Silver Loading Effect for the Activated Carbon Fibers Pre-treated with Acid

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Received April 1, 2004

The adsorption isotherms of N_2 onto the metallic silver treated activated carbon fiber samples after acid treatment are Type I with a small amount of capillary condensation hysteresis. Increasing amount of acid treatment leads to a decrease in S_{BET}s and external surface area. But, micropore volume and average pore diameter are presented in constant regular values with increasing amount of sulfuric acid treatment. SEM observes the surface morphology and crystal grown state of metal on the fiber surface. The results of EDX of Ag-activated carbon fiber pre-treated with acid show the spectra corresponding to almost all samples rich in silver with increasing the amount of acid treated. The FT-IR spectra of Ag-activated carbon fiber show that the acid pre-treatment is consequently associated with the homogeneous dispersion of metal with the increased surface acidity of the activated carbon fiber. The type and quality of oxygen groups are determined with Boehm titration method. From the those results, a positive influence of the acidic groups on the carbon fiber surface by acid treatment is also demonstrated by an increase in the contents of metallic silver with increasing of acidic groups.

Key Words : Adsorption isotherm, Silver-activated carbon fiber, SEM, EDX, Boehm titration

Introduction

Functional groups on the surface of microporous carbons are most likely subjected to a wide variety of inter- and intra-molecular interactions. The relatively large numbers of oxygen-containing surface groups lead to oxidation of carbon surfaces containing a more hydrophilic surface structure. In general, the oxygen-containing surface groups behave as Brønsted acid-base characteristics, which may severely alter molecular interaction of parent carbon compounds. This can be used in the preparation of carbon supported metal catalysis by exchange with cationic metal complexes. Although carbon is considered to be an inert material in comparison with other catalyst supports, its surface is not as inert as expected because of the formation of active sites by the heteroatoms. In terms of carbon supported catalyst preparation, the presence of oxygen bearing is of great interest. In the related literatures,[1,2] the influence of surface functional groups on the activity of carbon-supported catalysts has been clearly shown. Most of the chemical properties of activated carbon come from the incorporation of oxygen during its production, forming oxides like carboxylic, phenolic and lactonic groups. The modification of surface chemistry resulted in a significant change of the loading capacity and of the catalytic properties.[3] These functional groups may play role in the sorption and deposition of nonpolar molecules and metallic ions by creating obstacles for physical adsorption and occurring the molecule from occupying the most energetically favorable position on the carbon surface. Metal treated activated carbon is a material having adsorption and catalysis; these are of interest in several areas including medical applications, or water and air treatment for the catalytic removal of organic and inorganic pollutants and antibacterials. Especially, silver treated activated carbon by impregnation method is well known for its bacterial effects.[4,5]

In this paper, which is the first part of a study on the Ag-activated carbon fiber system pretreated with various sulfuric acids, the purpose is to investigate the effects of physical and textural change of activated carbon fiber, and chemical treatment sequence. Full characterizations of silver loading effects for activated carbon fiber were presented by nitrogen adsorption properties, SEM-EDX analysis, FTIR results and properties of surface functional groups by Boehm titration.

Experimental Section

Preparation procedures. Self-made activated carbon fiber used as a non-treated carbon fiber material was prepared from PAN based carbon fiber. The carbonized PAN fiber was heated first at 823 K for burn off, and the carbon fibers were activated by steam diluted with nitrogen in a cylinder quartz glass tube in the temperature range of 1053~1073 K for 30 min. These activated carbon fibers were washed with deionized water and dried for 24 h at ambient temperature. The molar concentration of from 0.01 to 0.1 M diluted sulfuric acid at boiling temperature was used in the oxidation treatment to increase the formation of functional groups without the damage of the activated carbon fiber surface. The oxidation was carried out at the boiling temperature for 1 h. The oxidized activated carbon fibers were washed and dried at 323 K for 24 h. We prepared series of solutions, mole concentrations of 0.01 to 0.1 of $AgNO_3$,

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for the metal loading effects. The doubly distilled water to dissolve the chemicals for the free from impurities was used. For the treatment, 2 g of chop typed ACFs were dipped in to 50 mL of each silver ion dissolved aqueous solutions and stirred for 12 hours at room temperature. Then, we removed air and bubbles in the solutions under the pressure of about 1.33 Pa for 30 minutes, and then discarded the solution. Finally, these samples were dried at 368 K for 72 hours in air atmosphere. In order to reduce the experimental error, sample dryness was conformed through the whole experiments prior to use.

