

Modifying functionalized-carbon-nanotube capacity to enhance water-vapor adsorption capacity from nitrogen gas

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Abstract

The primary objective of this paper is to enhance the water-vapor-adsorption capacity of multiwall-carbon-nanotube (MWCNT) from nitrogen gas by grafting sulfonic acid groups and doping palladium nanoparticles into the adsorbent. MWCNT has been selected to be modified because of having homogeneous adsorption energy compared to silica gel. As a result, it is capable of creating isotherm having sharp rising zone which is an important feature for gas dehydration application. For this purpose, MWCNT functionalized by hydroxyl groups (MWCNT-OH) was utilized to produce MWCNT functionalized by sulfonic acid groups (MWCNT-OSO₃H), MWCNT-OH doped by palladium nanoparticles (MWCNT-OH-Pd) and MWCNT-OSO₃H doped by palladium nanoparticles (MWCNT-OSO₃H-Pd). Thermal and mass stability, Fourier-transformation infrared and atomic absorption analyses supported the fact that the functional groups and palladium nanoparticles were placed successfully throughout the carbon nanotubes. Then, the water-vapor adsorption isotherms of MWCNT-OH, MWCNT-OSO₃H, MWCNT-OH-Pd and MWCNT-OSO₃H-Pd were obtained at two temperatures of 15 and 24 °C. The water-vapor adsorption experiments revealed that by substituting sulfonic acid groups for the hydroxyl ones the adsorption of water vapor was enhanced only for higher gas humidity. However, by intercalating palladium nanoparticles into MWCNT-OSO₃H the capacity for water-vapor adsorption was improved for lower gas humidity as well. The obtained isotherms followed the isotherms type of V which is prevailing in water-vapor adsorption systems.

Keywords

adsorption, gas dehydration, carbon nanotubes, functionalization

1. Introduction

Water vapor has been recognized as the most important impurity in natural gas product because of its adverse effect on heating value, pipeline corrosion, hydrate formation and pipeline efficiency (Gholami et al., 2010). With producing powerful adsorbent materials, gas adsorption has been considered as the most economical method for gas dehydration. Since the advent of carbon nanotubes (CNT), they have been examined as adsorbent materials by different researchers. The investigations about the adsorption of water vapor (Kim et al.,

2008), oxygen (Fujiwara et al., 2001), methane (Rasoolzadeh et al., 2008), hydrogen (Lamari et al., 2002), carbon dioxide (Khalili et al., 2012), several organic compounds (Agnihotri et al., 2005) and hydrogen sulfide (Oftadeh et al., 2013) on CNTs can be mentioned as examples. The adsorption capacity of CNTs can be enhanced by surface modifications such as functionalization. By performing appropriate functionalization of CNTs, they can be used to adsorb a wide range of materials (Hirsch and Vostrowsky, 2005). The functional groups can be grafted into the porous adsorbents by

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different techniques such as covalent, non-covalent, inner-structural and outer-structural (Adams et al., 2009). The adsorption of various gases on functionalized CNTs has been investigated extensively, e.g. CO₂ and CH₄ on the CNTs functionalized by carboxylate groups (Surapathi et al., 2012), CO₂ on CNTs functionalized by polyethylene glycol groups (Khan et al., 2012), H₂, O₂, CO₂ and CH₄ on CNTs functionalized by poly sulfonate (Kim et al., 2007) groups, CO and NH₃ on CNTs functionalized by carboxylate groups (Dong et al., 2013) and CO₂ on CNTs functionalized by amine group (Hsu et al., 2010).

The pristine CNTs cannot be considered as a powerful adsorbent for water vapor because of weak attraction between water molecules and the surface carbon atoms. However, this problem can be resolved by attaching appropriate functional groups to the surface carbon atoms of nanotubes (Do, 1998). The initial water molecules are adsorbed on the functional group as a result of hydrogen bonding. However, after making a cluster of water molecules around a functional group, further adsorption occurs by hydrogen bonding between two water molecules (Kim et al., 2008). Among many different hydrophilic functional groups examined so far, carboxylate (Kim and Agnihotri, 2008), hydroxyl (Yun et al., 2012), potassium carboxylate (Zhang et al., 2009), amines (Coccini et al., 2010, Fagnoni et al., 2009), acrylic acid (Mao et al., 2011) and poly acryl amid (Pei et al., 2008, Wang et al., 2007) can be mentioned as the most successful ones. Adding nanoparticles of the metals such as Au (Smorodin et al., 2005, Lin et al., 2013), Co (Nguyen et al., 2013), Pd (Su and Chuang, 2010), Pt (Penza et al., 2008) and Fe (Wadhawan et al., 2003) can lead to further improvement in water adsorption capacity. Metal nanoparticles serve as active sites inside CNTs for gas adsorption (Yun et al., 2009). Moreover, the electrical mutual influence of CNTs and metal nanoparticles speeds up the oxidation of the surface carbon atoms (Cho and Park, 2007). The investigations carried out on the application of metal nanoparticles have been focused on the hydrogen adsorption into nanostructures for fuel cell applications (Suehiro et al., 2007, Kong et al., 2001). Palladium nanoparticles have been widely employed as the catalyst for hydrogenation (Ruta et al., 2008), oxidation (Dimitratos et al., 2005), C-C bond formation (Beller et al., 1996) and fuel cell reactions (Kong et al., 2001). Palladium nanoparticles have been utilized to enhance capacity of single-wall carbon CNTs

