On the Nature of Oxygen-Containing Surface Groups on Carbon Nanofibers and Their Role for Platinum Deposition-An XPS and Titration Study

4 AUTHORS, INCLUDING:

Dangsheng Su
Chinese Academy of Sciences
643 PUBLICATIONS   13,189 CITATIONS

SEE PROFILE

Krijn P. De Jong
Utrecht University
317 PUBLICATIONS   11,815 CITATIONS

SEE PROFILE

J.H. Bitter
Wageningen UR
158 PUBLICATIONS   5,822 CITATIONS

SEE PROFILE

On the Nature of Oxygen-Containing Surface Groups on Carbon Nanofibers and Their Role for Platinum Deposition—An XPS and Titration Study

A. J. Plomp,[†] D. S. Su,[‡] K. P. de Jong,[†] and J. H. Bitter*,[†]

Inorganic Chemistry and Catalysis, Utrecht University, Utrecht, The Netherlands and Department of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

XPS and acid−base titrations were used to investigate the nature and stability of oxygen-containing surface groups on carbon nanofibers (CNF) and platinum-containing CNF. During heat treatments in inert atmosphere at 973 K all acidic (carboxylic) oxygen surface groups were removed for CNF. Introduction of platinum decreased the temperature at which the acidic oxygen surface groups could be removed to 773 K. It has been demonstrated that both carboxyl and phenol surface groups are able to bring about platinum ion adsorption during Pt/CNF synthesis.

Introduction

Carbon nanofibers (CNF) display considerable potential as catalyst support materials.[1,2] For obtaining highly dispersed platinum on CNF via wet chemical (aqueous) techniques such as homogeneous deposition precipitation (HDP), the presence of oxygen-containing surface groups is essential.[3] These groups can be introduced by, for example, oxidation via (oxygen) plasma treatment,[4] in air[5] or nitric acid.[5] We opt in our study for surface oxidation by concentrated nitric acid, which is expected to introduce primarily acidic oxygen surface groups (carboxylic groups).[6,7]

Earlier studies by Van der Lee et al.[7] and Toebes et al.[3] indicated that acidic surface groups are required to obtain either highly dispersed nickel or platinum on CNF via HDP. For nickel, carboxylic acid surface groups initially adsorb the metal ions, followed by nucleation and growth of the remaining nickel ions as a hydroxide phase during the pH increase.

It is claimed that platinum deposition on CNF via HDP does not result in the formation of a metal-hydroxide phase, but rather that a pH-induced ion adsorption takes place since the pH increased during the synthesis.[3] On the basis of titrations it was concluded that acidic oxygen-containing surface groups were essential for metal-ion adsorption. However, the nature of these oxygen surface groups remains unresolved.

Therefore, we investigated in this study which types of oxygen-containing surface groups are present on oxidized CNF, before and after heat-treatment, and on their platinum loaded equivalents. This approach will lead to a general characterization of the oxygen-containing surface groups present on CNF and to insights in their role during platinum deposition. XPS and acid−base titration were used to identify the nature of the different oxygen-containing surface groups. This study is complementary to and an extension of our earlier work on the characterization of oxygen-containing groups in CNF. Valuable information has been obtained by FT−IR spectroscopy, TPD/ TGA−MS and titration, as shown by us[5,6,8,9] and others.[10] The main advantages of XPS are its high sensitivity, thus allowing the study of low concentrations, and the low interaction of the

X-rays with the carbon. The latter is a major challenge to be addressed in low energy spectroscopic tools such as IR spectroscopy i.e., the incoming radiation is strongly absorbed by the CNF thus causing a high background adsorption. Moreover XPS can provide direct information on the chemical nature of the oxygen groups present in CNF.

Experimental Section

An Ni/SiO$_2$ (20 wt-% nickel) growth catalyst was prepared via HDP using 17.0 g silica (Degussa, Aerosil 200), 21.1 g nickel nitrate hexahydrate (Acros; 99%) and 13.9 g urea (Acros; p.a.) in 1 L demineralized water according to an earlier described procedure.[11] CNF were grown from CO/H$_2$/N$_2$ at 823 K using Ni/SiO$_2$ (2 g) as reported earlier.[12] The resulting CNF material (30 g) was collected and refluxed three times for 1 h per reflux in an aqueous KOH solution (1 M; 0.6 L; Merck; p.a.) to remove SiO$_2$. Subsequently, the material was refluxed two times for 1 h per reflux in concentrated nitric acid (0.6 L; Merck; 65%) to remove exposed nickel and introduce oxygen-containing surface groups on the CNF surface. Finally, the material was washed three times with demineralized water and dried overnight at 393 K. This sample is denoted as CNF-ox.

