

Theoretical Studies of the NO Effect on the Mercury Adsorption Capacity of a Carbonaceous Surface

Jing Liu,* Wenqi Qu, and Chuguang Zheng

State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China

Received June 21, 2010. Revised Manuscript Received July 19, 2010

This paper was withdrawn on September 20, 2010 (*Energy Fuels* 2010, 24, 5806).

A systematic theoretical study using the density functional theory is performed to provide a molecular-level understanding of the NO effect on the mercury adsorption on a carbonaceous surface. A six-fused benzene ring is examined to serve as a representative cluster species to model the carbonaceous surface. The edge atoms on the upper side of the models are unsaturated to simulate the active sites. All of the possible approaches in which NO is adsorbed on the edge sites of the carbonaceous surface are considered to examine their effects on Hg adsorption. The results indicate that NO adsorptions with side-on and N-down modes are thermally favorable, while the O-down mode is not energetically favorable for NO adsorption on the carbonaceous surface. The effects of NO on the Hg adsorption capacity of the carbonaceous surface are complicated, and they depend upon the concentration of NO in flue gas. A low concentration of NO promotes Hg adsorption on the carbonaceous surface, while higher concentrations of NO decrease the adsorption capacity of Hg because NO competes for the activate sites on the carbonaceous surface.

1. Introduction

Mercury is one of the heavy metals of greatest environmental concern because of its toxicity, ability to be transported in the environment, adverse effects on the ecosystem, and its neurological health impacts.¹ Many studies have shown that mercury released from anthropogenic sources eventually is deposited into rivers, lakes, and oceans, which is ultimately transformed by biological processes into more highly toxic organic forms of mercury that accumulates in fish and other organisms living in these waters. Human exposure of organic mercury through eating contaminated fish is also a great health concern.² Coal-fired power plants have been identified as the largest anthropogenic source of mercury emissions in the world.³ Reducing the emissions of mercury by coal-fired power plants has become a major challenging task in the near future for many countries.

Mercury in coal combustion flue gas has three different forms: particulate-bound mercury (Hg_p), elemental mercury (Hg^0), and oxidized mercury (Hg^{2+}). Most of the particulate-bound mercury can be removed using air pollution control devices (electrostatic precipitators and fabric filters). Oxidized mercury is soluble in water and, therefore, removed with high efficiency (>90%) by wet flue gas desulfurization (FGD) equipment. However, Hg^0 is highly volatile and insoluble in water. Thus, it is very difficult to reduce Hg^0 from the flue gas. Many studies have been performed to explore effective sorbents for the removal of Hg^0 from combustion flue gas. Injection of powder activated carbon (AC) upstream of particulate

control devices is one of the most popular technologies for Hg^0 control in coal-fired power plants.

Experimental studies have been previously carried out to understand the mechanism of mercury adsorption on a carbonaceous surface,^{4–9} and it has been made clear that the reaction mechanisms involved in mercury capture are very complex.¹⁰ The adsorption of Hg^0 on ACs is greatly affected by acidic species present in coal combustion flue gases.^{11–13} The flue gas composition, such as NO, could have a significant influence on the adsorption of Hg^0 on the carbonaceous surface.^{8,14–16} However, the mechanism of the NO effect on the Hg^0 adsorption on the carbonaceous surface is still not clear. Furthermore, there is even controversy on the effect of NO. Some researchers have concluded that adding NO to the baseline gases improved the mercury capture by carbonaceous sorbents. Miller et al.¹⁴ have reported that NO has a very positive effect on Hg^0 capture by AC. Upon exposure of the sorbent to NO added to the baseline gases (O_2 , N_2 , CO_2 , and

*To whom correspondence should be addressed. Telephone: 86-27-87545526. Fax: 86-27-87545526. E-mail: liujing27@mail.hust.edu.cn.