(SWCNT) to adsorb hydrogen (Chun et al., 2004), SO₂, CH₃OH and CH₄ (Zhou et al., 2010) at room temperature. They have been also used in CNTs to produce NO₂ gas sensor at atmospheric pressure (Yun et al., 2009). The study performed by Kim et al. is the only piece of research which directly deals with water vapor adsorption on functionalized CNTs. In this study, the adsorption of water vapor on SWCNTs functionalized using carboxyl groups has been investigated at room temperature. Su and Tsai (2008) have carried out an investigation on application of palladium in CNTs to improve their water vapor adsorption capacity. In this study, they doped a small amount of palladium to pristine CNTs and CNTs functionalised by carboxyl groups to produce Pd-CNT and Pd-CNT-COOH. Then, these two types of adsorbents were examined to find the effect of palladium on carbon nanotubes properties as a sensor.

The present study focused on examining the capability of sulfonic acid, as a hydrophilic functional group of CNTs, in water vapor adsorption. Sulfonic acid groups should have the two following characteristics to be considered as an effective functional group:

1. Having the high capacity in water vapor adsorption to adsorb a large number of water molecules
2. Forming adequately strong bond with surface carbon atoms to maintain attached during the regeneration stage.

Then, the synergy generated by addition of palladium nanoparticles to the CNTs functionalized by sulfonic acid groups was investigated. The beneficial effect of using palladium nanoparticles can be maximized when they are distributed uniformly throughout the CNTs. The CNT ability to adsorb water vapor is a function of many factors such as temperature, pressure, CNT size, CNT purity, CNT type, functional group concentration and CNT open-end percentage. As a result of this complexity, this ability was investigated by comparing the CNTs functionalized by sulfonic acid groups with the one functionalized by hydroxyl groups while keeping influencing factors the same.

2. Material and methods

MWCNT-OH were purchased from Horicon Company. The specifications of this material, which is produced by chemical precipitation method, are given in the following:

External diameter	10-20 nm
Internal diameter	5-10 nm
Length	30 μ m
OH percentage	3.06 wt%
Purity	95 wt%
Ash percentage	<1.5 wt%
Specific surface area	200 m ² /g
Open-end percentage	50%

Palladium salt, chlorosulfonic acid, Chloroform, Methanol and Sodium acetate were purchased from the Merck Company. FTIR (Perkin Elmer, Spectrum 65) spectra were obtained using the dry bromide potassium pills. Thermal gravitational analyses, DTG (Mettler, TG-50) were performed with the heating rate of 5°C/min within the temperature interval of 25 to 500°C. The palladium concentration doped into nanotubes was measured by ICP-AES (Liberty-RL). Atomic analysis was performed by using CHNS analyzer (Leco, CHNS-932).

2.1. The synthesis of MWCNT-OSO₃H

250 g MWCNT-OH was added to a beaker containing 5 ml chloroform and was stirred for 1 h. Next, the reaction continued for another 1h in an ultrasound bath. Figure 1 shows this reaction schematically. Then, the suspension was filtered to separate the solid residue. Finally, after several washing steps with chloroform, the solid was heated in a vacuum oven at 100°C for 48 h. The black solid residue is MWCNT-OSO₃H.

2.2. The synthesis of MWCNT-OSO₃H-Pd

24 mg PdCl₂ (0.136 mol) and 0.88 mg NaCl (0.152 mol) is combined in a beaker containing 5 mm methanol and the mixture was stirred for 24 hr at room temperature. The solution was filtered and diluted by 10 mm methanol. After adding 100 mg MWCNT-OSO₃H to this solution, it was agitated for 24 hr at 60°C. Then, after adding 0.76 mg sodium acetate to the mixture at room temperature, it was stirred for 1 hr. The reaction path is given in figure 2. The solution was filtered using a paper filter placed on the surface of a vacuum hopper. The solid residue was placed in vacuum oven for 48 hr. The final product is MWCNT-OSO₃H-Pd.

2.1. The synthesis of MWCNT-OH-Pd

MWCNT-OH-Pd was synthesized using the same way as described for MWCNT-OSO₃H-Pd synthesis. The only difference is using MWCNT-OH instead of MWCNT-OSO₃H. The reaction path is given in figure 3.

2.1. Characterization of the adsorbents

In order to examine the replacement of OH by SO₃H groups in the synthesized MWCNT-OSO₃H, FTIR, TGA-DTG and CHNS were employed. Palladium loading in synthesized MWCNT-OH-Pd and MWCNT-OSO₃H-Pd was evaluated by ICP-AES analysis.

