Creation of surface defects on carbon nanofibers by steam treatment

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Abstract

A direct strategy for the creation of defects on carbon nanofibers (CNFs) has been developed by steam treatment. Nitrogen physisorption, XRD, Raman spectra, SEM and TEM analyses proved the existence of the new defects on CNFs. BET surface area of CNFs after steam treatment was enhanced from 20 to 378 $m^2/g$. Pd catalysts supported on CNFs were also prepared by colloidal deposition method. The different activity of Pd/CNFs catalysts in the partial hydrogenation of phenylacetylene further demonstrated the diverse surfaces of CNFs could be formed by steam treatment.

Key words

carbon nanofibers; surface defects; steam treatment; palladium

1. Introduction

Carbon nanotubes (CNTs) and carbon fibers (CNFs) are interesting materials for different applications due to their special geometry and electronic, chemical, mechanical, and thermal properties [1–7]. The research on the modification and potential applications of CNTs and CNFs is of great significance since their feasible industrial production in large quantity [8,9]. Like other carbon materials, CNTs and CNFs are hydrophobic and inert in nature, which are not favorable for many applications. The surface modification of CNTs or CNFs is often performed by the introduction of surface functional groups, among which, oxygen- and nitrogen-containing functional groups have been most extensively studied in the last years [10–12]. The most commonly applied method for oxygen functionalization is chemical oxidation with acids [13–15]. The surface functionalization modifies not only the surface chemistry, but also the textural properties like specific surface area and porosity of CNTs [16]. The surface and textural properties can subsequently influence the CNTs application. In addition to surface functionalities, surface defects can also be used to tune the property of carbon materials for different applications [17]. For example, it was found that with the increase of defects the adsorption capacity of carbon materials can be greatly enhanced [18,19]. However, as compared to chemical functionalization, the creation of surface defects has been rarely studied experimentally. On the other hand, the types of defects and their potential applications have been mainly investigated from the theoretical aspect [17,20]. Hence, it is of high interest to develop simple and effective experimental methods for the creation of surface defects on CNTs or CNFs. Recently, Xia et al. reported a strategy for creating defects on the surface of CNFs in a controlled manner based on the catalytic steam gasification of carbon [21]. As a byproduct, the gasification reaction produces synthesis gas.

In this work, the surface modification of CNFs was performed by steam treatment. It is environmentally friendly and enables low-cost production in large-scale operations. A series of experiments were carried out to investigate the surface properties of CNFs treated by steam. The BET surface area of the treated CNFs has been greatly improved. Furthermore, colloidal Pd nanoparticles synthesized in ethylene glycol were deposited on the treated CNFs. The catalysts exhibited different activities in the hydrogenation of phenylacetylene, and further demonstrated that the diverse surfaces of the CNFs can be created by steam treatment.

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2. Experimental

2.1. Steam treatment of CNFs

The as-received CNFs were purchased from Applied Sciences Inc (Ohio, USA). The outer diameter of the CNFs was 70–200 nm, and the length was 50–100 μm. The BET surface area of the as-received CNFs was 10–20 m²/g. In order to remove the polymer impurities (e.g., polyaromatic hydrocarbons) from surface, the as-received CNFs were pretreated in helium (200 mL/min) at 800 °C for 1 h before steam treatment. The obtained pyrolytically stripped CNFs were designated as PS CNFs. The BET surface area of the PS CNTs was 20–30 m²/g.

A typical CNFs gasification process with steam involved the following steps: 0.200 g PS CNFs was placed in the middle part of the reactor using a quartz boat. The samples were heated under helium flow (100 mL/min) at a heating rate of 10 °C/min to the desired temperature, and then water vapor was introduced by flowing helium (100 mL/min) through a saturator filled with water at room temperature. The reaction was kept for a period of time. Then, the reactor was cooled down to room temperature in helium (100 mL/min). The obtained CNFs samples will be referred to as temperature (°C)–time (h). For example, the sample obtained by steam treatment at 850 °C for 3 h is designated as 850-3.

2.2. Catalyst preparation

Pd nanoparticles were synthesized from Pd(OAc)₂ (0.013 g) and ethylene glycol (25 mL) in 100 mL round bottomed flask by sonication at 30 °C for 3 h. Then CNFs support (0.500 g) was added. The slurry was stirred continuously for 21 h at room temperature. The obtained black suspension was filtered, washed by ethanol and dried at 60 °C for 24 h. No additional treatments were performed prior to catalytic activity measurements.