On part of CNF-ox the acidic surface groups, in particular the carboxylic acid groups, were converted to phenol groups as described by Van der Lee et al.[7] LiAlH$_4$ (1.36 g; Acros; 95%) was dissolved in dry tetrahydrofuran (THF; 135 mL) and after filtration added to dry CNF-ox (8.0 g). After stirring for 20 h, filtration and washing with dry THF, the sample was washed with demineralized water to protonate the alkoxide ions. All aforementioned steps were performed under argon conditions. The resulting material was washed for 1 h in an aqueous HCl solution (Merck; 250 mL; 1 M) to remove possible remaining metal oxides/alkoxides, washed again with demineralized water afterward, dried overnight at 393 K and denoted as CNF-OH.

Platinum was deposited on CNF-ox using HDP (intended metal loading 5 wt-%) as described earlier.[3,9] An acidified suspension (pH 3; 250 mL demineralized water) of CNF-ox (5 g) was stirred and heated to 363 K under inert atmosphere. Subsequently, urea (0.41 g; Acros) and Pt(NH$_3$)$_4$(NO$_3$)$_2$ (0.52 g; Aldrich) were added. After 18 h, the final pH of the slurry was 6.5−7. The material was filtered, washed with demineralized water, dried overnight at 393 K and reduced at 473 K for

* To whom correspondence should be addressed. E-mail: J.H.Bitter@uu.nl.
† Utrecht University.
‡ Fritz-Haber-Institut der Max-Planck-Gesellschaft.

TABLE 1: Physical Properties of the Catalysts

catalyst	metal loading (wt-%)	average metal particle size (nm based on TEM)	titrated mmol acidic groups/g (pH 5)	titrated mmol acidic groups/g (pH 7.5)	O/C atomic ratio
CNF-ox			0.16	0.22	0.082
CNF-red			0.13	0.18	0.071
CNF-OH			0.04	0.10	0.071
CNF-773			0.02	0.04	0.049
CNF-973			0.00	0.00	0.017
Pt/CNF	2.9	1.8	0.02	0.05	0.045
Pt/CNF-773	2.9	1.9	0.00	0.00	0.036
Pt/CNF-973	2.9	2.0	0.00	0.00	0.012
Pt/CNF-OH	1.4	1.9	n.d.[a]	n.d.[a]	n.d.[a]

[a] n.d. = not determined.

1 h (ramp 5 K/min) in H_2/N_2 (100 mL/min; 10% v/v). The resulting catalyst was denoted as Pt/CNF. Part of this catalyst was treated in N_2-flow at 773 or 973 K for 2 h (5 K/min) to remove the oxygen surface groups.[9] The resulting catalysts are denoted as Pt/CNF-773 or Pt/CNF-973.

Platinum catalysts (intended metal loading 5 wt-%) were also prepared on CNF-OH using HDP as described earlier.[3,9] An acidified suspension (250 mL demineralized water; pH 3) of CNF-OH (1 g) was stirred and heated to 363 K under inert atmosphere. Subsequently, urea (0.41 g; Acros) and $Pt(NH_3)_4(NO_3)_2$ (0.10 g; Aldrich) were added. After 18 h, the final pH of the slurry was 6.5−7. The material was filtered, washed with demineralized water, dried overnight at 393 K and reduced at 473 K for 1 h (ramp 5 K/min) in H_2/N_2 (100 mL/min; 10% v/v). The resulting material was denoted as Pt/CNF-OH.

For comparison, nonmetal containing CNF-ox were also reduced at 473 K for 1 h (ramp 5 K/min) in H_2/N_2 (100 mL/min; 10% v/v) and denoted as CNF-red. Nonmetal containing CNF-ox was heat-treated in N_2-flow at 773 or 973 K for 2 h (5 K/min) as well and denoted as CNF-773 or CNF-973.

The metal weight-loading of the samples was determined using ICP-OES. The measurements were performed using a SPECTRO CIROS[CCD] ICP-Spectrometer. Each sample was destructed by heating in aqua regia (1:3 mixture of concentrated HNO_3: HCl) before analysis.

