



Chemical treatment of CNTs in acidic KMnO_4 solution and promoting effects on the corresponding Pd–Pt/CNTs catalyst

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ARTICLE INFO

Article history:

Received 16 August 2011

Received in revised form 24 October 2011

Accepted 31 December 2011

Available online 9 January 2012

Keywords:

Carbon nanotubes

Chemical treatment

Acidic KMnO_4 solution

Carboxyls

Pd–Pt catalyst

ABSTRACT

Carbon nanotubes (CNTs) were chemically treated in acidic KMnO_4 solution. XRD, nitrogen physisorption, FTIR and chemical titration were used to investigate the influence of the treatment conditions on the surface structure, the bulk structure, the types and the amounts of the formed surface oxygen-containing functional groups of CNTs. The results show that the structure is not changed clearly after treatment and the formation of oxygen-containing groups, e.g., carboxyls, on the CNT surface is dependent on the treatment conditions. Under the present conditions, the concentration of the employed sulphuric acid and the weight ratio of the solid KMnO_4 and CNTs have clear influence on the formation of carboxyls, however, by comparison, the influence is slight when the treatment temperature is above 95 °C. With the increasing of the amount of carboxyls, the dispersion of the corresponding Pd–Pt metal particles supported on CNTs is increased and the catalytic activity is promoted in the profile reaction of naphthalene hydrogenation to tetralin.

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1. Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991, they have become one of the most active fields of nanoscience and nanotechnology due to their unique properties, which make them to qualify for many potential applications such as polymer reinforcements for composites or breakthrough materials for energy storage, electronics and catalysis [1–4]. In heterogeneous catalysis, compared with conventional carbon materials, like activated carbon, CNTs attract a growing interest as a catalyst support because of their specific characteristics, e.g., high mechanical strength, macroporous and mesoporous structure, possibility to control the surface chemistry and easy recovery of precious metals without introducing other metallic impurities by support burning [3,4]. Additionally, a theoretical investigation about the interaction of the supported nickel metal atoms with CNTs shows that the curvature of the surface graphite layers of CNTs significantly affects the values of magnetic moments of the nickel atoms and the charge transfer direction between nickel and carbon can be inverted [5]. Therefore, a certain peculiar metal–support interaction may exist in this catalyst system. The research results in the

published literature have shown that compared with the conventional catalyst supports, like Al_2O_3 , SiO_2 and activated carbon, the catalytic activity or the selectivity of the supported metal catalysts like Ni, Rh and Pt on CNTs can be promoted pronouncedly due to this peculiar interaction [3,4,6–9]. However, the surface of the primitive CNTs, which are generally produced from decomposition of hydrocarbons, is mostly covered with the inert C–H bonds and the corresponding interaction is very weak between the supported metal and the CNT surface [3,4,10–13]. Therefore, the surface of primitive CNTs has to be chemically pre-treated in the oxidants to generate some oxygen-containing functional groups, like carboxyls and phenolic hydroxyls, for anchoring the supported metal particles to improve the interaction between them [3,4,11–17].

The results in the published literature and in our lab show that the acidic potassium permanganate (KMnO_4) solution is an efficient method to generate oxygen-containing groups, especially strongly acidic groups, carboxyls [3,16–20]. Although there have been many publications about this topic, to our best knowledge, up to now there is no report concerning the influence of the treatment conditions on the formation of surface oxygen-containing functional groups, e.g., the ratio of the employed KMnO_4 and CNTs, the concentration of the employed acid and the treatment temperature. Additionally, the further relationship between the treatment conditions and the types and the amounts of the formed oxygen-containing groups has not been reported, either.

In this work, the influence of the chemical treatment conditions on the formation of the oxygen-containing functional groups

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was investigated in the details. Hydrogenation of naphthalene to tetralin was employed as a probe reaction to investigate the promoting effects of the formed functional groups on the activity of the supported Pd–Pt/CNTs catalyst.

2. Experimental

2.1. Treatment of CNTs

CNTs were obtained from Tsinghua University. They were produced from methane catalytic decomposition in a continuous commercial fluidized-bed reactor. The purity of the CNTs in the primitive samples is above 95%. The external diameter of CNTs is in the range of 10–30 nm with the majority around 20 nm. The inner diameters are typically about one-third of the corresponding external diameters. All the particle size of CNTs employed in this work is between 60 and 80 mesh.

For the chemical treatment of CNTs in the acidic KMnO_4 solution, solid KMnO_4 and CNTs were put in sulphuric acid solution in a flask with three necks and stirred for 100 min, then the suspension cooled down to room temperature (RT) and was filtered. The obtained solid mixture was washed with water, filtered, washed with concentrated HCl solution to remove the produced MnO_2 and then was re-filtered. Following this step, the obtained CNTs were washed with water for several times until the filtrate became neutral. Finally, CNTs were dried in air at 110°C for 16 h. The obtained CNT samples under different treatment conditions are listed in Table 1.

2.2. Characterization of CNTs

The XRD measurements of the CNT samples before and after the treatment were conducted with a Bruker D8 advance research X-ray diffractor (XRD) with $\text{Cu K}\alpha$ radiation at a scanning rate of 2°min^{-1} .

The texture structures of the samples were measured using nitrogen physisorption in a NOVA 1200 adsorption analyser (Quantachrome). The corresponding specific surface areas (S_g) were calculated by the Brunauer–Emmett–Teller (BET) equation at relative pressure (P/P^0) between 0.05 and 0.35. The total pore volumes were calculated from the amount of vapor adsorbed at the relative nitrogen pressure of 0.98, by assuming that all the pores were filled with liquid N_2 .