2.3. Characterization

Physisorption measurements were carried out with a Quantachrome Autosorb-1-MP system. BET surface area was determined by static nitrogen physisorption at 77 K subsequent to out-gassing at 300 °C until the pressure was lower than 5 mbar.

X-ray diffraction analysis of the samples was carried out using a Rigaku D/Max-RB diffractometer with Cu $K_{\alpha}$ monochromatized radiation source ($\lambda = 1.54178$ Å), operated at 40 kV and 100 mA. Diffraction data were collected in 2θ range of 5°–90° at a scanning rate of 10°/min. The interplane distance ($d_{002}$) between graphene layers of CNFs was determined from the diffraction peak (002) by the Bragg equation:

$$d_{002} = \frac{\lambda}{2\sin\theta} \quad (1)$$

where, $\lambda$ is the wavelength of Cu $K_{\alpha}$ radiation (nm) and $\theta$ is the diffraction angle in radians. The degree of graphitization (g) was calculated by the Maire and Mering formula [22]:

$$g = \frac{0.3440 - d_{002}}{0.3440 - 0.3354} \times 100\% \quad (2)$$

where, 0.3440 is the interlayer spacing of the fully non-graphitized carbon (nm) and 0.3354 is the interlayer spacing of the ideal graphite crystallite (nm).

Raman spectra were measured on a Jobin Yvon LabRAM HR 800 instrument with a 532 nm excitation laser. The power of the laser line at the sample was around 1 mW.

The morphology and structure of the samples were examined by scanning electron microscopy (NOVA NanoSEM 450) and transmission electron microscopy (Tecnai G² F30 S-Twin, 300kV Transmission Electron Microscope).

2.4. Phenylacetylene hydrogenation

Catalytic activity measurement for the partial hydrogenation of phenylacetylene was described in detail elsewhere [23]. The reaction was carried out in a 50 cm³ closed vessel with temperature controlled by a water bath. 0.020 g Pd catalyst was placed in the reaction vessel with 0.600 g phenylacetylene and 10 mL ethanol. The vessel was filled with H₂ to 0.40 MPa and vented three times to remove the air, finally filled with H₂ to 0.40 MPa. The reaction was carried out at 50 °C for 40 min with stirring. The analysis of the product was carried out using a gas chromatograph (SE-54/52 capillary column, FID detection). N-octane was used as internal standard.

3. Results and discussion

The gasification reaction of CNFs with steam can be described by the following equation:

$$C + H_2O \rightarrow CO + H_2 \quad (3)$$

The carbon atoms of CNFs could react with water vapor to produce CO and H₂ at high temperatures. Carbon atoms are missing in the form of CO from the hexagonal network of the CNFs and dangling bonds are saturated by hydrogen atoms, resulting in small vacancy defects (steps) or large defects in the form of holes and slits (3D defects) in the hexagonal network of the CNFs. The defects on the smooth surface of the CNFs can effectively increase the BET surface area of the CNFs. Figure 1 shows the BET surface areas with respect to the relative weight loss for the samples of CNFs obtained under the different conditions. There was almost no weight loss for the samples treated with steam at low temperatures, such as 600-1, 700-2, and 700-3, which indicated that the reaction could hardly occur when the temperature is below 700 °C. Corresponding to the samples of 800-3, 825-3, 850-2, 850-3, 900-0.5, 900-1, 900-1.5 and 900-2, the relative weight loss reached to 2.9%, 6.3%, 7.4%, 11.0%, 8.4%, 14.2%, 26.7% and 32.0%, respectively and the corresponding BET surface areas were 43, 73, 142, 170, 54, 56, 81 and 378 m²/g, respectively. Compared to the BET surface area of PS CNFs, the increased BET surface areas of the above samples can be
attributed mainly to the defects on the CNFs created in the reaction. It can be seen that the reaction was heavily affected by reaction temperature and time. First, the higher the temperature was, the faster the rate of the weight loss. For instance, the weight loss of 850-3 was approximate 4 times as much as 800-3, and the weight loss of 900-2 was more 4 times than that of 850-2. Second, comparing 850-2 with 850-3, as well as 900-0.5 with 900-2, both the weight loss and the BET surface areas increased as the steam treatment time increased. Third, BET surface area was not necessarily increased as the relative weight loss increased for the different samples. For example, the relative weight loss for 900-1 was higher than those for 825-3, 850-2 and 850-3, while the BET surface area was lower, which indicated that new and different defects could be produced at a higher temperature. From our point of view, when the temperature was below 850°C, the reaction was relatively mild and the vast majority of weight loss resulted from the missing of carbon atoms or groups of neighboring atoms on the surface of CNFs. The higher BET surface area of 850-3 could be attributed to the produced surface defects in the form of the step and terrace on the CNFs. Furthermore, when the temperature was 900°C, the reaction became relatively violent. As a result, the wall of the CNFs was partially destructed accompanied by great weight loss and the defect in the form of the hole was formed on the CNFs, which cannot significantly contribute to the increase of BET surface area, since the initial CNFs were open-ended. The highest BET surface area of 900-2 could be attributed to the large structural damages.