XPS was performed using a modified LHS/SPECS EA200 MCD system equipped with XPS (radiation source: Mg Kα 1253.6 eV and 168 W power). Fixed analyzer pass energy of 48 eV was used resulting in a resolution of 0.9 eV full-width at half-maximum of the Ag $3d_{5/2}$ intensity. The binding energy scale was calibrated using Au $4f_{7/2}$ = 84.0 eV and Cu $2p_{3/2}$ = 932.67 eV. The base pressure of the ultra high vacuum analysis chamber was 1.5×10^{-10} mbar. The sample was mounted on a stainless steel sample holder. To obtain O/C atomic ratios, Shirley backgrounds were subtracted from the experimental data and empirical cross sections were used.[13,14]

The O1s peaks were, before peak deconvolution, normalized at the C1s peak position. It is assumed that the C1s peak is invariant upon the different synthesis methods and treatments applied, since all CNF were graphite-like material. Moreover, all samples originate from the same CNF batch. Peak deconvolution (Gaussian distribution) was performed using Peakfit V4.12 of Systat Software.

Acid−base titrations were performed using a Titralab TIM 880 apparatus. To 60 mL of 0.1 M KCl 0.05 g of the material of interest was added. A solution of 0.01 M NaOH and 0.1 M KCl was used as titrant. The total titrant consumption at pH 5 and at pH 7.5 was used to calculate, respectively, the amount of strong acidic groups and the total amount of acidic groups on the catalysts.[6,7]
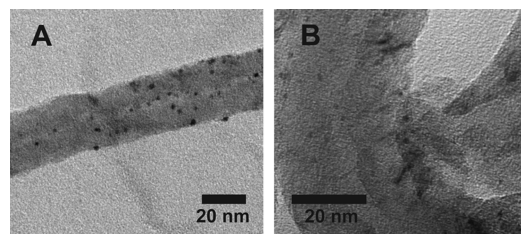
Figure 1. Representative TEM images of (A) Pt/CNF-773 and (B) Pt/CNF-OH.
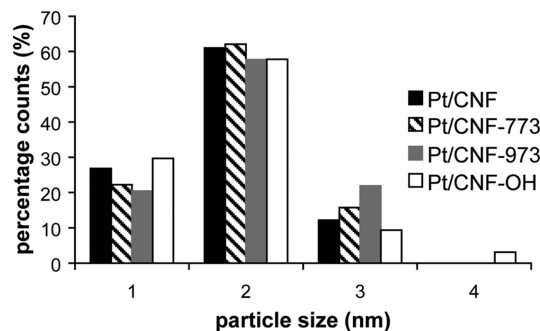
Figure 2. TEM particle size histograms of Pt/CNF, Pt/CNF-773, Pt/CNF-973, and Pt/CNF-OH.

Nitrogen physisorption was performed at 77 K using a Micromeritics Tristar 3000 V6.04 A. The obtained data were used to calculate the BET surface area. Prior to the physisorption measurements, the samples were dried at 473 K for about 14 h under nitrogen flow.

TEM was performed using a Tecnai 20 FEG operating at 200 kV and a point resolution of 2.7 Å. The samples were suspended in ethanol using an ultrasonic treatment and brought onto a holey carbon film on a copper grid.

Results and Discussion

BET surface areas were 179 m^2/g for CNF-ox and 177 m^2/g for CNF-OH with a mesopore volume of 0.26 mL/g. No micropores were found.

The platinum loading after metal deposition was 2.9 wt-% except for Pt/CNF-OH which contained 1.4 wt-% platinum (Table 1). Representative TEM-images of Pt/CNF-773 and Pt/CNF-OH are depicted in Figure 1. Histograms of the particle size distributions as determined using TEM were compiled for all samples (Figure 2). The particle size range for Pt/CNF, Pt/CNF-773, and Pt/CNF-973 was 1−3 nm with an average of 1.8 nm for Pt/CNF, 1.9 nm for Pt/CNF-773 and 2.0 nm for Pt/CNF-973 (Table 1). For Pt/CNF-OH the particle size range was broadened to 1−4 nm though still with an average of 1.9 nm (Table 1). Therefore, we concluded that, given the experi-

Oxygen-Containing Surface Groups on Carbon Nanofibers

J. Phys. Chem. C, Vol. 113, No. 22, 2009 **9867**

mental uncertainties, the platinum particle size was similar on all samples. The absence of sintering irrespective of the applied heat-treatment is in line with earlier observed results.[3,9]