The surface functional groups of the different CNT samples were observed in a Nicolet NEXUS Fourier transform infrared spectroscopy (FTIR). CNT samples and KBr particles were first ground into particles smaller than 300 mesh, dried in air at 110°C for 5 h, cooled to ambient, mixed physically with each other to uniformity and finally pressured into wafers. Since CNTs can strongly absorb IR light, the content of CNTs in the wafers was only 0.2–0.3 wt.%. During the investigation, the wafers were located on the sample shelf, which was exposed to the ambient in the instrument. IR absorptions in the range of $3800\text{--}800 \text{ cm}^{-1}$ were recorded.

According to the method suggested by Boehm [21–23], on carbon materials, e.g., activated carbon and carbon black, the surface oxygen-containing groups, which differ in their acidities, can be quantitatively measured in the process of chemical titration by neutralization with NaHCO_3 , Na_2CO_3 and NaOH , respectively. NaHCO_3 can only react with carboxyls (including carboxylic anhydride) and Na_2CO_3 can react with lactones and lactols besides carboxyls, and NaOH can react with carboxyls, lactone, lactols and phenolic hydroxyls. Therefore, the differences in acidity of the various types of functional groups allow differentiation by the simple titration method. For example, the difference between NaOH and Na_2CO_3 consumption corresponds to the phenolic groups.

For the measurement of the total content of the oxygen-containing groups, 50 ml of 0.01 M NaOH solution was firstly used for soaking 100 mg of CNTs in a container sealed under nitrogen for 24 h at RT in an ultrasonic bath and then the suspension was filtered to obtain the filtrate. The solution of 0.0098 M HCl was used to titrate 20 ml of the above filtrate to obtain the measurement titration curve. Additionally, by considering the disturbing of CO_2 , 20 ml of the same NaOH solution without soaking CNTs was titrated to obtain the reference titration curve. The consumed volumes of HCl to neutralize NaOH in the reference titration and in the measurement titration were referred as V_1 and V_2 , respectively. The total content of the oxygen-containing groups on CNT surface can be calculated out by the expression, $0.244 \times (V_1 - V_2) \text{ mmol g}^{-1}$. The total content of carboxyls, lactones and lactols and that of carboxyls can be obtained using HCl to back titrate Na_2CO_3 and NaHCO_3 , respectively, which have been used to soak CNTs. A PHS-2 pH meter was used for monitoring the pH change during the chemical titration.

2.3. Preparation and activity of Pd–Pt/CNTs catalyst

To investigate the promoting effects of the formed surface functional groups on the dispersion of the supported metal catalyst, Pd–Pt/CNTs were prepared by incipient wetness impregnation method. The mixture solution of $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ and $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$, in which the atomic ratio of Pd and Pt was 4:1, was used as the precursors of Pd–Pt. The results in our lab showed that the ionic exchange capacities of $[\text{Pd}(\text{NH}_3)_4]^{2+}$ and $[\text{Pt}(\text{NH}_3)_4]^{2+}$ on the treated CNT samples, were all above 1 wt.% of the total content of Pd–Pt metal. Therefore, to ensure the loading $[\text{Pd}(\text{NH}_3)_4]^{2+}$ and $[\text{Pt}(\text{NH}_3)_4]^{2+}$ can fully interact with the functional groups, 1 wt.% Pd–Pt/CNTs catalyst were prepared in this work. During the preparation, the mixed solution of $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ and $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ was dropped on CNTs at RT and then dried in the ambient for 24 h. Afterwards, the samples were dried in air at 110°C for 16 h and then calcinated in a tube furnace in an ultra-high purity nitrogen flow at 380°C for 2 h. The obtained catalysts supported on different CNT samples are referred as Pd–Pt-0# to Pd–Pt-7#, respectively. The actual loading content of Pd–Pt metal was measured using a Hitachi 180–80 atomic absorption spectroscopy (AAS).

Hydrogen chemisorption was employed to measure the dispersion of the metal particles at RT in a pulse system equipped with Thermo Finnigan TPDRO1100. The samples of 100 mg were reduced in a hydrogen flow at 300°C for 2 h, followed by flushing for 2 h in an ultrahigh purity helium stream of 30 ml min^{-1} at 300°C and then cooled in helium to ambient. Hydrogen pulses of $100 \mu\text{l}$ each were injected into an ultrahigh purity nitrogen flow and detected in the outlet gas by a thermal conductivity detector. By comparing the amount of hydrogen reaching the detector and the amount of hydrogen injected, the quantity of hydrogen adsorbed could be determined. Blank experiments on CNTs showed that there was no measurable uptake of hydrogen on the support itself. The metal dispersion, in terms of hydrogen to metal molar ratio, was calculated based on the moles of gas adsorbed on the catalyst and expressed into $\text{H}/(\text{Pd} + \text{Pt})$, the atomic ratio of the adsorbed hydrogen atoms and the total metal atoms of Pd and Pt in the catalyst system [24].

The hydrogenation of naphthalene was used as the probe reaction to investigate the promoting effects on the reactivity of Pd–Pt/CNTs catalysts. The reactions were carried out in a Parr 4842 high pressure autoclave. For each run, the catalyst sample of 300 mg was firstly reduced at 300°C for 2 h in hydrogen with a flow rate of 20 ml min^{-1} and then cooled to RT and moved to the reactor pre-filled with 120 ml solvent of tridecane under the protection of ultrahigh-purity nitrogen. Then 9 g of naphthalene were put in the reactor. When the temperature was heated to 220°C , the reaction solution began to be stirred. During the reaction, the hydrogen pressure was kept at 6.0 MPa, the reaction temperature was held

Table 1
Employed CNT samples before and after treatment in the acidic KMnO_4 solution under different conditions.