Figure 1. The relative weight loss and BET surface area of the CNFs obtained under different steam treatment conditions

Figure 2 shows the XRD patterns of PS CNFs. The diffraction peaks at 26.19° and 44.55° can be assigned to the graphite (002) plane and the Fe (110) plane, respectively. The appearance of a new peak at 35.64° for the sample 800-3 could be assigned to cubic Fe₂O₃, in conformity with the loss of Fe (110) for the samples of 850-3, 900-1, and 900-2. This indicated that the residual Fe catalysts in the CNFs could also react with H₂O at high temperature, resulting in Fe₂O₃. With the increase of temperature, the differences among the diffraction peaks of graphite (002) planes for the samples were already apparent and these peaks shifted slightly toward smaller diffraction angle. Usually, the degree of graphitization (Dg) is used to analyze these changes. If the dislocations and defects on the wall of CNFs increased, Dg would be reduced. According to the Maire and Mering formula (2), when the average interplane distance \( d_{002} \) is larger than 0.3440, the value of Dg should be less than zero. Whether the negative value of Dg has any real meaning or not, it could represent a structure that is far from the ideal graphite structure. Obviously, the higher the value of \( d_{002} \) is, the lower the value of Dg. The analysis results from XRD are listed in Table 1. As the temperature increased from 800 to 850 °C, the value of Dg decreased from 36% to 30%, which could be attributed to the defects produced on the wall of CNFs. Moreover, the trend became much stronger at 900 °C. Especially, for the sample of 900-2, the value of Dg decreased to −9%, implying that the structure of CNFs was seriously destroyed, which was in parallel with the relative weight loss shown in Figure 1.

![Figure 2. XRD patterns of the CNFs](image)

Table 1. Data from XRD patterns of the CNFs

<table>
<thead>
<tr>
<th>Samples</th>
<th>2θ (°)</th>
<th>Average interplane distance ( d_{002} ) (nm)</th>
<th>Degree of graphitization (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS CNFs</td>
<td>26.19</td>
<td>0.3402</td>
<td>44</td>
</tr>
<tr>
<td>800-3</td>
<td>26.14</td>
<td>0.3409</td>
<td>36</td>
</tr>
<tr>
<td>850-3</td>
<td>26.10</td>
<td>0.3414</td>
<td>30</td>
</tr>
<tr>
<td>900-1</td>
<td>26.00</td>
<td>0.3426</td>
<td>15</td>
</tr>
<tr>
<td>900-2</td>
<td>25.84</td>
<td>0.3448</td>
<td>−9</td>
</tr>
</tbody>
</table>

Raman spectroscopy was employed to further determine the structural order of CNFs treated by steam. Referring to Refs [24–26], the peak at 1500–1605 cm⁻¹ (G band) is related to the vibration of \( sp^2 \)-hybridized carbon atoms in a graphite layer. The peak at 1250–1450 cm⁻¹ (D band) is associated with the disorder-induced vibration of carbon atoms. The integrated intensity ratio \( R = I_G/I_D \) between G band and D band represents the graphitization degree of the CNFs. The corresponding Raman spectra are illustrated in Figure 3. With the increase of temperature, G band decreased and D band increased. The change of structural order evaluated by \( R \) was...
shown in Figure 3. $R$ decreased from 1.47 to 1.15, with respect to the sample from 800-3 to 900-1. The results of Raman spectra led to the same conclusion as XRD did. The destruction of the graphite structure in CNFs was weak when the temperature of the steam treatment was below 850 °C, and the new defects could be created on the surface of CNFs treated by steam to form a disordered region. However, it became serious at 900 °C. The reduced structural order was mainly attributed to the strong destruction of the structure of CNFs.

