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Characterization of multi-walled carbon nanotubes catalyst supports by point of zero charge

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ABSTRACT

Point of zero charge is a useful measurement to assess the surface acidity of multi-walled carbon nanotubes and to characterize functional groups on the multi-walled carbon nanotube surface. Knowledge of point of zero charge also assists the choice of an appropriate metal precursor to be used for electrostatic adsorption to prepare metal particles supported on multi-walled carbon nanotubes. Multi-walled carbon nanotubes with points of zero charge that range from 2.2 to 11.8 have been prepared and characterized. An efficient reduction method, utilizing ethanol at 20 atm and 180 °C, is described and can be used to reduce nitric acid functionalized multi-walled carbon nanotubes to convert the functional groups to mostly hydroxyls.

1. Introduction

The seminal work on Coulombic or electrostatic adsorption on oxide supports (of metal complex precursors to metal particles) may be attributed to Brunelle [1]. Electrostatic adsorption is based on the knowledge that oxide surfaces are populated with hydroxyl groups that become protonated at low pH and deprotonated at high pH producing anion exchange sites or cation exchange sites, respectively. That pH at which the surface is neutral is designated the point of zero charge (PZC). The PZC is an important characterization parameter in order to optimize loading and anchor the metal complex precursor to maximize dispersion (high dispersion and anchoring of the precursor leads to high dispersion of the metal on reduction). At extreme low or high pH, adsorption is inhibited over all surfaces by high ionic strength (see Spieker and Regalbuto [2] for a useful model of electrostatic adsorption, including ionic strength). This results in an optimum pH for maximum loading.

It has been suggested that molecular control of electrostatic adsorption might be achieved by changing the support PZC by doping with cations to increase the PZC, e.g., Na^+ on silica, or by doping with anions to decrease the PZC, e.g., Cl^- on alumina. This works, in so far as PZC change is concerned, but does not affect the electrostatic adsorption of metal complexes (because there is dissolution and reversal of the doping effect) [3]. The oxidation of a carbon support, on the other hand, is reasonably irreversible in the absence of strong reducing agents and can be tuned by both the oxygen loading and the mix of functionalities formed by nitric acid oxidation and modified by reduction. Liquid phase oxidation mainly produces carboxylic acids while gas phase oxidation mainly produces hydroxyl and carbonyl groups [4].

McPhail et al. [5] have reported that the carbon nanotube surfaces may have a wide range of PZC values resulting from different functionalization methods, e.g., refluxing in H_2SO_4/HNO_3 or the nitrosylation. The dispersion of metal nanoparticles may be controlled by the PZC of the carbon nanotube surface. This has been demonstrated for several metal cations, i.e., Co(II), Cu(II), Zn(II), and Mn(II), which exhibited increased adsorption when the pH of the carbon nanotube solution was made more basic [6]. Hao et al. [7] investigated three activated carbons, a graphite and a carbon black sample, and observed a varying PZC ranging from 2.5 to 8.6. Recently Regalbuto and co-workers have extended the PZC characterization to carbon xerogel supported catalysts used for benzene hydrogenation [8] and for fuel cell electrode catalysts [9]. Four carbon xerogels of varying pore sizes (18, 32, 68 and 90 nm) all have a PZC of 9.4 as-prepared and after nitric acid oxidation, the PZC is 2.4 [8]. The pH of maximum uptake was determined for both $[PtCl_6]^{2-}$ and $[Pt(NH_3)_4]^{2+}$. Loadings of 8–10 wt% Pt were achieved using $[PtCl_6]^{2-}$ at pH of 2.4–2.5 (as-prepared carbon xerogel) and with $[Pt(NH_3)_4]^{2+}$ at pH 11.0–11.2 (oxidized carbon xerogel). Using the optimized strong adsorption conditions determined for the as-prepared xerogel, Job et al. [9] prepared catalysts with Pt loadings of 7.5, 15.0 and 22.7 wt% Pt by adsorption of $[PtCl_6]^{2-}$ to saturation at pH 2.5 followed by drying and reduction at 200 °C, repeated three times on the same support. Somewhat surprisingly this resulted in higher density of Pt particles with increased loading but a nearly constant particle size of about 3 nm.

