Monte Carlo Simulation of Carbon Gasification Using Molecular Orbital Theory

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An attempt was made to simulate carbon gasification with the aid of molecular orbital theory. A simple Hückel method was applied to calculate molecular orbitals of a large polynuclear aromatic molecule, which was employed as a model crystallite for carbon. A free valence at each carbon atom in model crystallites of varying size and shape was determined, and this value was taken as a measure of reaction probability for the Monte Carlo simulation. Simulation of carbon gasification was performed by removing the carbon atoms from the model crystallites according to their corresponding reaction probabilities. This simulation made it possible to visualize how the shape of carbon crystallite is changed during gasification. It was found that the specific gasification rate depends on molecular size, but is essentially independent of the geometry of the starting model crystallite.

Introduction

Because of both the fundamental and industrial importance of carbon gasification reactions, the modeling of their kinetics has been a popular and rewarding research. Many kinds of simulation models have been proposed thus far. Among them, the random-pore models have been the most popular and versatile (Bhatia and Perlmutter, 1980; Gavalas, 1980). They simulate the gasification reaction by predicting the evolution of the pore structure of carbon during gasification. Such models provide no insight into reaction dynamics from the molecular point of view, for example, how carbon crystallites evolve during gasification and how the reactivity of carbon atoms varies as a function of carbon conversion.

Recently, we have proposed a new approach to the simulation of carbon gasification (Kyotani et al., 1993a,b), where polynuclear aromatic molecules (terminated with free-carbon sites instead of hydrogen) were employed as models for carbon crystallites, and the gasification reaction was simulated by removing the edge carbon atoms according to a prescribed reaction probability. In this approach we made, for simplicity, several unduly restrictive assumptions: the reaction probability depended only on the type of edge site (zigzag, armchair,

etc.) and each of the probabilities did not vary during the reaction. In the present study we evaluate the electronic state of each carbon atom to determine its reactivity (reaction probability). Because the carbon crystallite shrinks and its shape changes during the reaction, we also compute its electronic structure as a function of its extent of gasification.

Advances in computer hardware and software have made it possible to calculate molecular orbitals of complicated and large organic molecules, and thus adopt a quantum chemical approach to the modeling of carbon gasification. Stein and Brown (1987) have employed a simple Hückel molecular orbital (HMO) theory to calculate several electronic parameters for large polynuclear aromatic molecules (e.g., energy-level densities, bond orders, electron distributions, free valences, resonance energies). They found that these parameters strongly depend on the type of edge structure of polyaromatic molecules. More recently, more advanced molecular orbital theories (e.g., tight-binding extended HMO, INDO, etc.) have been used to improve our understanding of H_2 chemisorption on carbon (Chen and Yang, 1989), catalyzed gasification (Chen and Yang, 1992), and uncatalyzed gasification (Chen et al., 1993). These theories have also been used to simulate both uncatalyzed and catalyzed gas/carbon inter-

actions, including gasification (Janiak et al., 1993; Chen et al., 1993). The emphasis in the present study, however, is on predicting reaction probabilities at each carbon site during the entire process of carbon gasification. These predictions allow us to study the effect of different molecular shapes and sizes, as well as the reactivity vs. burnoff profiles. In this sense, the present study is the first attempt to simulate carbon gasification kinetics with the aid of simple HMO theory.

Modeling and Simulation Method

Molecular orbitals for carbon crystallites of different sizes and shapes (see Figure 1 and Table 1) were calculated using simple HMO theory. Free valence at a carbon atom r (FV_r) was adopted as the index of reaction probability at each carbon atom. It is commonly regarded as a measure of residual capability of bond formation. Generally an atom with a larger FV value is prone to be attacked by homolytic reagents. The free valence is calculated as the difference between the maximum bond order ($\sqrt{3}$) and the summation of bond orders at the object atom, as follows:

$$FV_r = \sqrt{3} - \Sigma_s P_{rs} \qquad (P_{rs} = \Sigma_i n_i c_{ir} c_{is}). \qquad (1)$$

In Equation 1 P_{rs} is the bond order between atom r and atom s, n_i is the number of π electrons, and c_{ir} and c_{is} are the atomic orbital coefficients at atoms r and s in the ith molecular orbital, respectively.