2.1. Water vapor adsorption experiment

The schematic diagram of the experimental batch system for adsorption experiment is shown in figure 4. This system consists of a cylindrical adsorption chamber with the volume of 873 cc, the humidification column, drying zeolite bed and the instruments for measuring temperature (± 0.1 K), pressure ($\pm 0.1\%$) and humidity ($\pm 2\%$ RH). Two streams of dry and humid nitrogen were combined in the adsorption chamber to attain the desired humidity. The humid stream is provided by passing nitrogen stream coming from the gas cylinder through the humidification column. The dry stream is supplied by passing the nitrogen gas coming from the gas cylinder through the zeolite adsorption bed. The pressure in the adsorption vessel was adjusted at 1 atm for all experiments by employing the regulator connected to the nitrogen gas cylinder. The whole system is kept in a lab room whose temperature was maintained at 10°C using air conditioning system. A heating jacket with PID temperature controller was employed to regulate the temperature at 15 and 24°C with the accuracy of ± 0.1 K.

20 mg of the adsorbent is heated in vacuum oven at the temperature of 100°C for 48 hr. Then, it is placed in the adsorption chamber and exposed to the humid nitrogen at desired temperature, pressure and initial humidity. The humidity is recorded during the adsorption process up to 24 hr. Afterwards it is assumed that the equilibrium is obtained. Having the initial and final humidity, the amount of water vapor adsorbed on the adsorbent can be calculated which is one point of isotherm. Then, the same procedure is performed at different initial humidity to fulfill the isotherm curve.

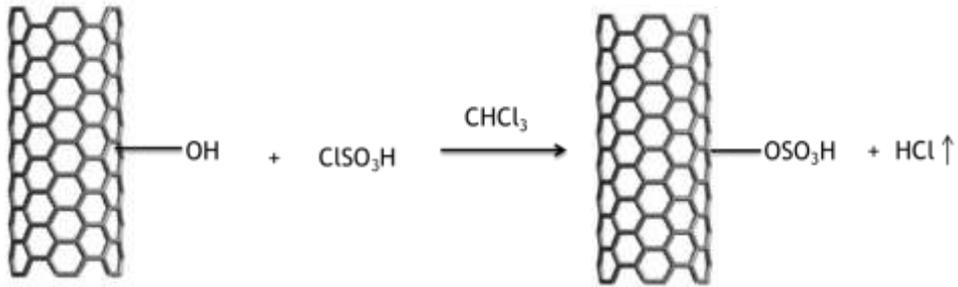


Fig. 1. The schematic picture of NT functionalization using sulfonic acid groups

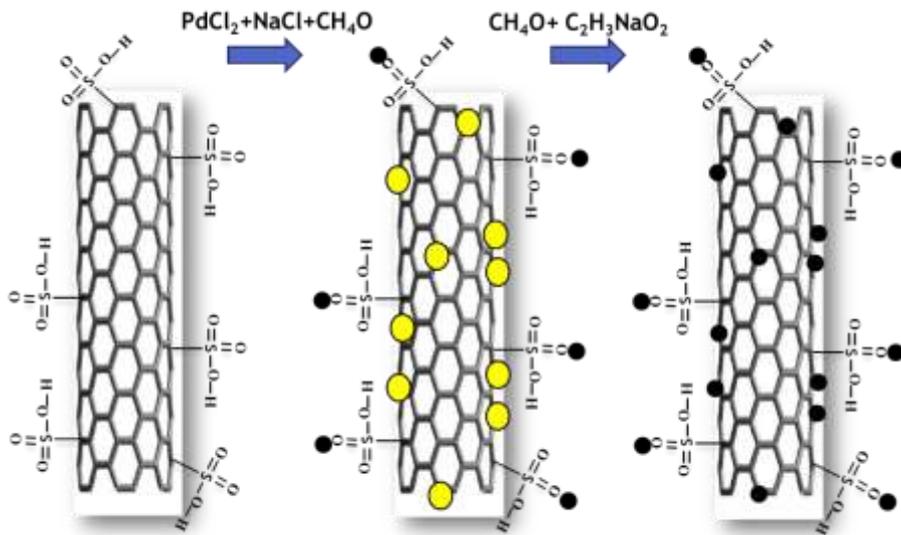


Figure 2. The schematic picture of palladium doping into MWCNT-OSO₃H, black circles: palladium nanoparticles and yellow circles: palladium chloride

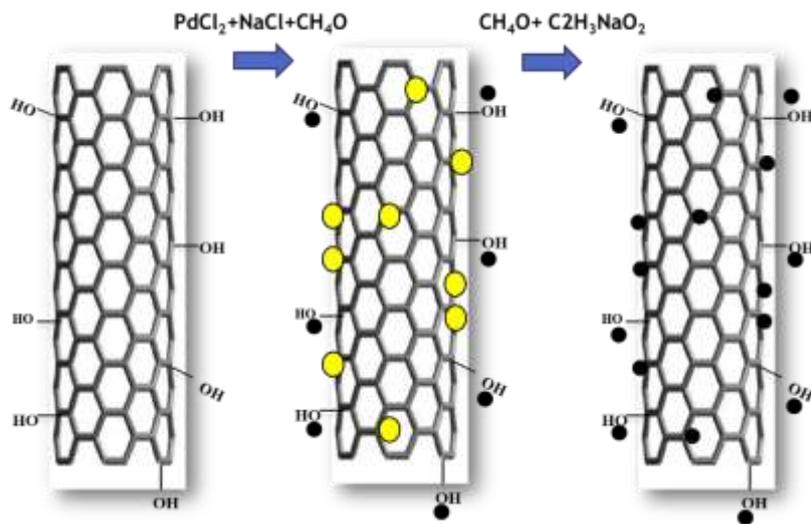


Figure 3. The schematic picture of palladium doping into MWCNT-OH, black circles: palladium nanoparticles and yellow circles: palladium chloride

