The Role of Oxygen- and Nitrogen-containing Surface Groups on the Sintering of Iron Nanoparticles on Carbon Nanotubes in Different Atmospheres

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The sintering of iron nanoparticles on carbon nanotubes (CNTs) under different atmospheres was investigated. CNTs were first treated with HNO₃ vapor at 200 °C to obtain O-functionalized CNTs (OCNTs). The OCNTs were treated in ammonia at 400 °C to obtain N-doped CNTs (NCNTs). Highly dispersed FeO nanoparticles were subsequently deposited by chemical vapor deposition from ferrocene under oxidizing conditions. The obtained FeO/OCNT and FeO/NCNT samples were allowed to sinter at 500 °C under flowing helium, hydrogen, or ammonia. The samples were studied by X-ray diffraction, transmission electron microscopy, and X-ray photoelectron spectroscopy. A significant increase in particle size and a decrease in Fe surface atomic concentration were observed in all the sintered samples. The sintering on OCNTs was more severe than on NCNTs, which can be attributed to stronger metal-substrate interactions and a higher amount of surface defects on NCNTs. The applied gas atmosphere had a substantial influence on the sintering behavior of the nanoparticles: treatment in helium led to the growth of particles and a significant widening of particle size distributions, whereas treatment in hydrogen or ammonia resulted in the growth of particles, but not in the widening of particle size distributions.

Introduction

Carbon nanotubes (CNTs) are very promising materials in heterogeneous catalysis because of their unique structural and electronic properties. CNT-supported transition metal catalysts have been used for hydrogenation reactions, Fischer–Tropsch synthesis, and in fuel cells. The application of CNTs relies strongly on their surface. Surface functional groups and surface defects can either be anchoring sites for catalyst nanoparticles, or active centers for catalytic reactions. Therefore, surface chemistry has been one of the major focuses in CNT research in recent years.

Oxygen functionalization, which is one of the most common methods for the modification of CNTs, can be achieved by treatment with nitric acid. In addition to oxygen, the incorporation of nitrogen into CNTs has offered new opportunities for tailoring their chemical and physical properties on the surface. The incorporation of nitrogen results in an enhancement of conductivity, owing to the contribution of additional electron density donated by nitrogen atoms. Moreover, the presence of nitrogen atoms in carbon has a profound effect on the surface chemical activity and electron transfer rates. Nitrogen-incorporated carbon as a catalyst support is also expected to improve the durability of the resultant catalyst, owing to enhanced π bonding and strong electron donor behavior of nitrogen. Various methods have been reported for the incorporation of nitrogen in CNTs, for example, catalytic growth using nitrogen-containing precursors, plasma treatment under nitrogen or ammonia atmospheres, and thermal treatment under ammonia. Treatment of pre-oxidized carbon materials by ammonia appears to be a simple, but very effective method for the creation of nitrogen-containing functional groups on CNTs. Moreover, the incorporation of nitrogen is frequently accompanied by the formation of surface defects on CNTs due to the different chemical bonds between carbon and nitrogen atoms. The modified CNTs, either with functional groups or with surface defects, are readily applicable as catalyst supports for nanoparticles.

Different methods were reported for the synthesis of nanoparticles supported on CNTs, including solution-based methods, such as incipient wetness impregnation, deposition-precipitation, and electrodeposition. We have shown that chemical vapor deposition (CVD) can lower the particle size, leading to highly dispersed nanoparticles with narrow size distributions.

Here, we demonstrate the effect of oxygen- and nitrogen-containing surface groups on the sintering of Fe nanoparticles on CNTs. The nitrogen-containing CNTs were prepared by the treatment of oxygen functionalized CNTs with ammonia. Extremely small iron oxide nanoparticles with diameters of about 1 nm were deposited on CNTs by CVD. The samples were treat-
The treatment of CNTs by HNO₃ vapor at high temperature led to a significantly greater amount of oxygen-containing functional groups, as compared to conventional treatment by heating under reflux in liquid HNO₃. Owing to the enhanced oxygen content, nitrogen can be readily incorporated into these CNTs through various reactions between the oxygen-containing groups and ammonia at elevated temperature, for example, at 400 °C. Both the oxygen- and nitrogen-containing groups can improve the hydrophilicity and the wetting properties of CNTs, and both of them can act as anchoring points for foreign species, for example, metal precursors. In addition to surface functional groups, surface defects also play an important role in the deposition of nanoparticles. This is especially important in the case of nitrogen-incorporated CNTs, for which a large number of surface defects, such as edge planes, are believed to be present, as suggested by earlier studies.