Measurement. Nitrogen adsorption isotherms were obtained by using BET surface area apparatus (ASAP 2010, Micrometrics) at 77 K. Before the experiment the samples were heated at 473 K and then outgassed at this temperature under a vacuum of 1.33×10^{-3} Pa to constant pressure. The isotherms were used to calculate the specific surface area and pore volume. The pore size distribution curves of micropores were obtained by the Hakins-Jura (H-J) method. Scanning electron microscopy (SEM, JSM-5200 JOEL, Japan) was used to observe the pore structure of silver treated activated carbon fiber and the treated silver particles state on the carbon fiber surfaces. For the elemental analysis of silver contents in activated carbon fibers treated with silver, EDX was also used. As one of the analysis of functional groups, FT-IR spectroscopy (FTS 3000MX, Biored Co.) was used to characterize of silver loading effect of Ag-activated carbon fibers. The silver supported activated carbon fibers after sulfuric acid treatment were examined by KBr method using the spectroscopy. Discs for the method were prepared by first mixing 1 mg of powdered Ag-activated carbon fiber with 600 mg of KBr (for FTIR spectroscopy) in an agitate mortar, and then pressing the resulting mixture successively under a pressure of 450 kg/cm^2 for 3 min. The spectra of the samples were measured between 4000 and 500 cm^{-1}.

Boehm titration. We used to Boehm titration method[6] for the identification of oxygenated surface group on the carbon fiber surfaces. One gram of Ag-activated carbon fiber sample was placed in 50 mL of the following 0.05 M solutions: sodium hydroxide, sodium carbonate, sodium bicarbonate, and hydrochloric acid. The elenmeyer flasks were sealed and shaken for 24 h and then 5 mL of each filtrate was pipetted and excess of base and acid was titrated with HCl and NaOH, respectively. The numbers of acidic sites of various types were calculated under the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups; Na_2CO_3, carboxylic and lactonic groups; and $NaHCO_3$, only carboylic groups. The number of surface basic sites was calculated from the amount of hydrochloric acid, which reacted with the carbon fiber.

Results and Discussion

The nitrogen adsorption isotherms at 77 K onto the silver supported activated carbon fiber samples after sulfuric acid treatments are shown in Figure 1. The S_{BET}s and porous structure of the Ag-activated carbon fibers are summarized in Table 1. The isotherms presented in this Figure 1 show that the total sorption uptake decreases with increasing amount of acid treatment. All of the Ag-ACFs gave Type I isotherms characterized by plateau that is nearly horizontal to the p/p_0 axis. This means that all the treated ACFs are microporous. It can be seen that both the external surface area and the total pore volume decreases as the distribution of silver on the activated carbon surfaces after acid treatments. Differences in the shape of these isotherms are not very significant, evidencing general similarities in the pore structure of the Ag-activated carbon fiber samples pretreated with sulfuric acid. Oh *et al.*[7,8] reported that the BET surface area is considerably decreased due to the blocking of the narrow pores by surface complexes introduced by pre-

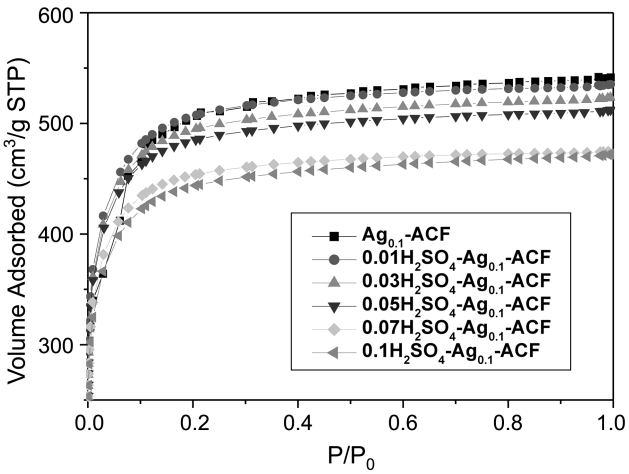

Figure 1. Adsorption isotherm of N_2 at 77 K onto the acid pretreated activated carbon fibers loaded with silver.

