

## Comparison of metal loading effect for the activated carbons pre-treated with various acids

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The adsorption/desorption isotherms of N<sub>2</sub> at 77K on metallic silver/activated carbons after acid treatment are Type I with a small amount of capillary condensation hysteresis. From the Pore Size Distribution (PSD) calculated for our materials using the density functional theory, these also confirm our hypothesis that the source of the microporosity is the metallic silver on the activated carbon surfaces after acid treatments. In the case of SEM results, one can observe the highly developed surface structures, and homogeneously distributed metals on the carbon surfaces. The IR spectra of metallic silver/activated carbons show that the acid treatment is associated with the homogeneous distribution of metal with the increased surface acidity of the activated carbons. The effect of surface acidity and basicity calculated from the Boehm titration method was also evaluated from correlations as a function of NaOH, NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> uptake. Finally, the results of typical EDX elemental microanalysis of Ag/activated carbons after acid treatment show spectra for almost all samples rich in silver with an increasing amount of acid treatment.

**Key words:** adsorption/desorption isotherm, silver/activated carbon, SEM, Boehm titration, EDX.

### Introduction

Granular activated carbon adsorption is a versatile technology and particularly suited to removing both regulated synthetic and volatile organic chemicals from air and dissolved naturally-occurring organic materials from water and waste water. Their materials are generally of concern for reasons relating directly to human health and are considered to be the major precursor to infectious byproducts formed during drinking water treatment operations. Applications of activated carbon are governed by a high surface area, a developed pore structure, and surface chemistry [1-3]. The surface chemical heterogeneity is due to the presence of heteroatoms such as oxygen, nitrogen, hydrogen, phosphorus and sulfur. The amount of these atoms present in the activated carbons depends on the origin of the carbon and method of activation [4]. The most important heteroatoms in activated carbon are oxygen, which is usually bonded to peripheral carbon atoms at the edges of the crystallites. The most common functional groups are carboxylic, carbonyls, phenols and lactones. Functional groups on the surface of microporous carbons are most likely subjected to a wide variety of inter- and intra-molecular interactions including inductive, mesomeric, tautomeric, steric and hydrogen bonding. These interactions may severely alter their Brønsted-acid-base

characteristics in such a way that in most cases they may not resemble the properties of parent chemical compounds. These functional groups may play a role in the sorption and deposition of nonpolar molecules and metallic ions by creating obstacles for physical adsorption and stopping the molecule from occupying the most energetically-favorable position on the carbon surface. Metal treated activated carbon is a material capable of 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 [5] and antibacterials. In particular, silver-treated activated carbon is well known for its bacterial effects [6, 7].

The purpose of the present paper is to prepare catalytic activated carbon supporting silver from activated carbon pretreated with various acids. Special emphasis is placed on the metal loading effect from adsorption characterization such as their surface, structural and functional properties.

### Experimental

#### Preparation procedures

Home made activated carbon used as a starting material was prepared from coconut shell based granular carbon. The carbonized coconut shell was heated first at 500 °C for burn off, then physically activated with water vapor in the temperature range of 750~780 °C. For the treatment, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, HNO<sub>3</sub> and AgNO<sub>3</sub> were obtained from Aldrich (99+%, ACS reagent) and used as received. In order to be free from impurities, doubly distilled

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water was used. For pretreatment with acid, 30 g of activated carbon was dipped into 100 ml of 0.05~0.1 M acid solution and stirred for 24 h at room temperature. Then, air and bubbles in the solution were removed under a pressure of about 1.33 Pa for 20 minutes, and then the solution was discarded. These samples were then dried at 110 °C for 48 h in an air atmosphere. For the metal treatment, 30 g of activated carbon was dipped into 100 ml of 0.1 M silver nitrate aqueous solution and stirred for 12 h at room temperature. After removal of the liquid, samples treated with silver were dried completely in an oven.

### Measurement

Nitrogen isotherms were measured using an 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  $1.33 \times 10^{-3}$  Pa to a constant pressure. The isotherms were used to calculate the specific surface area and pore volume. Scanning electron microscopy (SEM, JSM-5200 JOEL, Japan) was used to observe the surface state and pore structure of metal-treated activated carbon and the treated metal state. For the elemental analysis of metal contents in activated carbon, EDX was also used. The metal-supported activated carbons after acid treatment were examined by a KBr method using Fourier transform infrared (FTIR) spectroscopy. Discs for the method were prepared by first mixing 1mg of powdered metal-activated carbon with 600 mg of KBr (for FTIR spectroscopy) in an agitate mortar, and then pressing the resulting mixture successively under a pressure of 450 Pa for 3 minutes. The spectra of the samples were measured between 4000 and 500  $\text{cm}^{-1}$  using a FTS 3000MX (Bioered Co.) spectrophotometer.

### Boehm titration

A Boehm titration method [1] was used for the identification of oxygenated surface groups on the carbon surfaces. One gram of carbon 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;  $\text{Na}_2\text{CO}_3$ , carboxylic and lactonic groups; and  $\text{NaHCO}_3$ , only carboxylic groups. The number of surface basic sites was calculated from the amount of hydrochloric acid, which reacted with the carbon.