The presence of a large number of surface functional groups and surface defects allows the deposition of Fe at low temperatures without significant loss of Fe precursors. Therefore, the deposition of Fe oxides was performed at 200 °C, which is rather low compared to literature conditions. 19 mg of ferrocene was applied to 100 mg nanotubes leading to a theoretical weight loading of 6%. A rather small total flow rate of carrier and oxidation gases was applied, which allows sufficient time for the diffusion of the Fe precursor in the gas phase, leading to homogeneous deposition across the powder-like substrates. The decomposition of ferrocene was monitored by online mass spectrometry. It can be seen from Figure 1 that a higher Fe current of the C₅H₅ ligand (m/e = 65) was detected on the NCNTs than on the OCNTs, indicating more effective adsorption on NCNTs. Elemental analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES) gave Fe loadings of 3.59 and 3.96 wt % on the NCNTs and OCNTs, respectively. The Fe yield on NCNTs was slightly higher than that on OCNTs, which is in agreement with the results observed by online mass spectrometry. Notably, the samples were prepared by CVD and the overall loadings were in the low range. In wet chemistry, results can vary based on the amount of catalyst loading, since the numbers of anchoring sites are different on OCNTs and NCNTs.

Sintering experiments with FeO/OCNT and FeO/NCNT were performed simultaneously in one reactor under identical conditions, excluding the deviation of experimental conditions in different batches. The as-deposited and sintered samples in different atmospheres at 500 °C were studied by using TEM imaging. The histograms were obtained by measuring a sample of approximately 150 particles. It can be seen from Figure 2a and b that very small nanoparticles of 1–2 nm diameter were obtained on the OCNTs and NCNTs. The FeO nanoparticles are smaller on the NCNTs. The particle size distributions of both samples are very narrow, and the histograms show that those on the OCNTs and NCNTs are in the range of 1 to 2 nm (Figure 3a and b). More particles were measured with diameter below 1 nm and fewer particles were measured with diameter over 2 nm on the NCNTs compared to on the OCNTs. After thermal treatment in helium at 500 °C for 1 h, a significant increase in particle size and widening of size distribution was observed (Figure 2c and d). Particles over 15 nm were observed in both samples. The number of particles larger than 8 nm was found to be higher on the OCNTs than on the NCNTs, as can be seen from the histograms in Figure 3c and d. The FeO nanoparticle size on the NCNTs is smaller than on the OCNTs treated in hydrogen. Thermal treatment in hydrogen, rather than helium, led to very homogeneous nanoparticles with narrow size distributions as shown in Figure 2e and f. Sintering in hydrogen seems to be less severe than in helium. The difference in particle size on the OCNTs and NCNTs is clearly visible from the histograms (Figure 3e and f). Most of the particles are in the range of 4–6 nm on NCNTs, whereas they are 5–7 nm on OCNTs. Thermal treatment in ammonia caused the least sintering of the nanoparticles (Figure 2g and h); the obtained particles are clearly smaller than in the samples treated in hydrogen. Histograms show that the nanoparticle size is dominantly 3–6 nm on NCNTs and 4–7 nm on OCNTs. As a whole, although the Fe loading is slightly higher on NCNTs, the nanoparticles are, on average, smaller than on OCNTs, both before thermal treatment (as-deposited) and after sintering under different atmospheres at 500 °C.

XRD was used, as a bulk method, to determine the crystal structure and provide information on the size of crystallites and nanoparticles. Contributions from carbon were observed in all the samples, including peaks at around 42–45° and 54° (Figure 4). Given that the features from carbon are common in all the samples, the following discussion focuses on the iron species. As a result of extremely small particle size in the as-deposited samples (mainly 1–2 nm), only background signals were obtained from the nanotubes and no signal was detected that could be attributed to the Fe species. Magnetite (Fe₃O₄) was the main component observed in the two samples treated at 500 °C in helium (Figure 4a). Contributions from α-Fe were also detected. Hematite (Fe₂O₃), which is believed to be the...
dominant phase of Fe species after deposition under oxidizing atmosphere, was not detected. Clearly, partial reduction occurred during thermal treatment in helium, that is, the partial reduction of iron oxide by surface functional groups or carbon in inert atmosphere. Moreover, the intensities of the corresponding peaks of the OCNT sample are slightly higher than the NCNT sample indicating larger particles on the OCNTs, which is in agreement with the TEM results. For the two samples treated in hydrogen, a weak contribution at about 65° is identified that originates from Fe species (Figure 4b), which indicates small particle sizes. The peak can be assigned to α-Fe that is formed by reduction at 500 °C. The nanoparticle shell must have been re-oxidized upon exposure to air at room temperature after reduction. However, the core remains in the metallic state as indicated by the diffraction patterns. The samples treated in ammonia gave complicated diffraction patterns. To confirm the presence of nitride, the XRD measurements were repeated with a smaller step width and a longer collection time. The diffraction patterns obtained are shown in Figure 4c. Iron nitride of the type ε-Fe₃N was clearly resolved. The peak between 44° and 45°, which may be related to graphite and/or α-Fe, appeared to be much weaker than in Figure 4a and b. The peak at 65°, which is solely related to α-Fe, was not present in the range scanned for these two samples. Therefore, the presence of α-Fe in ammonia-treated samples cannot be fully excluded.