Table 1. Comparison of physical parameters of metallic silver supported activated carbon fibers after sulfuric acid treatment

Sample	Parameter			
	S_{BET} (m^2/g)	Micropore Volume (mL/g)	External Surface Area (m^2/g)	Average Pore Diameter (Å)
$Ag_{0.1}$-ACF	1923	0.554	527.7	17.39
$0.01H_2SO_4$-$Ag_{0.1}$-ACF	1924	0.568	411.6	17.13
$0.03H_2SO_4$-$Ag_{0.1}$-ACF	1881	0.574	475.9	17.17
$0.05H_2SO_4$-$Ag_{0.1}$-ACF	1845	0.570	442.3	17.17
$0.07H_2SO_4$-$Ag_{0.1}$-ACF	1730	0.544	355.8	16.95
$0.1H_2SO_4$-$Ag_{0.1}$-ACF	1686	0.511	396.9	17.27

treated acids.

The pore size distributions (PSD) calculated for Ag-ACFs using the H-J method[7] are shown in Figure 2. There is one major peak 0-20 Å, which is located in the micropore ranges. And another minor peak is located in ranging from 30 to 45 Å. The pore volume of micropores decreases with increasing amount of acid treatment, which is result of chemical and physical changes by sulfuric acid treatment of both internal and external surface in the Ag-activated carbon fibers. As shown in Table 1, S_{BET}s were distributed between 1685 and 1923 m^2/g. In addition to, external surface areas were distributed between 355.8 and 527.7 m^2/g. Increasing amount of acid treatment leads to a decrease in S_{BET}s and external surface area. But, micropore volume and average pore diameter are presented in constant regular values with increasing amount of sulfuric acid treatment. That is, the number of pores decreases with acid treatment, but the micropores of activated carbon fiber are not sufficiently created as acid pre-treatment effect with decreasing of S_{BET}s.

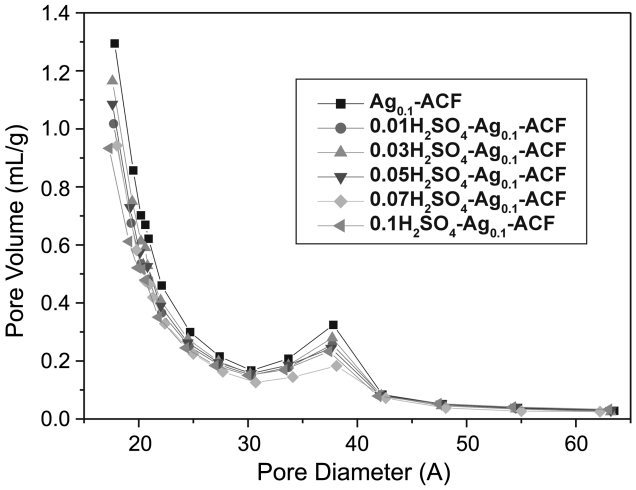

Figure 2. Pore size distributions of the acid pre-treated activated carbon fibers loaded with silver.

