

CHARACTERIZATION OF ACTIVATED CARBONS' PHYSICAL AND CHEMICAL PROPERTIES IN RELATION TO THEIR MERCURY ADSORPTION

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Introduction

Mercury (Hg) has been identified by the U.S. Environmental Protection Agency (EPA) as a toxic pollutant of great environmental health concern that is emitted from coal-fired power plants. Regulations governing Hg emissions from coal-fired power plants are to be issued by EPA by December 15, 2004 [1]. One potential method for controlling Hg emissions from coal-fired utility boilers is the injection of an activated carbon sorbent upstream of a particulate control device such as an electrostatic precipitator or a bag filter. The control of Hg emissions is strongly dependent on the form of Hg emitted (oxidized vs. elemental). A major portion of the Hg emitted from many coal-fired power plants is in the elemental form (Hg^0). It is known that Hg^0 is more difficult to capture than its oxidized forms from combustion flue gases, due to its higher volatility and insolubility in water [2].

Many studies have been carried out to evaluate the effectiveness of Hg^0 adsorption by activated carbons [3-7]. It has been shown that carbon sorbent type and its associated properties are the most important factors influencing Hg^0 adsorption [6]. Different activated carbons have been examined in bench-, pilot-, and full-scale tests; however, correlations between carbon physical and chemical properties and Hg^0 adsorption have not been established. The mechanism involved in Hg^0 adsorption is not well understood. A previous study [8] of Hg^0 adsorption by activated carbons performed at room temperature suggests that carbon surface moisture has a strong enhancement effect to promote Hg^0 adsorption. Results of the temperature-programmed desorption (TPD) measurement of adsorbed Hg and X-ray absorption fine structure (XAFS) spectroscopy analysis of surface Hg bonding suggest that chemisorption of Hg^0 is a dominant process over physisorption for the moisture-containing samples [8]. Hg^0 bonding on the carbon surface appears to be associated with oxygen [8]. It was also suggested that

surface oxygen complexes are most likely to provide the active sites for Hg^0 bonding. Electron transfer processes are likely to be involved during the chemisorption of Hg^0 . However, it is not clear what particular surface functional groups are participating in Hg^0 adsorption due to the lack of chemical characteristic information of the carbons tested. Characterization of the carbon oxygen surface groups in relation to the carbon's Hg^0 adsorption capacity could provide important mechanistic information on Hg^0 adsorption. The objective of this study was to characterize the physical and chemical properties of the carbons used for Hg^0 adsorption, in order to understand the role of oxygen surface functional groups on the mechanism of Hg^0 adsorption by activated carbons.

Experimental

Sample preparation

The samples tested were two commercially available, bituminous-coal-based activated carbons (WPL, BPL, Calgon Carbon Corporation, Pittsburgh, PA). The samples were washed with de-ionized (DI) water and air dried at 383 K, and designated as -AR. Acid treatments were also performed to the above two carbons in order to modify the surface chemical characteristics of the carbons. They were treated in a 6 N nitric acid (HNO_3) solution at room temperature for 5 hrs, then washed with DI water and dried at 383 K in an oven overnight, and designated as - HNO_3 . The two -AR samples were air oxidized at 693 K. The -AR sample was first heated in a quartz tube reactor under a helium (He) atmosphere to 1200 K for 2 hrs to remove the surface oxygen complexes present originally on the carbon surfaces, and cooled to 693 K under a He atmosphere. Then, an air flow (55 cm^3/min , standard temperature and pressure, STP) was introduced into the reactor for 10 hrs. The gas flow was switched back to He and cooled to room temperature. The weight loss of the sample was determined to be about 25% for both the BPL and WPL carbons during air oxidation.

