COMPUTATIONAL STRATEGY FOR STUDYING CHEMICAL PROCESSES ON CARBONACEOUS SURFACES

Thanh N. Truong, * *Alejandro Montoya,*‡ *and Fanor Mondragón,*‡

‡Department of Chemistry, University of Antioquia, Medellin, Colombia, A.A 1226
*Henry Eyring Center for Theoretical Chemistry, Department of Chemistry, University of Utah, 315 South 1400 East, rm 2020, Salt Lake City, Utah 84112

Introduction

Char materials existed in coal gasification and combustion are known to have a macrostructure consisting of aromatic units of different sizes from 3 to 14 six-carbon rings.[1] The aromatic units are bonded together to form a three-dimensional network with random orientations. The number of rings per aromatic unit and the average height of the crystallites depend on the pyrolysis temperature and the nature of the raw material. Chemical processes taken places on char surfaces are known to occur at the active sites, which are the unsaturated carbon atom sites as shown in Figure 1. In order to obtain accurate structural, energetic and spectroscopic properties of surface species on char to provide insights into the mechanisms of the gasification or combustion processes, accurate correlated quantum mechanical methods are required. The computational demand for such methods so far has limited the physical models of char to a two-dimensional single-layer graphene molecular systems. Furthermore, the large number of possible surface oxygen species and the number of chemical transformations involving such species raise the need for developing a cost-effective computational strategy for carrying such studies.

The goal of this study is to develop a cost-effective computational strategy for studying chemical processes on carbonaceous surfaces. It is reasonable to think that since the chemistry occurs locally at the active sites, it is possible to treat the reactive region consisting of the active site and the adsorbate more accurate while the spectator region less accurate using the well-known multi-layer ONIOM approach.[2] However, the delocaliztion of the π-bond network in the graphene layer would make such a partition questionable. We examined the accuracy for determinations of structural, energetic, and IR spectra for two representative surface oxygen species using different partition schemes. We also examined factors that affect the accuracy of the calculated properties, for instance the spin contamination in the Hartree-Fock (HF) wavefunction. Since the physical models of char are highly open-shell systems, spin contamination is expected to be large in the HF method. In other words, our main objective is to establish an accurate theoretical framework for future computational studies of chemical and physical processes on carbonaceous materials using quantum chemistry methods.

Computational details

Physical model. A carbon model with five-six member ring in zigzag shape was selected and it is presented in Figure 1. The boundary conditions are capped with hydrogen atoms as termination element and left some unsaturated carbon atoms to represent the active sites of a char. Carbon atoms in the model are differenciated by its topology. For instance, active site (a), Inactive exposed site (ie) and inactive buried site (ib) as shown in Figure 1. Although char has a much larger aromatic units and different shapes of the active sites, the model proposed in this study is adequated for the purposed of this study.

Theoretical model. Single-point energy calculations were performed at the B3LYP DFT functional using the 6-31G(d) basis set at different electronic states and the lowest energy was selected as the ground state of the molecular model. Then, models were fully optimized at the B3LYP DFT functional, HF and at different ONIOM levels. Unrestricted wave functions were used in all open shell cases. Restricted, Restricted-open and Unrestricted single determinant wavefunction was study in a separate report.[3] B3LYP functional were selected because this functional has been know to produce fairly accurate bond energies. Ab-initio Hartree-Fock level was used because it has been used for estimating geometries of carbonaceous models.[4] The 6-31G(d) and 3-21G basis sets were used in this study.
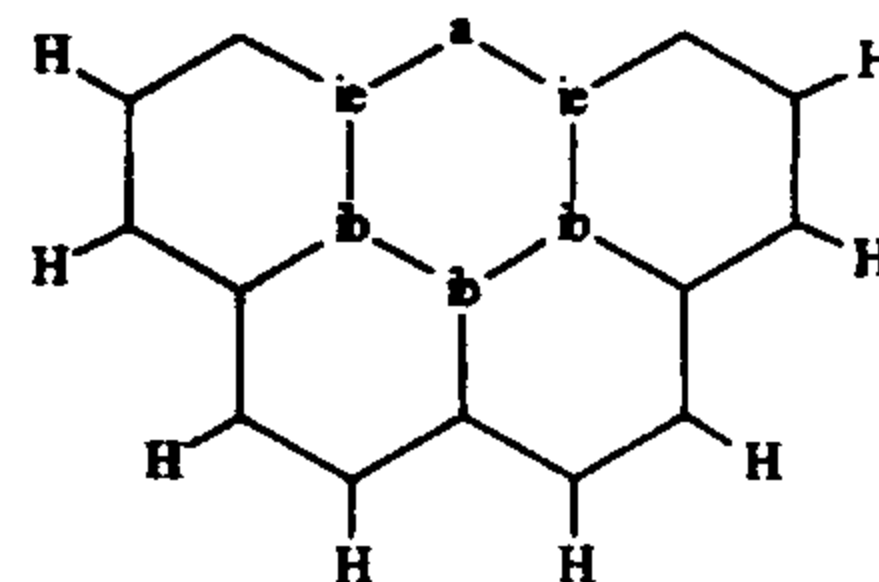

Figure 1. Representation of the carbon model in zigzag shape. a = active site. ie = inactive exposed site. ib = inactive buried site.