## Results and Discussion

Figure 1 shows the adsorption/desorption isotherms of  $\text{N}_2$  at 77 K on the metallic silver-supported activated

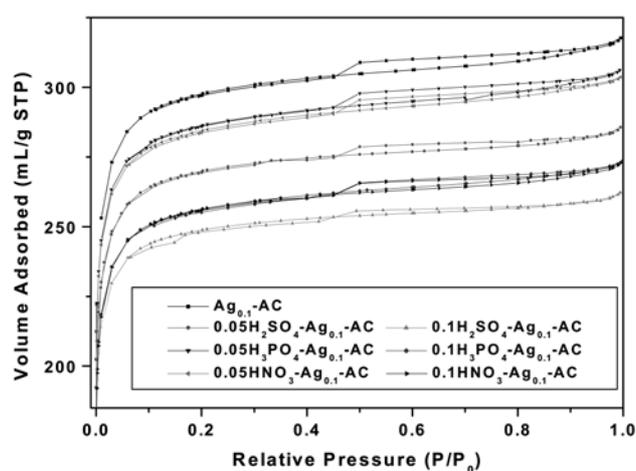


Fig. 1. Adsorption/desorption isotherm of  $\text{N}_2$  at 77 K on metallic silver-supported activated carbons after various acid treatments.

carbon samples after various acid treatments. The isotherms presented in this Fig. show that the total sorption uptake decreases with an increasing amount of acid treatment. All of the isotherms are Type I with a small amount of capillary condensation hysteresis. It can be seen that both the external surface area and the total pore volume decreases with the distribution of metallic silver on the activated carbon surfaces after acid treatments. Hysteresis exists mainly due, among other factors such as the silt-shaped pores, to the presence of ink-bottle shaped of pores [8]. The development of micropores and mesopores can be clearly confirmed by the shape of the isotherms. According to the Kelvin equation, the ink-bottle shaped of pores have a large pore size, given that for these samples hysteresis occurs at a high relative pressure ( $P/P_0 > 0.5$ ). The smaller amount of adsorption and narrow hysteresis loop for the metallic silver-supported activated carbon samples after various acid treatments indicate the existence of a larger amount of porous spaces and ink-bottle pores. Differences in the shape of these

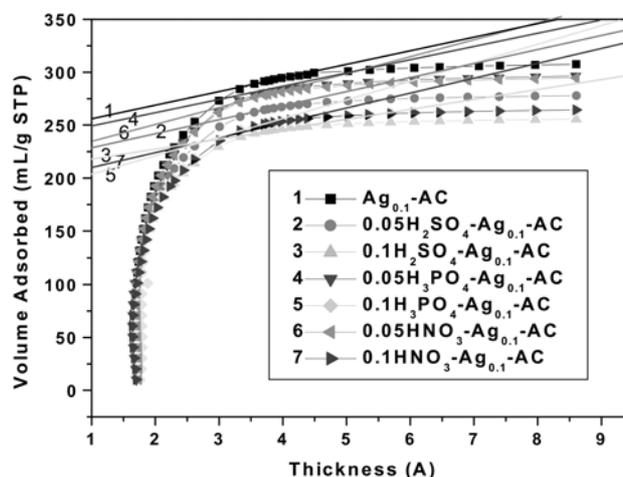
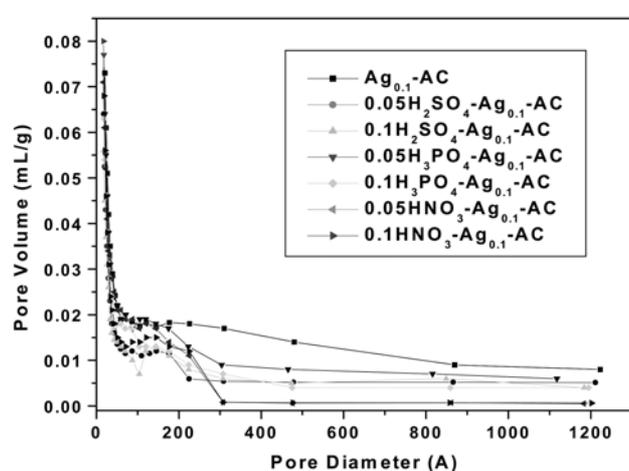


Fig. 2. t-plots of metallic silver-supported activated carbons after various acid treatments.



**Fig. 3.** Pore size distributions of metallic silver-supported activated carbons after various acid treatments.

isotherms are not very significant, evidencing general similarities in the pore structure of the metallic silver-supported activated carbon samples after various acid treatments.

Figure 2 shows t-plots of the metallic silver-supported activated carbon samples after various acid treatments. The t-plots of these samples have a c-swing indicating the presence of both ultra- and supermicropores. The t-plot method was used to test for microporosity.