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In this study, we have investigated the systematic variation of the PZC of the surface of nitric acid oxidized multi-walled carbon nanotubes (MWCNT) where the density and functionality of the oxygen containing groups has been varied by reduction and high temperature treatment in an inert atmosphere. Initially, reduction was achieved using $LiAlH_4$, but the residual alumina (and Li^+) impurity complicated interpretation. Among several reducing agents investigated, reduction by ethanol in the liquid phase at high temperature and pressure provides the best results with respect to formation of a high density of hydroxyl groups. The PZC has been varied from 2.2 to 11.8 and the acidity correlated with functionality of oxygen and nitrogen surface groups. An independent measure of MWCNT surface acidity by catalytic reaction was obtained using a 2-methylpent-2-ene isomerization as a probe reaction catalyzed by Brönsted acid sites [10].

2. Materials and methods

2.1. Catalyst preparation

2.1.1. Nitric acid oxidation of MWCNT

The multi-walled carbon nanotubes (MWCNT), synthesized by the chemical vapor deposition (CVD) method, were purchased from Cheap Tubes Inc. Their outer diameter and length are 10–20 nm and 10–30 μm, respectively. Combustion of the MWCNT produces a residual mass of non-volatiles of 2.3 wt%. All other reagents, unless stated otherwise, were used as received and were supplied by Aldrich.

The raw MWCNT were refluxed in 70% nitric acid (15 M HNO_3) at the boiling temperature for 2 h. The mixture was filtered and washed with 100 ml deionized water for 3 or 15 times. The pH of the washing solution was about 1 after three washings and increased to about 7 after 15 washings. The resulting material was then dried overnight at 100 °C in a thermostated oven and crushed to powder.

2.1.2. Grafting of ZrO_2 on MWCNT

The MWCNT were oxidized by nitric acid, and reduced by various reducing agents, e.g., NH_3 and H_2 in the gas phase. After dehydration in refluxing toluene purged by Ar, the hydroxylated MWCNT were grafted with zironium acetylacetoneate ($Zr(acac)_4$) for 6 h in refluxing toluene solution, dried at 120 °C and heat treated in flowing Ar at 450 °C. When ethanol was used as the reducing agent and the solvent, the reduction and grafting were performed simultaneously in ethanol at 20 atm and 180 °C for 6 h. After washing and filteration, the samples were dried at 90 °C and heat treated in flowing Ar at 450 °C. Generally, the reduced MWCNT (0.5 g) were grafted with 0.0115 M $Zr(acac)_4$ solution in 50 ml ethanol.

2.1.3. Sulfation of ZrO_2/MWCNT

The resulting ZrO_2/MWCNT was impregnated with aqueous $(NH_4)_2SO_4$ and again heat treated in flowing Ar at 450 °C to form S-ZrO_2/MWCNT.

2.2. MWCNT characterization

2.2.1. Point of zero charge (PZC) measurement

To measure the point of zero charge, the mass titrations were performed following the method proposed by Solhy et al. [11]. Ten ml solutions with a given initial pH (adjusted by NaOH and HCl) were prepared. MWCNT were added successively in 10 mg increments and the resulting pH values were measured after 20 min stirring to reach an equilibrium pH value. The pH of each suspension was then measured using a digital pH meter (AB 15 from Accumet Basic) calibrated by NBS buffers. The PZC is easily determined from the appearance of a plateau in the plot of pH vs. mass.

2.2.2. Thermogravimetric analysis (TGA)

Because the preparation procedure may cause some loss of Zr cations, the final Zr content of all samples was determined by TGA. TGA was conducted on a Setaram Setsys 1750 instrument in flowing air (Ultra Zero grade, from Airgas). The as-synthesized sample was first loaded in an alumina crucible, which was then placed in the instrument. The temperature was held at 200 °C for 30 min to remove any water adsorbed on the sample and then heated to 1000 °C at 10 °C/min and held at 1000 °C for 30 min. The same temperature profile was repeated immediately after the previous run to obtain the background signal to minimize the error caused by buoyancy and drag forces. The mass loss was also corrected by the mass residue formed by TGA of the as-received MWCNT.