For the sample of 900-2, the relative weight loss is too large which leads to a seriously destroyed structure. Obviously, it is not suitable to treat the CNFs under the kind of severe condition. Thus, Pd/PS, Pd/800-3, Pd/850-3 and Pd/900-1 catalysts were prepared to further investigate the effect of the defects on the surface of CNFs on catalytic properties. Corresponding to Pd/PS, Pd/800-3, Pd/850-3 and Pd/900-1, the Pd loadings were 1.04, 0.80, 1.18 and 1.27 wt% by inductively coupled plasma (ICP) analysis, respectively.

Figure 6 shows the XRD patterns of the Pd/CNFs samples. The reflections at about 40° assigned to Pd (111) were detected in all samples, which indicated that Pd nanoparticles deposited on CNFs were synthesized. The intensity of the peaks at about 26° decreased sequentially from Pd/800-3 to Pd/900-1, which was consistent with the XRD in Figure 2. On the contrary, the intensity of the peaks at about 26° for Pd/PS was weaker than Pd/800-3. This might be associated with the defective surface of Pd/800-3. For the smooth surface of PS CNFs, the deposited Pd nanoparticles could make it rough and disordered. Thus, the intensity of the peaks at about 26° could be decreased. When Pd nanoparticles were deposited on the defective surface of CNFs, Pd atoms could saturate the defect site. For instance, the vacancy could be saturated by the deposition of Pd atoms, which formed pseudo-hexagons. It could increase the structural order of the treated CNFs to some extent.

Partial hydrogenation of phenylacetylene to styrene was used to test the catalytic performance of Pd/PS, Pd/800-3, Pd/850-3, and Pd/900-1 catalysts. We have tested the hydrogenation of phenylacetylene in the presence of the supports (PS, 800-3, 850-3 and 900-1) at 50 °C, 0.40 MPa for 40 min. The results showed that almost no hydrogenation reactions could be detected. Figure 7 shows the conversion and selectivity of the partial hydrogenation of phenylacetylene to styrene. For Pd/PS, Pd/800-3, Pd/850-3 and Pd/900-1 catalysts, the conversions of phenylacetylene are 86%, 84%, 82% and 65%, with respect to the selectivities to styrene of 98.7%, 98.7%, 98.8% and 98.8%, respectively. For the catalysts of Pd/PS, Pd/800-3 and Pd/850-3, the conversion of phenylacetylene decreased slightly from 86% to 82%. However, for the catalyst of Pd/900-1, the conversion decreased obviously to 65%. These could be attributed to the different active cites.
Figure 4. SEM images of the CNFs at the scale of 20 µm and 200 nm: (a, a’) PS CNFs, (b, b’) 800-3, (c, c’) 850-3, (d, d’) 900-1, (e, e’) 900-2
Figure 5. TEM images of the CNFs: (a, b) 850-3, (c, d) 900-2

Figure 6. XRD patterns of the Pd/CNFs samples

Figure 7. The conversion and selectivity of the partial hydrogenation of phenylacetylene to styrene

of Pd resulted from the different surface of CNFs, since the hydrogenation of phenylacetylene is structure sensitive [27]. For 900-1, it might be possible that Pd nanoparticles deposit in the holes on the wall of CNFs, which could greatly reduce the number of the effective Pd sites. For Pd/800-3 and Pd/850-3, Pd nanoparticles were believed to be on the surface of the CNFs, while it might also gathered in the defects of the CNFs, resulting in a small loss of Pd exposed sites. Thus the reduced conversion is relatively slight. Even though there is no obvious improvement for the treated CNFs supported Pd catalyst in the phenylacetylene hydrogenation, it has still evidenced that the new defects produced on the surface of the CNFs through their gasification with steam affect the catalytic performance.

4. Conclusions

PS CNFs were treated by steam in the different conditions. It is a novel way to effectively increase BET surface area of the CNFs, though the structural order of CNFs reduced with the increased temperature. The increased BET surface area was mainly attributed to the new produced defects on the surface of CNFs. In our case, the sample of 850-3 has a larger BET surface area with an appropriate relative weight loss and a slight variation of the structure order. Colloidal Pd nanoparticles were first synthesized in ethylene glycol without other protective stabilizers by sonication and deposited on the samples of CNFs. As expected, the different results of the catalytic performance in the phenylacetylene hydrogenation provide further evidence of the new defects produced on
CNFs through their gasification with steam.

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References