The FeOₓ/OCNT and FeOₓ/NCNT samples with and without thermal treatment were further studied by XPS. As an averaging method, the XPS instrument used in this study typically measures an area of 3000 μm² by 60 μm². [22] As is shown above, Fe deposited in air led to the formation of iron oxide nanoparticles. After thermal treatment at 500 °C, under different atmospheres, the samples were exposed to air at room temperature. Therefore, Fe exists at least partially in the oxidized state even in the reduced samples. The formation of surface oxides is especially important for the interpretation of experimental data obtained from surface sensitive techniques such as XPS. Figure 5a and b show the Fe 2p spectra of FeOₓ/OCNT and FeOₓ/NCNT samples, respectively. The Fe 2p core levels are split into the 2p₁/₂ and 2p₃/₂ components as a result of spin-orbit coupling. All samples show characteristic Fe 2p₃/₂ peaks at
711 eV indicating the presence of Fe$^{3+}$ species. For the as-synthesized and hydrogen-treated samples both on OCNTs and on NCNTs, shake-up satellites can be clearly observed at 719 eV, which is a typical feature of Fe$^{3+}$ species.[23] It is known that metallic iron can be easily oxidized in air even at room temperature, which explains the presence of Fe$^{3+}$ species in the reduced samples in hydrogen. Additional contributions appear at 707.3 eV in the samples treated in ammonia (Figure 5a and b, NH$_3$), which can be assigned to iron nitride species and is in agreement with the XRD studies. Nitride was also detected in the FeO$_x$/NCNT sample after treatment in helium, as indicated by the clear peak at 707.3 eV (Figure 5b, He). Given that the treatment was performed in helium for this sample, the surface nitrogen groups other than ammonia must be the nitrogen source for nitride formation. The XP spectra plotted in Figure 5 were normalized to the corresponding C 1s peaks. Hence, the peak intensities reflect the dispersion and, correspondingly, the particle size. It can be seen that the intensities of the Fe 2p spectra of the NCNT samples are higher than those of the corresponding OCNT samples, which can be attributed to smaller particle size for the NCNT samples. Moreover, it is known from elemental analysis that the Fe loading on NCNTs is higher than that on OCNTs, which also contributes to higher peak intensities. The surface atomic concentrations of Fe, C, O, and N derived from XPS studies are listed in Table 1. It can be seen that the Fe concentrations of all NCNT samples are higher than the corresponding OCNT samples. As a result of the small particle size, the as-is samples show high Fe concentrations. The as-is FeO$_x$/NCNT gives a maximum Fe concentration of 7.1%. Thermal treatment led to a decrease in Fe concentrations. The Fe is in agreement with literature results.[8] Quantitative analysis showed that the samples treated in helium have the smallest amount of oxygen in iron oxides (Table 1). This low oxide concentration can be attributed to the reduction of the oxides by carbon at high temperatures and the formation of stable surface Fe species, such as carbides, which cannot be oxidized by air during sample transfer. For the samples reduced in hydrogen, re-oxidation occurred upon exposure to air. Hence, the samples treated in hydrogen showed higher amounts of oxides than those treated in helium (Table 1). Additionally, there are further factors influencing the amount of oxygen on the sample surfaces. The deposited Fe species can catalyze the decomposition of O-groups upon heating. In this respect, Fe oxides and metallic Fe on OCNTs are believed to be more effective than Fe–N species (nitrides and oxynitrides) on NCNTs. This could be one reason that less O was detected on FeO$_x$/NCNT than on FeO$_x$/OCNT. Also the high Fe dispersion on NCNTs led to high oxygen levels as a result of the formation of surface iron oxides and/or oxynitrides during sample transfer to XPS in air.