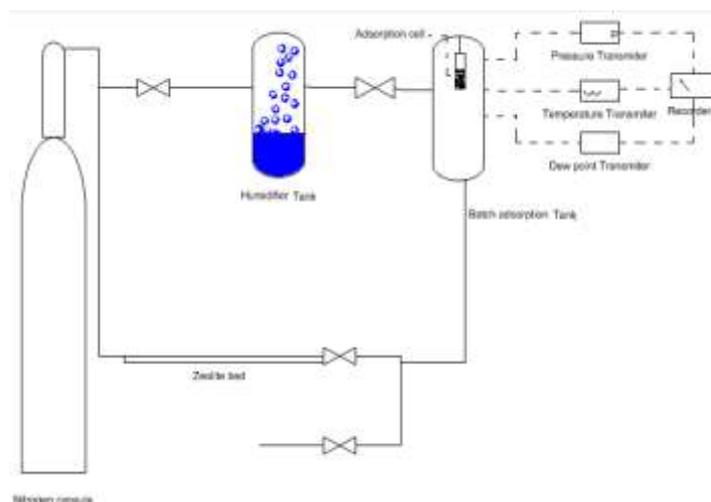


Figure 4. The schematic diagram of the adsorption setup.

Results and discussion

2.2. Characterization

Figure 5 shows FTIR spectra of the MWCNT-OSO₃H and MWCNT-OH samples. The peak observed within the range 3000-3500 cm⁻¹ is associated with OH-group and the one within the range 1000-1500 cm⁻¹ can be ascribed to S=O group (Mansur et al., 2008). This fact can support the formation of sulfonic acid group. Figures 6 and 7 show DTG analyses of both dry and wet MWCNT-OSO₃H-Pd samples. The material removal occurring at the temperature less than 200°C is associated to solvent and crystal water evaporation. The peak within the temperature interval of 200-300°C can be attributed to the decomposition of organic

parts (functional group). Thus, the adsorbent regeneration temperature was selected equal to 100°C which is far from the instability temperature of attached sulfonic acid groups. Also, the CHNS elemental analysis was performed on MWCNT-OSO₃H to determine the weight percentage of sulfur element. Using this value the amount of sulfonic acid group was calculated equal to 12.76wt%. In the present study, the weight percentage of palladium doped into MWCNT-OH and MWCNT-OSO₃H was evaluated respectively equal to 4.5wt% and 8.1wt% which is equivalent to 0.25 and 0.45 mmol/g respectively.