The following simplifying assumptions were made for the simulation of carbon gasification kinetics:

(1) Carbon crystallites are composed only of sp^2 carbon atoms. No other types of carbon atoms or heteroatoms (e.g., H or O) are considered at this stage.

(2) Carbon atoms with higher FV values are more easily gasified.

(3) Edge atoms that are bonded to only one adjacent atom are so reactive that they are gasified as soon as they are formed. The reaction probability at such a site is set to unity. Atoms without any bonds, which can be formed in this simulation method, also have a reaction probability of unity.
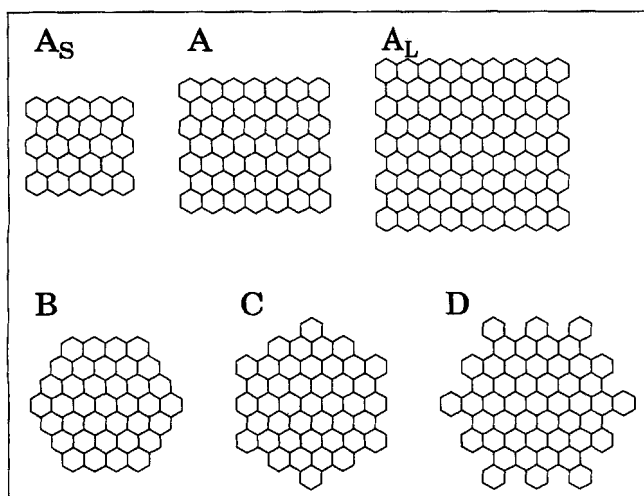

Figure 1. Models of carbon crystallites.

Table 1. Structural and Reactivity Parameters for Model Carbon Crystallites

Model	No. of Carbon Atoms	No. of Rings	Zigzag Sites	Arm-chair Sites	Avg. FV at Edge Atoms
A_S	66	23	6	12	0.484
A	120	46	10	16	0.492
A_L	190	77	14	20	0.497
B	96	36	12	12	0.495
C	114	43	0	24	0.440
D	138	49	0	24	0.433

As seen in Figure 1 and Table 1, models A_S, A, and A_L have a rectangular shape but they differ in size. In contrast, models A, B, C, and D have similar sizes, but they differ in shape. Model crystallite A is reactangular; B, C, and D are hexagonal, but they differ in the type of edge termination. The distribution of carbon atoms and the other structural parameters for these models are summarized in Table 1.

A program for the calculation of molecular orbitals was written in FORTRAN 77 and executed on a supercomputer (NEC, SX-3R). The flow sequence of the program is summarized in Figure 2. The coordinates of the carbon atoms are first specified for a given model crystallite. The FV values are then determined for all atoms from the calculation of molecular orbitals (Eq. 1). In the next step, a random number in the range 0–10 is generated at a given carbon atom r; in accordance with assumption (2), if this number is less than FV_r, it is gasified (removed from the structure). The effect of the random number range on the simulation will be discussed
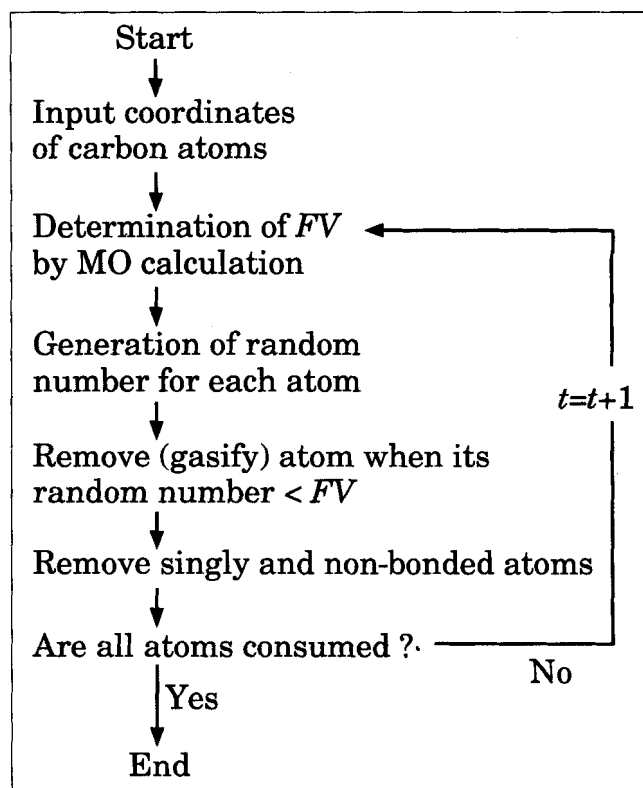