Nitrogen was detected in the FeO$_x$/NCNT samples after treatment in helium and ammonia, as indicated by XPS (Figure 7). Ammonia treatment also led to the formation of nitrogen species in FeO$_x$/OCNT. However, treatment at 500 °C in hydrogen removed all the nitrogen surface groups on FeO$_x$/NCNTs. Fitting of the XP N 1s spectra resolved two prominent peaks in the samples: pyridinic at 398.8 eV and pyrrolic at 400.4 eV.[15] Traces of pyridine oxides were also detected as indicated by the peak at around 403 eV. The amount of nitrogen is higher on the samples treated in ammonia (Table 1). It can be seen
that the treatment of the FeOx/NCNT sample in helium led to an increase of nitrogen concentration from 2.4 to 3.3%. This increase may be a result of the sintering of the Fe particles and the exposure of surface nitrogen groups.

As can be seen from the TEM, XRD, and XPS studies, the applied atmosphere has a significant influence on the sintering behavior of the nanoparticles on the OCNTs and NCNTs. Treatment in helium led to significant sintering and widening of particle size distributions, which could be related to reaction of iron oxide with carbon, that is, high temperature carbothermic reactions. Iron oxide can be reduced by the carbon substrate in inert atmosphere forming metallic Fe at high temperatures. Additionally, reaction at the particle-substrate interface can enhance the mobility of the nanoparticles leading to sintering. However, in hydrogen and ammonia the nanoparticles were reduced by the applied reduction gas at lower temperatures compared with the carbothermal reduction. Furthermore, metallic Fe can hardly react with the carbon substrate under reducing conditions at the applied temperatures, and the particles are therefore less mobile. As a result, sintering of the nanoparticles was less severe in hydrogen and ammonia, and substantial widening of particle size distributions was not observed.

Clearly, the surface functional groups play a vital role in the sintering of Fe nanoparticles. We believe that at least two factors have contributed to the less severe sintering on NCNTs.

![Figure 4. XRD patterns of FeOx/OCNT and FeOx/NCNT samples after treatment at 500 °C for 60 min in helium (a), hydrogen (b), and ammonia (c).](image)

![Figure 5. XP Fe 2p spectra of FeOx/OCNT (a) and FeOx/NCNT (b) samples after treatment at 500 °C for 60 min under different atmospheres.](image)

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(a) Oxygen in iron oxides calculated from the fitted peaks at 530.2 eV of the O 1s spectra.
than on OCNTs: the strong iron-nitrogen interaction at the metal-carbon interface and the surface defects created as a result of incorporation of nitrogen in carbon. The strong iron-nitrogen bond enhanced metal-support interactions limiting the coalescence of neighboring nanoparticles. Edge plane defects are typically present on the nitrogen-doped carbon surface, which may help to lower the mobility of the nanoparticles. Furthermore, the thermal stability of the surface oxygen- and nitrogen-containing groups may also influence the sintering behavior of the iron nanoparticles. It is known that nitrogen-containing surface groups are significantly more stable than oxygen-containing groups. [8, 11, 15] Therefore, the treatment at 500 °C does not cause a significant loss of anchoring sites on NCNTs, which is not the case on OCNTs. The presence of these anchoring sites can also help securing the nanoparticles on their original positions upon heating thus hindering the sintering of these nanoparticles.

Conclusions

Highly dispersed iron oxide nanoparticles were deposited on CNTs functionalized by oxygen- or nitrogen-containing groups. Thermal treatment was performed in different atmospheres to study the sintering of the nanoparticles. A significant increase in particle size and a decrease in surface atomic concentration of Fe were observed in all the samples after thermal treatment. It was found that sintering on OCNTs was more severe than on NCNTs, indicating stronger metal-substrate interactions on NCNTs. The incorporation of nitrogen into carbon led to the formation of surface defects, which also helped to stabilize the nanoparticles against sintering. Additionally, the high thermal stability of nitrogen-containing groups is beneficial for maintaining small particle sizes at high temperatures. The applied atmosphere had a significant influence on the sintering behavior of the nanoparticles. The treatment in helium led to a significant widening of particle size distributions, which is believed to be related to the carbothermic reaction between iron oxide and carbon at high temperatures. Under reducing atmosphere iron oxide can be reduced at lower temperatures. Hence, thermal treatment in hydrogen or ammonia led to less sintering of the nanoparticles. As a next step for this work, we will be applying the obtained results to Fischer–Tropsch synthesis.