The pore size distributions (PSD) calculated for our materials using the density functional theory [9] are shown in Fig. 3. There is one major peak 0-10 Å, which is located in the micropore ranges. The development of micropores (smaller than 20 Å) is observed with increasing amounts of acid treatment. Moreover, the volume of mesopores smaller than 100 Å significantly decreases with an increasing amount of acid treatment, which is the result of chemical and physical changes of both internal and external surfaces in the metal-activated carbon. These PSDs also confirm our hypothesis about the source of the microporosity being the metallic silver on the activated carbon surfaces after various acid treatments. Pore structures and physical parameters of the metallic silver-supported activated carbon samples after various acid treatments are listed

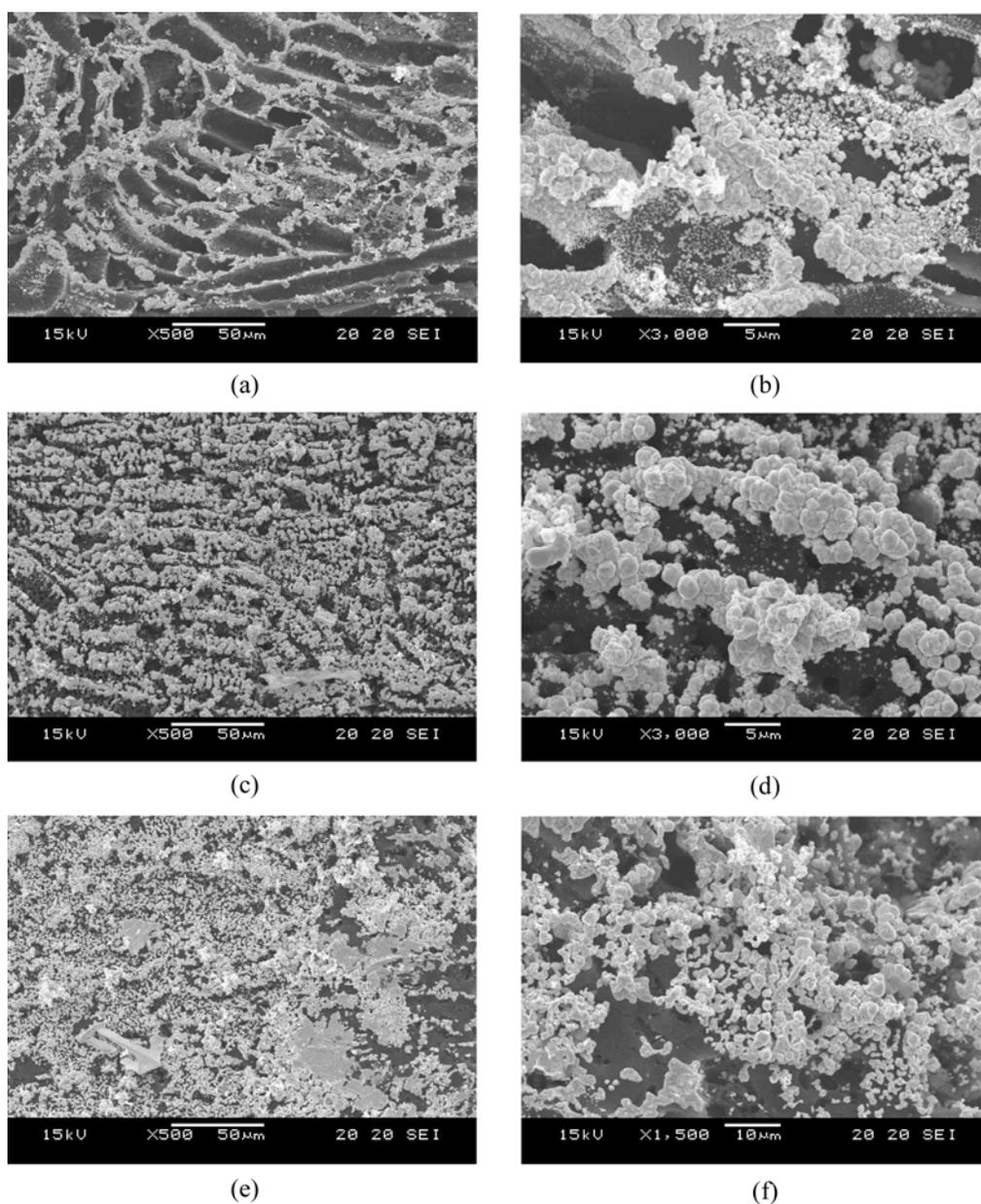
in this Table 1. As shown in Table,  $S_{\text{BET}}$ s were distributed between 973.9 and 1145  $\text{m}^2/\text{g}$ . An increasing amount of acid treatment leads to a decrease in micropore volume, external surface area and average pore diameter. That is, the number of pores decreases with acid treatment, but the creation of micropores is more significant as an acid pre-treatment effect with decreasing of  $S_{\text{BET}}$ s.

The surface morphology and crystal grown state of metal on the activated carbon surfaces were observed by scanning electron microscopy. Fine particles and aggregated metallic Ag particles were observed on the surfaces of some carbons as indicated in Fig. 4, 5 and 6. From these results, one can obviously observe the highly developed cracks and cavities, and homogeneous distributed metals and grown crystal particles on the carbon surface. Treated metallic silvers give considerable transformation to the outer surface states of activated carbon treated with acid. Comparing acid-free samples, samples treated with acid were revealed to have homogeneous distributions of fine particles. Also, it was shown that coalescing and particles blocking up some micropores on the surface increase with increasing the acid concentration used in the treatment. In the case of treatment with phosphoric acid, one can clearly observe a special homogeneous distribution of fine silver particles.