CNT samples	Treatment conditions		
	Temperature ($^{\circ}\text{C}$)	Concentration of H_2SO_4 (M)	Weight ratio of KMnO_4 and CNTs
0#	–	–	–
1#	75	4.5	3:1
2#	95	4.5	3:1
3#	115	4.5	3:1
4#	95	3	3:1
5#	95	6	3:1
6#	95	4.5	1:1
7#	95	4.5	5:1

at 250°C , the stirring speed was 660 rad min^{-1} . The samples were taken in the interval of 20 min and were analyzed using a gas chromatography equipped with a hydrogen flame ionization detector and a HP-PONA methyl silicone capillary column.

3. Results and discussion

3.1. Influence on structure of CNTs

Fig. 1 shows that the XRD profiles of the CNTs before and after chemical treatment under the different conditions. It can be found that all the eight CNT samples possess the crystal structure similar to that of graphite. The structures of CNTs after treatment under the different conditions remain unchanged, which indicates that the treatment does not change the bulk structure of the CNTs.

The specific surface areas, S_g , and the total pore volumes, V_p , of CNTs obtained using N_2 physisorption, are shown in Table 2. It can be seen that there are only some small changes after treatment, which may be attributed to the surface modification from the oxidization of some active carbon layers on the surface, e.g., the unsaturated carbon atoms in the defects or the carbon layers like pentagon and heptagon located on the ends of CNTs [3,18].

The above results of XRD and N_2 physisorption indicate that the treatment in acidic KMnO_4 solution can not clearly alter the bulk structure and the texture, which is advantageous to the use of CNTs as a support.

3.2. Formation of surface functional groups

Fig. 2A–C shows FTIR spectra of CNT samples from 0# to 7#. To allow comparison, transmission levels of all spectra were kept approximately same. It was ascertained that, within the

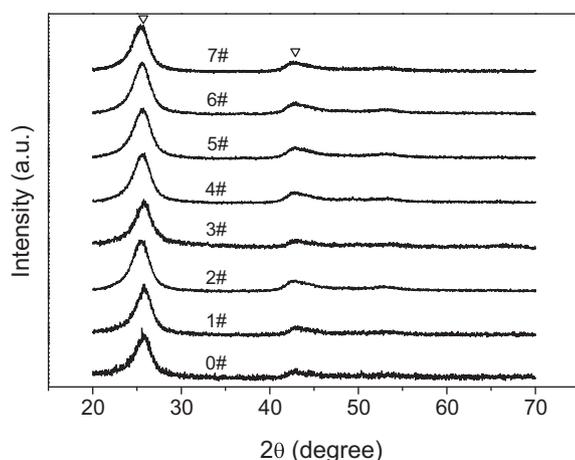


Fig. 1. XRD profiles of the CNT samples before and after treatment in the acidic KMnO_4 solution; $\text{Cu K}\alpha$; ∇ , graphite.

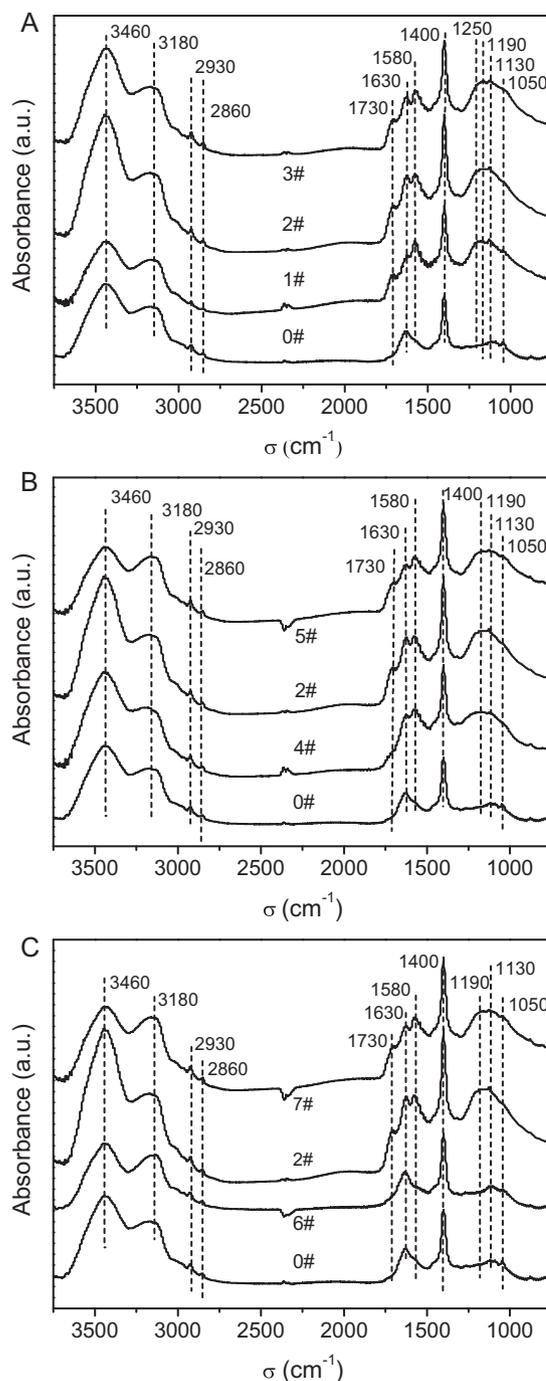


Fig. 2. IR spectra of the CNT samples before and after treatment in the acidic KMnO_4 solution.

