



CO₂ adsorption on carbonaceous surfaces: a combined experimental and theoretical study

Alejandro Montoya^a, Fanor Mondragón^a, Thanh N. Truong^{b,*}

^a*Institute of Chemistry, University of Antioquia, Medellin A.A 1226, Colombia*

^b*Department of Chemistry, Henry Eyring Center for Theoretical Chemistry, Rm 2020, University of Utah, 315 South 1400 East, Salt Lake City, UT 84112, USA*

Received 24 June 2001; accepted 14 July 2002

Abstract

We present an experimental and theoretical study to provide further insight into the mechanism of CO₂ chemisorption on carbonaceous surfaces. The differential heat of CO₂ adsorption at low and high coverages was determined in the temperature range 553–593 K. We found that the heat profile has two distinct energetic zones that suggest two different adsorption processes. In the low-coverage region, the heat of adsorption decreases rapidly from 75 to 24 kcal/mol, suggesting a broad spectrum of binding sites. In the high-coverage region, the heat becomes nearly independent of the loading, from 9 to 5 kcal/mol. A systematic molecular modeling study of CO₂ chemisorption on carbonaceous surfaces was performed. Several of the carbon–oxygen complexes that have been proposed in the literature were identified and characterized. The calculated adsorption energies are within the experimental uncertainty of the heat of adsorption at low coverage. Pre-adsorbed oxygen groups decrease the exothermicity of CO₂ adsorption. In the high-coverage region, our theoretical results suggest that CO₂ molecules are likely to adsorb on surface oxygen complexes and on graphene planes.

© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: A. Char; B. Gasification; C. Chemisorption, Molecular simulation; D. Surface oxygen complexes

1. Introduction

The carbon–CO₂ reaction has been used as an energy source and to partially oxidize carbonaceous surfaces to obtain microporous materials with valuable properties in the chemical industry. The identification of the surface oxygen complexes is very important since it provides insights into the detailed gasification mechanism and surface characterization of carbonaceous materials. The chemisorption reaction can be represented as follows:



where a gas-phase CO₂(g) molecule chemisorbs on an active site C_f to produce a surface carbon–oxygen complex C(CO₂). The CO₂ chemisorption is a complex reaction that is further complicated by the heterogeneity of

the carbonaceous surface. For instance, some studies have argued multiple chemisorption active sites [1] and that molecular [1,2] or dissociative modes of adsorption are possible [3,4]. There have been a number of experimental studies attempting to identify and quantify the carbon–oxygen complexes during this reaction [1,2,5–9]. This is important for deducing the mechanism for CO gas release in the subsequent step of the reaction. The stability of the surface oxygen complexes has been studied mainly from the desorption features of the CO molecule after the carbon–CO₂ reaction using either temperature-programmed desorption [5,6,10,11] or transient kinetic techniques [12–14]. These studies suggested that there are more than two surface oxygen complexes formed with different stabilities [15,16]. In fact, several complexes have been proposed so far, namely lactone [1,7,8], ether [5], pyrone [6,9], carbonyl [2,9] and semiquinone [2,9]. Other groups, such as acid anhydride [17,18] and epoxy oxygen groups [19,20], have also been proposed in the gasification with oxygen. Identifying in-situ surface oxygen complexes in the chemisorption process is difficult for several

*Corresponding author. Tel.: +1-801-581-7272; fax: +1-801-581-4353.

E-mail address: truong@chemistry.utah.edu (T.N. Truong).

reasons, namely (1) thermal transformation to different species on the char surface, (2) diffusion of gaseous agents on the micropore network and (3) re-adsorption of CO desorbed species [5,21].

Our goal in this study was to identify the carbon–oxygen complexes formed due just to the interaction of CO₂ with the carbonaceous surface. One of the properties used was the differential enthalpy of adsorption, the amount of heat released when an adsorbate adsorbs on a substrate that contains many adsorption sites. When this quantity is determined for low coverages, the value of the heat of adsorption is due only to the interaction between the adsorbate and the substrate. The heat of CO₂ adsorption has been measured by volumetric experiments below 273 K on graphite and amorphous carbon surfaces [22,23]. At this temperature the process is mainly a physical interaction between the CO₂ molecules and the carbonaceous surface. Few studies have been carried out to measure the differential enthalpy of adsorption of CO₂ on carbonaceous surfaces above its critical temperature. Complications may arise due to the possible in-situ gasification of the solid material [24]. However, it has been shown that the surface oxygen complexes formed with CO₂ at low surface coverage at 573 K are stable up to 873 K [3].

This study is divided into two main sections. First, the isosteric heat of CO₂ adsorption was measured at low and high surface coverage between 553 and 593 K. Second, as a complementary tool, a state-of-the-art quantum chemical method was used to characterize the nature of the carbon–oxygen complexes and to predict heats of adsorption. The results from these calculations were then compared with the experimental data. Several fundamental questions regarding the adsorption process were examined, in particular molecular structures and stability of the carbon–CO₂ complexes, and the effects of neighboring surface oxygen complexes on the calculated CO₂ adsorption properties.

2. Experimental

The adsorption of CO₂ was carried out on a pure carbon material in order to avoid mineral matter contamination that can affect the measured CO₂ adsorption properties. The carbonaceous material was obtained by pyrolysis of a pure phenol–formaldehyde resin under high-purity N₂ flow. Phenol–formaldehyde resin was heated to 1273 K at 10 K/min in a horizontal quartz tube and held at this temperature for 2 h. After this time, the reactor was allowed to cool to room temperature under He flow to prevent oxidation. The small amount of mineral matter on the char (0.6 wt%, daf) suggested that chemisorption takes place mainly on the aromatic network of the char, for instance on the active sites of the carbonaceous surface.

The reactivity of carbonaceous material with CO₂ was measured in a thermogravimetric balance at 0.84 atm.

About 20 mg of the sample was heated at 10.0 K/min to 1073 K and held at this temperature for 30 min in N₂ flow. The sample temperature was then lowered to the reaction temperature and N₂ was switched to CO₂. Weight changes of the char sample were analyzed as chemisorption (weight gain) or gasification (weight loss) of the material. This procedure was carried out at different temperatures to determine a suitable temperature range where CO₂ can be chemisorbed without gasification. Then, a fresh carbon sample was subjected to CO₂ adsorption at different pressures in a volumetric equipment to obtain the CO₂ adsorption profile at different CO₂ loadings. The procedure used was as follows. The carbon material was outgassed for 24 h at 573 K at a residual pressure of 5×10^{-3} mmHg N₂ to eliminate humidity and trapped gases and the weight of the sample was recorded. Then, the sample was heated to 1073 K at a pressure of 1.5×10 mmHg He to eliminate some of the oxygen complexes that could have been formed during handling of the sample after pyrolysis. The sample was cooled to the chemisorption temperature and CO₂ adsorption was recorded at different pressures. The CO₂ equilibrium pressure in the adsorption chamber was considered to be reached when the pressure change per equilibrium time interval was less than 0.01% of the average pressure during the interval. For the determination of the low-coverage heat of adsorption, 10 pressure points were recorded in the range 0.05–5 Torr. For the determination of the high-coverage heat of adsorption, 20 points were recorded in the range 10–650 Torr. The adsorbed volume was calculated assuming ideal behavior. All gases were of high purity. The experimental error was 1 K in measuring the temperature and 0.15% in pressure.