Figure 7 shows the IR spectra of metallic silver-supported activated carbon samples after various acid treatments. Observation of the absorption bands shows that the changes between the oxidized (acid treatment) and non-oxidized (non treatment) carbon samples are mainly due to the formation of functional groups. From the Fig. (a), the presence of absorption bands at  $1116\text{ cm}^{-1}$  is assigned to the  $\nu$  (C-O) coordinated methoxy species. The  $\nu$  (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 supported and unsupported metal catalysts. The frequency of  $\nu$  (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

**Table 1.** Comparison of physical parameters of metallic silver-supported activated carbons after various acid treatments

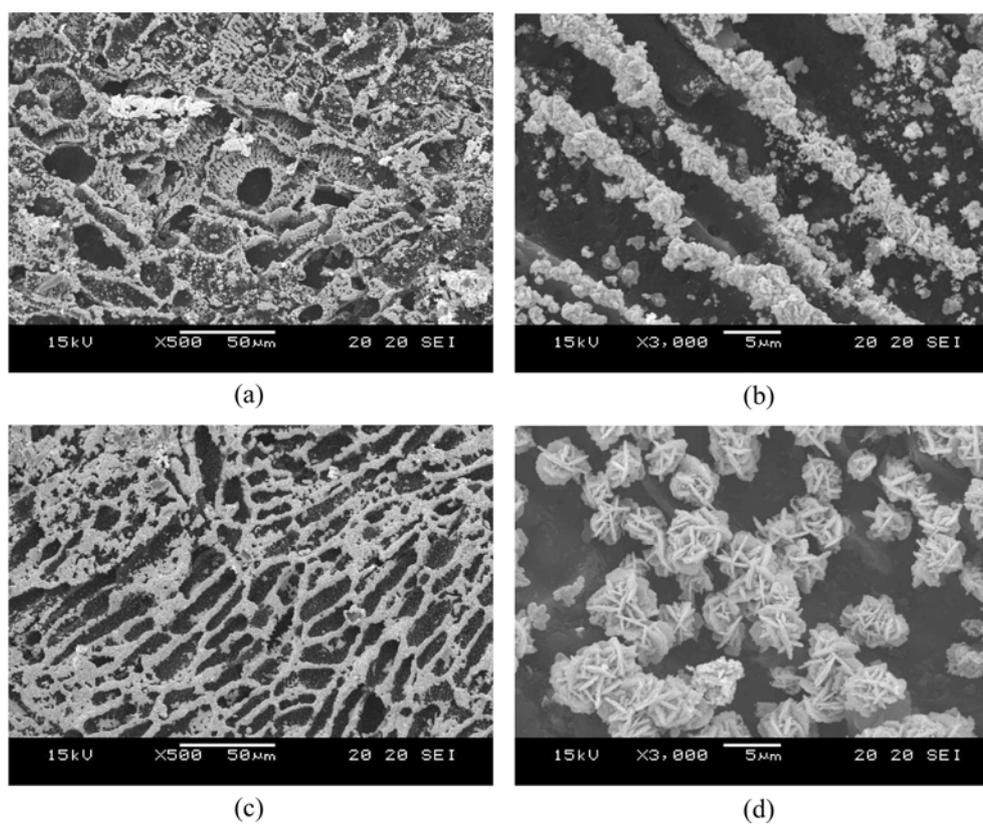
Sample	Parameter			
	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Micropore Volume ( $\text{cm}^3/\text{g}$ )	External Surface Area ( $\text{m}^2/\text{g}$ )	Average Pore Diameter (Å)
$\text{Ag}_{0.1}\text{-AC}$	1145	0.399	1140	17.04
$0.05\text{H}_2\text{SO}_4\text{-Ag}_{0.1}\text{-AC}$	1054	0.363	930.2	16.62
$0.1\text{H}_2\text{SO}_4\text{-Ag}_{0.1}\text{-AC}$	973.9	0.338	867.2	16.54
$0.05\text{H}_3\text{PO}_4\text{-Ag}_{0.1}\text{-AC}$	1117	0.385	985.7	16.83
$0.1\text{H}_3\text{PO}_4\text{-Ag}_{0.1}\text{-AC}$	1001	0.344	881.8	16.77
$0.05\text{HNO}_3\text{-Ag}_{0.1}\text{-AC}$	1110	0.382	977.9	16.81
$0.1\text{HNO}_3\text{-Ag}_{0.1}\text{-AC}$	1002	0.344	882.2	16.72