Table 2
Specific surface area (S_g) and pore volume (V_p) of the CNT samples.

	CNT samples							
	0#	1#	2#	3#	4#	5#	6#	7#
S_g ($m^2 g^{-1}$)	158	149	162	150	153	139	154	138
V_p ($ml g^{-1}$)	0.37	0.36	0.38	0.35	0.37	0.34	0.37	0.34

transmission window used, the intensity of the bands did not depend upon the transmission level of the spectra. The absorptions in the spectra can be assigned according to Refs. [25–31].

The peaks at 1050 and 1120 cm^{-1} are because of the stretching vibration of C–O in ethers [26,27]; the peaks at 1190 and 1250 cm^{-1} originate from the stretching vibration of C–O in phenols [26,27]; the peak at 1400 cm^{-1} may be associated with H–O bending vibration in water, phenols and carboxyls [25,28,29] and the peak at 3164 cm^{-1} may be attributed to H–O stretching vibration in phenols and carboxyls [26,27]; the peak at 1580 cm^{-1} can be ascribed to the stretching vibration of aromatic rings in the surface of CNTs. The absorptions at 1630 cm^{-1} are due to water adsorbed on the KBr and CNTs, possibly during the wafer preparation and the observation [25,28]; the peak at 1715 cm^{-1} can be assigned to the C=O stretching vibration in carboxyls or carbonyls [25,26,28]; the peaks of 2846 and 2930 cm^{-1} are in the range of CH_3/CH_2 stretching vibration [25,26]. The absorptions at 3440 cm^{-1} are due to the H–O stretching vibration of the adsorbed water on the KBr and CNTs [30,31]. The absorptions at 1400, 1630 and 3440 cm^{-1} are also observed to be present in the KBr backgrounds.

Based on the above analysis, before treatment, there are only small amounts of C–O on the surface of CNTs, mainly in ethers and a few in phenols. Oxygen in air may be chemisorbed at low temperatures on unsaturated carbon atoms at some defects or dislocations that occur on the surface of the CNTs and may react further to generate some surface oxygen-containing groups [10]. By comparison, some bands are formed apparently after treatment: one is at 1580 cm^{-1} originating from an aromatic ring vibration [25,26]; and the other is at 1715 cm^{-1} which can be assigned to the C=O stretching vibration in carboxyls or carbonyls [25,26,28]. The peak at 1580 cm^{-1} indicates aromatic skeleton rings sticking out of the surface of CNTs after the oxidization of the surface and the formation of C=O shows the generation of carbonyls or carboxyls in the surface of CNTs. The absorptions at 1190, 1250 cm^{-1} (C–O stretching vibrations in phenols) are enhanced indicating that more phenols were formed [26,27]. In Fig. 2A, it can be seen that the amount of the formed C=O or the phenols is higher at 95 and 115 °C than at 75 °C. In Fig. 2B and C, they are both higher using 4.5 M and 6.0 M sulphuric acid than using 3.0 M or higher with the proportion of $KMnO_4$ and CNTs of 3:1 and 5:1 than with that of 1:1. Since the surface functional groups are very complex and their vibration ranges are adjacent to one another, it is difficult to make further quantitative assignments. However, it can be found that after treatment, phenols and carboxyls are formed on CNT surface and the amount of them has a relationship with the treatment conditions.

According to the method suggested by Boehm [21–23], the amounts of the different oxygen-containing surface groups can be measured by using HCl to back titrate the solution of NaOH, $NaHCO_3$ and Na_2CO_3 , respectively, which have been used to soak CNT samples. As an example, the reference titration curves and the measurement titration curves of two CNT samples 1# and 2# are shown in Fig. 3A–C. The types and amounts of the surface functional groups on CNTs were calculated out and listed in Table 3. The relationship of them with treatment conditions is further illustrated in Fig. 4. It can be found that before treatment the amount of the total oxygen-containing groups is very low and only a few weakly acidic phenolic groups are existed, which is consistent with

