DENSITY FUNCTIONAL THEORY STUDY OF CARBON-H₂O REACTIONS DURING GASIFICATION WITH STEAM

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Introduction

Carbon gasification is an alternative process to the combustion of coal since it produces less pollution and is more efficient. Basically, carbon gasification is the reaction of carbon with an oxidant agent such as oxygen, steam and/or carbon dioxide. Steam gasification is a process that has been widely studied by experimental techniques. Several mechanisms have been proposed for this reaction.[1-9] However, it is still not clear which of the proposed mechanisms is correct. Furthermore, these mechanisms do not provide any molecular-level details due to the complexity of the system.

In a recent theoretical study of the carbon-H_2O reaction a novel mechanism for the formation of molecular hydrogen was proposed which does not imply dissociation of the water molecule on the surface rather than a rearrangement of the hydrogen atoms.[10] This shows that molecular modeling is a powerful tool for improving our understanding of the gasification process.

The goal of this study is to carry out a Density Functional Theory study of thermodynamics of selected reactions that can take place during the steam gasification process. Particularly, we studied the interaction of the H_2O molecule with the active sites of clean carbonaceous models and possible pathways for the evolution of molecular hydrogen during the carbon-H_2O reaction.

Computational Details

Carbonaceous materials are macrostructures formed mainly by aromatic clusters. For char, it is known from solid-state ¹³C-NMR experiments that it has structures of randomly connected graphene clusters consisting of 12-25 aromatic carbon atoms (3-7 benzene rings).[11] Since the gasification reactions take place at high temperatures, the active sites are simulated as edge carbon atoms of a graphene layer that have lost a hydrogen atom. In the carbonaceous model used for the calculations the other edge carbon atoms are terminated with hydrogen atoms. It has been reported previously that the use of H to terminate the boundaries of finite graphite models is a good choice.[12] The models shown as the reactants in Figures 1 and 2 are reasonable representations of the active sites environment in zigzag and armchair edges, respectively. Note that the π-bond network is implied in these figures. It is important to note that although the char has a highly condensed aromatic ring structure where the graphene units may have different sizes and orientations, the size of the carbonaceous models used in this study correspond to those suggested from NMR experimental data. In previous investigations it was also shown that the reactivity of a carbon material depends more strongly on the local structure of the active site rather than on the size of the graphene layer.[13,14]

In order to investigate the reaction of steam with the carbonaceous models we fully optimized each structure and some of the complexes that can be formed. All calculations (energies, optimizations, and frequencies) were done at B3LYP Density Functional Theory level (DFT), using the 6-31G(d) basis set for all atoms except for the hydrogen atoms in the water molecule where the 6-31G(d,p) basis set was used. In a previous study it was shown that

spin contamination in unrestricted wave function at B3LYP level of theory is small for carbonaceous models.[15] Each model was optimized in its electronic ground state. Question on the roles of the excited states in these reactions is deferred to a separate study. This was done by performing single-point energy calculations at the same level of theory for several electronic states using geometries that were optimized at the AM1 semiempircal method for a given species, the ground state was taken as the one with the lowest energy. Furthermore, frequency calculations were done in order to confirm the stability of the optimized structures. All calculations were done using the Gaussian 98 program.[16]

Results and Discussion

Reaction of Steam with Clean Surfaces. The reaction of steam with the active sites of the carbonaceous models is a highly exothermic reaction either on zigzag or armchair configuration as can be seen in Figures 1 and 2. These reactions involve the production of a hydroxyl group after the dissociative chemisorption of the water molecule. If there is an active site next to the hydroxyl group, the hydrogen atom of this group would potentially further react with that active site to form a semiquinone group, in a reaction that is exothermic on both zigzag and armchair configurations.
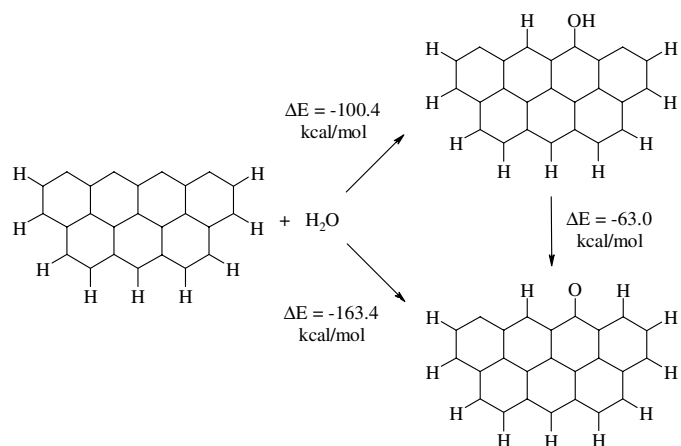