2.2.3. Temperature-programmed desorption (TPD) with mass spectra (MS) analysis

The surface functionalities of all samples were measured by TPD and the correlation of functional groups with temperature of decomposition to CO and/or CO_2 tabulated by Figueiredo et al. [4]. A sample of 50 mg of was loaded into TPD cell. The temperature was increased to 800 °C at a rate of 10 °C/min and held there for 1 h. The signal was collected with an RGA equipped with a quadruple MS detector. The carrier gas (He) flow rate was 20 ml/min.

2.3. Catalytic reaction

2.3.1. Two-methylpent-2-ene isomerization as a catalytic probe

We have used the 2-methylpent-2-ene isomerization as a probe reaction to characterize the activity and acidity (selectivity to trans-3-methylpent-2-ene) of ZrO_2/MWCNT [8]. A sample of 50 mg was loaded into a Pyrex reactor, operated at a space velocity of 25,000 ml/g-cat h at 1 atm and a reaction temperature of 400 °C. Prior to isomerization, the reactor was purged by ultra high purity grade Ar at room temperature. The 2-methylpent-2-ene was injected into the sample cell by using a syringe pump, and the products (trans-3-methylpent-2-ene and 4-methylpent-2-ene) were analyzed by the FID detector.

3. Results

The PZC of the MWCNT, as-received, is 8.7, somewhat lower than the 9.4 reported by Lambert et al. [8] for as-prepared carbon xerogels, but after oxidation (refluxing in 15 M HNO_3 for 2 h, washed three times), it decreases to 2.2. However, some of the functional groups producing the PZC of 2.2 are not stable against multiple washings. That is, 15 washings (after which the PZC does not change) brings the PZC to 3.7.

To investigate the nature of the functional groups that are removed by vigorous washing, we have performed TPD-MS, see Fig. 1. The analysis of the TPD-MS curves for CO and CO_2 was guided by the temperatures of desorption of different functional groups tabulated by Figueiredo et al. [4]. After oxidation by nitric acid and three washings, we observe a substantial desorption of NO, that is essentially removed after 15 washings. The CO_2 peak below 200 °C results from carboxylic acid groups on the surface of the MWCNT, and the higher temperature (500–800 °C) CO_2 peak may be attributed to carboxylic anhydrides and lactones [4]. Before the ethanol reduction, the major oxygen functional group on the MWCNT surface is carboxylic acid. Some functionalization that is decomposed between 200 and 400 °C to produce CO_2 also decreases with vigorous washing. The lactone groups are formed by the ethanol reduction. After ethanol reduction, the CO peak is decreased and the H_2O peak is increased. Therefore, the quinone groups also may be reduced by ethanol. Because there is a simultaneous burst of CO_2, CO and NO below 200 °C, see Fig. 1, we interpret this as combustion of surface groups by adsorbed NO_3^- that is