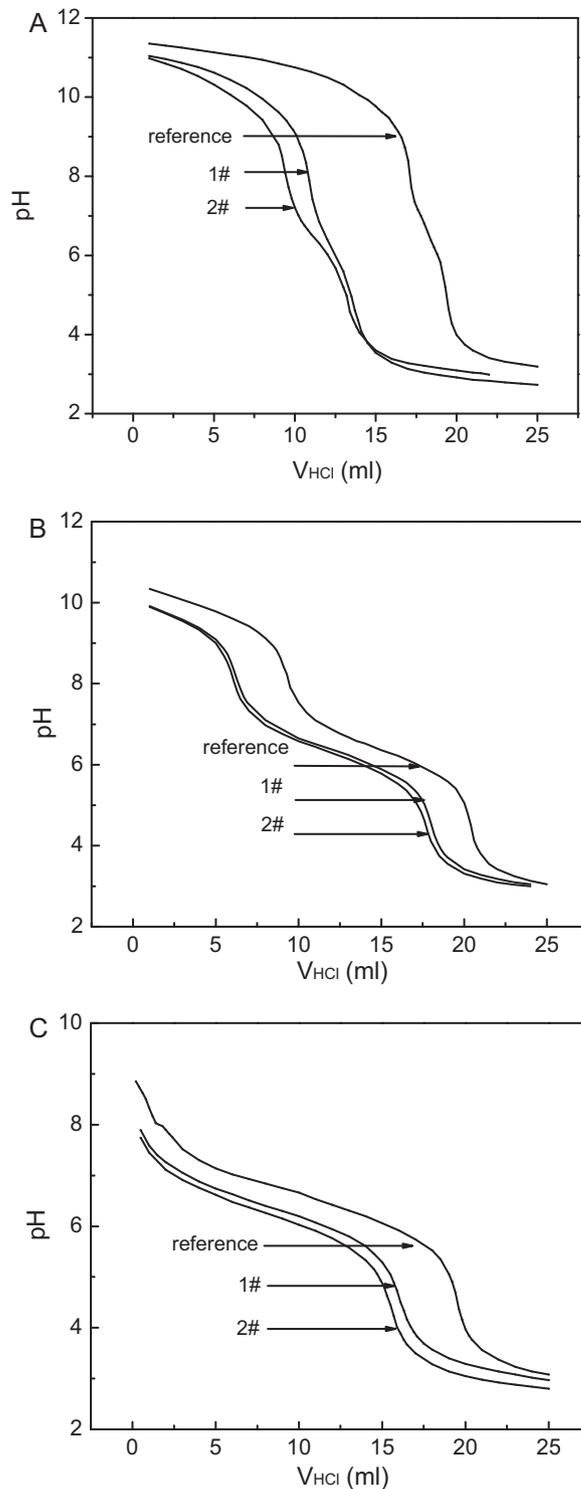


Fig. 3. Chemical titration curves using HCl to back titrate NaOH (A), Na_2CO_3 (B) and $NaHCO_3$ (C) for the quantitative measurement of the oxygen-containing groups on CNT samples 1# and 2#.

Table 3
Amounts of the surface oxygen-containing groups on the CNT samples.

	CNT samples							
	0#	1#	2#	3#	4#	5#	6#	7#
Carboxyl (mmol g^{-1})	–	0.38	0.54	0.55	0.47	0.71	0.28	0.65
Lactone and lactol (mmol g^{-1})	–	0.35	0.27	0.26	0.14	0.21	0.29	0.3
Phenolic hydroxyl (mmol g^{-1})	–	0.52	0.5	0.53	0.45	0.52	0.41	0.53
Total (mmol g^{-1})	0.013	1.25	1.31	1.34	1.06	1.44	0.98	1.48

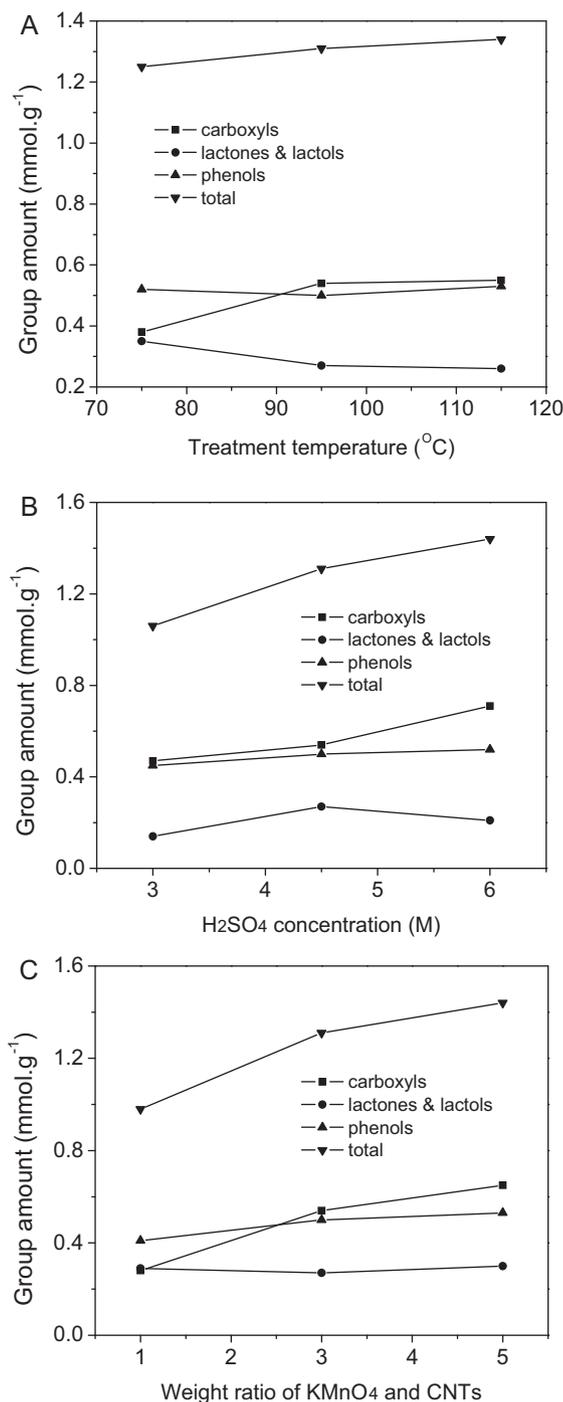


Fig. 4. Effect of treatment condition on the formation of surface oxygen-containing groups on CNTs: (A) treatment temperature; (B) concentration of H_2SO_4 ; (C) weight ratio of KMnO_4 and CNTs.