(1) Panta, Y. M.; Liu, J.; Cheney, M. A.; Joo, S. W.; Qian, S. Z. *J. Colloid Interface Sci.* **2009**, *333*, 485–490.

(2) Fitzgerald, W. F.; Engstrom, D. R.; Mason, R. P.; Nater, E. A. *Environ. Sci. Technol.* **1998**, *32*, 1–7.

(3) Yang, H. Q.; Xu, Z. H.; Fan, M. H.; Bland, A. E.; Judkins, R. R. *J. Hazard. Mater.* **2007**, *146*, 1–11.

(4) Liu, W.; Vidic, R. D.; Brown, T. *Environ. Sci. Technol.* **2000**, *34*, 154–159.

(5) Rubel, A.; Andrews, R.; Ganzalez, R.; Groppo, J.; Robl, T. *Fuel* **2005**, *84*, 911–916.

(6) Sandhya, E.; Stenger, H. G. *Energy Fuels* **2007**, *21*, 852–857.

(7) Seneviratne, H. R.; Charpentreau, C.; George, A.; Millan, M.; Dugwell, D. R.; Kandiyoti, R. *Energy Fuels* **2007**, *21*, 3249–3258.

(8) Chi, Y.; Yan, N. Q.; Qu, Z.; Qiao, S. H.; Jia, J. P. *J. Hazard. Mater.* **2009**, *166*, 776–781.

(9) Dunham, G. E.; Dewall, R. A.; Senior, C. L. *Fuel Process. Technol.* **2003**, *82*, 197–213.

(10) Hutson, N. D.; Attwood, B. C.; Scheckel, K. G. *Environ. Sci. Technol.* **2007**, *41*, 1747–1752.

(11) Olson, E. S.; Miller, S. J.; Sharma, R. K.; Dunham, S. A.; Benson, S. A. *J. Hazard. Mater.* **2000**, *74*, 61–79.

(12) Laumb, J. D.; Benson, S. A.; Olson, E. A. *Fuel Process. Technol.* **2004**, *85*, 577–585.

(13) Hower, J. C.; Senior, C. L.; Suuberg, E. M.; Hurt, R. H.; Wilcox, J. L.; Olson, E. S. *Prog. Energy Combust. Sci.* **2010**, *36*, 510–529.

(14) Miller, S. J.; Dunham, G. E.; Olson, E. S.; Brown, T. D. *Fuel Process. Technol.* **2000**, *65–66*, 343–363.

(15) Carey, T. R.; Hargrove, O. W.; Richardson, C. F.; Chang, R.; Meserole, F. B. *J. Air Waste Manage. Assoc.* **1998**, *48*, 1166–1174.

(16) Eswaran, S.; Stenger, H. G. *Energy Fuels* **2007**, *21*, 852–857.

H₂O), the mercury capture improved to 90–100%. In contrast, Carey et al.¹⁵ studied the effects of individual gas components on Hg⁰ capture by active carbon; they found that increasing NO_x alone from 0 to 100 ppm causes the Hg⁰ adsorption capacity to increase from 0 to 640 μg/g of C and then increasing NO_x from 100 to 400 ppm causes the Hg⁰ adsorption capacity to decrease from 640 to 250 μg/g of C.

Although many experimental studies have been performed to find the mechanism of NO effects on Hg⁰ adsorption on carbonaceous materials, limited success has resulted because of problems associated with experiment conditions and the mechanisms involved in the NO effect on the Hg⁰ adsorption are not well-understood. Understanding the details of the interactions between mercury and flue gas components (NO) on carbonaceous surfaces is important to the design of carbons with faster kinetics and greater capacities for mercury sorption in utility flue gas streams.¹⁷ Therefore, it is required to have knowledge of molecular-level detailed mechanisms of NO impact on the Hg adsorption on carbonaceous surfaces. Molecular orbital theory calculation has been used in the investigations of the mechanisms in both homogeneous^{18,19} and heterogeneous^{20,21} systems, which prove to be powerful tools that can solve problems beyond the ability of experiments. A theoretical understanding and prediction of the adsorption behavior and mechanism at the molecular level have thus far been limited. Such studies would help to give a better understanding of the NO effects on Hg adsorption and, thus, to improve the efficiency of the process. Progress in quantum chemical calculations has made it possible to make reliable predictions of molecular structures, relative energies, potential surfaces, vibrational properties, reactivities, reaction mechanisms, etc.