The crystal-grown state and surface morphology of silver on the activated carbon fiber surface were observed by scanning electron microscopy. The fine particles and aggregated metallic Ag particles were observed on the surfaces of some carbon fibers as indicated in Figure 3. As shown in this Figure 3, the aggregated metallic Ag particles are presented in increase with increasing amount of sulfuric acid treatment. From these results, one can obviously observe the highly developed creaks and cavities, and heterogeneous distributed metallic Ag particles on the carbon fiber surface. Comparing acid free samples, samples treated with acid were revealed to homogeneously distribution of fine silver particles. It can be considered that treated metallic silvers give considerable transformation to the outer surface states of activated carbon fiber treated with acid. And, it is shown that coalescing and particles blocked up some micropores on the surface increase with increasing the acid concentration treated. For the elemental analysis of metal supported activated carbons after acid treatment, samples were analyzed by Energy disperse X-ray (EDX). Energy disperse X-ray (EDX) spectra of Ag-activated carbon fibers pre-treated with sulfuric acid are shown in Figure 4. From the

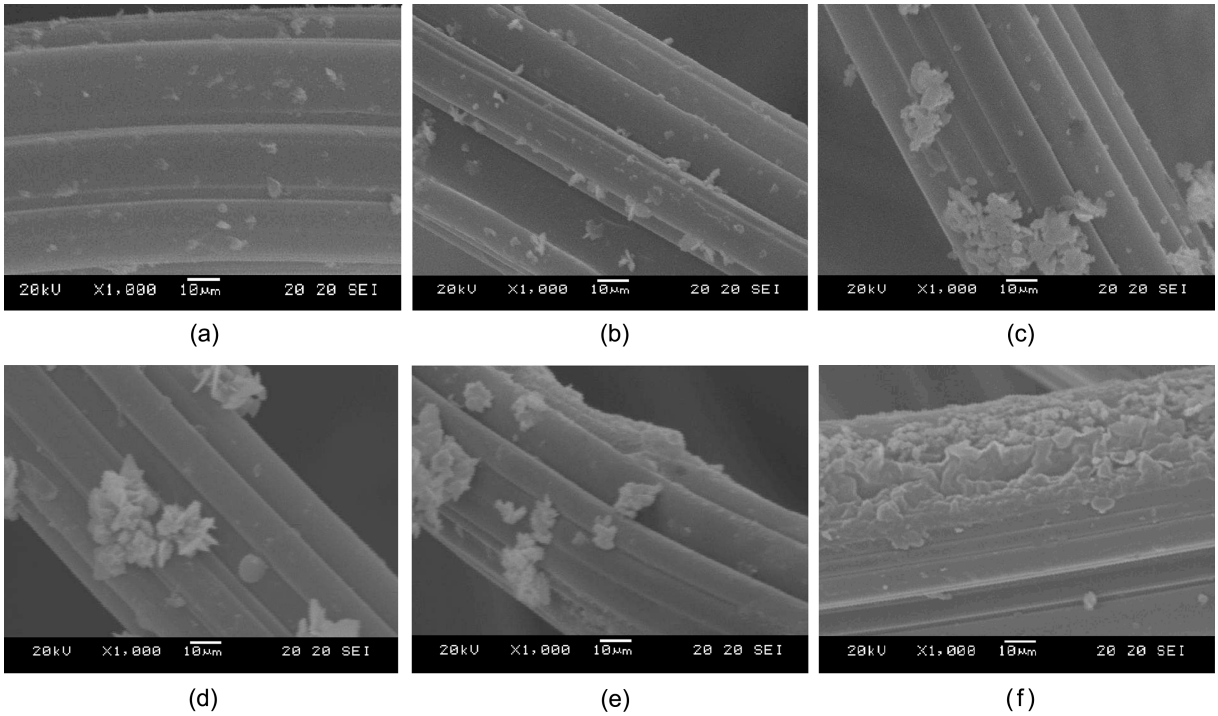

Figure 3. SEM micrographs of acid free metallic silver supported activated carbon fiber and metallic silver supported activated carbon fibers after sulfuric acid treatments; (a) $Ag_{0.1}$-ACF, (b) $0.01H_2SO_4$-$Ag_{0.1}$-ACF, (c) $0.03H_2SO_4$-$Ag_{0.1}$-ACF, (d) $0.05H_2SO_4$-$Ag_{0.1}$-ACF, (e) $0.07H_2SO_4$-$Ag_{0.1}$-ACF and (f) $0.1H_2SO_4$-$Ag_{0.1}$-ACF.