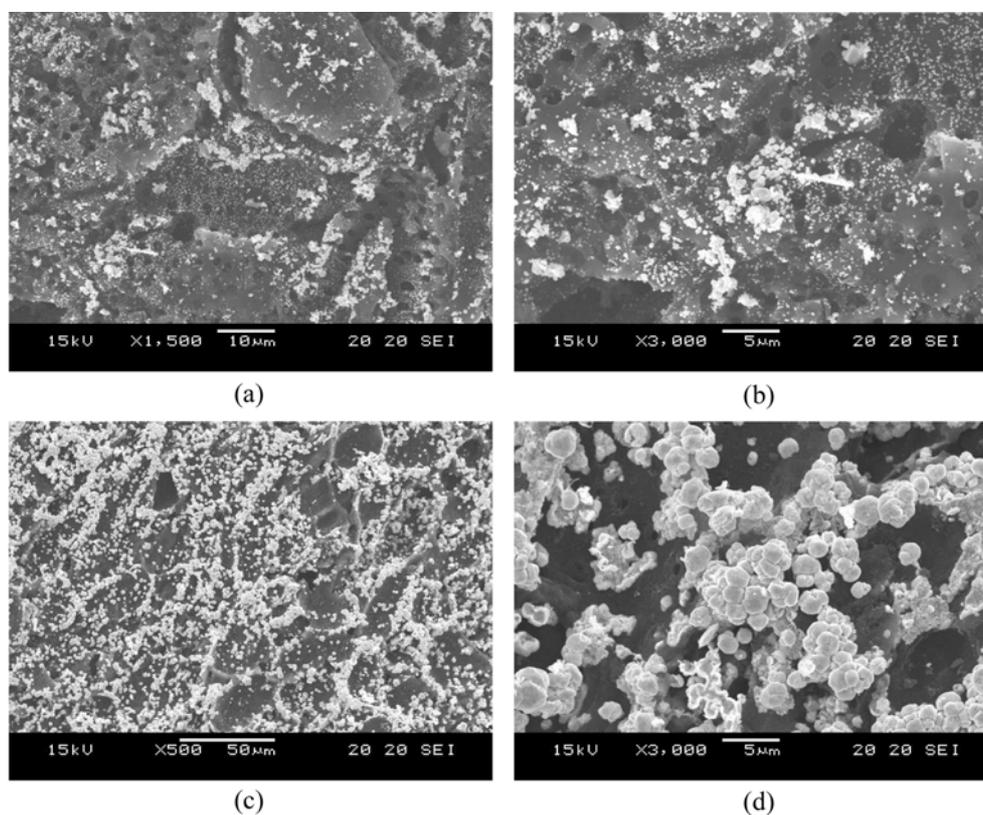
**Fig. 4.** SEM micrographs of acid free metallic silver-supported activated carbons and metallic silver-supported activated carbons after sulfuric acid treatments; (a)  $\text{Ag}_{0.1}\text{-AC}$  ( $\times 500$ ), (b)  $\text{Ag}_{0.1}\text{-AC}$  ( $\times 3000$ ), (c)  $0.05\text{H}_2\text{SO}_4\text{-Ag}_{0.1}\text{-AC}$  ( $\times 500$ ), (d)  $0.05\text{H}_2\text{SO}_4\text{-Ag}_{0.1}\text{-AC}$  ( $\times 3000$ ), (e)  $0.1\text{H}_2\text{SO}_4\text{-Ag}_{0.1}\text{-AC}$  ( $\times 500$ ) and (f)  $0.1\text{H}_2\text{SO}_4\text{-Ag}_{0.1}\text{-AC}$  ( $\times 3000$ ).

differently on the solid surface. The presence of at least two types of surface bound CO species is recognized by the characteristic position of the  $\nu$  (C-O) bands. The most characteristic changes are observed at  $1380$ ,  $1570$  and  $1719\text{ cm}^{-1}$  showing the presence of C-O- and N-O-containing structures. The band centered at  $1719\text{ cm}^{-1}$  is ascribed to the stretching vibrations of carboxyl groups on the edges of layer planes or to conjugated carbonyl groups. The weak bands appearing at  $1380$  and  $1570\text{ cm}^{-1}$  are ascribed to the formation of oxygen function groups like a highly conjugated C=O stretching in carboxylic groups, and carboxylate moieties [10]. These results indicate that acid treatment gave rise to a greater increase in C=O bonds in carboxylic