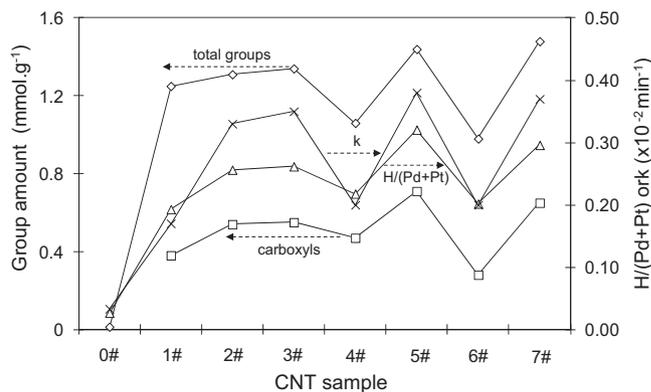


Fig. 5. Amount of total oxygen-containing functional groups and that of carboxyls on CNTs, the atomic ratio of $\text{H}/(\text{Pd} + \text{Pt})$ during the measurement of metal dispersion of Pd-Pt/CNTs and the pseudo-first-order reaction rate constant, k , in naphthalene hydrogenation to tetralin.

the FTIR observation. After treatment, the amount of the functional groups can be increased pronouncedly. From Fig. 4A, it can be seen that the amount of carboxyls is increased clearly when the treatment temperature is increased from 75 to 95 °C (1# → 2#) and is almost not changed from 95 to 115 °C (2# → 3#). The amount of phenols is unchanged with the increase of the treatment temperature. The amount of lactones and lactols is decreased from 75 to 95 °C, then keeps flat from 95 to 115 °C. This indicates that the oxidation ability of acidic KMnO_4 solution can be enhanced from 75 to 95 °C and cannot be promoted further above 95 °C. In Fig. 4B, the amount of carboxyls is flatly increased when the concentration of the employed sulphuric acid is increased from 3 to 4.5 M (4# → 2#) and is clearly increased when it is from 4.5 to 6 M (2# → 5#). The amount of phenols keeps flat in the full range. The amount of lactones and lactols is increased when it is from 3 to 4.5 M and then decreased when it is from 4.5 to 6 M. In Fig. 4C, when the weight ratio of KMnO_4 and CNTs is increased from 1 to 5, the amount of carboxyls is increased and that of phenols is flatly increased and that of lactones and lactols remains unchanged. In the acidic KMnO_4

Table 4

Actual loading content of Pd-Pt/CNTs, the atomic ratio of $\text{H}/(\text{Pd} + \text{Pt})$ during the measurement of metal dispersion of Pd-Pt/CNTs and the corresponding pseudo-first-order reaction rate constant, k , in naphthalene hydrogenation to tetralin.

Catalyst samples	Actual loading content (%)	$\text{H}/(\text{Pd} + \text{Pt})$	k (min^{-1})
Pd-Pt-0#	1.13	0.027	0.00033
Pd-Pt-1#	0.985	0.193	0.0017
Pd-Pt-2#	0.937	0.256	0.0033
Pd-Pt-3#	0.956	0.262	0.0035
Pd-Pt-4#	1.01	0.218	0.0020
Pd-Pt-5#	0.936	0.321	0.0038
Pd-Pt-6#	0.991	0.202	0.0020
Pd-Pt-7#	0.946	0.296	0.0037