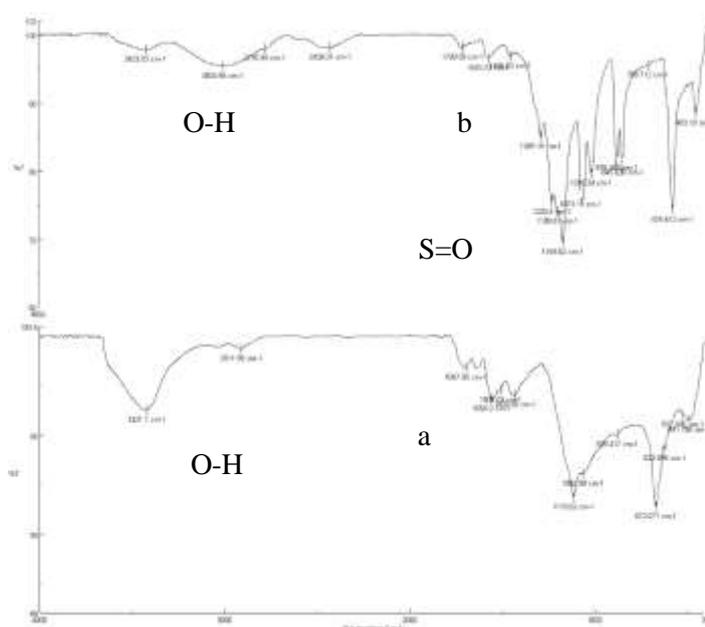


Figure 5. The FTIR spectra of a) MWCNT-OH b) MWCNT-OSO₃H

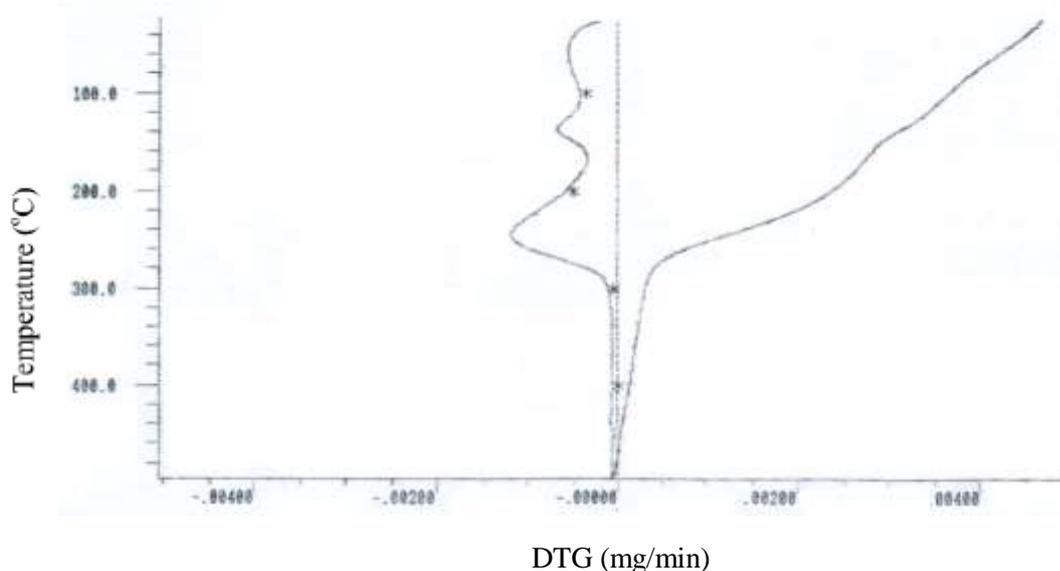


Figure 6. DTG diagrams of wet MWCNT-OSO₃H for the sample mass of 10.471 g

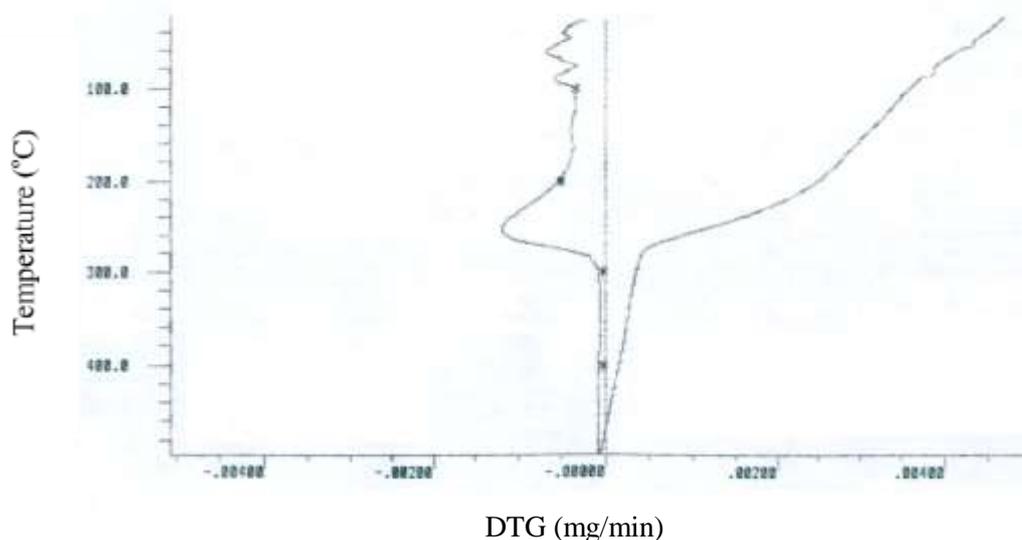


Figure 7. DTG diagrams of dry MWCNT-OSO₃H for the sample mass of 10.264 g

2.1. Water-vapor adsorption isotherm

The isotherms are shown by the plots of adsorbate uptake (mmol of adsorbate uptaken per gram of adsorbent) versus relative humidity (RH). Figure 8 shows the water-vapor adsorption isotherm for MWCNT-OH at

24°C. As it can be seen, the equilibrium adsorbed water vapor begins rising from relative humidity of 25% and reaches the saturation at relative humidity of 40% for both MWCNT-OH and MWCNT-OSO₃H samples. The adsorbent saturation loading are 6.7 and 2.5 mmol/g for MWCNT-OH and

MWCNT-OSO₃H samples, respectively. Higher saturation value associated to nanotube functionalized by sulfonic acid group is ascribed to the high tendency of this group to adsorb water molecules compared to the hydroxyl ones. This figure also reveals that the adsorption amount at the relatively low RH (less than 20%) are approximately similar for both samples. This fact can be related to the high tendency of large-size sulfonic acid groups to form a bond with their neighboring groups. It makes them less effective to adsorb water molecules at low humidity. However, for higher humidity the affinity between the large number of water molecules and the sulfonic acid groups breaks the above-mentioned bond. Figure 9 shows the same isotherms for the temperature of 15°C. Similar trend can be observed in this figure. Thus, in order to examine this hypothesis and increase the water adsorption capacity at lower humidity, palladium nanoparticles were intercalated into the porous structure of MWCNT-OSO₃H which is called as MWCNT-OSO₃H-Pd. Palladium nanoparticles are electrophile. The presence of these particles can raise the polarity of S=O groups and hence increases their