3. Computational approach

We have published several studies on computational methodologies and their applications to adsorption/desorption processes on char surfaces [25–27]. Many computational details have been discussed previously and thus they are only briefly summarized here. To calculate the geometries and CO₂ adsorption energies, carbon models and their corresponding CO₂ surface oxygen complexes were fully optimized in their ground states. To determine the correct ground state for each system, we have performed single-point energy calculations at the same level of theory for different electronic states, the ground state being selected to be the lowest energy state. Normal mode analyses were performed for selected complexes to provide some information on the IR spectra of the surface oxygen complexes and to characterize the stationary points as stable equilibrium structures or as saddle points. All calculations were performed at the B3LYP DFT level of theory, i.e. Becke's hybrid three-parameter non-local exchange functional [28–30] with Lee, Yang, and Parr's non-local correlation functional [31], using the 6-31G(d) basis set. It

is known that B3LYP produces fairly accurate bond energies and thermodynamic properties of reactions and the basis set used is adequate. An unrestricted open-shell wave function was used in all open-shell cases. In a previous study we have shown that the spin contamination in unrestricted B3LYP is reasonably small and has small effects on the energetic properties of graphene layers [25]. All calculations were performed using the GAUSSIAN 98 program [32].

4. Results

4.1. CO₂ isosteric heat of adsorption

The isosteric heat of adsorption on phenol–formaldehyde char at different CO₂ loadings was determined from the variation of the CO₂ adsorbed volume with temperature. The temperature range was obtained from reactivity measurements of CO₂ with the char surface in a thermogravimetric balance. No decrease in weight was observed when the sample was exposed to CO₂ below 673 K (with a soak time of 60 min under N₂ flow). Then, to avoid in-situ gasification not detected in the TGA, the CO₂ adsorption isotherms were obtained in the temperature range 553–593 K. The adsorption isotherms at different temperatures are shown in Fig. 1. As can be seen, the CO₂ volume adsorbed decreased when the adsorption temperature was increased. However, notice that, in the low-pressure region, there is a small difference in the adsorbed volume at different adsorption temperatures, but the adsorbed volume increases faster than in the high-pressure region. This suggests that the CO₂ molecule occupies the same number of sites and is being adsorbed on high-energy binding sites.

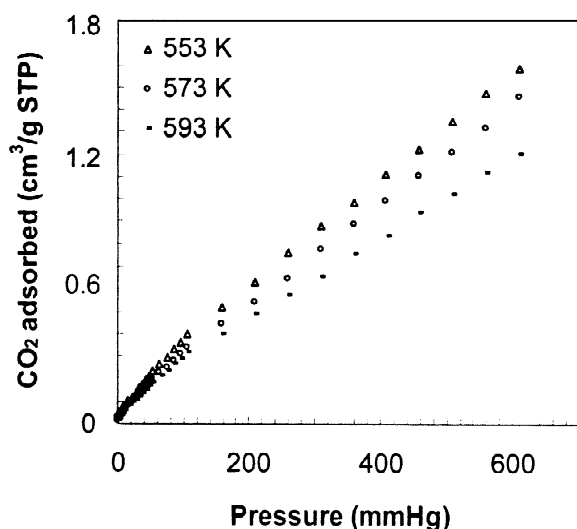


Fig. 1. CO₂ adsorption isotherms at different temperatures on phenol–formaldehyde char.

The temperature affects the volume adsorbed at a higher surface coverage where CO₂ may adsorb on the external surface. In general, two regions can be distinguished in the adsorption isotherm, one below 60 mmHg, where the CO₂ uptake increases to 0.2 cm³/g, and the second after 60 mmHg, where the CO₂ uptake increases to 1.6 cm³/g.

The differential heat of adsorption ($\Delta\bar{h}$) was obtained from the CO₂ adsorption isotherms shown in Fig. 1. The heat was obtained in terms of differences between data points in isotherms measured at different temperatures for the same value of the amount of gas adsorbed on the carbon surface using the Clausius–Clapeyron equation. A detailed procedure can be found elsewhere [33]. The ideal gas law is assumed and the adsorbed phase molar volume is not considered in this case. This assumption is reasonable since errors in the isosteric heat of adsorption due to non-ideality are noticeable only when the pressure is over 4.6 atm [34]. Furthermore, it is known that errors from neglecting the adsorbed phase volume are smaller than those from the assumption of the ideal gas law [34,35]. Since the experiments were done below 650 mmHg, we expect that these errors are not significant.

Because adsorption is spontaneous and this process is associated with a loss of entropy, the enthalpy of adsorption is exothermic, and $\Delta\bar{h}$ is negative in sign [36]. Therefore, the temperature and pressure should increase at constant loading for exothermic adsorption. In other words, the amount of gas adsorbed decreases as the adsorption temperature is increased, as seen in the CO₂ adsorption isotherms in Fig. 1. By definition, the isosteric heat is a positive number and therefore $q_{\text{isost}} = -\Delta\bar{h}$. The isosteric heat of CO₂ adsorption at different loadings on the carbonaceous surface is shown in Fig. 2. The isosteric heat decreases rapidly and then remains constant at high surface coverage. This process implies heterogeneous binding site states of the char that saturate quickly as the amount of CO₂ increases. The isosteric heat as a function of CO₂ loading can be separated into two regions. First, in the low-loading region the isosteric heat of adsorption decreases rapidly from 75 to about 24 kcal/mol. Second, in the high-loading region, above 0.03 mol/kg, the heat of adsorption remains essentially constant in the range 9–4 kcal/mol, becoming nearly independent of the loading. These values may indicate that, in the low-loading region, the CO₂ molecules chemisorb at the highest binding energy sites available to form stable carbon–oxygen species. When most of the active sites have already been covered, CO₂ molecules may adsorb either on the graphene planes or on the surface oxygen complexes. Our results are consistent with those obtained by Chen and Yang, where it was found that CO₂ adsorbs preferentially on the active edge sites, but also on the basal carbon plane of the char surface even at low temperatures [37]. These results do not provide any information on the structure of the different carbon–oxygen complexes that could be formed at different surface coverages. However, the energy