The acidic properties of the oxygen-containing surface groups on the different materials were determined using acid−base titrations.[15] The amount of strong acidic groups was calculated based on the amount of titrant required to reach pH = 5 to establish the number of carboxylic acid surface groups (Table 1).[7] In addition, the titrant consumption to reach pH 7.5 was used to determine the total amount of acidic oxygen surface groups (Table 1).[6,7] The difference between titration results at pH 5 and pH 7.5 is defined as the amount of weak acidic groups. For CNF-ox and CNF-red, the majority of the groups present consists of carboxylic acid surface groups (pH < 5). For the nonmetal containing materials, i.e., CNF-ox, CNF-red, CNF-773, and CNF-973, a strong decrease of the amount of acidic oxygen surface groups was found with increasing severity of the heat-treatment. Treatment at 973 K resulted in complete decomposition of acidic groups. Most likely, CO, CO_2, and H_2O were the decomposition products.[6]

Platinum deposition and subsequent reduction resulted in larger removal of acidic groups going from CNF-ox to Pt/CNF, when compared to going from CNF-ox to CNF-red. Thus, the decrease in oxygen surface groups going from CNF-ox to Pt/CNF must be induced by the presence of platinum and its reduction. It has been described in the literature that during reduction of platinum on carbon supports, hydrogen might be dissociated on the metal and migrate onto the support. This reactive hydrogen can assist in the decomposition of oxygen-containing surface groups into CO, CO_2, and H_2O.[16] Going from CNF-ox to Pt/CNF, 0.17 mmol acidic groups/g were removed (titration up to pH 7.5), while 0.14 mmol/g of strong (carboxylic) acid groups were removed (titration up to pH 5). It is therefore concluded that the majority of the removed groups were carboxylic acid groups.

Heat-treatment in N_2-flow of Pt/CNF at 773 K resulted in complete removal of the acidic groups. For nonmetal containing materials, the temperature had to be increased to 973 K (i.e., CNF-973) to remove all acidic groups (Table 1). This clearly shows the assisting role of platinum in the decomposition of acidic oxygen surface groups.

Treatment of CNF-ox with $LiAlH_4$, thus producing CNF-OH, resulted in a decrease of the amount of carboxylic acid groups (titrations up to pH = 5) on the CNF surface (Table 1). This is expected since this treatment converts carboxylic acid surface groups toward, weaker acidic, phenolic groups. The total amount of titrated groups decreased as well indicating that oxygen surface groups were removed upon the $LiAlH_4$-treatment, which is in agreement with results of Van der Lee et al.[7]

In addition to titrations, XPS was also used to study the nature of the oxygen surface groups on the different samples. The advantage of XPS is that nonacidic surface groups and subsurface oxygen surface groups (i.e., 1−2 nm below the surface) can also be analyzed. Via peak deconvolution of the O1s peak, the amount and nature of the different oxygen surface groups can be established.[15,17−19] Peak deconvolution of the XPS binding energies are influenced by the somewhat arbitrary inputs for the number, shape, and width of the peaks.[15] As will be discussed later for the individual samples, XPS peaks obtained in this research clearly showed three different contributions in the O1s region and therefore peak deconvolution into these three contributions is applied. A summary of peak assignments based on a literature review is given in Table 2.[17,18,20−22] Distinction is made between carbonyl groups (peak 1: 530−531.5 eV),

TABLE 2: Comparison of O1s Peak Deconvolution Positions

	peak 1 C=O	peak 2 C−OH/ C−O−C	peak 3 chem. H_2O/O_2
Proctor (1983)[18]	531.5	533	
Schlögl (1983)[19]	530	533	535
Stöhr (1991)[20]	531	533	
Gardner (1995)[16]	531.2−531.6	532.8−533.1	535.4−535.8
Biniak (1997)[15]	530.4−530.8	532.4−533.1	534.8−535.6

phenol and/or ether groups (peak 2: 532.5−533.1 eV) and chemisorbed water and/or O_2 (peak 3: 534.8−535.8 eV). Some authors, who resolved the O1s peak in four components, agreed with the positions of carbonyl and phenol groups bonded to aromatic systems, but resolved an additional peak at 533.1−533.8 eV which was attributed to the oxygen in the C−O−C linkages in esters and anhydrides. The fourth position, i.e., peak 3 here, is then attributed to oxygen atoms in carboxyl groups.[19,23] The published binding energies for carbonyl and phenol/ether groups are in line with the reference spectra of polymers measured by Louette et al.[24−26] for poly(vinyl alcohol), poly(ether ether ketone), and poly(vinyl butyral). The limitations of comparing polymers with oxygen surface groups on carbon is stressed here as well: the absolute binding energy for oxygen in poly(acroleine) (532.65 eV) is not in agreement with the expected binding energy (530−531.5 eV).[27] Such discrepancies upon comparison of absolute binding energies for oxygen functionalities on carbon and oxygen functionalities on polymers were already observed by Proctor et al.[20] Still, the trend observed for, e.g., poly(ether ether ketone) shows that binding energies for ether-type bonded oxygen (533.40 eV) and carbonyl bonded oxygen (531.31 eV) are well separated, which is therefore used in this study.