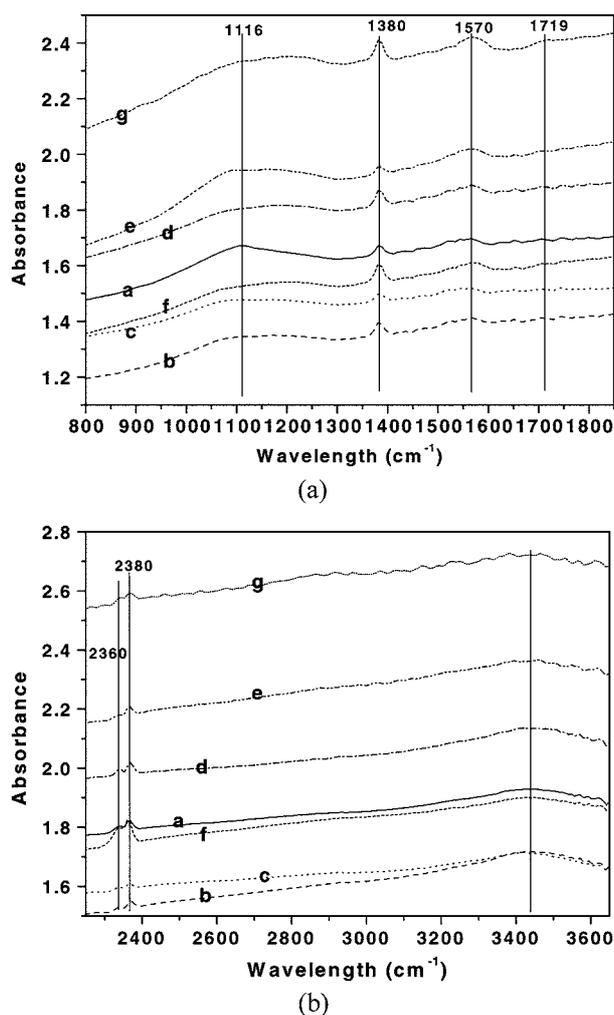
acid and lactone groups. The acid treatment is consequently associated with the homogeneous distribution of metal with increased surface acidity of the activated carbons. The band observed at  $2360\text{ cm}^{-1}$  is usually ascribed to the presence of aliphatic compounds. Observation of absorption bands in the range above  $3000\text{ cm}^{-1}$ , appearing as intense and broad peaks, are associated with the stretching vibrations of hydroxyl groups involved in hydrogen bonding, probably with the participation of water adsorbed on the carbon [11]. A broad band in the  $3100\text{-}3500\text{ cm}^{-1}$  region, typically attributed to O-H stretches from hydroxyl, phenolic and carboxylic groups is absent. Thus FTIR spectra confirm the formation of carbonyl



**Fig. 5.** SEM micrographs of metallic silver-supported activated carbons after phosphoric acid treatments; (a)  $0.05\text{H}_3\text{PO}_4\text{-Ag}_{0.1}\text{-AC}$  ( $\times 500$ ), (b)  $0.05\text{H}_3\text{PO}_4\text{-Ag}_{0.1}\text{-AC}$  ( $\times 3000$ ), (c)  $0.1\text{H}_3\text{PO}_4\text{-Ag}_{0.1}\text{-AC}$  ( $\times 500$ ) and (d)  $0.1\text{H}_3\text{PO}_4\text{-Ag}_{0.1}\text{-AC}$  ( $\times 3000$ ).



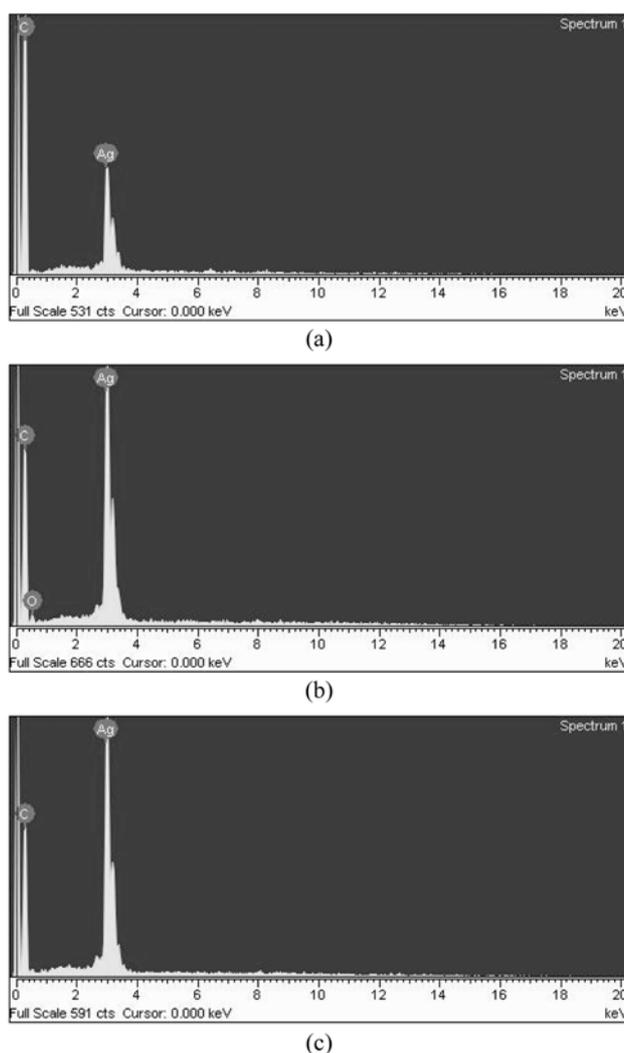
**Fig. 6.** SEM micrographs of metallic silver-supported activated carbons after nitric acid treatments; (a)  $0.05\text{HNO}_3\text{-Ag}_{0.1}\text{-AC}$  ( $\times 500$ ), (b)  $0.05\text{HNO}_3\text{-Ag}_{0.1}\text{-AC}$  ( $\times 3000$ ), (c)  $0.1\text{HNO}_3\text{-Ag}_{0.1}\text{-AC}$  ( $\times 500$ ) and (d)  $0.1\text{HNO}_3\text{-Ag}_{0.1}\text{-AC}$  ( $\times 3000$ ).