results, it shows the presence of C, Ag and O. In case of most of samples, carbon and silver are present as major elements in the activated carbon treated with metal. And, these results presented for each samples are shown the spectra corresponding to almost all samples rich in silver with increasing of the amount of acid treated. Note that a increasing of the amount of Ag contents (52.31%) with increasing O contents (7.32%) is observed for the $0.1H_2SO_4$-$Ag_{0.1}$-ACF (Fig. 4(f)), which becomes more homogeneous as the carbon fiber surface is oxidized. The results of SEM and EDX indicate that the functional groups of activated carbons fiber surface by acid treatment are affects to the dispersion of the metallic silver. As already known from another study,[9] the stability of the graphene layers (basal planes) is high. Therefore, oxygen surface groups are expected to be located at the edges of the basal planes, which are relatively weak sites of carbon structure and oxidation progresses slowly into the basal planes.

The FT-IR spectra of an Ag-activated carbon fiber pre-treated with sulfuric acid treatment are shown in Figure 5. Observation of the absorption bands shows that the changes between the oxidized (acid treatment) and non-oxidized (non treatment) carbon fiber samples are mainly due to the formation functional groups. As shown in Figure 5, the intensity of spectra decreases with increasing amount of sulfuric acid treatment. The ν (C-O) mode of the methoxy groups depends on the chemical structure of the adsorption sites. Absorption of C-O followed by IR spectra has been used to characterize treated and non-treated metal catalysts. The frequency of ν (C-O) of adsorbed carbon monoxide is often treated as an indicator characterizing the local coordination. This is also suitable for examining the state of metal ions situated differently on the solid surface. The most characteristics changes are observed at 1366 cm^{-1} of the presence of C-O- containing structures (ν_s of COO^-). The spectra show the presence of an absorption band at 1600 cm^{-1}.