The resulting O/C atomic ratios for our materials are compiled in Table 1. Heat-treatment of the CNF-materials resulted in a decreased amount of oxygen surface groups, which is in agreement with the titration results.

Deposition of platinum and subsequent reduction in hydrogen (i.e., Pt/CNF) resulted also in a lower amount of oxygen surface groups present when compared to CNF-red. Heat-treatment of the platinum-containing CNF samples revealed the same trends as observed by titrations, i.e., a lower amount of oxygen surface groups is present on the platinum-containing materials when compared to the nonmetal containing CNF samples, which were heat-treated under similar conditions.

$LiAlH_4$ reduction (i.e., CNF-OH) resulted in removal of oxygen surface groups as well when compared to CNF-ox. The XPS results observed here, i.e., removal of oxygen surface groups upon heat-treatment, platinum deposition/reduction, and $LiAlH_4$ reduction, are in line with the titration results, though the latter technique is only limited to accessible acidic oxygen surface groups.

As described earlier, peak deconvolution of the O1s scan may reveal more information about the amount and nature of the different oxygen-containing surface groups. In Figure 3, the O1s scans for the different materials are compiled. Peak deconvolution for the O1s signals was performed into three contributions. For three representative examples, i.e., CNF-ox, CNF-OH, and Pt/CNF, the raw data and peak deconvolutions are depicted in Figure 4. The peaks were ascribed to the following oxygen groups: peak 1 to carbonyl groups (at 531 eV) and peak 2 to phenol and/or ether type groups (at 533 eV). Peak 3 has been tentatively ascribed to chemisorbed water and/or O_2 (at 535−536 eV).[17,18,21] Going from CNF-ox to CNF-OH, a decrease of peak
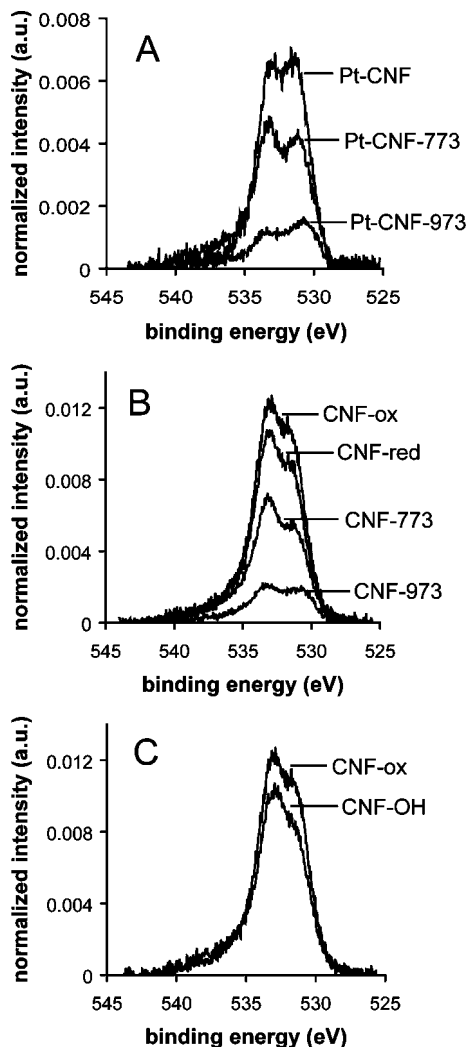
Figure 3. XPS O1s scans normalized at C1s position. (A) Pt-containing samples; (B) nonmetal containing samples; and (C) comparison of CNFox and CNF-OH.