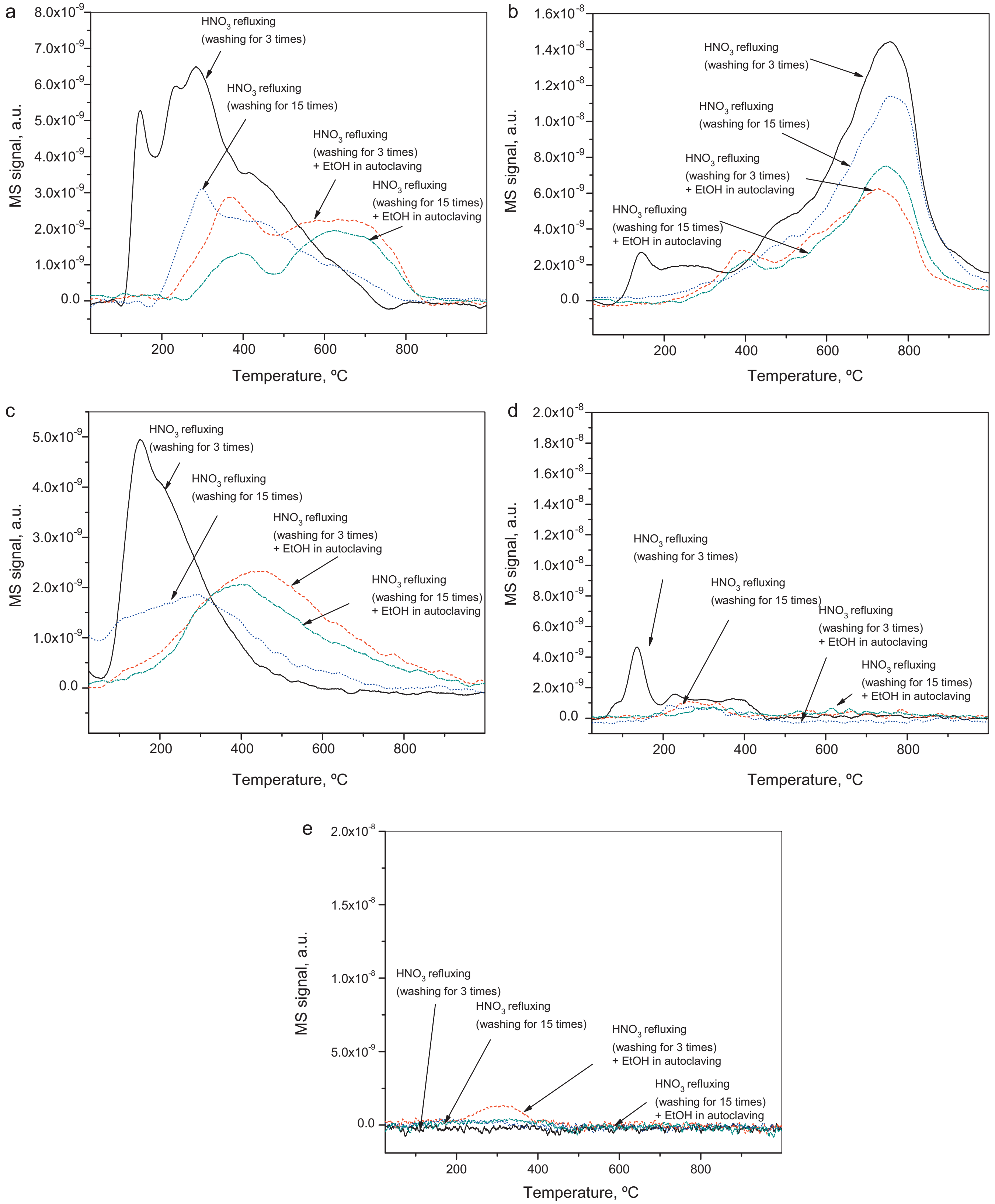

Fig. 1. TPD-MS curves for MWCNT oxidized by nitric acid and reduced by ethanol at 20 atm and 180 °C: (a) CO_2, (b) CO, (c) H_2O, (d) NO, and (e) NH_2.

mostly removed by the 15 washings. However, we believe that the primary effect on PZC is the removal of adsorbed NO_3^- that decomposes during TPD, but survives three washings and a heating to 450 °C, see Fig. 1d.

Thus, nitric acid oxidation followed by varying degrees of washing only affects the PZC of MWCNT in the range of 2.2–3.7. A much more profound change in PZC can be affected by reduction. The goal of reduction was to attempt to maximize conversion

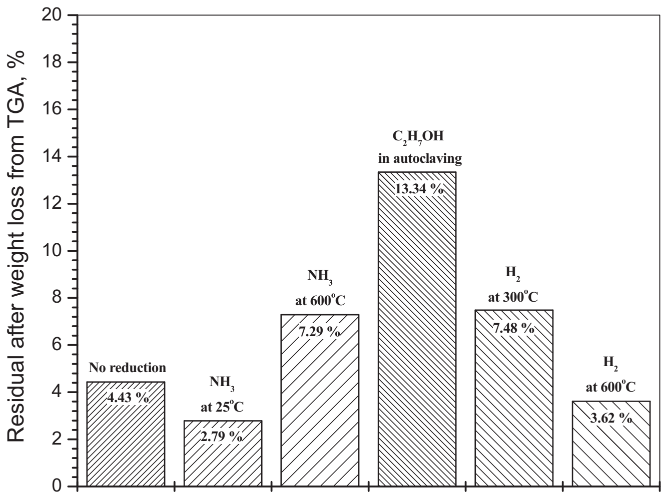

Fig. 2. Weight loss from TGA in air of MWCNT oxidized by nitric acid, reduced by H_2, NH_3 or ethanol. In all cases except ethanol reduction, the grafting of $Zr(acac)_4$ was performed in refluxing toluene at 1 atm. Ethanol reduction and $Zr(acac)_4$ grafting were performed simultaneously at 20 atm and 180 °C.