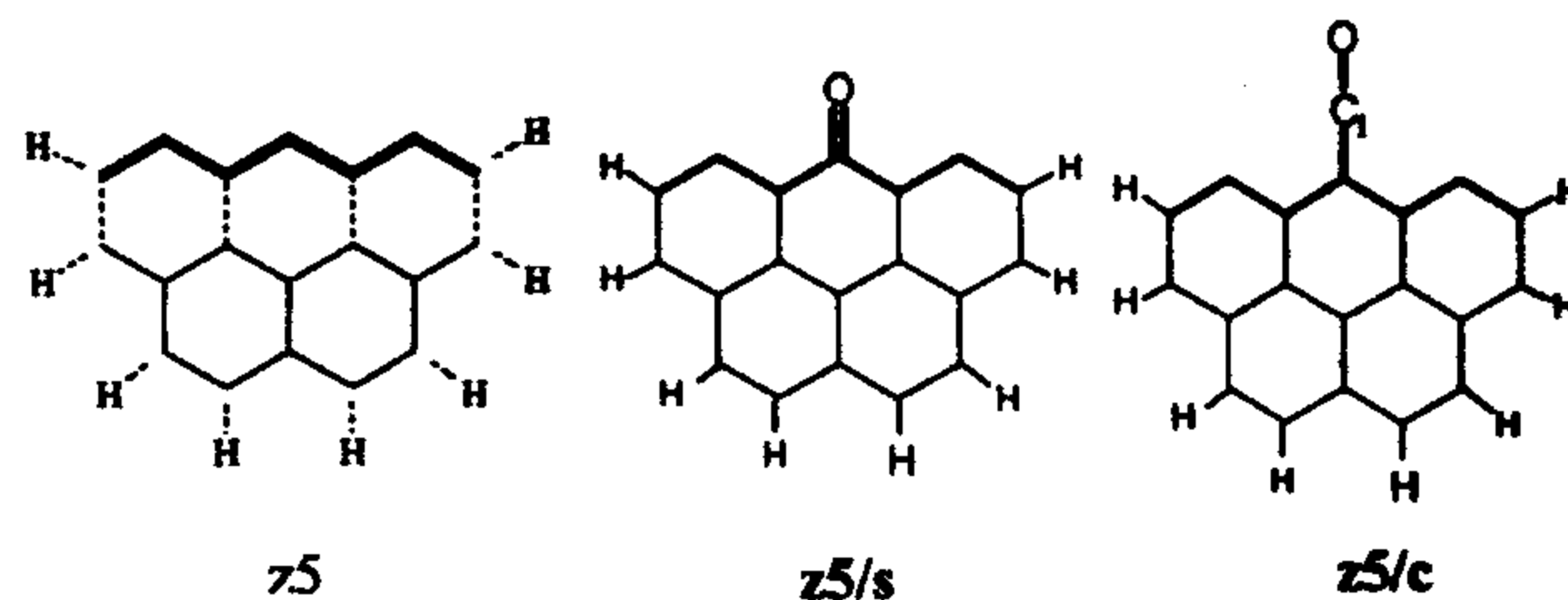z5   z5/s   z5/c

Figure 2. Representation of different layers used in the ONIOM method. z5: carbonaceous model. z5/s: semiquinone model. z5/c: carbonyl model. (▬): High Level of theory. (▬): Medium Level of theory. (—): Low Level of theory.

The three and two-layer ONIOM method were used to fully optimize the structures and estimating their energies. Different layers were selected and treated using different levels of theory. Figure 2 shows the partition of the carbonaceous, semiquinone and carbonyl oxygen models used in this study where the first layer corresponds to the first row of carbon atoms and the oxygen group. The second layer corresponds to the carbon atoms on the basal plane. The third layer corresponds to the hydrogen atoms. The nomenclature of the ONIOM method will be given in the following order "high level: medium level: low level". The two-layer ONIOM method was used when the second and third layers were modeled at the same level of theory. The first ONIOM level selected is the B3LYP/6-31G(d):B3LYP/3-21G:B3LYP/STO-3G, (O-L3(ONIOM three layer)). The second ONIOM level corresponds to the B3LYP/6-31G(d):HF/3-21G, (O-L2(ONIOM two layer)). The linking bonds between layers in the ONIOM models are represented in Figure 2 with doted lines and they were selected to be hydrogen atoms to compensate dangling bonds at the border of each layer. All calculations were performed using the GUASSIAN 98 program.[5]

Results and discussion

Geometrical parameters. The z5, z5/s and z5/c models were fully optimized at different levels of theory and the most important geometrical parameters are shown in Table 1. Unfortunately, there is no experimental data of the geometry of the surface oxygen complexes formed in the gasification and combustion of coal. Hence, our reference point is the geometry obtained at the highest theoretical level used. Bond lengths are shown for the B3LYP/6-31G(d) level, column two. The other columns show the difference with the geometrical parameters at the B3LYP/6-31G(d) level. For instance, a-ie bond length at the HF level is 0.58 pm bigger than the B3LYP/6-31G(d) level in the z5 model. It is found that the parameters obtained at the B3LYP functional converge with the basis set. Hence, the deviation obtained at the O-L3 ONIOM level is small. The parameters obtained at the HF level are different from those obtained at the DFT functional. Especially, the C-C$_1$ bond in the carbonyl oxygen group. Hence, the O-L2 ONIOM level has the largest deviation.