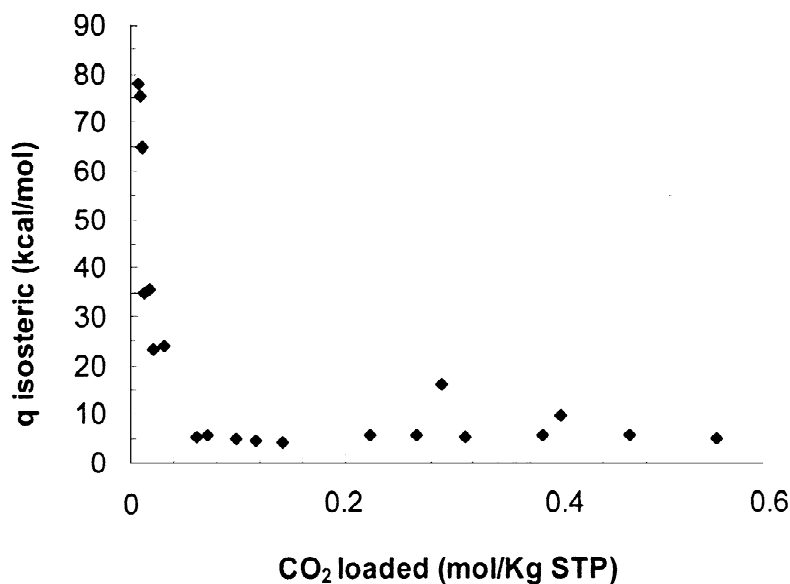


Fig. 2. Isosteric heat of CO₂ adsorption on phenol–formaldehyde char at different CO₂ loadings in the range 553–593 K.

profile can be a reference point for comparisons with the predicted heats of formation of different possible carbon–oxygen complexes from our quantum molecular modeling described below.

4.2. Molecular modeling

Since the reaction of CO₂ with char usually takes place at high temperatures, CO₂ can be vibrationally excited, particularly in the low-frequency bending modes. This suggests four possible CO₂ adsorption configurations, as shown in Fig. 3. Different molecular models (also shown in Fig. 3) of the char in zig-zag, armchair and tip shapes were used. In these models, several carbon atoms at the edge are left unsaturated to simulate the active sites. Such models have been used in our previous study [38], and those of Chen and Yang [39], and Kyotani and Tomita [40]. Radovic et al. [41] suggested a broad distribution of carbon active sites with different heats of chemisorption as entities for char oxidation. Although char has a much more complex structure, where graphene layers of various sizes have random orientations and translations, our previous study [38] has shown that the models considered here give appropriate representations of different local environments of an active site.

4.3. CO₂ surface oxygen complexes

We found that adsorption of CO₂ on a clean surface can produce four different surface oxygen complexes, namely lactone, carbonyl-type, furan, and heterocyclic oxygen groups, as shown in Fig. 4. Selected optimized geometrical parameters are shown in the same figure. Horizontal adsorption can form either the lactone or heterocyclic

oxygen groups. Vertical adsorption can form a carbonyl-type oxygen group in the zig-zag and tip models. In the armchair model, it can form a furan group and a gas-phase CO molecule. The chemical nature of each surface oxygen complex was analyzed by a normal mode analysis. The carbonyl-type and the heterocyclic in the armchair model were found to have at least one imaginary frequency and thus do not correspond to local equilibrium structures and will not be discussed further.

4.4. Size convergence

The stable oxygen complexes were optimized at different molecular sizes. Char models in zig-zag, armchair and tip shapes were used and are indicated by ‘z’, ‘a’ and ‘t’, respectively, followed by the number of six-membered rings. The size convergence analysis was performed on the heat of adsorption. The adsorption energies were obtained as the difference between the total energy of the optimized surface oxygen complexes and those of the reagents. The standard heat of adsorption was calculated by adding corrections for the zero-point energy and thermal energy at 298 K to the adsorption energy. These corrections for lactone and heterocyclic oxygen groups in the seven six-membered ring zig-zag carbon models are 6.90 and 4.57 kcal/mol, respectively. These two oxygen complexes have the same number of atoms, but different oxygen groups. As discussed below, we found that the zero-point and thermal energy corrections depend strongly on the type of surface complex rather than on the size of the molecular model. Therefore, we used the results from the z7, a5, and t4 models as estimates for the corrections in the other models with different sizes.