The objective of the current study is to apply the density functional theory (DFT) to study the NO effects on the Hg adsorption mechanism on the carbonaceous surface. All of the possible approaches in which NO was adsorbed on the edge sites of the carbonaceous surface were considered to examine their effects on Hg adsorption. This is performed with the purpose of finding the possible adsorption sites, the structure, and stability of the adsorbed species. To our knowledge, this is the first theoretical study involving the NO effect on the Hg adsorption by the carbonaceous surface at the molecular level.

2. Computational Methods

The DFT was extensively employed because of its balanced computational efficiency and accuracy. In our previous work,²² the use of the quantum mechanical method and basis set combinations have been validated through a comparison of theoretically determined geometries, frequencies, and reaction enthalpies involving mercury to experimental values found in the literature. The results showed that QCISD/RCEP28DVZ combination leads to the most accurate results. Also, B3PW91/RCEP28DVZ combination provides reasonably accurate results for these

systems. Because of the huge computational costs of QCISD and because the B3PW91 method of the DFT is within acceptable errors for predicting geometries compared to the larger and more expensive calculation method, B3PW91/RCEP28DVZ was used for the Hg atom. The Pople 6-31G(d) basis set was used for non-metal elements (C, N, O, and H).

The geometries of carbonaceous surface models and their corresponding NO- and Hg-adsorbed intermediates were fully optimized in their electronic ground state. This was performed by performing single-point energy calculations at the same level of theory for several electronic states. The ground state is taken as the one with the lowest energy. Furthermore, frequency calculations were performed to confirm their stability. The energies were calculated by adding the zero-point energy (ZPE) and thermal (temperature-dependent) corrections. All calculations were made at 120 °C because it is known that most of the experiments involving Hg adsorption are performed close to this temperature. Calculations were carried out using the Gaussian 03 software package in this work.²³

In addition, bond populations and net charge distribution were calculated by performing Mulliken population analysis. Mulliken population was used for charge determination and as a measure of bond strength. Although absolute values of populations have little physical meaning, their relative values can be useful. For example, positive and negative values of bond population mean that the atoms are bonded or anti-bonded, respectively. A large positive value indicates that the bond is largely covalent, whereas there is no interaction between the two atoms if the bond population is close to zero.²⁴

The adsorption energy (E_{ads}) of an adsorbate “A” on a solid surface “B” can be calculated as

$$E_{\text{ads}} = E(\text{AB}) - (E(\text{A}) + E(\text{B})) \quad (1)$$

where $E(\text{A})$ is the total energy of the adsorbate, $E(\text{B})$ is the total energy of the substrate, and $E(\text{AB})$ is the total energy of adsorbate/substrate system in the equilibrium state. Adsorption of the adsorbate is exothermic if E_{ads} is negative. A higher negative value of E_{ads} corresponds to a stronger adsorption.

3. Results and Discussion

3.1. Modeling the Carbonaceous Surface. It is very important to establish an appropriate model for studying adsorption and surface reactions involving electron transfer between a molecule and a solid surface because these interactions involve finite and infinite systems. In any surface calculation with density functional or *ab initio* methods, it was impossible to completely model the entire surface, even with robust computer codes and highly efficient supercomputers.²⁵ Cluster models are commonly used to represent the surface.

(17) Olson, E. S.; Azenkeng, A.; Laumb, J. D.; Jensen, R. R.; Benson, S. A.; Hoffmann, M. R. *Fuel Process. Technol.* **2009**, *90*, 1360–1363.