of oxygen functional groups to hydroxyls, the species that is most proficient in grafting reactions. As an example of grafting of catalytic interest, we have used zirconium acetylacetonate, $Zr(acac)_4$, that reacts with oxygen funcationalized MWCNT and can be transformed to ZrO_2/MWCNT after heat treatment at 450 °C in an inert atmosphere. In general, transition metals that form acetylacetonate complexes are useful for reacting (grafting) with surface hydroxyls and this probe reaction allowed us to determine the effectiveness of several possible reducing reagents to form hydroxyls. In the experiments illustrated in Fig. 2, two gas phase reducing agents (H_2 and NH_3) and a liquid phase reducing agent (ethanol) are compared. In these experiments, stoichiometric reaction would have resulted in 13 wt% ZrO_2 (1.4 at%) if there were sufficient hydroxyls to react with all the $Zr(acac)_4$ charged to the reactor. As-prepared (without reduction) the grafting by $Zr(acac)_4$ only produced 4.43 wt% ZrO_2/MWCNT. Neither gas phase reducing reagent (H_2 and NH_3) was particularly effective for increasing reduction of hydroxyls but ethanol at 20 atm and 180 °C provided sufficient reduction to hydroxyls to achieve stoichoimetric reaction of $Zr(acac)_4$ to form ZrO_2 at a loading of 13 wt% (1.4 at%) of ZrO_2. These results were consistent with TPD-MS results. After reduction, the H_2O desorption temperature was shifted to higher temperature due to the formation of hydroxyl groups on the surface.

Fig. 3 shows the TEM images of as-received, oxidized and ZrO_2 grafted MWCNT. The HNO_3 oxidation of MWCNT would contribute to metal removed as shown in Fig. 3. Solhy et al. [11] reported that the amorphous carbon was consumed at the beginning of the oxidation process. The ends of oxidized MWCNT were opened by HNO_3 oxidation resulting in an increase in surface area by about a factor of 2 (results not shown). Fig. 3c shows the TEM image of S-ZrO_2. There is no evidence of ZrO_2 particle formation suggesting a high dispersion.

In Fig. 4, we show schematically the functional groups after three treatments (washing 3 or 15 times, and ethanol reduction) of MWCNT functionalized by refluxing in 15 M HNO_3 for 2 h and the associated PZC. When the functionalized MWCNT is reduced in ethanol at 20 atm and 180 °C, the PZC increases to 11.8. The primary change appears to be reduction of NO_3^- groups (the nature of the nitrogen groups is not known but the removal by water might imply an ion bound electrostatically) to NH_2 groups, see Fig. 1e. This is demonstrated by a comparison of the TPD-MS of MWCNT simply washed three times after oxidation with nitric acid, where NO is detected as a desorption product between 200 and 450 °C, but the ethanol reduced functionalized MWCNT which shows no detectable NO desorption, but a very substantial NH_2 desorption across the whole temperature range. We note that there is also a measurable NH_2 desorption after 15 washings (but no reduction).