**Fig. 7.** Infrared spectra recorded from silver-supported activated carbons after acid treatment (a) lower band region, (b) higher band region: a.  $\text{Ag}_{0.1}\text{-AC}$ , b.  $0.05\text{H}_2\text{SO}_4\text{-Ag}_{0.1}\text{-AC}$ , c.  $0.1\text{H}_2\text{SO}_4\text{-Ag}_{0.1}\text{-AC}$ , d.  $0.05\text{H}_3\text{PO}_4\text{-Ag}_{0.1}\text{-AC}$ , e.  $0.1\text{H}_3\text{PO}_4\text{-Ag}_{0.1}\text{-AC}$ , f.  $0.05\text{H}_3\text{PO}_4\text{-Ag}_{0.1}\text{-AC}$  and g.  $0.1\text{H}_3\text{PO}_4\text{-Ag}_{0.1}\text{-AC}$ .

groups during the oxidation process of acid treatment.

The changes described above are due to an alternation of the carbon surface via introduction of oxygen groups and removal of some carbon atoms from matrix. The type and quality of oxygen groups are determined by the Boehm titration method. The results

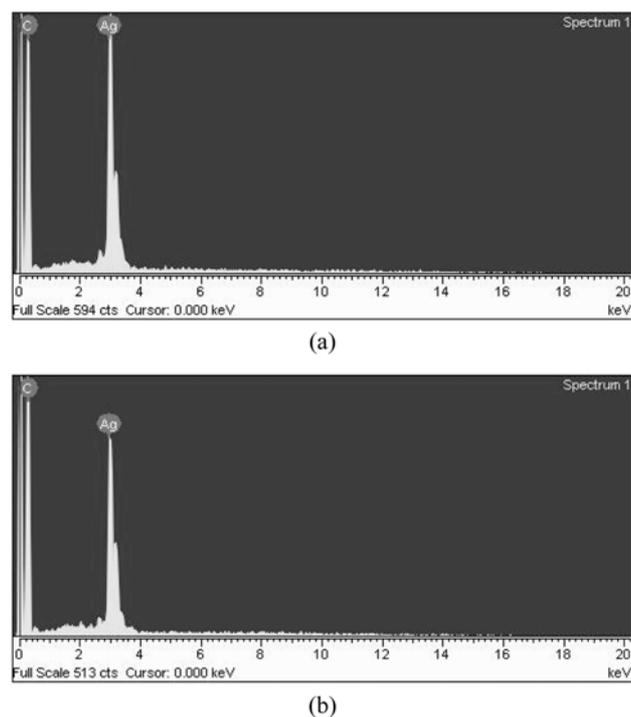


**Fig. 8.** EDX elemental microanalysis of acid free metallic silver-supported activated carbon and metallic silver-supported activated carbons after sulfuric acid treatments; (a)  $\text{Ag}_{0.1}\text{-AC}$ , (b)  $0.05\text{H}_2\text{SO}_4\text{-Ag}_{0.1}\text{-AC}$  and (c)  $0.1\text{H}_2\text{SO}_4\text{-Ag}_{0.1}\text{-AC}$ .

obtained from the method proposed by Boehm are collected 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  $\text{NaOH}$ ,  $\text{NaHCO}_3$  and

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

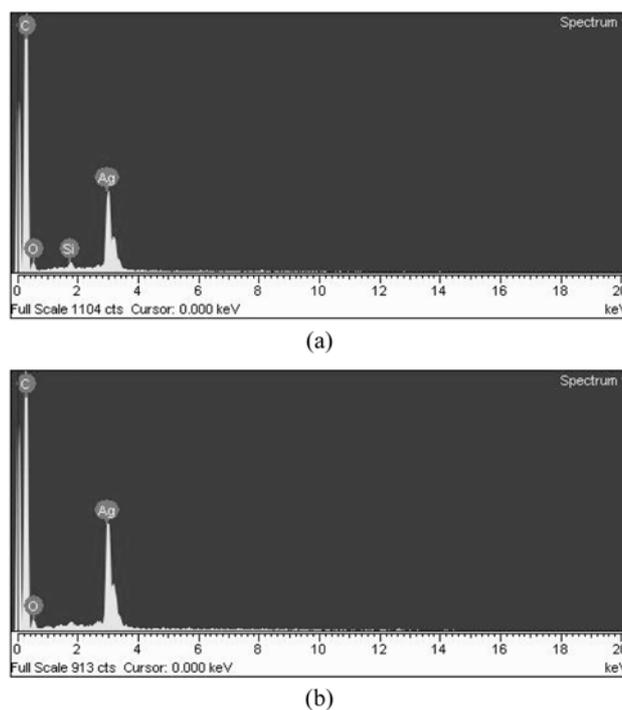
Sample	Functional Group (meq/g)				
	Carboxylic	Lactonic	Phenolic	Acidic	Basic
$\text{Ag}_{0.1}\text{-AC}$	2.00	1.62	2.96	6.58	3.73
$0.05\text{H}_2\text{SO}_4\text{-Ag}_{0.1}\text{-AC}$	2.89	1.74	6.23	10.86	3.24
$0.1\text{H}_2\text{SO}_4\text{-Ag}_{0.1}\text{-AC}$	4.82	3.41	29.07	38.0	2.17
$0.05\text{H}_3\text{PO}_4\text{-Ag}_{0.1}\text{-AC}$	3.13	2.30	3.19	8.62	3.78
$0.1\text{H}_3\text{PO}_4\text{-Ag}_{0.1}\text{-AC}$	3.65	3.29	8.69	15.63	2.30
$0.05\text{HNO}_3\text{-Ag}_{0.1}\text{-AC}$	3.25	1.30	4.38	8.93	3.47
$0.1\text{HNO}_3\text{-Ag}_{0.1}\text{-AC}$	3.86	2.00	7.35	13.16	3.79