Figure 2. Flow chart of the computer program used for simulation.

in the following section. This interrogation routine for atom removal is carried out for all remaining carbon atoms. As a result of this process, some singly bonded edge atoms and nonbonded atoms may be produced; if this is the case, they are removed unconditionally, according to assumption (3). The number of gasified carbon atoms and their coordinates are then recorded. This molecular orbital calculation and atom-removal sequence is then performed again for the resulting partially gasified model crystallite. It is repeated until all carbon atoms are consumed. The number of calculation loops (counts) is taken to be a measure of the gasification time. The relationship between gasification time thus obtained and actual time requires calibration with experimental data and will be pursued in our future work. For the time being, the gasification rate is simply measured in "count" units. From the number of removed carbon atoms in each loop, carbon conversion (X) and specific gasification rate (R, normalized by the number of residual carbon atoms) are calculated as follows:

$$X(\%) = \frac{\text{no. of gasified carbon atoms}}{\text{no. of initial carbon atoms}} \times 100 \quad (2)$$

$$R = \frac{1}{100 - X} \frac{dX}{dt}, \quad (3)$$

where t is the number of loops, that is, a measure of gasification time.

The key improvement of the present work with respect to our earlier one (Kyotani et al., 1993a) is as follows. We assumed in the earlier work that the reactivity at each edge carbon is determined by whether it is on zigzag site, armchair site, or tip site, and the reactivities of these sites are assumed to be constant during the entire process of gasification. In the present model, however, the reactivity of each site is determined on a more reasonable basis (molecular orbital theory) and the reactivity thus determined may change when the size of crystallite shrinks due to its gasification.

Results and Discussion

Reactivity at each carbon atom

Figure 3 shows the FV values at each carbon atom in a portion of Model A crystallite. As expected, edge atoms have larger FV values than the carbon atoms in the basal plane. Therefore, they will be gasified more easily. This is consistent with the general understanding of carbon gasification (Walker et al., 1959). Furthermore, zigzag edge sites are predicted to be more reactive than armchair sites. Indeed, based on measurements of etch-pit enlargements in graphite during gasification with O_2 at 800–900°C, Thomas (1965) had reached the same conclusion. For the other model crystallites, the FV values for zigzag and armchair sites varied from 0.55 to 0.60 and from 0.44 to 0.49, respectively, regardless of the differences in size and shape.

Table 2 summarizes the distribution of FV values for model crystallites $A - D$. Each one is seen to have a different FV distribution. Crystallites A and B have sites whose FV values are larger than 0.5 because they have zigzag edges. Since gasification occurs mainly at edge sites (see the next section), the average of FV values at all edge sites can be taken as a
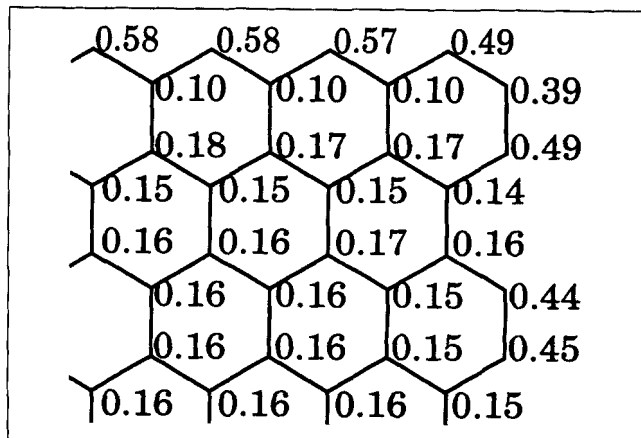