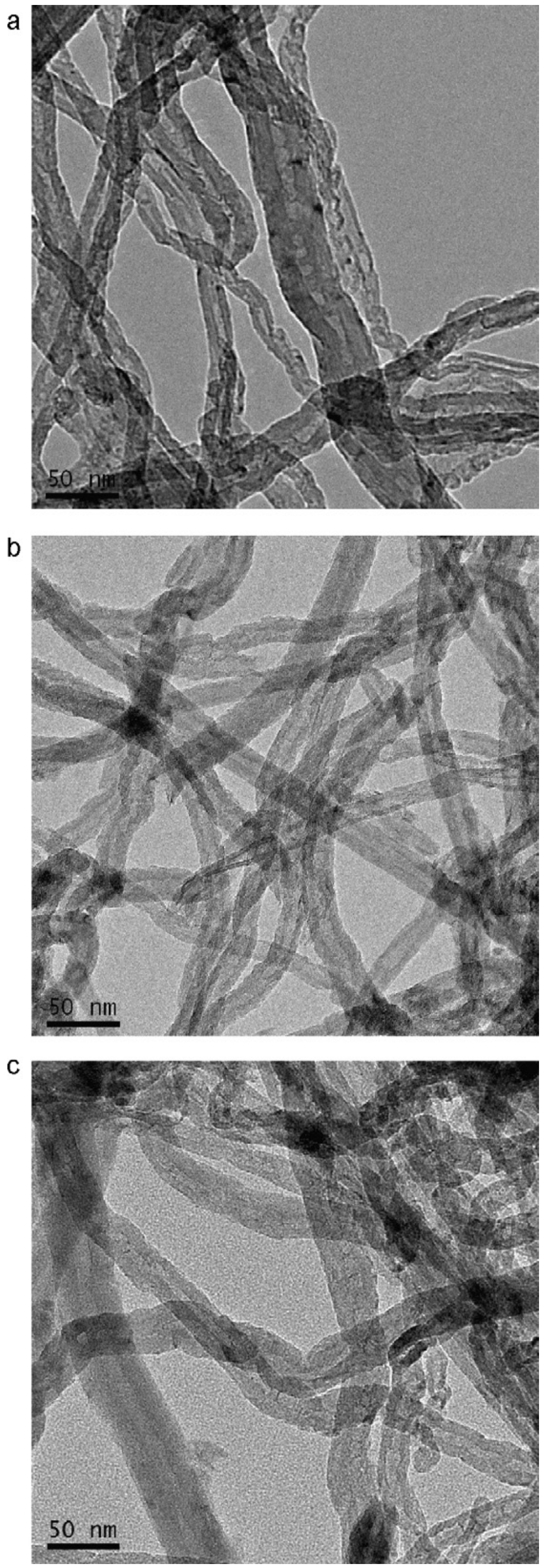

Fig. 3. TEM image of (a) as-received MWCNT, (b) 15 M HNO_3 treated MWCNT and (c) 13 wt% ZrO_2 on MWCNT (after sulfation).