Characterization of samples

BET (Brunauer-Emmett-Teller) and DR (Dubinin-Radushkevich) surface areas of the carbons were measured

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Table 1 Pore structure characterization results

Sample	S_{BET} (m ² /g)	S_{CO_2} (m ² /g)	V_t (cm ³ /g)	V_{micro} (cm ³ /g)	L (nm)
BPL-AR	1136	976	0.58	0.37	1.5
BPL-1200	1246	1013	0.62	0.38	1.5
BPL-HNO ₃	1088	929	0.57	0.35	1.4
BPL-693	1656	970	0.96	0.37	1.5
WPL-AR	1057	825	0.62	0.31	1.4
WPL-1200	1064	802	0.62	0.30	1.4
WPL-HNO ₃	931	805	0.54	0.31	1.4
WPL-693	1407	919	0.83	0.35	1.5

by nitrogen (N₂) adsorption at 77 K with P/P₀ up to 0.99, and carbon dioxide (CO₂) adsorption at 273 K with P/P₀ up to about 0.03, respectively, using a volumetric adsorption apparatus (ASAP 2400, Micromeritics). The total pore volume was evaluated from the N₂ adsorption isotherm at P/P₀ = 0.99, and the micropore volume was estimated from CO₂ adsorption at 273 K using the DR equation.

Temperature-programmed desorption (TPD) of the carbon samples was carried out by heating the sample to 1200 K under a He flow of 55 cm³/min (STP), and at a heating rate of 10 K/min. About 200 mg of sample was placed in a quartz reactor on a fine frit of 25 mm diameter. The reactor exit was connected to a quadrupole mass spectrometer (Dycor, Model M200) set up for continuous measurement of evolving gases. The responses of carbon monoxide (CO), CO₂, and water (H₂O) of the spectrometer were calibrated periodically using the weighted amounts of calcium oxalate monohydrate (CaC₂O₄·H₂O). The temperature of the carbon was measured by a thermocouple positioned into the carbon bed.

Base-acid titration of the carbons based on Boehm's method [9] was performed to measure the oxygen functionalities of the samples. About 0.8 g of carbon was placed in 50 mL of the following 0.05 N solutions: sodium bicarbonate (NaHCO₃), sodium carbonate (Na₂CO₃), sodium hydroxide (NaOH), and hydrochloric acid (HCl). The vials were sealed and shaken for 24 hrs, and then filtered. A total of 10 mL each of the filtrate was pipetted, and the excess of base and acid of the filtrate was titrated with HCl and NaOH, respectively. The specific surface oxygen functional groups were estimated by using the data measured from the base titration and the TPD experiment, based on the following assumptions: NaHCO₃ titrates carboxyl groups only; NaOH titrates carboxyl, lactone, and phenol groups; CO₂ is a decomposition product of carboxyl and lactone groups, and CO is a decomposition product of phenol and carbonyl groups [10].

Mercury adsorption

Hg⁰ adsorption experiments were performed at a temperature of 398 K under a N₂ atmosphere, and in a fixed-bed reactor surrounded by a temperature-controlled electrical furnace. The detailed experimental setup and procedures were described elsewhere [8]. Hg⁰ adsorption experiments were also performed on the heat-treated

samples (designated as -1200). The sample was heated at a constant heating rate (10 K/min) to 1200 K under a N₂ atmosphere, and then held for 2 hrs. The reactor was then cooled to the Hg⁰ adsorption temperature (398 K) under a N₂ flow, before the adsorption experiment was started. Therefore, re-oxidation due to exposure of the carbon sample to the atmosphere could be avoided. A Hg⁰ concentration of 55±2 ppb (450 µg/Nm³) in N₂ at a total flow rate of 370 mL/min (STP) was generated and used for all the Hg⁰ adsorption experiments.