Figure 4. Raw data and peak deconvolutions of the XPS O1s scans. (A) CNF-ox, (B) CNF-OH, and (C) Pt-CNF.
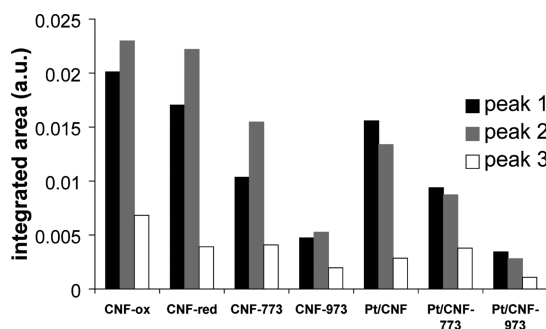
Figure 5. Integrated areas (a.u.) of the O1s signal deconvolutions to the total intensity.

1 (carbonyl groups) and a relative increase of peak 2 (533 eV; phenol and/or ether groups) is visible (Figure 4). Since it is expected that CNF-OH has a high concentration of phenol type groups, it is concluded that the peak at 533 eV must be attributed to the binding energy of oxygen in phenol type groups and confirms thereby earlier reported phenol peak positions.[17−23]

In Figure 5, the absolute integrated areas for all three XPS-contributions are depicted. For the nonmetal containing materials, peak 2 (phenol and/or ether-type bonded oxygen) resulted in the highest surface area irrespective of the applied heat-treatments. After metal deposition and reduction, peak 1 (carbonyl groups) resulted in the highest surface area throughout all heat-treatments applied. This means that upon metal deposition and reduction, XPS results show that mainly phenol groups are removed from the CNF surface. It is important to note here that using XPS, oxygen originating from the carboxylic acid surface groups cannot be resolved (see peak assignments above). Therefore, XPS and titrations are complementary techniques, since titrations showed that platinum deposition and reduction resulted in a substantial removal of carboxylic acid surface groups (Table 1).

The amount of carboxylic acid surface groups for CNF-ox (0.16 mmol acidic groups/g material; pH < 5) is close to the amount of platinum incorporated (i.e., 0.15 mmol Pt/g material), which is theoretically possible assuming a 1/1 ratio. On the basis
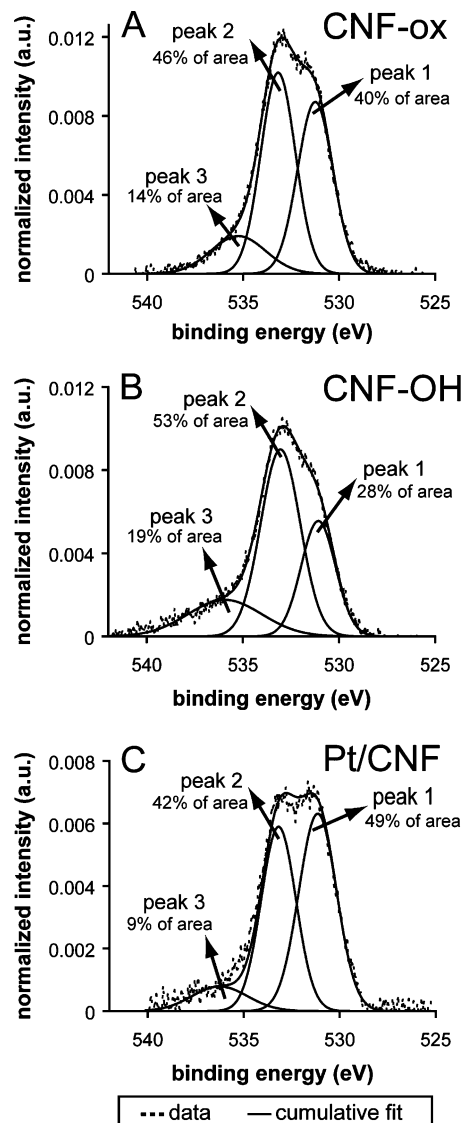
of the metal loading and assuming a surface area of 1.98 nm^2 for a hydrated $Pt(NH_3)_4^{2+}$-complex,[28] it was calculated that the surface coverage is close to a monolayer. Thus, we cannot distinguish whether the amount of carboxylic groups or the surface area of the support determines the platinum loading. Therefore, we continued our investigations by deposition of platinum via HDP on CNF-OH, which contained less carboxylic acid surface groups then CNF-ox. This synthesis resulted in deposition of platinum on CNF-OH, but a lower metal loading