**Fig. 9.** EDX elemental microanalysis of metallic silver-supported activated carbons after phosphoric acid treatments; (a)  $0.05\text{H}_3\text{PO}_4\text{-Ag}_{0.1}\text{-AC}$  and (b)  $0.1\text{H}_3\text{PO}_4\text{-Ag}_{0.1}\text{-AC}$ .

$\text{Na}_2\text{CO}_3$  uptake. It is noteworthy that  $0.1\text{H}_2\text{SO}_4\text{-Ag}_{0.1}\text{-AC}$  has the highest number of carboxylic, lactonic and phenolic groups and the lowest number of basic ones. 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 surface by acid treatment is also demonstrated by an increase in the content of metals with an increase of acidic groups calculated from Boehm titration. It is considered that the affinity of activated carbon for metal depends on the amount of surface functional groups. When a distribution of acidic groups is properly introduced, active sites on the carbon surface should play an 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.

For the elemental analysis of metal-supported activated carbons after acid treatment, samples were analyzed by Energy dispersive X-ray (EDX). EDX spectra of metal-supported activated carbons are shown in Fig. 8, 9 and 10. The results of typical EDX elemental microanalysis of metal-supported activated carbons after acid treatment are shown in Table 3. The results show 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. Fig. 8, 9 and 10 for each sample show spectra corresponding to almost all the samples are rich in silver with an increasing the amount of acid treatment. Note that for the  $0.1\text{HNO}_3\text{-}$



**Fig. 10.** EDX elemental microanalysis of metallic silver-supported activated carbons after nitric acid treatments; (a)  $0.05\text{HNO}_3\text{-Ag}_{0.1}\text{-AC}$  and (b)  $0.1\text{HNO}_3\text{-Ag}_{0.1}\text{-AC}$ .

**Table 3.** EDX Elemental Micro-Analysis of Ag-ACs

Sample	Elements (%)		
	C	Ag	O
$\text{Ag}_{0.1}\text{-AC}$	65.25	34.75	0
$0.05\text{H}_2\text{SO}_4\text{-Ag}_{0.1}\text{-AC}$	34.16	64.84	1.00
$0.1\text{H}_2\text{SO}_4\text{-Ag}_{0.1}\text{-AC}$	36.82	55.97	7.22
$0.05\text{H}_3\text{PO}_4\text{-Ag}_{0.1}\text{-AC}$	44.81	53.9	1.29
$0.1\text{H}_3\text{PO}_4\text{-Ag}_{0.1}\text{-AC}$	49.13	42.44	8.43
$0.05\text{HNO}_3\text{-Ag}_{0.1}\text{-AC}$	67.74	22.93	8.75
$0.1\text{HNO}_3\text{-Ag}_{0.1}\text{-AC}$	60.09	29.48	10.4

$\text{Ag}_{0.1}\text{-AC}$  (Fig. 10(c) and (d)) an increasing of amount of Ag content (55.97%) with increasing O content (7.22%) is observed, which becomes more homogeneous as the carbon surface is oxidized. These results seem to indicate that the functional groups of activated carbon surfaces by acid treatment are affected due to the dispersion of the Ag.

## Conclusions

The adsorption/desorption isotherms of  $\text{N}_2$  at 77 K on metallic silver-supported activated carbon samples after various acid treatments are Type I with a small amount of capillary condensation hysteresis. From the micro-positivity test, the t-plots of these samples have a c-swing indicating the presence of both ultra- and super-micropores. The pore size distributions (PSD) calculated for our materials using the density functional theory,

those also confirm our hypothesis that the source of the microporosity is the metallic silver on the activated carbon surfaces after various acid treatments. In the case of SEM results, one can clearly observe the highly developed surface structures, and homogeneous distribution of metals and grown crystal particles on the carbon surface. The IR spectra of metallic silver-supported activated carbon samples show that the acid treatment is associated with a homogeneous distribution of metal with an increased surface acidity of the activated carbons. The effect of surface acidity and basicity was also evaluated from correlations as a function of NaOH, NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> uptake. A positive influence of the acidic groups on the carbon surface by acid treatment is also demonstrated by an increase in the content of metal with an increasing amount of acidic groups calculated from Boehm titration. Finally, the results of typical EDX elemental microanalysis of metal-supported activated carbons after acid treatment show the spectra corresponding to almost all the samples are rich in silver with increasing amount of acid treatment.

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