Fig. 5 shows the heats of adsorption of different CO₂

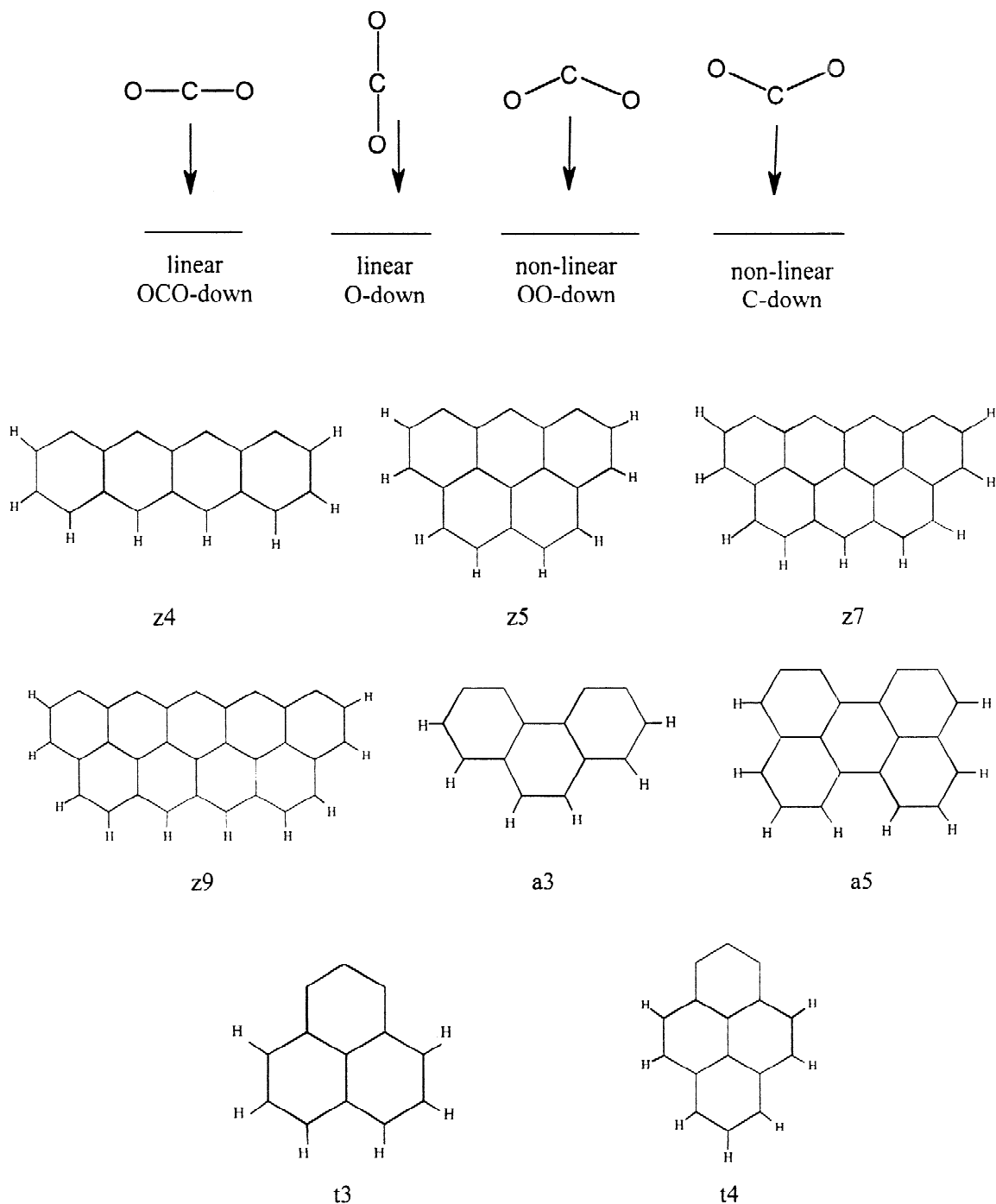


Fig. 3. Illustration of four different CO₂ adsorption orientations on different carbon models of char. z, zig-zag shape; a, armchair shape, t, tip shape. Numbers after the letters represent the number of six-membered rings.

oxygen complexes on different model sizes and different local environments of the active sites. It was found that adsorption of CO₂ is an exothermic process in all cases. The adsorption energy depends strongly on the type of the local active site rather than on the size of the molecular

model. The heats of adsorption remain nearly constant as the model size increases. However, the adsorption energies are distinctively different for formation of the same complex on different types of active sites. For instance, the average CO₂ adsorption energies to form the lactone group

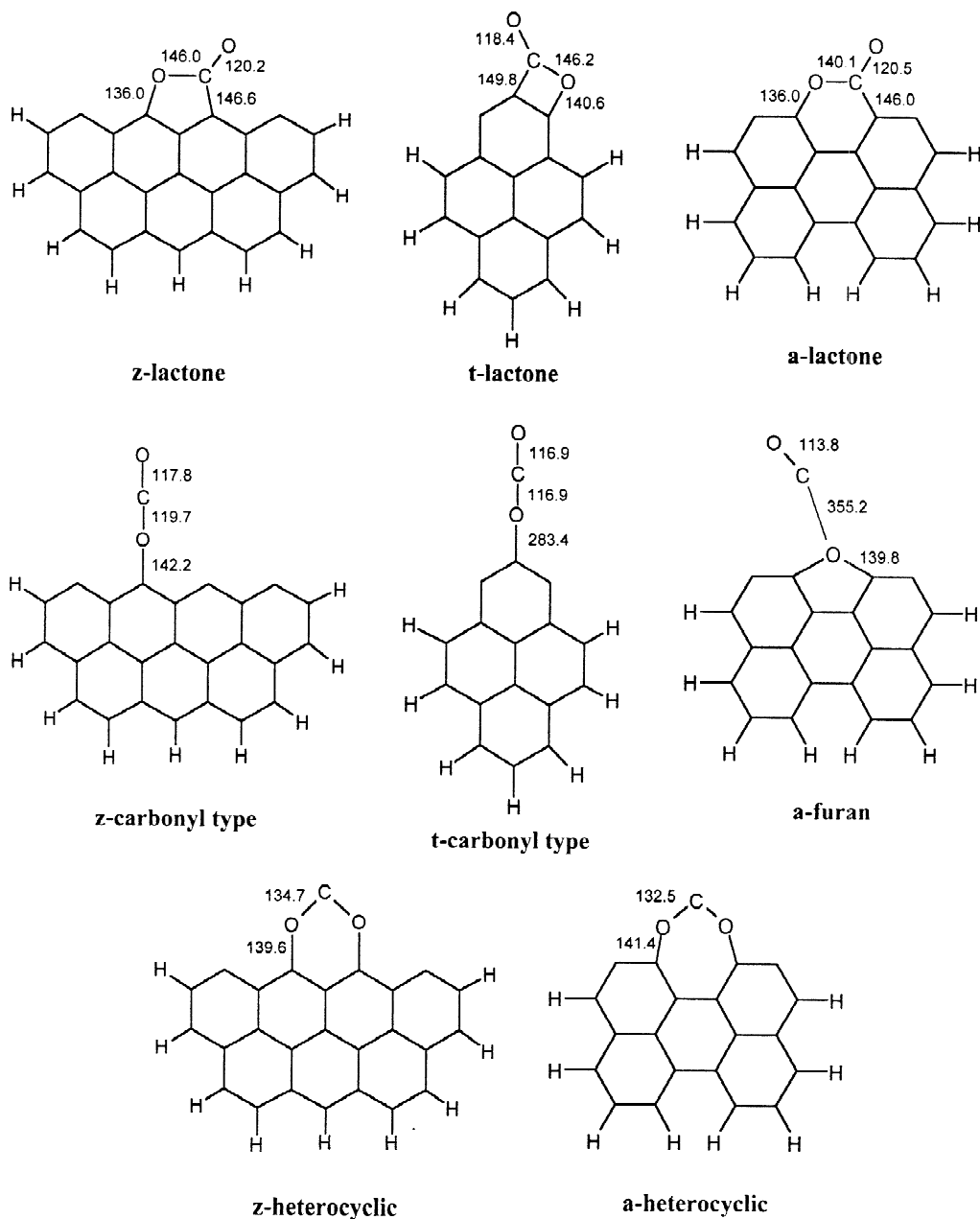


Fig. 4. Structures of different surface oxygen complexes formed after CO_2 adsorption. Numbers are selected optimized bond lengths in pm.

are -85 , -47 and -24 kcal/mol for the zig-zag, armchair and tip active site, respectively.