Oxygen-Containing Surface Groups on Carbon Nanofibers

J. Phys. Chem. C, Vol. 113, No. 22, 2009 **9869**

was obtained as compared to deposition on CNF-ox (1.4 wt-% for Pt/CNF-OH vs 2.9 wt-% for Pt/CNF) and therefore shows that carboxylic acid surface groups are important for metal deposition. Since in the latter experiment the amount of platinum (i.e., 0.07 mmol Pt/g material) exceeded the amount of carboxylic acids present on CNF-OH (i.e., 0.04 mmol groups/g material at pH < 5), it is concluded that also other types of oxygen surface groups are involved in platinum deposition. Using XPS analysis, it has been found that after platinum deposition, reduction, and heat-treatment (i.e., Pt/CNF, Pt/CNF-773, and Pt/CNF-973), the majority of the oxygen surface groups are of the carbonyl type, but when platinum is absent (i.e., CNF-ox, CNF-red, CNF-773 and CNF-973), the majority of the oxygen surface groups are of the phenol type. This means that upon metal deposition and reduction, mainly phenol groups are removed from the CNF surface. As described earlier, deposition of platinum is not solely related to the amount of carboxylic acid surface groups. Since mainly phenol groups are present on CNF-OH, and these groups are removed upon metal deposition and reduction in large amounts when compared to carbonyl groups, it is concluded that phenol oxygen surface groups may also enable platinum deposition next to carboxylic acid surface groups. After removal of these oxygen surface groups, the platinum metal particles are probably stabilized directly on carbon via, e.g., defects in the structure or other types of oxygen surface groups.[29,30]

These results differ from the observations of Van der Lee et al.[7] that only carboxylic acid surface groups are required for nickel deposition on CNF. For nickel, a hydroxide phase is formed upon increasing pH (5.5−6.4) which starts to nucleate on nickel ions which were adsorbed at low pH. Since only carboxylic acid surface groups become deprotonated at the low pH range, one requires these groups to adsorb and deposit nickel ions prior to complete nucleation of the nickel hydroxide.[7] Platinum does not form a hydroxide phase in the pH range of HDP synthesis and, therefore, deposition of platinum is more a result of pH-induced ion adsorption than deposition precipitation.[3] During HDP, phenol groups become deprotonated as well at higher pH range.[31,32] Therefore, phenol groups are, next to carboxyl groups, also responsible for platinum ion adsorption. The ion adsorption observed here as a function of pH is in line with the revised physical adsorption model as described by the group of Regalbuto, namely that at pH well above the point of zero charge (i.e., pH 2−3 for oxidized CNF[33,34]), adsorption of cationic platinum occurs on the negatively charged support material.[35,36]

Conclusions

A study on the nature and role of oxygen-containing surface groups, using XPS and acid−base titrations, for platinum deposition on CNF is herein reported. Removal of acidic oxygen surface groups is observed when heat-treatments in inert atmosphere at 973 K were performed. Platinum deposition and reduction on CNF resulted in decreasing decomposition temperature of the acidic oxygen surface groups to 773 K. Synthesis of platinum on CNF via homogeneous deposition precipitation results in metal anchoring on carboxyl as well as phenol oxygen surface groups. It is proposed that during synthesis, both groups become deprotonated and are able to bring about platinum ion adsorption.

References and Notes

(1) de Jong, K. P.; Geus, J. W. *Cat. Rev. -Sci. Eng.* **2000**, *42*, 481.

(2) Serp, P.; Corrias, M.; Kalck, P. *Appl. Catal., A* **2003**, *253*, 337.

(3) Toebes, M. L.; van der Lee, M. K.; Tang, L. M.; Huis in 't Veld, M. H.; Bitter, J. H.; van Dillen, A. J.; de Jong, K. P. *J. Phys. Chem. B* **2004**, *108*, 11611.

(4) Haiber, S.; Ai, X. T.; Bubert, H.; Heintze, M.; Bruser, V.; Brandl, W.; Marginean, G. *Analyt. Bioanalyt. Chem.* **2003**, *375*, 875.

(5) Ros, T. G.; van Dillen, A. J.; Geus, J. W.; Koningsberger, D. C. *Chem.−Eur. J.* **2002**, *8*, 1151.

(6) Toebes, M. L.; van Heeswijk, J. M. P.; Bitter, J. H.; van Dillen, A. J.; de Jong, K. P. *Carbon* **2004**, *42*, 307.

(7) van der Lee, M. K.; van Dillen, A. J.; Bitter, J. H.; de Jong, K. P. *J. Am. Chem. Soc.* **2005**, *127*, 13573.

(8) Ros, T. G.; van Dillen, A. J.; Geus, J. W.; Koningsberger, D. C. *ChemPhysChem* **2002**, *3*, 209.