tendency to adsorb more water molecules even at lower gas humidity. Figures 10 and 11 compare the water-vapor adsorption isotherms on MWCNT-OSO₃H and MWCNT-OSO₃H-Pd at the temperatures of 24 and 15 °C. As it is obvious, doping palladium nanoparticles increases the adsorption capacity, especially at low gas humidity. This increase in adsorption capacity can be ascribed to palladium capability to adsorb water molecules as well. In order to investigate this hypothesis, the performance of MWCNT-OH containing palladium nanoparticles (MWCNT-OH-Pd) to adsorb water vapor molecules was compared with the pristine ones. The water-vapor adsorption isotherms on MWCNT-OH and MWCNT-OH-Pd were compared at two temperatures of 24 and 15°C through figures 12 and 13. These figures illustrate that adding palladium nanoparticles cannot improve the adsorption capacity of MWCNT-OH. It means that palladium nanoparticles cannot be responsible for the capacity improvement by themselves. Indeed, their interaction with sulfonic acid groups can make such an improvement in water-vapor adsorption on MWCNT-OSO₃H-Pd.

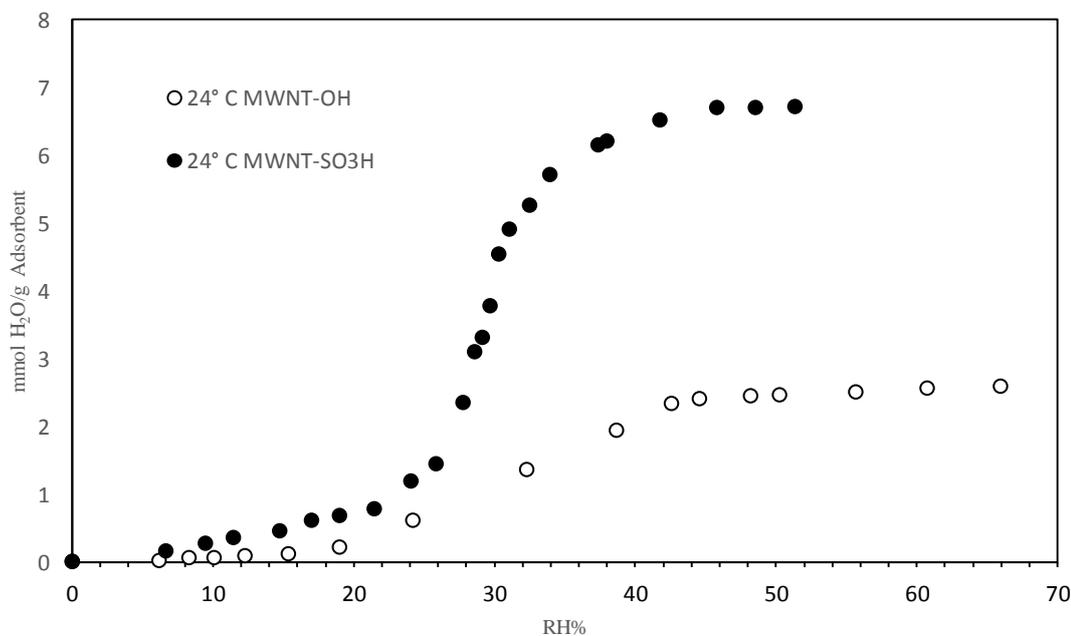


Figure 8. The water-vapor adsorption isotherms on MWCNT-OH and MWCNT-OSO₃H at 24°C.

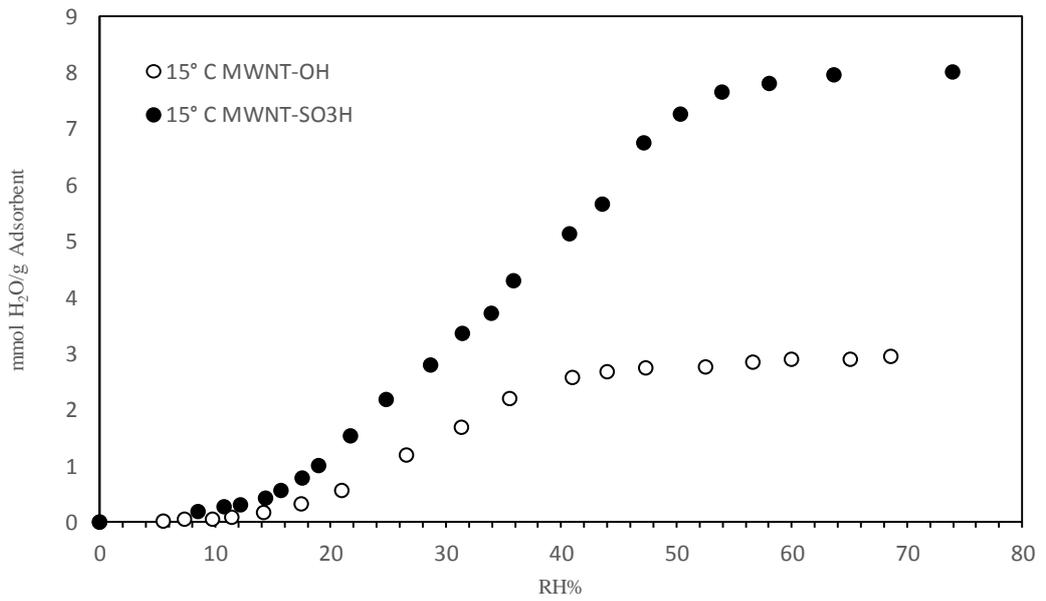


Figure 9. The water-vapor adsorption isotherms on MWCNT-OH and MWCNT-OSO₃H at 15°C.