5. Discussion

5.1. Heats of adsorption

The heat of CO_2 adsorption on the char models depends strongly on the chemical nature of the active sites rather

than on the size of the aromatic cluster. Formation of the lactone carbon–oxygen group is the most exothermic reaction, followed by heterocyclic and furan oxygen groups. However, a special consideration should be given to the formation of the furan carbon–oxygen complex. The formation of this complex takes place in two stages: first, chemisorption of CO_2 , and then desorption of CO , although adsorption is a concerted process, i.e. adsorption of CO_2 to form the furan complex and gas-phase CO , which shows a monotonic decrease in energy from the reactants

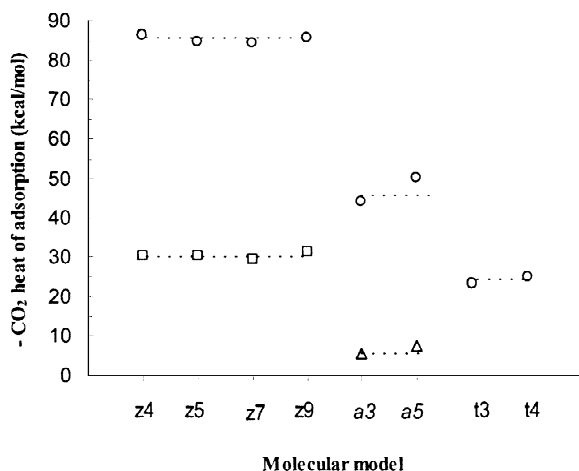


Fig. 5. Heat of adsorption of a single CO₂ molecule on a clean carbon surface. (○) Lactone oxygen group. (□) Heterocyclic oxygen group. (△) Furan oxygen group. z, zig-zag models; a, armchair models; t, tip models.

to the products. It is possible that the CO molecule released upon the formation of the furan group can be re-adsorbed on a new active site. For instance, if such re-adsorption forms a carbonyl surface complex, the adsorption energy would be lowered by -31 – 49 kcal/mol [38] and the total heat of adsorption makes the chemisorption of CO₂ along this pathway favorable. In narrow micropores, formation of lactone and ether groups is thought to be difficult due to the size of the oxygen groups. The formation of the furan or ether group would then be thermodynamically and sterically more favorable at very low surface coverage in narrow pores.

Both experimental and modeling results of CO₂ adsorption on carbon surfaces indicate that this is an exothermic process. The predicted theoretical heats of CO₂ adsorption are from -6 to -85 kcal/mol. The predicted upper limit is about 10 kcal/mol higher than the experimental heat of adsorption at low surface coverage. Note that the basis set superposition error (BSSE) [42] is

not included in the predicted heats of adsorption. For instance, the BSSE for the z-lactone model in Fig. 4 raises the adsorption energy by 4.88 kcal/mol; thus it brings theoretical data in better agreement with experimental results. Since experimental heats of adsorption can also be influenced by neighboring graphene layers, in-situ gasification, mass transport or by the small amount of mineral impurities, the observed discrepancies may be within the experimental uncertainty.

So far we have discussed calculated results for adsorption of a single CO₂ molecule. These should be compared with the experimental heats of adsorption obtained at very low surface coverage. The isosteric energy obtained experimentally decreases rapidly with increasing surface coverage in the first chemisorption zone. This suggests that high-energy binding sites are saturated with CO₂ and that pre-adsorbed oxygen groups can affect the CO₂ adsorption energy.

5.2. Influence of surface coverage

To study the effects of surface coverage on CO₂ chemisorption, three different models were adopted. In the first model, two CO₂ molecules adsorb on nearby active sites, as shown in Fig. 6. Two stable oxygen groups were used, namely lactone and the heterocyclic oxygen groups. In the second model, a single CO₂ molecule adsorbs on an oxidized carbon surface, i.e. CO₂ adsorbs on the free active sites in the presence of pre-adsorbed oxygen atoms, as shown in Fig. 7. A char model with one and two oxygen atoms was selected in order to represent increasing surface coverage. Our goal here is to provide a qualitative understanding of such effects; thus, the dependence on the location of the pre-adsorbed group is not needed. In the third model, a single CO₂ molecule adsorbs on an oxidized carbon surface to form a carbonate surface oxygen complex, as shown in Fig. 8. In this case, the CO₂ molecule interacts with the semiquinone group and with the two neighboring active sites. These models were fully optimized in the ground state and the adsorption energies of a single CO₂ molecule were calculated.

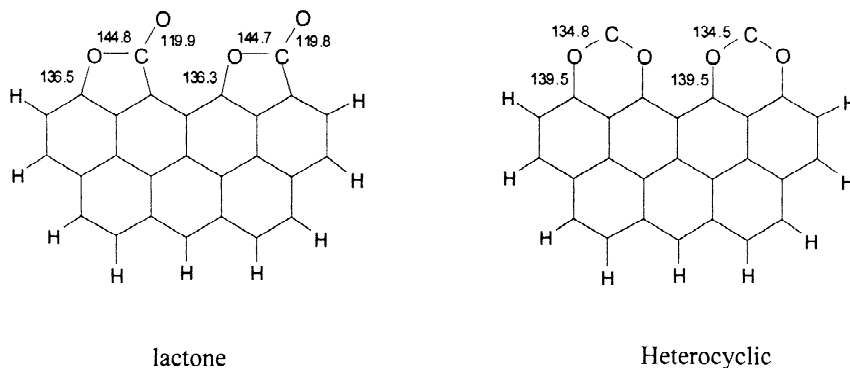


Fig. 6. Model for coverage dependence study of CO₂ adsorption. Numbers are selected optimized bond lengths in pm.

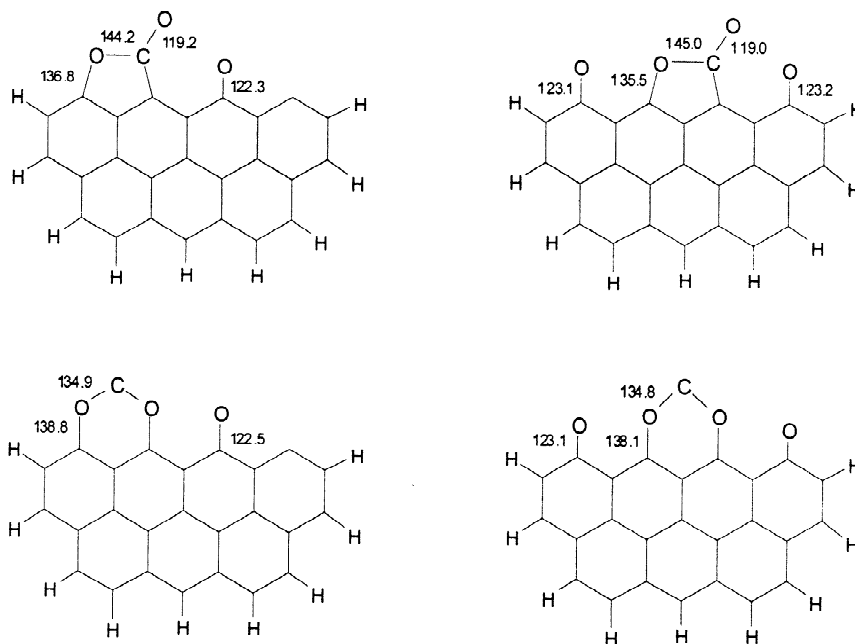


Fig. 7. Models of adsorption of a single CO_2 molecule on carbon models with pre-adsorbed oxygen groups. Numbers are selected optimized bond lengths in pm.

