a resinous product. If such polymerization does not occur, the main products should be phenol that results from the neighbor insert hydrogen (NIH) shift [25,26]. In the reported mechanism, the main products were 3-hydroxyl-cyclohexene. This can be explained as follows: the oxene species add to conjugated carbon–carbon unsaturated bond and then 3-hydroxyl-cyclohexene resulted from the NIH shift. When styrene was used as substrate, oxene species add to conjugated carbon–carbon unsaturated bonds and the intermediates of the reaction easily polymerize, and resinous products were obtained.

Hence, the possible hydroxylation reaction mechanism can be described as follows. Firstly H2O2 molecular chemisorption occurred on the surface of the MWCNTs and the oxygen atoms were “fixed” by mismatched pi-orbital on the carbon nanotube surfaces. At the same time, H2O2 was decomposed into oxygen atom and water. In some sense, the “fixed” oxygen atoms on the MWCNTs surface should have an oxene character; they are electrophilic and tend to attack the ring to yield the methyl group. A perfect graphite sheet surface (with a large amount of well-conjuncted pi-orbitals) could be disadvantageous to create active oxygen species, and a seriously curved sp2-hybridized carbon surface (with mismatched pi-orbitals) could not stabilize these active species. As a result, the active oxygen species would quickly be consumed by the aromatic hydrocarbons. Such a process should be repeated in the catalytic process, as illustrated in Fig. 7. On the other hand, the products (phenols) could be transferred quickly into the benzene phase through the strong π–π interaction, which would prevent further oxidation of the products. These may explain how the high selectivity could be obtained when benzene was oxidized by H2O2 with MWCNTs as catalyst. To verify such a proposition, we examined the electrocatalysis action of MWCNTs for hydrogen peroxide decomposition in a conventional three-electrode electrochemical cell. Paste electrodes were constructed using MWCNTs and graphite powder mixed with mineral oil, respectively. The electrochemical behavior of such electrodes prepared with MWCNTs was compared with that of graphite paste electrodes using a cyclic voltammeter. Fig. 8 shows the cyclic voltamograms of the graphite paste electrode in 0.05 M phosphate buffer (pH 7.4) in the absence (curve a) and presence (curves b–e) of H2O2 at a scan rate of 10 mV/s. In Fig. 8, curve a shows the cyclic voltamograms (CVs) of the graphite powder paste electrode in 0.05 M phosphate buffer (pH 7.4) at scan rates of 10 mV/s. Curves b–e show the cyclic voltamograms (CVs) of the graphite powder paste electrode in the presence of different concentrations of H2O2: 2.5, 5.0, 7.5, and 10.0 mM, respectively. In Fig. 9, curve
a shows the CVs of the MWCNTs (diameter, 15–20 nm) paste electrode in 0.05 M phosphate buffer (pH 7.4) at scan rate of 10 mV/s. Curves b–e show the CVs of the MWCNTs (diameter, 15–25 nm) paste electrode in the presence of different concentrations of H$_2$O$_2$: 2.5, 5.0, 7.5, and 10.0 mM, respectively. When the graphite powders were modified on the electrode, the peak currents were only about 0.48 μA. When MWCNTs were modified on the electrode, the peak currents remarkably increased and reached up to 23 μA. From the distinctive reductive current difference between Figs. 8 and 9, it can be seen that the catalytic ability toward H$_2$O$_2$ of modified electrode is mainly determined by the presence of MWCNTs.

4. Conclusion

In summary, multi-walled carbon nanotubes were directly used as catalyst for the hydroxylation of aromatic hydrocarbons. Curved sp$^2$-hybridized carbon surfaces of MWCNTs play an important role in the selective catalytic reactions. The active oxygenated species, with strong oxene characters, may be generated through the interaction between the hydrogen peroxide and the MWCNTs. Without the assistance of any solvent or additive, a high selectivity, up to 98%, was obtained. CNTs were proved to be a highly-active, highly-selective, and well-reproductive heterogeneous catalyst. This provides a wide prospect for the application of CNTs and a simple and easily controlled one pot process at low temperature may be practical in chemical process.

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