(18) Xu, M. H.; Qiao, Y.; Liu, J.; Zheng, C. G. *Powder Technol.* **2008**, *180*, 157–163.

(19) Zheng, C. G.; Liu, J.; Liu, Z. H.; Xu, M. H.; Liu, Y. H. *Fuel* **2005**, *84*, 1215–1220.

(20) Liu, J.; He, M. F.; Zheng, C. G.; Chang, M. *Proc. Combust. Inst.* **2010**, doi: 10.1016/j.proci.2010.06.023.

(21) Indrakanti, V. P.; Schobert, H. H.; Kubicki, J. D. *Energy Fuels* **2009**, *23* (10), 5247–5256.

(22) Liu, J.; Qu, W. Q.; Yuan, J. Z.; Wang, S. C.; Qiu, J. R.; Zheng, C. G. *Energy Fuels* **2010**, *24*, 117–122.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, revision B.04*; Gaussian, Inc.: Wallingford, CT, 2003.

(24) Hu, Q. K.; Wu, Q. H.; Sun, G.; Luo, X. G.; Liu, Z. Y.; Xu, B.; He, J. L.; Tian, Y. J. *Surf. Sci.* **2008**, *602*, 37–45.

(25) Neurock, M. J. *Catal.* **2003**, *216*, 73–88.

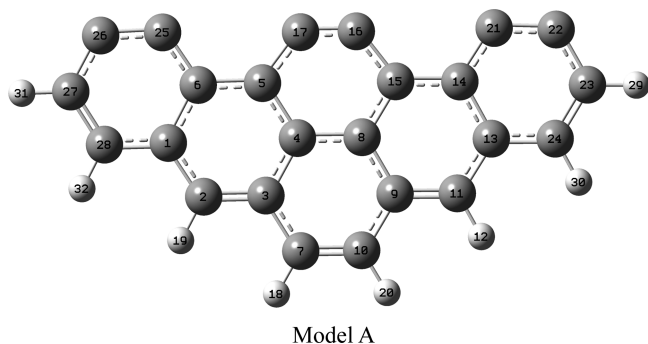


Figure 1. Cluster model of the carbonaceous surface.

Table 1. Optimized Parameters of the Carbonaceous Surface Model

average parameter	model	experiment
C–C (Å)	1.40	1.42
C–H (Å)	1.09	1.07
∠C–C–C (deg)	121	120
∠C–C–H (deg)	120	120

Carbonaceous materials, including graphite, active carbon, and char, are considered macrostructures formed mainly by aromatic clusters that are parallel graphene layers. For the theoretical model, it is assumed that the carbonaceous molecular framework is similar to that of graphite. The cluster models consisting of 4–7-fused benzene rings have been used in several studies of different applications to simulate carbonaceous surfaces.^{26–30} The previous studies showed that the reactivity of the active sites, which are the unsaturated carbon atoms at the edge of the graphene layers, mainly depends upon its local shape rather than the size of the graphene cluster.²⁶ Thus, on the basis of previous studies, we use a 6-fused benzene ring with armchair edge sites to simulate the carbonaceous surface (model A), as shown in Figure 1. The edge atoms on the upper side are unsaturated to simulate the free active sites, whereas others are terminated with hydrogen atoms. The carbon atoms are labeled to facilitate the discussion below. The optimized bond lengths and bond angles were given in Table 1. The dihedral angles are either 0° or 180°. Both bond lengths and angles of the optimized structure are in good agreement with the experimental data.³¹ The calculations used provide a reasonable balance between accuracy and computational expense.

Mulliken total atomic charges for selected atoms of model A were calculated and given in Table 2. It is clear from the data that the atoms C(16), C(17), and C(25) have a considerable excess of negative charge than other carbon atoms; thus, they are the most active sites for adsorption.