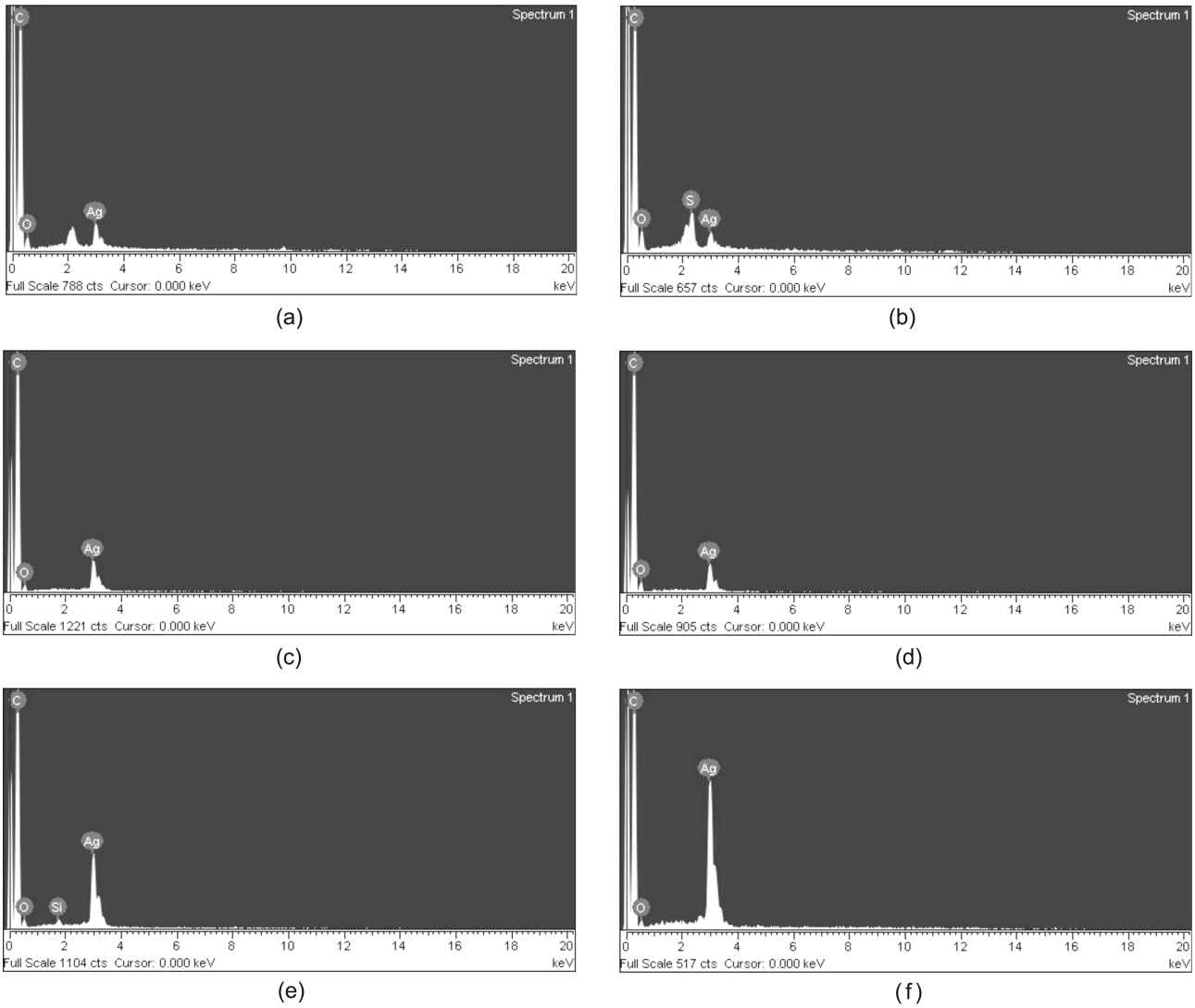

Figure 4. EDX elemental micro-analysis of acid free metallic silver supported activated carbon fiber and metallic silver supported activated carbon fibers after sulfuric acid treatments; (a) $Ag_{0.1}$-ACF, (b) $0.01H_2SO_4$-$Ag_{0.1}$-ACF, (c) $0.03H_2SO_4$-$Ag_{0.1}$-ACF, (d) $0.05H_2SO_4$-$Ag_{0.1}$-ACF, (e) $0.07H_2SO_4$-$Ag_{0.1}$-ACF and (f) $0.1H_2SO_4$-$Ag_{0.1}$-ACF.

Table 2. Number of Surface Species (meq/g) Obtained from Boehm Titration

Sample	Functional Group (meg/g)				
	Carboxylic	Lactonic	Phenolic	Acidic	Basic
$Ag_{0.1}$-ACF	1.01	0.52	0.90	2.43	1.31
$0.01H_2SO_4$-$Ag_{0.1}$-ACF	1.56	0.73	0.95	3.24	1.12
$0.03H_2SO_4$-$Ag_{0.1}$-ACF	1.66	1.32	2.87	5.85	1.22
$0.05H_2SO_4$-$Ag_{0.1}$-ACF	2.03	1.85	2.33	6.21	1.11
$0.07H_2SO_4$-$Ag_{0.1}$-ACF	1.95	2.01	3.88	7.84	1.13
$0.1H_2SO_4$-$Ag_{0.1}$-ACF	4.56	3.21	3.09	10.86	1.45