Table 1 shows the relevant heats of adsorption. The second column shows the heat of adsorption of a single CO_2 molecule on a clean carbon surface for comparison. The third column shows the heat of adsorption of a CO_2 molecule in the presence of another CO_2 molecule. The fourth and fifth columns show the heat of adsorption in the presence of one and two semiquinone groups, respectively. The last column shows the heat of adsorption of a CO_2 molecule to form a carbonate surface complex. In all cases, chemisorption of CO_2 is an exothermic process. However, the exothermicity of the chemisorption is reduced by 3–8 kcal/mol due to pre-adsorbed oxygen atoms. Therefore, the amount of CO_2 adsorbed on the char surface should

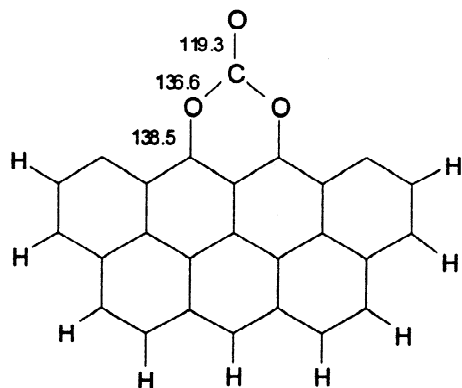


Fig. 8. Structure of the carbonate surface complex formed by adsorption of CO_2 on a semiquinone surface oxygen complex. Numbers are selected optimized bond lengths in pm.

decrease with the surface coverage, as observed by Skokova and Radovic for the $\text{C}-\text{O}_2$ reaction [43,44]. The carbonate oxygen complex is formed with an exothermicity of -27.2 kcal/mol. Furthermore, a normal mode analysis of this complex shows that it is a stable species. To our knowledge, this surface oxygen complex has not been proposed as an intermediate in the uncatalyzed CO_2 gasification reaction.

The above results show that the exothermicity of chemisorption decreases with the surface coverage due to the presence of chemisorbed oxygen groups and due to the formation of new oxygen complexes on the char surface, as was observed experimentally. Notice that the lowest heat of adsorption in Table 1 is -26.5 kcal/mol, which corresponds to the first zone of the experimental isosteric energy profile in Fig. 3. Although no theoretical CO_2 adsorption energy was obtained at a higher O/C ratio in the char model, a different adsorption process should influence the second zone of the isosteric heat. For instance, once the most active sites are covered, CO_2 molecules may adsorb on the graphene planes or on carbon–oxygen complexes to form a second layer.

Simulation of adsorption of a CO_2 molecule on the basal plane of an oxygen-free carbon structure was performed using a finite graphene $\text{C}_{22}\text{H}_{12}$ model. It contains seven six-membered carbon rings where all edge carbon atoms are capped with hydrogen atoms. Three different configurations were assumed, as shown in Fig. 9. In calculations of CO_2 adsorption energies, the graphite model was fully optimized, first at the B3LYP/6-31G(d) level, then held fixed while optimizing the CO_2 /graphene distance. The

Table 1
Predicted heats of adsorption (kcal/mol) of the CO₂ molecule on carbonaceous surfaces

| | Single CO ₂ molecule (reference) | Next to a CO ₂ molecule | Next to a semiquinone group | Between two semiquinone groups | New group |
|--------------|--|--|-----------------------------------|--------------------------------------|--------------|
| Lactone | −85.0 | −82.9 | −77.7 | −77.2 | −27.2* |
| Heterocyclic | −30.0 | −28.1 | −29.9 | −26.5 | |

* Carbonate.

approximated potential curves were also calculated by scanning the CO₂/graphene distance from 20 to 80 pm in intervals of 1 pm. The distance between the planar graphene and the CO₂ molecule is defined by the perpendicular line dropped from the carbon atom of the CO₂ molecule to the graphene plane.

Fig. 9 also shows the potential energy curves in the three cases. It was found that at the B3LYP functional that adsorption over the C–C bond is the most attractive, although the potential energy differences in comparison with the other configurations are small. We found that CO₂ adsorption on the basal plane is rather weak and has an adsorption energy of less than 1 kcal/mol. Since adsorption of CO₂ on a graphene sheet is governed mainly by dispersion interactions, which are not accounted for in the DFT theory, we also recalculated the adsorption energy by single-point MP2 calculations for the most favorable adsorption configuration. The adsorption energy curve is also shown in Fig. 9. The adsorption energy is about −4 kcal/mol.

Another possibility is that, at high coverage, CO₂ can adsorb on the surface oxygen complexes themselves, as illustrated in Fig. 10. In this example, CO₂ adsorbs on the heterocyclic oxygen groups in a zig-zag carbon model. Because our goal here is to provide a qualitative understanding of such effects, only the adsorbed CO₂ molecule was optimized. Selected optimized parameters are also

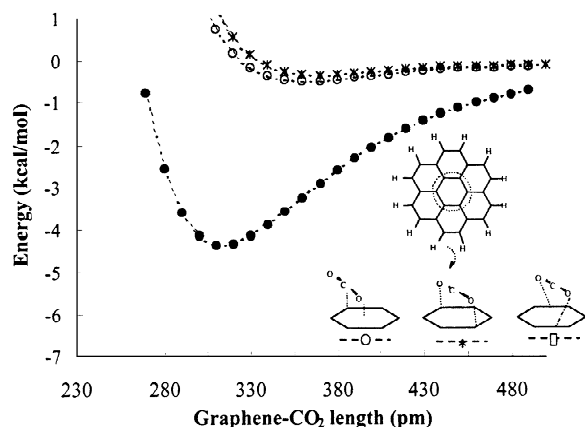


Fig. 9. Potential energy curves for the adsorption of a CO₂ molecule on the basal plane of a graphite carbon model at different relative orientations. (○) B3LYP/6-31G(d), (●) MP2/6-31G(d)//B3LYP/6-31G(d).

shown in the figure. It was found that the CO₂ bond axis is perpendicular to the carbon plane and the adsorption of CO₂ does not change the bonding characteristics of the heterocyclic surface complexes. It was found that adsorption ‘in the second layer’ is also favorable with a calculated adsorption energy of about −7.5 kcal/mol at the MP2/6-31G(d)//B3LYP/6-31G(d) level of theory. Our results suggest that the weak adsorption region is mostly influenced by CO₂ adsorption on the basal plane and on the surface complexes.