3.2. NO Adsorption on the Carbonaceous Surface. To study the NO effect on the mercury adsorption on the carbonaceous surface, the NO adsorption on the carbonaceous surface is discussed first. There are three possible approaches (N-down, O-down, and side-on modes) for the adsorption of the NO molecule, as shown in Figure 2. For N-down

(model B) and O-down (model C) modes, the NO bond axis was perpendicular to the edge line with the N and O atoms down, respectively. For side-on (model D) mode, the bond axis is parallel to the edge line of carbon on the carbonaceous surface.

Table 3 indicates the atomic bond population and bond length for NO adsorption on the carbonaceous surface. When NO is in the N-down and side-on approaches to the surface, the resultant structures were found to be in one plane; namely, all dihedral angles are either 0° or 180°. However, not all of the atoms were in the same plane in the O-down mode. The N-down approach to the C(17)–C(16) bond of the carbonaceous surface gave structure B with an adsorption energy of $-103.5 \text{ kJ mol}^{-1}$. The N–O bond length is 1.25 Å, and the atomic bond population is 0.265 (Table 3) for the N-down mode. However, in the case of the O-down mode, the N–O bond length is 2.48 Å and the atomic bond population is 0.001 (Table 3). This very small bond population suggests that the N atom has only a very small interaction with the O atom, namely, the release of a single N atom from NO during its O-down approach. As can be expected, the process that produces an unstable N atom has a positive value of adsorption energy (51.5 kJ mol^{-1}). In other words, the O-down approach to the armchair site of the carbonaceous surface is not energetically favorable. Thus, it will not be considered in the following calculations involved Hg adsorption. On the other hand, the side-on mode produced very stable species that consists of a six-membered ring (model D), whose adsorption energy is $-496.8 \text{ kJ mol}^{-1}$. The N–O bond length is 1.38 Å, and the atomic bond population is 0.112 for the side-on mode (Table 3). For all of these cases, the adsorption of NO reduced the bond strength of the most neighboring C–C bonds [C(17)–C(16), C(5)–C(17), and C(16)–C(15)]. Such bond strength reduction results in the increase of the bond length. From the above discussion, it can be concluded that NO is strongly bound to the carbonaceous surface, which is compatible with the available experimental results.³² The chemisorption of the side-on mode is stronger than that of the N-down mode.

A similar observation could be seen from the Mulliken population analysis given in Table 2. For all of the cases, NO adsorption on the carbonaceous surface yielded the electric charge transfer among atoms. For model B (N-down mode), the charge of the neighboring C(16) and C(17) changed from -0.05 to 0.087 after NO adsorption. The N atom of the gas-phase NO molecule has a positive charge (0.121) and becomes -0.077 after NO adsorption. It can be seen that the N-down mode adsorption is an electrophilic addition process. For model C (O-down mode), the charge of the N atom is nearly zero after NO adsorption and the bond population of NO is nearly zero (Table 3), which means that the N atom is almost dissociative. For model D (side-on mode), the number of electron transfer from the neighboring C(25) and C(17) to N and O atoms is the largest. The large charge transfer means that the adsorption of the side-on mode is the strongest, which is in good agreement with the above discussion involving adsorption energy.

3.3. NO Effect on Hg⁰ Adsorption on the Carbonaceous Surface. The adsorptions of Hg⁰ on the carbonaceous surface with and without NO were investigated to study the NO

(26) Montoya, A.; Truong, T. T.; Mondragón, F.; Truong, T. N. *J. Phys. Chem. A* **2001**, *105*, 6757–6764.

(27) Montoya, A.; Mondragón, F.; Truong, T. N. *J. Phys. Chem. A* **2002**, *106*, 4236–4239.

(28) Wu, X. X.; Radovic, L. R. *J. Phys. Chem. A* **2004**, *108*, 9180–9187.

(29) Radovic, L. R. *Carbon* **2005**, *43*, 907–915.