Experimental Section

Incorporation of oxygen and nitrogen in CNTs

Carbon nanotubes (CNTs), with inner diameters of 20–50 nm and outer diameters of 70–200 nm, were obtained from Applied Sciences Inc. (Ohio, USA). The as-received CNTs were first thermally treated under flowing helium for 1 h at 800 °C to remove the polyaromatic impurities on the surface. The thermally treated CNTs were then functionalized by HNO₃ vapor treatment at 200 °C for 24 h, which is reported to be highly effective for oxygen functionalization of CNTs. [9] After cooling, the CNTs were dried at 60 °C to obtain oxygen-containing CNTs (OCNTs). To introduce nitrogen-containing functional groups, 200 mg of the OCNTs were loaded into a vertical quartz-tube reactor with an inner diameter of 20 mm. The sample was treated at 400 °C for 6 h in flowing ammonia (8 vol.% NH₃ in He) at a flow rate of 25 sccm. The obtained nitrogen-containing CNTs were designated as NCNTs.

Deposition of iron by chemical vapor deposition

The obtained OCNTs and NCNTs were used as substrates for the deposition of iron oxides in a fixed-bed reactor with ferrocene (Merck, 98%) as an iron source. Helium (purity 99.9999%) was used as the carrier gas and synthetic air (20.5% O₂ in N₂) as the oxidizing gas. The flow rates were adjusted by mass flow controllers. In a typical experiment, 100 mg of OCNTs or NCNTs were loaded into the reactor, and 19 mg ferrocene (corresponding to a Fe loading of 6 wt%) was placed in the sublimation chamber. The deposition was performed in two steps. First, the reactor was heated to 200 °C at 10 °C min⁻¹ using a resistance heating wire, and the subli-
The reactor was heated to 350 °C, air (25 sccm) was introduced to the reactor. The sublimation chamber was heated to 110 °C in an oven. Simultaneously, helium (25 sccm) was passed through the sublimation chamber and air (25 sccm) was introduced to the reactor. The sublimation finished within about 1 h, as indicated by an online mass spectrometer. Subsequently, the reactor was heated to 350 °C at 10 °C min⁻¹ under the same flow conditions. The calcination was performed for 2 h. The reactor was then cooled down to room temperature to obtain the as-synthesized CNT-supported iron oxide (designated as FeO_x/OCNT and FeO_x/NCNT, respectively).

Sintering experiment

Sintering the iron oxide nanoparticles supported on OCNTs and NCNTs was performed in a horizontal quartz tube reactor with an inner diameter of 30 mm. The thermal treatment was performed always with two samples in parallel, i.e., FeO_x/OCNT and FeO_x/NCNT. The samples in two quartz boats were loaded into the center of the reactor, which was then heated to 500 °C at a rate of 10 °C min⁻¹ and maintained at that temperature for 60 min. The following atmospheres with a total flow of 100 sccm were used for the treatment: (1) pure helium; (2) hydrogen and helium, 1:1; (3) 10 vol. % ammonia in helium. After treatment, the samples were cooled to room temperature in flowing helium (100 sccm).

Characterizations

Inductively coupled plasma optical emission spectrometry (ICP-OES) was used for elemental analysis. A Hitachi H-8100 microscope operated at 200 kV was applied for transmission electron microscopy (TEM) measurements. X-ray diffraction was measured using a PANalytical MPD diffractometer equipped with CuKα radiation, a secondary graphite monochromator and 0.04 rad incident/secondary beam Soller slits. Measurement conditions were 45 kV, 40 mA, 0.5° divergence slit, and 0.2 mm receiving slit width. X-ray photoelectron spectroscopy (XPS) measurements were carried out in an ultra-high vacuum (UHV) set-up equipped with a monochromatic AlKα X-ray source (1486.6 eV; anode operating at 14 kV and 55 mA) and a high resolution Gammatrada–Scienta SES 2002 analyzer. The base pressure in the measurement chamber was maintained at about 7 × 10⁻¹⁰ mbar. The measurements were carried out in the fixed transmission mode with a pass energy of 200 eV, resulting in an overall energy resolution better than 0.5 eV. A flood gun was applied to compensate for the charging effects. The binding energies were calibrated based on the graphite C1s peak at 284.5 eV. The CASA XPS program with a Gaussian–Lorentzian mix function and Shirley background subtraction was used to analyze the XP spectra. The peak positions for all the samples were reproducible along with the fixed Gaussian to Lorentzian mix function and Shirley background subtraction was used to analyze the XP spectra. The XP spectra were normalized to the corresponding C1s peaks.

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