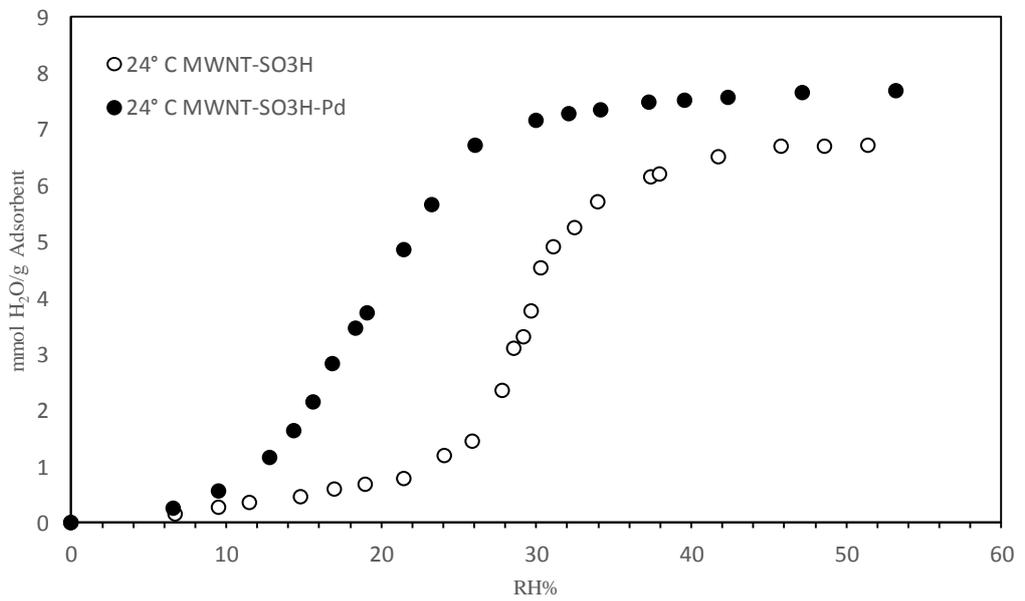


Figure 10. The water-vapor adsorption isotherms on MWCNT-OSO₃H and MWCNT-OSO₃H-Pd at 24°C.

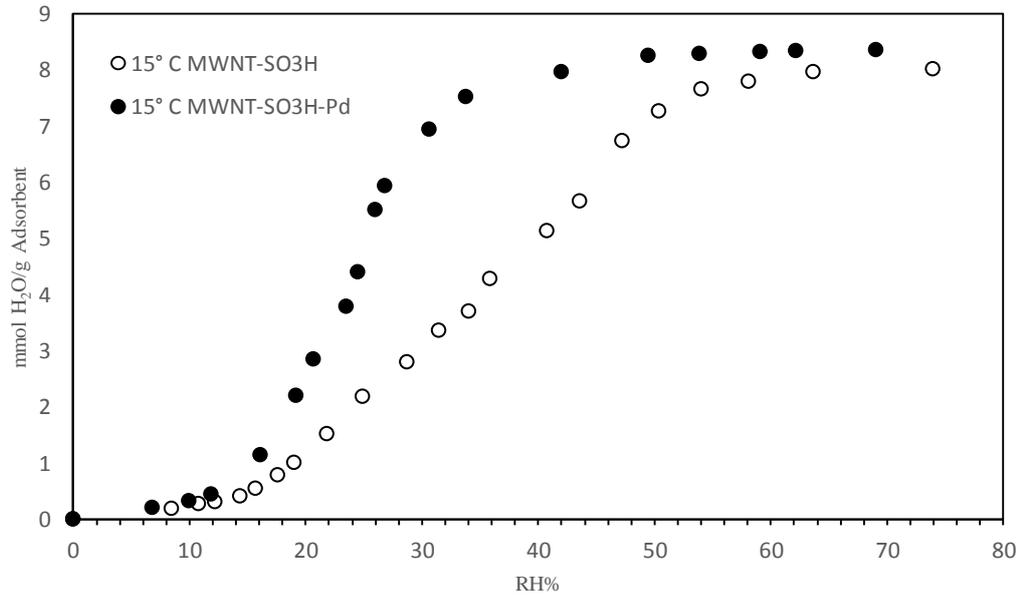


Figure 11. The water-vapor adsorption isotherms on MWCNT-OSO₃H and MWCNT-OSO₃H-Pd at 15°C.