Results and Discussions

Sample characterization

The characteristics of the samples' pore structures are shown in Table 1. It can be seen from the table that both BPL-AR and WPL-AR are microporous carbons. Heat treatment at 1200 K under N₂ did not significantly change their measured pore structures. A decrease in surface area and pore volume was observed for the HNO₃-treated samples, possibly as a result of the destruction of some of the thin pore walls and blocking of the pore entrances by oxygen functional groups [11]. As expected, air oxidation treatment of the carbons performed at 693 K increased the surface area and pore volume of the samples significantly, as the results of carbon burnoff lead to pore development. The base-acid titration and the TPD results are summarized in Table 2. The oxygen surface complex concentration, [O] (mmol/100g), was calculated from the measured total amounts of CO₂, CO, and H₂O thermally desorbed from the carbon surface during the TPD experiment. As shown in Table 2, significant differences in the base-acid titration values and the CO₂, and CO decomposition values between the BPL-AR and the WPL-AR samples were observed. The oxygen content of the WPL-AR (293 mmol/100g) measured by TPD is much higher than that (106 mmol/100g) of the BPL-AR sample. In general, the acidity and basicity of the carbon can be estimated approximately by its NaOH and HCl titration values, respectively. It can be seen that the amount of basicity (53 meq/100g) is about double that of the acidity (25 meq/100g) for the BPL-AR. This indicates that BPL-AR is a basic carbon as reported previously in the

Table 2 Base-acid neutralization and TPD experiment results

Sample	Base-acid neutralization				TPD			
	NaHCO ₃	Na ₂ CO ₃	NaOH	HCl	[CO ₂]	[CO]	[O]	CO/CO ₂
	(meq/100g)				(mmol/100g)			
BPL-AR	2	4	25	53	11	67	106	6.1
BPL-HNO ₃	29	50	81	17	75	262	442	3.5
BPL-693	37	67	148	32	38	397	489	10.4
WPL-AR	7	16	51	42	46	158	293	3.4
WPL-HNO ₃	13	30	80	7	77	235	413	3.1
WPL-693	42	72	176	19	60	475	609	7.9

Table 3 Surface acidic functional groups of samples

Samples	Carboxyl	Lactone	Phenol	Carbonyl
	(mmol/100g)			
BPL-AR	2	9	14	53
BPL-HNO ₃	29	46	6	256
BPL-693	37	1	110	287
WPL-AR	7	39	5	153
WPL-HNO ₃	13	64	3	232
WPL-693	42	18	116	359

literature [12]. On the other hand, the basicity of the WPL-AR is lower than its acidity.

The effects of HNO₃ treatment and air oxidation on surface chemistry are pronounced. The total oxygen concentration increased significantly after the two samples were treated with a HNO₃ solution. Similar increases in oxygen concentration were also observed after the samples were air oxidized at a temperature of 693 K. More acidic groups were formed, resulting in high NaOH titration values and low HCl titration values, for both the HNO₃-treated and the air-oxidized samples. It can be seen from Table 2 that the amount of surface acidic groups, titrated by NaOH, is almost equal to that of the CO₂ desorbed from the TPD experiment for the two HNO₃-treated samples, as well as for the WPL-AR sample. For the air-oxidized samples, it was found that high NaOH titration values and more CO-forming complexes were obtained, which results in a higher CO/CO₂ ratio as shown in Table 2. Although significant amounts of CO were measured from the TPD experiments for the HNO₃-treated samples and for the WPL-AR samples, their CO/CO₂ ratios remain low (3.1-3.5). These may be due to the CO₂-forming complexes produced through oxidation of the carbon during HNO₃ treatment remained on the surface, which decomposed to yield CO₂ later during the TPD experiment to produce a low CO/CO₂ ratio. However, some of the CO₂-forming complexes produced during air oxidation at 693 K may not be stable, resulting in a higher CO/CO₂ ratio.

Both the HNO₃ treatment and the air oxidation at 693 K were found to increase the total oxygen content of the treated samples. However, the surface functional groups formed from these two treatment processes are different, resulting in different chemical characteristics of these two

treated samples. Table 3 shows the different acidic groups estimated from the base-acid titration and from the TPD experiment. It can be seen from the table that more lactone (39 mmol/100g) and carbonyl (153 mmol/100g) groups are present in the WPL-AR sample compared to those (9 mmol/100g and 53 mmol/100g, respectively) in the BPL-AR sample. However, much more phenol groups (14 mmol/100g) are present in the BPL-AR sample than those (5 mmol/100g) in the WPL-AR. For the HNO₃-treated samples, almost all the acidic functional groups measured had increased, except for the phenol groups. On the other hand, more phenol groups and relatively less lactone groups were measured after the samples were air oxidized at 693 K, and more carboxyl groups were also found.