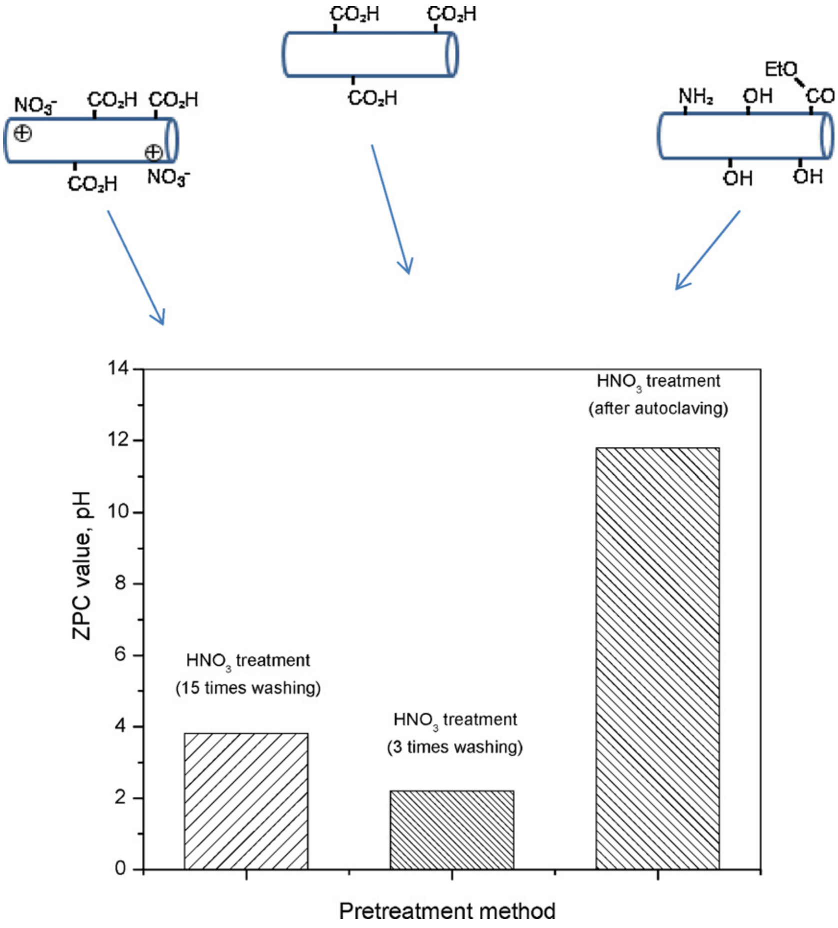

Fig. 4. PZC of MWCNT oxidized by nitric acid and (a) washed 3 times, (b) washed 15 times and (c) reduced by ethanol at 20 atm and 180 °C and schematic of probably dominant functional groups after each treatment.

This is consistent with the rise in PZC from 2.2 to 3.7 between 3 and 15 washings. However, it is likely that there still remains some nitric acid residue such as NO_3^- or NO_2^- that are reduced by hydrogen containing functional groups in the process of TPD.

Fig. 5 exhibits the Noh and Schwartz [12] mass titration measurement of PZC for four samples. The lowest PZC (2.2), is that of MWCNT functionalized by refluxing in 15 M HNO_3 for 2 h and washed three times. The highest PZC (11.8) is that sample reduced (autoclaved at 20 atm and 180 °C) in ethanol. Heat treatment of the reduced MWCNT at 450 °C in Ar lowers the PZC to 8.7 and heat treatment at 650 °C results in a further lowering of the PZC to 7.0, about the same as as-received MWCNT. The former may be attributed to desorption of NH_2 groups (see Fig. 1e) and, according to Figueiredo et al. [4], the decomposition in the range of 450–650 °C is primarily attributed to phenol (hydroxyl) decomposition to form CO, but it is not clear how that accords with a decrease in PZC.

Protonation of 2-methylpent-2-ene produces a tert-cation or alkoxy-compound which rearranges by a 1,2 hydride shift to a secondary ion. Proton loss results in double bond isomerization to cis or trans-4-methylpent-2-ene. Methyl migration requires stronger acidity (more carbonium ion character in the transition state than does double bond migration), but is observed even on γ-alumina to a small extent, to form trans-3-methylpent-2-ene. Under the conditions used here, the activity of a reference silica-alumina (grade 135) is 9.5 mmol/(g-cat h). The activity for a sulfated ZrO_2/MWCNT and four MWCNT samples are compared in Table 1. None of these catalysts without ZrO_2 produce any methyl migration, i.e., they are all weak catalytic acids. About two-thirds of the activity of the reference silica-alumina is due to methyl migration so the remainder, ~3 mmol/(g-cat h) is due to double bond isomerization, i.e., the activity of the two most active MWCNT catalysts is comparable to the weak acid sites on silica-alumina. Sulfated ZrO_2/MWCNT catalyst is substantially more active for acid catalysis than the ref-

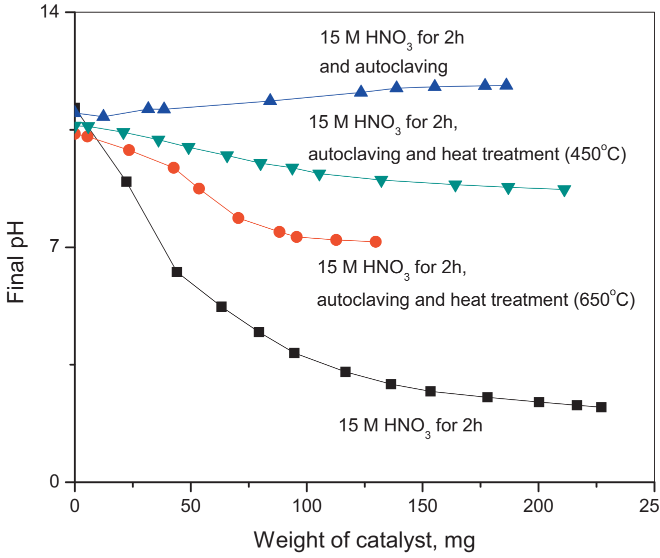

Fig. 5. Titration by mass of MWCNT after consecutive treatments of oxidation by nitric acid (squares), reduction by ethanol at 20 atm and 180 °C (triangles pointing up), heat treatment in He at 450 °C (triangles pointing down) and heat treatment in He at 650 °C.