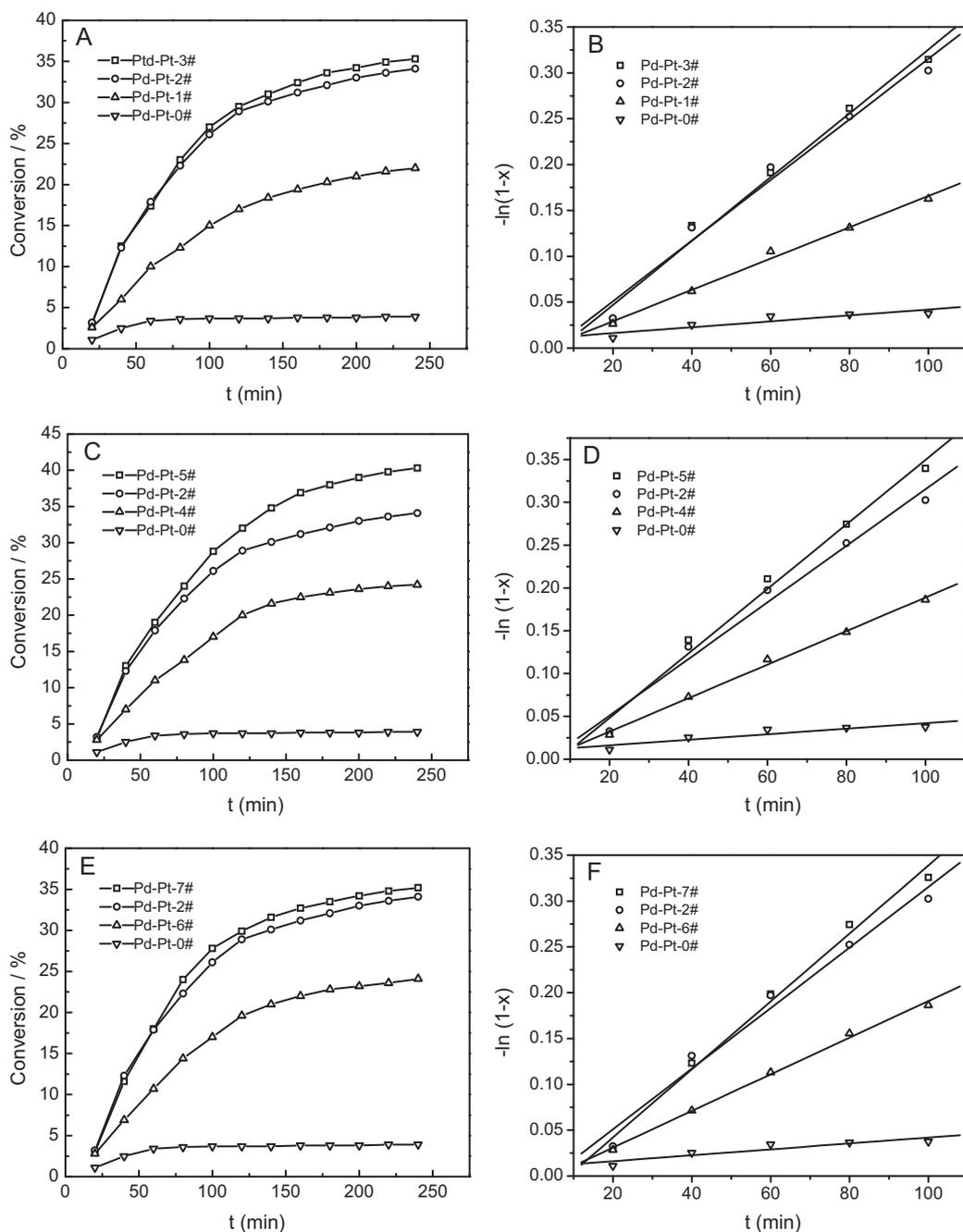


Fig. 6. Influence of the treatment of CNTs on conversion of naphthalene to tetralin on Pd-Pt/CNTs: (A, C and E) activity curves; (B, D and F) pseudo-first-order kinetic plots.

solution, the oxidation process of solid carbon materials could occur according to the reaction as below [32]:



Therefore, with the increase of the concentration of sulphuric acid or the amount of the employed $KMnO_4$, the reactivity of the acidic $KMnO_4$ solution is enhanced. Therefore, the unstable groups, phenols, lactones or lactols could be further oxidized into carboxyls. In Fig. 5, it can be seen that except 3#, the tendency of the amount of the total oxygen-containing groups is similar to that of carboxyls, which indicates that the contribution of the amount increase of the total oxygen-containing groups is mainly from carboxyls. The above results show that the types and the amounts of the functional groups are dependent on the treatment conditions. When the treatment becomes more severe, more carboxyls are

generated. Under the present treatment conditions, the concentration of the employed sulphuric acid and the weight ratio of solid $KMnO_4$ and CNTs have clear influence on the formation of carboxyls, however, by comparison, the influence is slight when the treatment temperature is above $95^\circ C$.

3.3. Dispersion and activity of Pd-Pt/CNTs

The actual loading content of Pd-Pt metal in the eight Pd-Pt/CNTs catalysts was measured by AAS and is listed in Table 4. It can be seen that they are all around 1 wt.% as expected.

Hydrogen chemisorption was employed to measure the dispersion of the metal particles and the results are listed in Table 4. Fig. 5 illustrates the relationship between the metal dispersion of the Pd-Pt/CNTs and the amount of the carboxyls. It can be found

that the order of the former is the same as that of latter. More carboxyls are formed on the surface, is higher dispersion of the corresponding catalyst obtained here. Carboxyls on the surface of solid carbon support can have strong interaction with the loaded metal precursors $[\text{Pd}(\text{NH}_3)_4]^{2+}$ and $[\text{Pt}(\text{NH}_3)_4]^{2+}$ through the formation of chemical bonds, like $-\text{COO}^- [\text{Pt}(\text{NH}_3)_4]^{2+} -\text{OOC}-$, which serve to hinder agglomeration and surface diffusion of metal ions, and minimize the sintering propensity of the formed Pd–Pt particles across the CNT surface to obtain the high metal dispersions in the calcination and reduction process [10]. The results in Fig. 5 indicate that the amount of the carboxyls is vital to the dispersion of the Pd–Pt metal particles.

Hydrogenation of naphthalene to tetralin was employed as the profile reaction to further show the promoting effect of the surface groups on the activity of the supported metal catalyst because the activity of the Pd–Pt metal particles in this reaction is increased with the decrease of their size [33]. During the hydrogenation process, tetralin is the only product. From the curve of conversion with the reaction time extension in Fig. 6, it can be found that the activity of Pd–Pt-0# is very low and after treatment, the activity of Pd–Pt/CNTs is promoted obviously. Additionally, in an ideal stirring batch reactor, the hydrogenation of naphthalene to tetralin can be regarded as a pseudo-first-order reaction [34]. The relationship between the conversion, x , and reaction time, t , can be expressed by the equation, $-\ln(1-x) = kt$, in which k is the reaction rate constant. Therefore, the first five conversions are used to show the plot of the relationship, $-\ln(1-x) \sim t$. The obtained k are listed in Table 4. The tendency of both k and dispersion of Pd–Pt metal particles of the corresponding catalysts is illustrated in Fig. 5. It can be found that the order of k is the same as that of the Pd–Pt dispersion. Since the catalyst samples have the similar loading content and are obtained from the same preparation method, the difference in activity should be attributed to the dispersion of the metal particles. Therefore, the formation of carboxyls during treatment in the acidic KMnO_4 solution can improve the dispersion of Pd–Pt metal particles, which can promote the activity of the corresponding catalyst. With the increasing of the amount of carboxyls, the Pd–Pt dispersion is increased and the activity of the catalyst is enhanced as well.