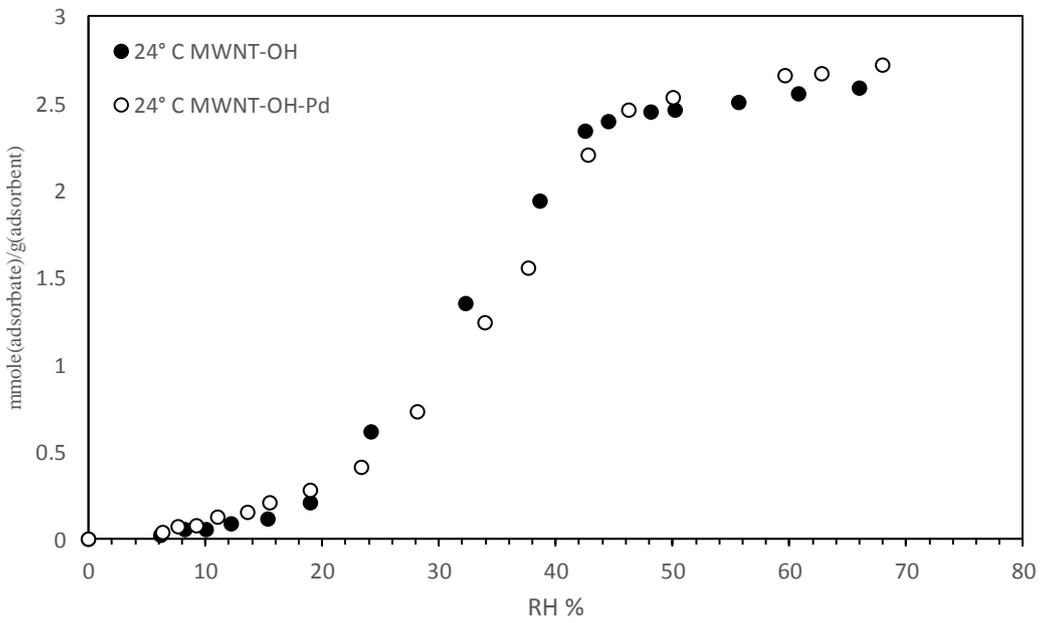


Figure 12. The water-vapor adsorption isotherms on MWCNT-OH and MWCNT-OH-Pd at 24°C.

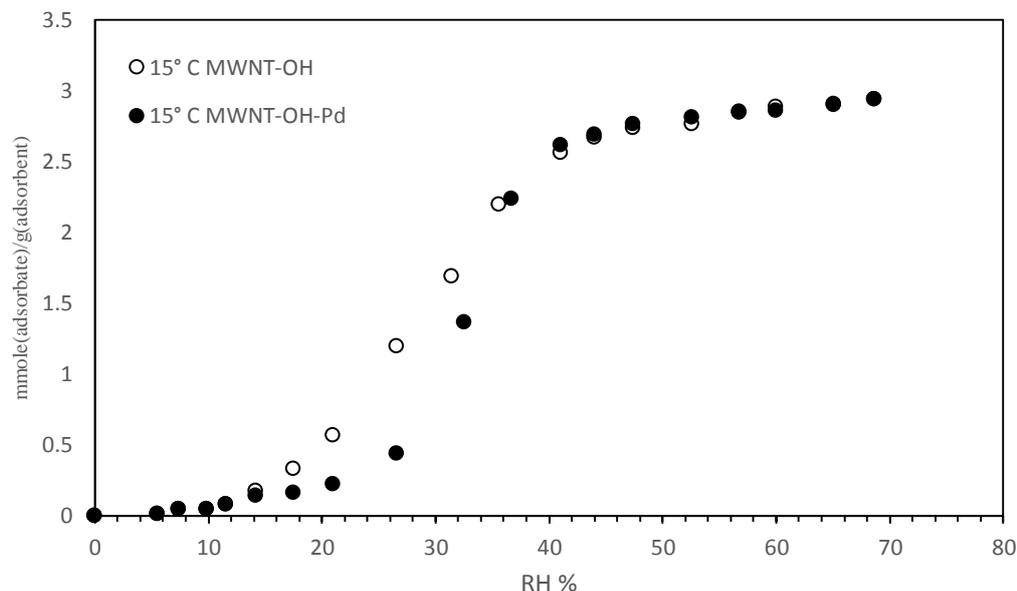


Figure 13. The water-vapor adsorption isotherms on MWCNT-OH and MWCNT-OH-Pd at 15°C.

3. Conclusions

In this study MWCNT-OSO₃H was synthesized using MWCNT-OH. Both types of MWCNT were doped by palladium nanoparticles to examine their influence on the improvement of their water-vapor adsorption capacity. The equilibrium adsorption of water vapor on both MWCNT-OSO₃H and MWCNT-OH was investigated experimentally. The results revealed that these two adsorbents demonstrate different performance. Adsorption capacity for MWCNT-OSO₃H compared with MWCNT-OH shows an increase in higher gas humidity. However, no significant difference was observed for lower gas humidity. It was attributed to the high tendency of large-size sulfonic acid groups to form hydrogen bond with one another. This hypothesis was supported strongly by comparing the adsorption capacity of both MWCNT-OSO₃H and MWCNT-OH doped by palladium nanoparticles with the pristine ones. The results showed that MWCNT-OSO₃H-Pd had better performance than MWCNT-OSO₃H. However, no significant difference was obtained between the performances of MWCNT-OH-Pd and MWCNT-OH. Eventually, it was concluded that MWCNT-OSO₃H-Pd can be much-more-suitable adsorbent for water-vapor adsorption compared to the rest of the nanotubes.

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