Table 1. Optimized Bond Lengths (in pm) of the zigzag carbon model

	B3LYP 6-31G(d)	3-21G	O-L3	HF 3-21G	O-L2
			z5 model		
a-ie	139.37	0.09	0.14	0.58	0.49
ie-ib	145.38	0.48	0.43	-0.71	0.91
ib-ib	142.70	0.08	0.09	-0.42	- 0.10
			z5/s model		
C-O	122.54	-0.03	0.30	-0.74	-8.7
			z5/c model		
C-C$_1$	133.53	-0.04	0.23	-2.3	-2.46
C$_1$-O	116.54	-0.09	0.03	-0.7	1.14

Adsorption energy. Adsorption energy of gasifying molecules on the carbonaceous structure of the char is usually compared with experimental data in order to analyze reaction mechanisms. Thus, the theoretical levels were used to predict the adsorption energy of atomic oxygen and CO molecules in order to form the z5/s and z5/c models. The adsorption energy was determined as the difference between the absolute energy of the reagents and products. Table 2 shows the adsorption energy at different theoretical levels, namely, B3LYP/6-31G(d), O-L3, O-L2, HF/3-21G and B3LYP/6-31(G)//HF/3-21G. The last one performs a single point energy calculation on the optimized structure using the HF/3-21G level. Because we want to compare different theoretical levels, the absolute adsorption energy is not important at this point. What it is important is the trend with our reference, in this case, the B3LYP/6-31G(d) level. It is seen that the adsorption energy can be well predicted by the O-L3 ONIOM level of theory. When a Hartre-Fock level is included in the basal carbon plane, For instance O-L2, it affects the adsorption energy by about 20% as it is shown in the atomic oxygen adsorption. Although, the O-L2 level deviates from our reference point, it has the same trend. The adsorption is an exothermic process in all cases. A different trend is found at the HF/3-21G level. The adsorption of a CO molecule is an endothermic process and the energy of atomic oxygen has an error of 84%. The high deviation of the HF level can be due to the electron correlation effect and also by the spin contamination of the electronic state of the wavefunction. For instance, the HF wavefunction of the carbonyl and semiquinone models has a spin contamination of 0.2 and 0.3, respectively. The

mixture of electronic states makes the energetic prediction ambiguous. The adsorption energy predicted at the B3LYP/6-31G(d)//HF/3-21G level is the closest to the reference point. Thus, the single point energy at the HF level corrects the adsorption energy.

Table 2. Adsorption energy (kcal/mol) of atomic oxygen and CO molecule on the z5 model

	Atomic oxygen	CO molecule
Level	z5/s	z5/c
B3LYP/6-31G(d)	-161.7	-54.8
O-L3	-166.6	-56.2
O-L2	-130.2	-42.4
HF/3-21G	-25.2	25.9
B3LYP/6-31G(d)// HF/3-21G	-160.0	53.1

IR spectra. The identification of the surface oxygen complexes can be done by the Infrared (IR) spectra. Table 3 shows the harmonic vibrational frequency of the oxygen group region using the B3LYP/6-31G(d) and the O-L3 levels. The frequency values are not corrected by the anharmonicity. As can be seen, the frequency values and their intensity obtained at the O-L3 ONIOM level is comparable to the highest theoretical level.

Table 3. Harmonic vibrational frequency (cm^{-1}) for carbonyl and semiquinone oxygen groups

	B3LYP/6-31G(d)	O-L3
Semiquinone (C-O)	1741.3/100	1800/100
Carbonyl (C-O)	2199.7/100	2100/100

Conclusions

It is shown that carbonaceous models and their surface oxygen complexes need to be studied at a theoretical level that takes into account electron correlation. Thus, B3LYP functional should be used for estimating geometries and predict adsorption/desorption energy of gasifying molecules. A different alternative for bigger molecular models is the well-known ONIOM method approach. Partitioning the carbonaceous structure in different layers depending on its reactive towards the chemisorption of gasifying agents seems to be adequate when it is used the same theoretical level at different basis sets.

References
(1) Berkowitz, N. *The Chemistry of Coal*; Elsevier: New York, 1985; pp 238.
(2) Dapprich, S.; Komiromi, I.; Byun, K. S.; Morokuma, K.; Frisch, M. J. *Theochem* 1999, *461-462*, 1.
(3) Montoya, A.; Truong, T. N.; Sarofim, A. F. *J. Phys. Chem. A* 2000, *104*, 6108.
(4) Chen, N.; Yang, R. T. *Carbon* 1998, *36*, 1061.
(5) M. J. Frisch, et al. Gaussian 98; Revision A.9.; Gaussian, Inc.: Pittsburgh PA, 1998.