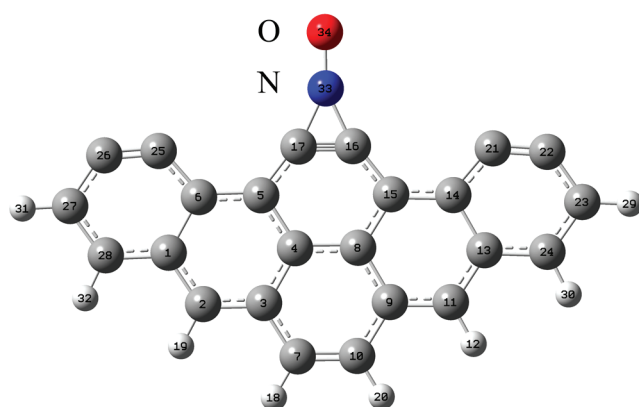
(30) Chen, N.; Yang, R. T. *J. Phys. Chem. A* **1998**, *102*, 6348–6356.

(31) Chen, N.; Yang, R. T. *Carbon* **1998**, *36*, 1061–1070.

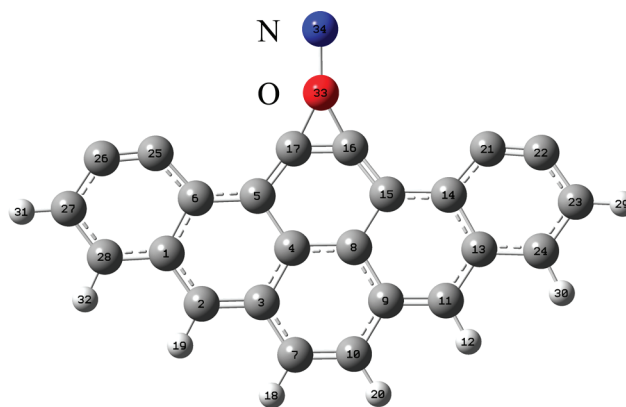
(32) Xia, B.; Phillips, J.; Menendez, J. A.; Radovic, L. R. *Extended Abstracts of 23rd Biennial Conference on Carbon*; The American Carbon Society: University Park, PA, 1997; pp 418–419.

Table 2. Mulliken Total Atomic Charges for Selected Atoms in Different Models

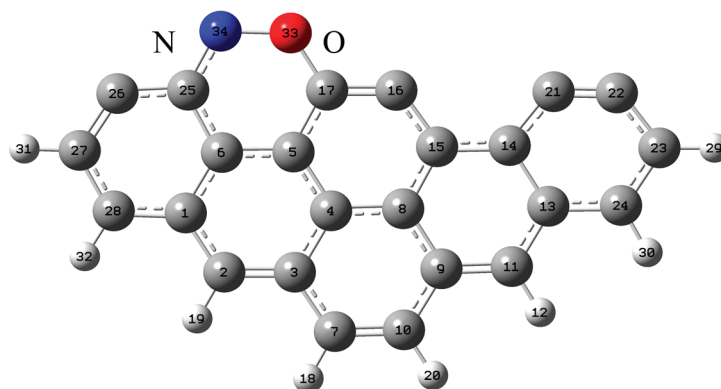
atom	model A	model B	model C	model D	model E	model F	model G
N		−0.077	−0.001	−0.139		−0.049	−0.141
O		−0.362	−0.473	−0.424		−0.381	−0.442
Hg					0.077	0.185	0.302
C(26)	−0.005	−0.001	−0.002	0.009	0.001	0.016	0.015
C(25)	−0.044	−0.049	−0.052	0.141	−0.031	−0.186	0.142
C(6)	0.009	0.047	0.027	0.037	0.007	0.047	0.029
C(5)	0.044	0.077	0.075	−0.026	0.065	0.024	0.015
C(17)	−0.050	0.087	0.155	0.352	−0.117	0.116	0.262
C(16)	−0.050	0.087	0.155	−0.089	−0.113	0.075	−0.194



Model B (N-down)



Model C (O-down)



Model D (Side-on)

Figure 2. Models for NO adsorption on the carbonaceous surface.

effect on the Hg^0 adsorption, and the optimized structures were shown in Figure 3.