5.3. IR spectra of carbon–oxygen complexes

From our quantum chemistry study, we found four stable surface oxygen complexes, i.e. lactone, heterocyclic, furan and carbonate. Table 2 shows the frequencies and the intensity values of the most important vibration modes of the oxygen groups. A scale factor of 0.9614 was used to convert the predicted harmonic vibrational frequencies (ω) to the fundamental frequencies (ν) observed experimentally [45]. As can be seen, lactone and carbonate oxygen groups have the most intense frequency values which correspond to the C=O stretching mode. They are centered at 1770 and 1839 cm^{−1}, respectively. Heterocyclic and furan groups have the most intense frequency values

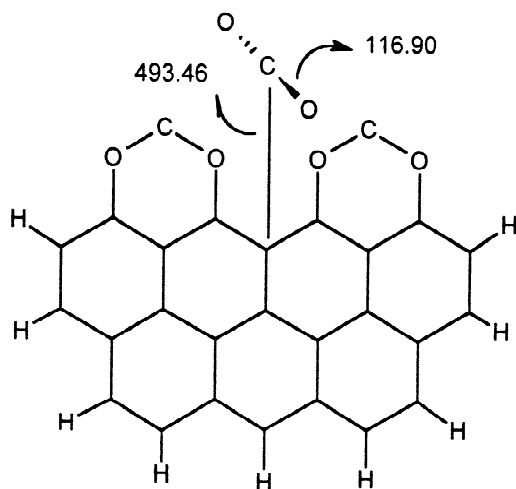


Fig. 10. A model of the adsorption of a CO₂ molecule on surface oxygen complexes. Numbers are selected optimized bond lengths in pm.

Table 2

Predicted infrared vibrational frequencies (cm^{-1}) and their intensities for different surface oxygen models

| | z7-lactone | z7-di-ether | a5-furan | z7-carbonate |
|----------------|------------|-------------|----------|--------------|
| C–O Stretching | 1170/4 | 994.8/47 | 938/34 | 949/4 |
| | 1180/2 | 1132/100 | 974/19 | 1070/7 |
| | 1328/6 | 1157/87 | 1155/39 | |
| | 1364/8 | 1321/44 | 1175/18 | |
| C=O Stretching | 1772/100 | | | 1839/100 |

corresponding to the C–O stretching mode. They are in the range 900–1300 cm^{-1} . Furan and heterocyclic oxygen groups show frequency values that correspond to the frequency assignment of ether oxygen groups in char surfaces [46,47]. Although a carbonate intermediate has not been proposed previously, its frequencies overlap with those proposed for the acid anhydride oxygen group [18]. All frequencies of the four oxygen groups can be assigned to those found experimentally.

6. Conclusions

We have carried out combined experimental and theoretical studies to provide insights into the mechanism of CO_2 chemisorption on carbonaceous surfaces. The heat of CO_2 adsorption was obtained in the range 553–593 K using volumetric experiments. The heat of adsorption was related to the isosteric heat of adsorption obtained from variation of the volume adsorbed at different pressures with temperature. We confirmed that adsorption is an exothermic process. At low coverage the heat of adsorption decreases and then remains constant at high coverage. There exist two distinct adsorption energy regions, which suggests two different adsorption processes. In the first region, at low surface coverage, the adsorption energy decreases rapidly due to the broad distribution of binding site states. In the second region, at high surface coverage, the adsorption energy remains nearly constant, in the range 9–5 kcal/mol.

From our quantum chemistry calculations, at low surface coverage we found that CO_2 forms stable surface oxygen complexes with the active sites of the char. Three stable carbon–oxygen complexes are formed due to the interaction of CO_2 with a clean carbon model, i.e. lactone, heterocyclic and furan-type complexes. Furan complex formation implies dissociative CO_2 chemisorption. As the surface coverage increases, the CO_2 adsorption energy decreases by virtue of the presence of surface oxygen atoms and by the formation of new surface oxygen complexes such as carbonate. In the high-coverage region, our theoretical result shows a low adsorption energy, suggesting that CO_2 molecules chemisorb on the surface oxygen complexes and on the graphene planes. Our calculated results for heats of adsorption are consistent with experimental values.

Acknowledgements

F.M. and A.M. wish to thank Colciencias and the University of Antioquia for financial support of this project (No. 1115-05-10853). T.N.T. acknowledges financial support from NSF. A.M. wishes to thank the seed grant given by the University of Utah. We also thank the Utah Center for High Performance Computing for computer support. The authors are grateful for the comments of Dr. Ljubisa Radovic.

References

- [1] Koenig PC, Squires RG, Laurendeau NM. Evidence for two-site model of char gasification by carbon dioxide. *Carbon* 1985;23(5):531–6.
- [2] Marchon B, Tysoe WT, Carrazza J, Heinemann H, Somorjai GA. Reactive and kinetic properties of carbon monoxide and carbon dioxide on a graphite surface. *J Phys Chem* 1988;92(20):5744–9.
- [3] Kelemen SR, Freund H. A comparison of dioxygen and carbon dioxide oxidation of glassy carbon surfaces. *Carbon* 1985;23(6):723–9.
- [4] Bonner F, Turkevich J. Study of the carbon dioxide–carbon reaction using C as a tracer. *J Am Chem Soc* 1951;73:561–4.
- [5] Calo JM, Hall PJ. Applications of energetic distributions of oxygen surface complexes to carbon and char reactivity and characterization. In: *Fundamental issues in control of carbon gasification reactivity*, NATO ASI series E, vol. 192, Dordrecht: Kluwer Academic, 1991, pp. 329–68.
- [6] Fritz OW, Huettinger KJ. Active sites and intrinsic rates of carbon–gas reactions—a definite confirmation with the carbon–carbon dioxide reaction. *Carbon* 1993;31(6):923–30.
- [7] Barton SS, Harrison BH. Acidic surface oxide structures on carbon and graphite. *Carbon* 1975;13(4):283–8.
- [8] Marchon B, Carrazza J, Heinemann H, Somorjai GA. TPD and XPS studies of oxygen, carbon dioxide, and water adsorption on clean polycrystalline graphite. *Carbon* 1988;26(4):507–14.
- [9] Moulijn JA, Kapteijn F. Towards a unified theory of reactions of carbon with oxygen-containing molecules. *Carbon* 1995;33(8):1155–65.
- [10] Huettinger KJ, Fritz OW. The carbon–carbon dioxide reaction: an extended treatment of the active-site concept. *Carbon* 1991;29(8):1113–8.
- [11] Zhang ZG, Kyotani T, Tomita A. TPD study on coal chars chemisorbed with oxygen-containing gases. *Energy Fuels* 1988;2(5):679–84.