Table 1
Activity for 2-methylpent-2-ene isomerization.

	PZC (pH)	Activity (mmol/(g-cat h))	Selectivity[a] (mmol/(g-cat h))
As-received	7.1	0.19	0
15 M HNO_3 for 2 h	2.2	2.02	0.01
15 M HNO_3 for 2 h and autoclaving	11.8	0.35	0.01
15 M HNO_3 for 2 h, autoclaving and thermal treatment at 450 °C	8.7	4.6	0.03
Sulfated ZrO_2/MWCNT	2.8	88.2	55.63

[a] Selectivity is the rate of production of trans-3-methylpent-2-ene, the product of a methyl shift of 2-methylpent-2-ene.

erence silica-alumina. The activity of the sulfated ZrO_2/MWCNT is 88.25 mmol/(g-cat h). The selectivity for methyl shift to double bond shift is 63%.

4. Discussion

While it had already been established that the PZC is a useful concept for a variety carbons [6,7], we have extended this measurement to MWCNT. In particular, we have demonstrated that reduction of a nitric acid oxidized MWCNT surface can modify the oxidized MWCNT surface to introduce new functional groups and reach very high PZC. This provides a new route to amine functionalization of MWCNT via nitrogen containing groups adsorbed on the MWCNT being reduced to NH_2.

The reduction of nitric acid oxidized MWCNT by ethanol (at 20 atm and 180 °C) is an efficient method to convert –COOH (and other oxygen containing groups) to hydroxyls, but it also introduces new functional groups such as surface ethyl esters and probably other ethoxide groups. Some evidence for these groups can be seen in the comparison of the TPD-MS of Fig. 1e with Fig. 1a, i.e., a substantial desorption of NH_2 over the whole TPD range and low temperature desorption of CO below 400 °C that did not exist before the ethanol reduction.

One of the important discoveries of this work is a route to oxygen functionalization of MWCNT that is predominantly hydroxyls as demonstrated by the grafting of Zr(acac)$_4$. Here we demonstrate this for a loading of 13 wt% loading, but much higher loadings are possible, e.g., up to 47 wt% (8.6 at%). Assuming an average of 25 layers in our MWCNT, this is equivalent to greater that 60 at% of the external surface or approximately a monolayer of ZrO_2. No evidence for ZrO_2 particles can be observed in transmission electron images at a resolution of <1 nm, but observable particles do form on heat treatment at temperatures in the range of 450–750 °C.

The results for the activity of the variously functionalized MWCNT for isomerization of 2-methylpent-2-ene generally correlate with the measurement of PZC. None of these catalysts have significant strong acidity required to isomerize 2-methylpent-2-ene to 3-methylpent-2-ene (methyl shift), i.e., only products of double bond isomerization are observed. The exception to the correlation with PZC is the MWCNT that have been consecutively treated by nitric acid (oxidation), ethanol reduction and then heat treatment at 450 °C, which has a PZC of 8.7 but is more active for 2-methylpent-2-ene double bond isomerization than is the MWCNT only treated by nitric acid oxidation and washed 3 times (PZC = 2.2). The sites that cause double bond isomerization on this material would appear not to be proton donors (based on the slightly basic PZC) but have not yet been identified.

5. Conclusion

Treatment of nitric acid oxidized MWCNT by ethanol reduction at 20 atm and 180 °C is an efficient method of reduction to a high density of hydroxyls which provide a convenient method to graft metal acetylacetonate metal complexes to the surface of MWCNT. Measurement of PZC of MWCNT can guide the choice of cation/anion metal precursors and adjustment of pH to maximize loading and anchoring of metal particles when MWCNT are used as a catalyst support.

Acknowledgements

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