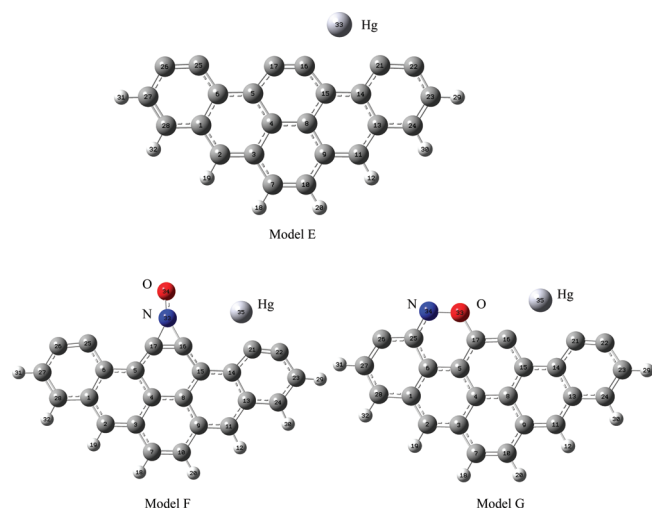
First, the adsorption energy of Hg on the carbonaceous surface (model E) was calculated to be $-64.6 \text{ kJ mol}^{-1}$, which is smaller than those of NO on the carbonaceous surface ($-103.5 \text{ kJ mol}^{-1}$ for N-down mode and $-496.8 \text{ kJ mol}^{-1}$ for side-on mode). Therefore, it can be concluded that NO adsorption on the carbonaceous surface is more stable than Hg adsorption. NO is easier to be adsorbed on the activate sites of the carbonaceous surface than Hg^0 . Then, the adsorption energies of Hg on the carbonaceous surface with NO were calculated to be $-100.1 \text{ kJ mol}^{-1}$ for model F and $-81.2 \text{ kJ mol}^{-1}$ for model G. They are bigger than the adsorption energy of Hg on the carbonaceous surface without NO ($-64.6 \text{ kJ mol}^{-1}$), which indicated that NO promotes the chemisorption of Hg^0 . Therefore, from the

viewpoint of adsorption energy, the effects of NO on the Hg adsorption capacity of the carbonaceous surface are complicated and depend upon the NO concentration in flue gas. When the NO concentration in flue gas is high, the competitive mechanism is the main effect. A higher concentration NO will restrain the Hg^0 adsorption because NO is easier to be adsorbed on the activate sites of the carbonaceous surface than Hg^0 . However, when the NO concentration in flue gas is low, the synergetic mechanism is the main effect because NO in the carbonaceous surface promotes the chemisorption of Hg^0 .

The Mulliken total atomic charges were listed in Table 2. It can be seen that NO in the carbonaceous surface increases electrons from the neighboring active carbon centers, making them more electronegative, and thus increases the propensity for Hg adsorption. In addition, the charge of the

Table 3. Bond Population and Bond Length for NO Adsorption on the Carbonaceous Surface

model	bond	bond population	length (Å)
A	C(26)–C(25)	0.452	1.38
	C(25)–C(6)	0.470	1.40
	C(6)–C(5)	0.274	1.43
	C(5)–C(17)	0.470	1.40
	C(17)–C(16)	0.670	1.24
	C(16)–C(15)	0.470	1.40
	C(15)–C(14)	0.274	1.43
	N–O	0.265	1.25
B (N-down mode)	C(16)–N	0.145	1.46
	C(17)–N	0.145	1.46
	C(5)–C(17)	0.418	1.38
	C(17)–C(16)	0.120	1.36
	C(16)–C(15)	0.418	1.38
	N–O	0.001	2.48
C (O-down mode)	C(16)–O	0.130	1.46
	C(17)–O	0.130	1.46
	C(5)–C(17)	0.410	1.38
	C(17)–C(16)	0.348	1.30
	C(16)–C(15)	0.410	1.38
	N–O	0.112	1.38
D (side-on mode)	C(25)–N	0.349	1.36
	C(17)–O	0.158	1.37
	C(26)–C(25)	0.447	1.39
	C(25)–C(6)	0.373	1.43
	C(6)–C(5)	0.290	1.41
	C(5)–C(17)	0.380	1.42
	C(17)–C(16)	0.417	1.36