(9) Toebes, M. L.; Zhang, Y.; Hájek, J.; Nijhuis, T. A.; Bitter, J. H.; van Dillen, A. J.; Murzin, D. Y.; Koningsberger, D. C.; de Jong, K. P. *J. Catal.* **2004**, *226*, 215.

(10) Gorgulho, H. F.; Mesquita, J. P.; Goncalves, F.; Pereira, M. F. R.; Figueiredo, J. L. *Carbon* **2008**, *46*, 1544.

(11) Toebes, M. L.; Bitter, J. H.; van Dillen, A. J.; de Jong, K. P. *Catal. Today* **2002**, *76*, 33.

(12) Plomp, A. J.; Vuori, H.; Krause, A. O. I.; de Jong, K. P.; Bitter, J. H. *Appl. Catal., A* **2008**, *351*, 9.

(13) Shirley, D. A. *Phys. Rev. B* **1972**, *5*, 4709.

(14) Briggs, D.; Seah, M. P. In *Practical Surface Analysis*; 2nd ed.; Wiley: New York, 1990; Vol. 1, Auger and X-ray Photoelectron Spectroscopy; pp 635.

(15) Boehm, H. P. *Carbon* **2002**, *40*, 145.

(16) Fraga, M. A.; Jordao, E.; Mendes, M. J.; Freitas, M. M. A.; Faria, J. L.; Figueiredo, J. L. *J. Catal.* **2002**, *209*, 355.

(17) Biniak, S.; Szymanski, G.; Siedlewski, J.; Swiatkowski, A. *Carbon* **1997**, *35*, 1799.

(18) Gardner, S. D.; Singamsetty, C. S. K.; Booth, G. L.; He, G. R.; Pittman, C. U. *Carbon* **1995**, *33*, 587.

(19) Kvande, I.; Oye, G.; Hammer, N.; Ronning, M.; Raaen, S.; Holmen, A.; Sjoblom, J.; Chen, D. *Carbon* **2008**, *46*, 759.

(20) Proctor, A.; Sherwood, P. M. A. *Carbon* **1983**, *21*, 53.

(21) Schlögl, R.; Boehm, H. P. *Carbon* **1983**, *21*, 345.

(22) Stöhr, B.; Boehm, H. P.; Schlögl, R. *Carbon* **1991**, *29*, 707.

(23) Lakshminarayanan, P. V.; Toghiani, H.; Pittman, C. U. *Carbon* **2004**, *42*, 2433.

(24) Louette, P.; Bodino, F.; Pireaux, J.-J. *Surf. Sci. Spectra* **2006**, *12*, 106.

(25) Louette, P.; Bodino, F.; Pireaux, J.-J. *Surf. Sci. Spectra* **2006**, *12*, 149.

(26) Louette, P.; Kohler, L.; Bodino, F.; Pireaux, J.-J. *Surf. Sci. Spectra* **2006**, *12*, 159.

(27) Louette, P.; Bodino, F.; Pireaux, J.-J. *Surf. Sci. Spectra* **2006**, *12*, 154.

(28) Santhanam, N.; Conforti, T. A.; Spieker, W.; Regalbuto, J. R. *Catal. Today* **1994**, *21*, 141.

(29) Zhang, Y.; Toebes, M. L.; van der Eerden, A.; O'Grady, W. E.; de Jong, K. P.; Koningsberger, D. C. *J. Phys. Chem. B* **2004**, *108*, 18509.

(30) Hull, R. V.; Li, L.; Xing, Y. C.; Chusuei, C. C. *Chem. Mater.* **2006**, *18*, 1780.

(31) Boehm, H. P.; Diehl, E.; Heck, W.; Sappok, R. *Angew. Chem.* **1964**, *76*, 742.

(32) Boehm, H. P. *Carbon* **1994**, *32*, 759.

(33) Geus, J. W.; Van Dillen, A. J.; Hoogenraad, M. S. *Mater. Res. Soc. Symp. Proc.* **1995**, *368*, 87.

(34) Hoogenraad, M. S. *PhD-thesis*, Utrecht University, 1995.

(35) Hao, X.; Spieker, W. A.; Regalbuto, J. R. *J. Colloid Interface Sci.* **2003**, *267*, 259.

(36) Hao, X.; Quach, L.; Korah, J.; Spieker, W. A.; Regalbuto, J. R. *J. Mol. Catal. A: Chem.* **2004**, *219*, 97.