4. Conclusions

The treatment in the acidic KMnO_4 solution cannot clearly change the bulk structure and the surface texture of CNTs under the present conditions, however, different oxygen-containing functional groups can be formed on the surface. The types and the amounts of the formed functional groups, e.g., carboxyls, are dependent on the treatment conditions. The concentration of the employed sulphuric acid and the weight ratio of the solid KMnO_4 and CNTs have clear influence on the formation of carboxyls, however, by comparison, this influence is slight when the treatment

temperature is above 95°C . The presence of carboxyls on CNT surface can improve the dispersion of the supported Pd–Pt metal particles and promote their activity in hydrogenation of naphthalene to tetralin. It seems that acidic KMnO_4 solution is an efficient treatment method for CNTs before being employed as the catalyst support.

Acknowledgment

This work was supported by the Natural Science Foundation of China under contract number 20006012.

References

- [1] S. Bose, R.A. Khare, P. Moldenaers, *Polymer* 51 (2010) 975–993.
- [2] A. Reyhani, S.Z. Mortazavi, S. Mirershadi, A.Z. Moshfegh, P. Parvin, A.N. Golikand, *J. Phys. Chem. C* 115 (2011) 6994–7001.
- [3] P. Serp, M. Corrias, P. Kalck, *Appl. Catal. A* 253 (2003) 337–358.
- [4] K.P. de Jong, J.W. Geus, *Catal. Rev.-Sci. Eng.* 42 (2000) 481–510.
- [5] M. Menon, A.N. Andriotis, G.E. Froudakis, *Chem. Phys. Lett.* 320 (2000) 425–434.
- [6] C. Park, R.T.K. Baker, *J. Phys. Chem. B* 103 (1999) 2453–2459.
- [7] C.A. Bessel, K. Laubernds, N.M. Rodriguez, R.T.K. Baker, *J. Phys. Chem. B* 105 (2001) 1115–1118.
- [8] R. Giordano, P. Serp, P. Kalck, Y. Kihn, J. Schreiber, C. Marhic, J.L. Duvail, *Eur. J. Inorg. Chem.* 4 (2003) 610–617.
- [9] J.Z. Luo, L.Z. Gao, Y.L. Leung, C.T. Au, *Catal. Lett.* 66 (2000) 91–97.
- [10] F. Rodriguez-Reinoso, *Carbon* 36 (1998) 159–175.
- [11] C. Lu, H. Chiu, *Chem. Eng. J.* 139 (2008) 462–468.
- [12] J.L. Chen, Z.H. Zhu, Q. Ma, L. Li, V. Rudolph, G.Q. Lu, *Catal. Today* 148 (2009) 97–102.
- [13] J.L. Chen, Z.H. Zhu, S.B. Wang, Q. Ma, V. Rudolph, G.Q. Lu, *Chem. Eng. J.* 156 (2010) 404–410.
- [14] R.I. Jafri, T. Arockiadoss, N. Rajalakshmi, S. Ramaprabhu, *J. Electrochem. Soc.* 157 (2010) B874–B879.
- [15] M.A.M. Motchelaho, H.F. Xiong, M. Moyo, *J. Mol. Catal. A* 335 (2011) 189–198.
- [16] T.J. Aitchison, M. Ginic-Markovic, J.G. Matison, G.P. Simon, P.M. Fredericks, *J. Phys. Chem. C* 111 (2007) 2440–2446.
- [17] Q.H. Chen, H. Liu, J.L. Chen, Y.D. Li, *Tansu* 3 (2006) 8–14.
- [18] K. Hernadi, A. Siska, L. Thien-Nga, L. Forro, I. Kiricsi, *Solid State Ionics* 141–142 (2001) 203–209.
- [19] N.Y. Zhang, J.N. Xie, V.K. Varadan, *Smart Mater. Struct.* 11 (2002) 962–965.
- [20] M.O. Danilov, A.V. Melezhyk, *J. Power Sources* 163 (2006) 376–381.
- [21] H.P. Boehm, E. Diehl, W. Heck, R. Sappok, *Angew. Chem. Int. Ed. Engl.* 3 (1964) 669–678.
- [22] H.P. Boehm, *Carbon* 32 (1994) 759–769.
- [23] H.P. Boehm, *Carbon* 40 (2002) 145–149.
- [24] S. Jongpatiwut, N. Rattapanuchapong, T. Rirksomboon, S. Osuwan, D.E. Resasco, *Catal. Lett.* 122 (2008) 214–222.
- [25] T.G. Ros, A.J. van Dillen, J.W. Geus, D.C. Koningsberger, *Chem. Eur. J.* 8 (2002) 1151–1162.
- [26] P.E. Fanning, M.A. Vannice, *Carbon* 31 (1993) 721–730.
- [27] E. Papirer, E. Guyon, N. Perol, *Carbon* 16 (1978) 133–140.
- [28] M.S.P. Shaffer, X. Fan, A.H. Windle, *Carbon* 36 (1998) 1603–1612.
- [29] C. Moreno-Castilla, M.V. Lopez-Ramon, F. Carrasco-Marin, *Carbon* 38 (2000) 1995–2001.
- [30] H. Kandori, Y. Shichida, *J. Am. Chem. Soc.* 122 (2000) 11745–11746.
- [31] W. Neagle, C.H. Rochester, *J. Chem. Soc. Faraday Trans.* 86 (1990) 181–183.
- [32] J.F. Colomer, P. Piedigrosso, A. Fonseca, J.B. Nagy, *Synth. Met.* 103 (1999) 2482–2483.
- [33] B.H. Cooper, B.B.L. Donniss, *Appl. Catal. A* 137 (1996) 203–223.
- [34] A. Corma, A. Martinez, V. Martinez-Soria, *J. Catal.* 169 (1997) 480–489.