- [12] Radovic LR, Jiang H, Lizzio AA. A transient kinetics study of char gasification in carbon dioxide and oxygen. *Energy Fuels* 1991;5(1):68–74.
- [13] Kapteijn F, Meijer R, Moulijn JA, Cazorla-Amoros D. On why do different carbons show different gasification rates: a transient isotopic CO₂ gasification study. *Carbon* 1994;32(7):1223–31.
- [14] Kapteijn F, Meijer R, Moulijn JA. Transient kinetic techniques for detailed insight in gas–solid reactions. *Energy Fuels* 1992;6(4):494–7.
- [15] Huettinger KJ. Active sites and carbon gasification kinetics: theoretical treatment and experimental results. In: *Fundamental issues in control of carbon gasification reactivity*, NATO ASI series E, vol. 192, Dordrecht: Kluwer Academic, 1991, pp. 163–73.
- [16] Kapteijn F, Meijer R, Eck BV, Moulijn JA. Active sites in carbon gasification with CO₂ transient kinetic experiments. In: *Fundamental issues in control of carbon gasification reactivity*, NATO ASI series E, vol. 192, Dordrecht: Kluwer Academic, 1991, pp. 221–33.
- [17] Starsinic M, Taylor RL, Walker Jr. PL, Painter PC. FTIR studies of saran chars. *Carbon* 1983;21(1):69–74.
- [18] Zhuang QL, Kyotani T, Tomita A. DRIFT and TK/TPD analyses of surface oxygen complexes formed during carbon gasification. *Energy Fuels* 1994;8(3):714–8.
- [19] Pan Z, Yang RT. Strongly bonded oxygen in graphite: detection by high-temperature TPD and characterization. *Ind Eng Chem Res* 1992;31(12):2675–80.
- [20] Dubsy J, Beran S. Quantum chemical study of oxygen adsorption on graphite. II. Molecular orbital study of dissociation of molecular oxygen on graphite. *Surf Sci* 1979;79(1):53–62.
- [21] Huettinger KJ. Transport and other effects in coal gasification. In: *New trends in coal science*, NATO ASI series C, vol. 244, Dordrecht: Kluwer Academic, 1988, pp. 453–80.
- [22] de Torre LEC, Flores ES, Llanos JL, Bottani EJ. Gas–solid potentials for N₂, O₂, and CO₂ adsorbed on graphite, amorphous carbons, Al₂O₃, and TiO₂. *Langmuir* 1995;11(12):4742–7.
- [23] Bottani EJ, Bakaev V, Steele W. A simulation/experimental study of the thermodynamic properties of carbon dioxide on graphite. *Chem Eng Sci* 1994;49(17):2931–9.
- [24] Lussow RO, Vastola FJ, Walker Jr. PL. Kinetics of oxygen interaction with graphon between 450 and 675 °C. *Carbon (Oxford)* 1967;5(6):591–602.
- [25] Montoya A, Truong TN, Sarofim AF. Spin contamination in Hartree–Fock and density functional theory wavefunctions in modeling of adsorption on graphite. *J Phys Chem A* 2000;104(26):6108–10.
- [26] Montoya A, Mondragón F, Truong TN. Adsorption on carbonaceous surfaces: cost-effective computational strategies for quantum chemistry studies of aromatic systems. *Carbon* 2002;40(11):1863–72.
- [27] Montoya A, Truong TN, Sarofim AF. Application of density functional theory to the study of the reaction of NO with char-bound nitrogen during combustion. *J Phys Chem A* 2000;104(36):8410–8.
- [28] Becke AD. Density-functional thermochemistry. II. The effect of the Perdew–Wang generalized-gradient correlation correction. *J Chem Phys* 1992;97(12):9173–7.
- [29] Becke AD. Density-functional thermochemistry. I. The effect of the exchange-only gradient correction. *J Chem Phys* 1992;96(3):2155–60.
- [30] Becke AD. Density-functional thermochemistry. III. The role of exact exchange. *J Chem Phys* 1993;98(7):5648–52.
- [31] Lee C, Yang W, Parr RG. Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B: Condens Matter* 1988;37(2):785–9.
- [32] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR et al. *Gaussian 98*, Rev. A.9. Pittsburgh, PA; 1998.
- [33] Webb PA, Orr C, editors, *Analytical methods in fine particle technology*, Norcross: Micromeritics Instrumental, 1997, pp. 253–6.
- [34] Pan H, Ritter JA, Balbuena PB. Examination of the approximations used in determining the isosteric heat of adsorption from the Clausius–Clapeyron equation. *Langmuir* 1998;14(21):6323–7.
- [35] Al-Muhtaseb SA, Ritter JA. Roles of surface heterogeneity and lateral interactions on the isosteric heat of adsorption and adsorbed phase heat capacity. *J Phys Chem B* 1999;103(13):2467–79.
- [36] Myers AL. Thermodynamics of adsorption in porous materials. *AIChE J* 2002;48(1):145–60.
- [37] Chen SG, Yang RT. Titration for basal plane versus edge plane surface on graphitic carbons by adsorption. *Langmuir* 1993;9(11):3259–63.
- [38] Montoya A, Truong T-TT, Mondragon F, Truong TN. CO desorption from oxygen species on carbonaceous surface: 1. Effects of the local structure of the active site and the surface coverage. *J Phys Chem A* 2001;105(27):6757–64.
- [39] Chen N, Yang RT. Ab initio molecular orbital calculation on graphite: selection of molecular system and model chemistry. *Carbon* 1998;36(7/8):1061–70.
- [40] Kyotani T, Tomita A. Analysis of the reaction of carbon with NO/N₂O using ab initio molecular orbital theory. *J Phys Chem B* 1999;103(17):3434–41.
- [41] Radovic LR, Walker Jr. PL, Jenkins RG. Importance of carbon active sites in the gasification of coal chars. *Fuel* 1983;62(7):849–56.
- [42] van Duijneveldt FB, van Duijneveldt-van de Rijdt JGCM, van Lenthe JH. State of the art in counterpoise theory. *Chem Rev (Washington, DC)* 1994;94(7):1873–85.
- [43] Skokova K, Radovic LR. Role of carbon–oxygen complexes in the CO/CO₂ ratio during carbon oxidation. In: *Extended Abstracts, 23rd Biennial Conference on Carbon*, State College, PA, American Carbon Society, 1997, pp. 414–5.
- [44] Skokova K, Radovic LR. On the role of carbon–oxygen surface complexes in the carbon/oxygen reaction mechanism. *Am Chem Soc, Div Fuel Chem* 1996;41(1):143–7.
- [45] Scott AP, Radom L. Harmonic vibrational frequencies: an evaluation of Hartree–Fock, Moeller–Plesset, quadratic configuration interaction, density functional theory, and semiempirical scale factors. *J Phys Chem* 1996;100(41):16502–13.
- [46] Meldrum BJ, Rochester CH. Infrared spectra of carbonaceous chars under carbonization and oxidation conditions. *Fuel* 1991;70(1):57–63.
- [47] Fanning PE, Vannice MA. A DRIFT study of the formation of surface groups on carbon by oxidation. *Carbon* 1993;31(5):721–30.