Figure 1. Reaction of the H_2O molecule on the active sites of the clean zigzag model and thermodynamic data.
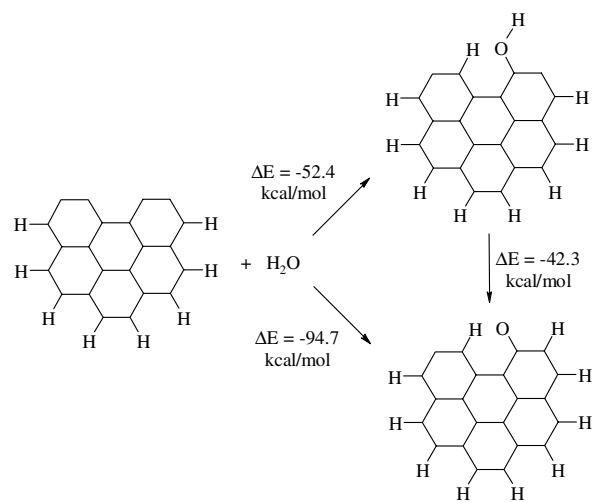
Figure 2. Reaction of the H_2O molecule on the active sites of the clean armchair model and thermodynamic data.

The reactions shown in Figures 1 and 2 are in agreement with the published experimental results where it was reported that after adsorption of water on graphite at low temperatures (25°C) the water molecule is chemisorbed and phenol and carbonyl (semiquinone) groups would be formed.[17] From the data shown, the dissociation of the water molecule at the active sites of carbonaceous materials is a thermodynamically favorable process.

Hydrogen Evolution. We studied several possibilities for the production of molecular hydrogen during the carbon-H_2O reaction on zigzag and armchair configurations. One possible pathway for the evolution of hydrogen is shown in Figure 3.
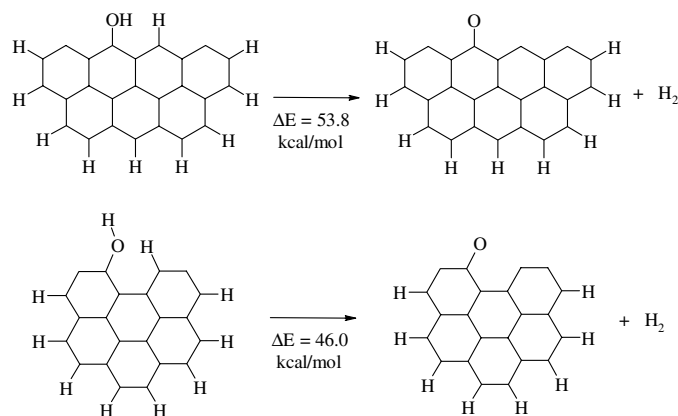
Figure 3. Possible pathways for molecular hydrogen evolution after chemisorption of one water molecule on the carbon surface.

Another route for the evolution of molecular hydrogen is found when two water molecules react on consecutive active sites as shown in Figure 4. From a thermodynamic point of view, the reactions shown in Figure 4 are more favorable ways to produce hydrogen from zigzag and armchair edges.
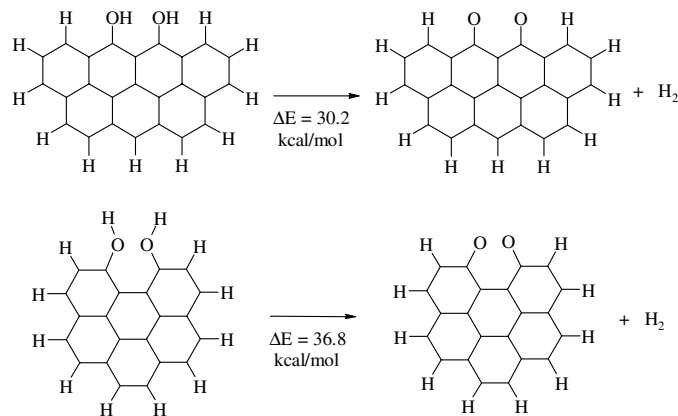
Figure 4. Molecular hydrogen evolution after carbon reaction with two water molecules and thermodynamic data.

The reactions shown in Figure 4 involve the dissociative chemisorption of two water molecules in such a way that two neighbor hydroxyl groups are obtained. These groups are precursors for subsequent hydrogen evolution leaving two semiquinone groups on the surface that could desorb as carbon monoxide or carbon dioxide as the gasification reaction proceeds.[18,19]

Conclusions

The reaction of steam with the active sites of the carbonaceous models is a highly exothermic reaction either on zigzag or armchair configuration. This reaction produces a hydroxyl group after the dissociative chemisorption of the water molecule. We propose an alternative pathway for hydrogen evolution that involves two neighbor hydroxyl groups that are precursors for molecular hydrogen production leaving two semiquinone groups.

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