Mercury adsorption

Table 4 summarizes Hg⁰ adsorption capacities of the samples. It was found that the Hg⁰ adsorption capacity of the BPL-AR is very low (40 µg/g), which is in agreement with that reported in the literature for the same sample measured at the similar experimental conditions [13]. As shown in Table 4, there are no Hg⁰ uptakes of both the BPL and WPL after they were heat-treated at a temperature of 1200 K under a N₂ atmosphere. The breakthrough curve obtained matches that of the blank experiment when only sand particles and quartz wool were present in the reactor. It can be assumed that most of the oxygen surface complexes are removed after the carbons are heat treated at 1200 K under a N₂ atmosphere. The elimination of Hg⁰ adsorption capacity of these two samples after heat treatment provides further evidence that oxygen surface complexes are the most likely active sites

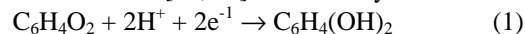
for Hg^0 capture [8]. It is noted that the surface area and pore volume of the heat-treated samples are still preserved. A comparison of the Hg^0 adsorption capacity and the characteristics of the surface functional groups between BPL-AR and WPL-AR suggests that Hg^0 adsorption capacity seems to have a strong dependence on the carbon's chemical characteristics. Both lactone and carbonyl groups appear to be the possible active sites for Hg^0 adsorption. It is well known that both lactone and carbonyl are the reducible functional groups on carbon surfaces [14]. Results obtained from this study suggest that Hg^0 adsorption on carbon surfaces seems to follow the oxidation-reduction mechanism. Upon treatment with a HNO_3 solution, Hg^0 adsorption capacity of the BPL- HNO_3 shows a sharp increase and reaches the highest value (1,520 $\mu\text{g/g}$). However, the capacity of another HNO_3 -treated sample, WPL- HNO_3 , is lower than that of its untreated counterpart (925 $\mu\text{g/g}$); but it is still maintaining a high value (700 $\mu\text{g/g}$). A 12% reduction in BET surface area was observed for the HNO_3 -treated WPL carbon. The difference in Hg^0 adsorption capacity between WPL- HNO_3 and WPL-AR may be explained by the reduction in total surface area of the WPL- HNO_3 sample.

Table 4 Mercury adsorption capacity and the phenol/carbonyl

Sample	Hg^0 ($\mu\text{g/g}$)	Phenol/carbonyl
BPL-AR	40	0.26
BPL-1200	0	n.a.
BPL- HNO_3	1520	0.02
BPL-693	40	0.38
WPL-AR	925	0.03
WPL-1200	0	n.a.
WPL- HNO_3	700	0.01
WPL-693	20	0.32

The Hg^0 adsorption capacities of the two air-oxidized samples were found to be reduced to very low values (20–40 $\mu\text{g/g}$) as a result of air oxidation. It can be seen from Table 3 that the most distinguishing feature of the surface chemical characteristics associated with the air-oxidized samples is their high phenol groups concentrations (110 – 116 mmol/100g) and their CO/CO_2 ratio shown in Table 2. These two parameters seem to correlate with the Hg^0 adsorption capacity. The samples with a low CO/CO_2 ratio and phenol group concentration tend to give a high Hg^0 adsorption capacity, indicating that phenol groups may prohibit Hg^0 oxidation reaction or they affect the equilibrium concentrations of the lactone or carbonyl groups. It has been shown that the apparent ability of the carbon surfaces to catalyze both oxidation and reduction reactions can be explained by equilibrium considerations [10]. The resonance-stabilized structures of the surface

functional groups (e.g., quinonoid complexes) could behave as an electrode [10, 15] as shown by:



The potential (E_h) of the electrode can be expressed as

$$E_h = E_0 - \frac{RT}{2F} \ln \frac{a_{[\text{C}_6\text{H}_4(\text{OH})_2]}}{a_{[\text{C}_6\text{H}_4\text{O}_2]} a_{[\text{H}^+]}^2} \quad (2)$$

where E_0 is the characteristic constant potential, and a is the activity (= concentration \times activity coefficient). As shown in Equation (2), higher hydroquinone or phenol [$\text{C}_6\text{H}_4(\text{OH})_2$] concentration could significantly reduce the potential of quinhydrone electrodes (E_h) and result in a lower potential difference (ΔE), which would be required for a given oxidation-reduction reaction system. It was found that the carbonyl groups on the carbon surface are also associated or chelated with the phenolic hydroxyl groups through hydrogen bonding [14]. It is interesting to see if reaction (1) would proceed forward during Hg^0 adsorption. The last column of Table 4 shows the ratios of phenol and carbonyl groups of the samples evaluated. It appears that a high Hg^0 adsorption capacity is associated with a low phenol/carbonyl ratio, which would give a higher potential of the quinhydrone electrode (E_h) according to Equation (2). This suggests that the mechanism of Hg^0 adsorption involves an electron transfer process, and the carbon surface possibly acts as an electrode for Hg^0 oxidation. However, the kinetics and mechanism of such reactions may be more complex, and other surface functional groups, such as lactones, could also participate in the electron transfer process [10]. Further studies to investigate carbon electrochemistry would be useful for gaining more mechanistic insights of Hg^0 adsorption.

Conclusion

The physical and chemical properties, and Hg^0 adsorption capacity of two as-received and treated activated carbons were characterized. Heat treatment of the samples, performed at a temperature of 1200 K under N_2 , did not cause significant changes in their pore structure characteristics. A decrease in surface area and pore volume was observed after the samples were treated with a HNO_3 solution. Air oxidation of the samples, performed at a temperature of 693 K, significantly increased both the surface area and the pore volume. Significant differences in chemical characteristics were found in the two as-received samples. The total oxygen content of the WPL-AR, measured by the TPD experiment, is much higher than that of the BPL-AR sample. More lactone and carbonyl groups are present in the WPL-AR sample compared to those present in the BPL-AR. Significantly more phenol groups are present in the BPL-AR sample than those present in the WPL-AR. The total oxygen concentration increased significantly

after the samples were treated with a HNO₃ solution. Air oxidation of the samples at 693 K also raised the total oxygen concentration of the samples. It was found that all the functional groups measured were higher, except for the phenol groups, as a result of HNO₃ treatment. More phenol groups and relatively less lactone groups are formed upon air oxidation at 693 K, significantly more carboxyl groups are also created.

The results of Hg⁰ adsorption of the as-received and oxidized samples suggest that Hg⁰ adsorption capacity tends to have a strong dependence on the sample's chemical characteristics. No Hg⁰ uptakes were measured for the samples after they were heat-treated at 1200 K under a N₂ gas atmosphere, although significant surface area and pore volumes of the samples are still largely preserved after the heat treatment. Such observation provides further support that oxygen surface complexes are the possible active sites for Hg⁰ capture. Both lactone and carbonyl groups are the likely active sites for Hg⁰ adsorption, and Hg⁰ adsorption seems to follow the oxidation-reduction mechanism. It was found that the CO/CO₂ ratio measured by the TPD experiment, and concentration of the phenol groups estimated from titration appear to be correlated with the sample's Hg⁰ adsorption capacity. The samples, which have a lower CO/CO₂ ratio and phenol group concentration tend to have a higher Hg⁰ adsorption capacity, indicating that phenol groups present in carbon prohibit Hg⁰ adsorption. It is also found that a high Hg⁰ adsorption capacity is associated with a low ratio of the phenol/carbonyl groups. The results of this study suggest that the mechanism of Hg⁰ adsorption involves an electron transfer process, and the carbon surface may act as an electrode for Hg⁰ oxidation.

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