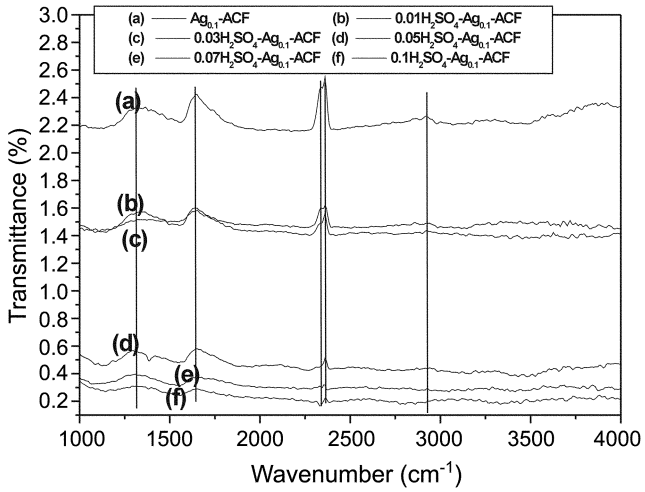

Figure 5. Infrared spectra recorded from the acid pre-treated activated carbon fibers loaded with silver; (a) $Ag_{0.1}$-ACF, (b) $0.01H_2SO_4$-$Ag_{0.1}$-ACF, (c) $0.03H_2SO_4$-$Ag_{0.1}$-ACF, (d) $0.05H_2SO_4$-$Ag_{0.1}$-ACF, (e) $0.07H_2SO_4$-$Ag_{0.1}$-ACF and (f) $0.1H_2SO_4$-$Ag_{0.1}$-ACF.

These bands are due to C=C stretching modes that weakly active in the IR because of breakdown of selection rules. The weak band appearing at 1366 cm^{-1} is ascribed to the formation of oxygen function groups like a highly conjugated C=O stretching in carboxylic groups, and carboxylate moieties.[3] These results indicate that acid treatment gave rise to a greater increase in C=O bonds in carboxylic acid and lactone groups. The acid treatment is consequently associated with the homogeneous distribution of silver with the increased surface acidity of the activated carbon fibers. The band observed at 2360 cm^{-1} is usually ascribed to the presence of aliphatic compounds. A broad band in the 3100-3500 cm^{-1} region, typically attributed to O-H stretches from hydroxyl, phenolic and carboxylic groups are absent. Thus FTIR spectra confirm the formation of carbonyl groups during the oxidation process of acid treatment. The main goal of oxidation is to obtain a more hydrophilic surface with a relatively large number of oxygen containing oxygen groups on the fiber surfaces.

The FT-IR spectra transformation described above are due to an alternation of the carbon surface via introduction of oxygen groups and removal some carbon atoms from matrix by acid treatment. The type and quality of oxygen groups are determined with Boehm titration method. The results obtained from the method proposed by Boehm are listed in Table 2. It can be observed that the total acidity and the distributions of groups of various strengths have very different values. The effect of surface acidity and basity was also evaluated from correlations as a function of NaOH, $NaHCO_3$ and Na_2CO_3 uptake. The surface acidity increases with increasing of the amount of acid treated. It is presented that $0.1H_2SO_4$-$Ag_{0.1}$-ACF has the highest number of oxidation groups such as carboxylic, lactonic and phenolic groups. This may contribute to the lowest local pH of this carbon surface due to acid treatment. A positive influence of the acidic groups on the carbon fiber surface by acid treatment is also demonstrated by an increase in the contents of metallic silver with increasing of acidic groups calculated from Boehm titration. It is believe that the affinity of activated carbon fiber for silver depends on the amount of surface functional groups. When distribution of acidic groups is properly introduced, active sites on the carbon fiber surface should be play important role in the deposition of metallic ions. As expected, acid oxidation introduces a significant number of oxygen containing groups in almost each category classified by Boehm.

Conclusion

The adsorption isotherms of Ag-ACFs pre-treated with sulfuric acid are Type I. From the pore size distributions (PSD) calculated for our materials using the H-J method, these also confirm our hypothesis about the source of the microporosity being the metallic silver on the activated carbon fiber surfaces after various acid treatments. In case of SEM results, one can obviously observe the highly developed surface structures, and homogeneous distributed metals and grown crystal particles on the carbon fiber surface. The results of typical EDX elemental microanalysis of Ag-activated carbon fibers pre-treated sulfuric acid show the spectra corresponding to almost all samples rich in silver with increasing the amount of acid treated. The FT-IR spectra of Ag-activated carbon fiber samples show that the acid treatment is consequently associated with the homogeneous distribution of metal with the increased surface acidity of the activated carbon fibers. The effect of surface acidity and basity was also evaluated from correlations as a function of NaOH, $NaHCO_3$ and Na_2CO_3 uptake. A effects of the acidic groups introduced on the carbon fiber surface by acid treatment is also demonstrated by an increase in the

contents of metallic silver with increasing of acidic groups calculated from Boehm titration.

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