**Figure 3.** Models for Hg adsorption on the carbonaceous surface with and without NO.

Hg atom increases from 0.077 to 0.185 (model F) and 0.302 (model G), which means NO in the carbonaceous surface promotes the charge transfer of Hg and promotes the Hg adsorption. Therefore, the increase in the Hg adsorption energy in the presence of NO in the carbonaceous surface is mostly due to the electronic effects.

The bond population and length of the related atoms before and after Hg adsorption on different models were given in Table 4. When the bond populations of the Hg atom were compared to the near C atoms, it becomes clear that Hg

Table 4. Bond Population and Bond Length for Hg Adsorption on the Carbonaceous Surface with and without NO

model	bond	bond population	length (Å)
E	C(16)–Hg	0.181	2.39
	C(21)–Hg	0.205	2.34
	C(26)–C(25)	0.707	1.23
	C(25)–C(6)	0.512	1.39
	C(6)–C(5)	0.204	1.42
	C(5)–C(17)	0.399	1.41
	C(17)–C(16)	0.444	1.35
	C(16)–C(15)	0.476	1.41
	N–O	0.222	1.26
	C(21)–Hg	0.210	2.27
F	C(16)–Hg	0.000	3.41
	C(17)–N	0.161	1.48
	C(16)–N	0.121	1.44
	C(22)–C(21)	0.442	1.36
	C(21)–C(14)	0.473	1.42
	C(14)–C(15)	0.304	1.43
	C(15)–C(16)	0.403	1.40
	C(16)–C(17)	0.227	1.34
	C(17)–C(5)	0.382	1.40
	N–O	0.114	1.38
G	C(16)–Hg	0.242	2.23
	C(21)–Hg	0.199	2.35
	C(25)–N	0.374	1.35
	C(17)–O	0.174	1.38
	C(26)–C(25)	0.433	1.40
	C(25)–C(6)	0.359	1.44
	C(6)–C(5)	0.274	1.40
	C(5)–C(17)	0.288	1.42
	C(17)–C(16)	0.429	1.37
	C(16)–C(15)	0.399	1.42

is interacting with the two carbon atoms C(16) and C(21) for models E and G. However, for model F, Hg is only interacting with C(21) because electrons were transferred from C(16) to the N atom and there is a positive charge in C(16). The bond populations of Hg–C in models F and G are higher than that of model E, which indicates that Hg is more strongly bound to the surface with NO.

4. Conclusions

DFT and cluster models are used to provide a molecular-level understanding of the NO effect on the mercury adsorption on the carbonaceous surface. The NO effects on the Hg adsorption on the carbonaceous surface are complicated and depend upon the NO concentration in flue gas. If the NO concentration is high, NO will compete for the activate sites on the carbonaceous surface and inhibit the Hg adsorption. If the NO concentration is low, it will promote the adsorption. These results agree well with the experimental results conducted by Carey et al.¹⁵ and also can explain the seemingly conflicting experimental results reported in the literature concerning the NO influence on the mercury adsorption on the carbonaceous surface. This work shows that the DFT is a promising means for understanding the fundamental aspects of the heterogeneous adsorption reaction.

Acknowledgment. This work was supported by the Natural Science Foundation of China (20877030 and 50936001) and 973 Program of China (2006CB705806 and 2010CB227003).