Figure 3. FV values at each carbon atom for model crystallite A.

measure of carbon reactivity for crystallites of similar size. This value is shown in the last column of Table 1. There is a slight monotonic increase for crystallites of increasing size. A much more pronounced difference is seen between model crystallites A and B, on the one hand, and crystallites C and D, on the other. Differences in reactivity among polynuclear aromatic molecules with different edge structures have already been discussed theoretically by Stein and Brown (1987), who also used a simple HMO theory and calculated several reactivity parameters, including FV. They concluded that the molecule with zigzag edges should be the most reactive one. As shown below, however, a crystallite with zigzag edges is not always the most reactive during simulated gasification.

Simulated gasification of model crystallites

Since a Monte Carlo technique was applied to the present simulation, it was necessary to check how many times a simulation run should be repeated to obtain statistically meaningful values of reaction parameters such as conversion and specific rate. Figure 4 shows the gasification profile (X vs. t) for model crystallite A, which was obtained after 50 repeated simulations. The solid curve in this figure was drawn from the average of the conversion values. The standard deviation for each conversion value was calculated to be about $\pm 10\%$ in 50 repeated runs. The presence of such scatter in the simulated values means that the results from only one simulation run cannot be used for the calculation of the reaction parameters. Simulations were also performed by repeating the calculations 100 times for the same model crystallite. The resultant average profile was identical to the profile shown in

Table 2. Distribution of FV Values in Model Carbon Crystallites

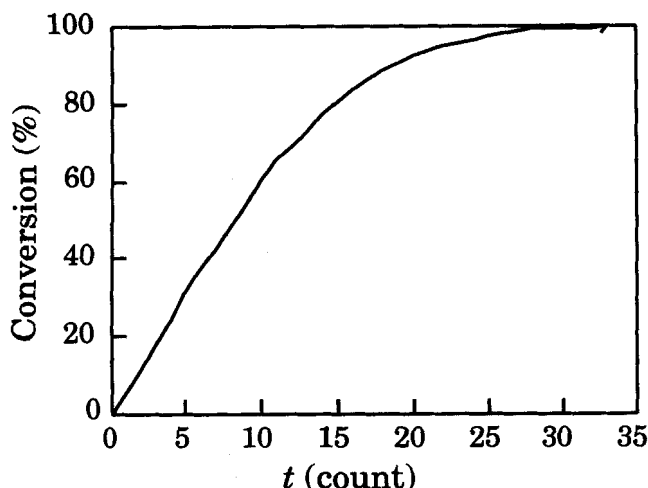| Range of FV	Model			
	A	B	C	D
$0.5 \leq FV$	10	12	0	0
$0.4 \leq FV < 0.5$	16	12	24	36
$0.3 \leq FV < 0.4$	4	0	6	6
$0.2 \leq FV < 0.3$	0	0	0	0
$0.1 \leq FV < 0.2$	90	72	84	96

Figure 4. Gasification profile (conversion vs. time) obtained from the average of 50 simulation runs for model crystallite A.

Figure 4. This finding indicates that 50 repeated runs are sufficient for obtaining meaningful values of the reactivity parameters. A similar simulation was performed for each model crystallite, and the specific rate was calculated from the average conversion using Eq. 3.

In the present Monte Carlo simulation, the computer produced a random number in the range from 0 to 10 at each carbon atom and then compared this number with FV at the atom. In order to investigate the effect of the range selected on the specific rate, we made the simulation run for model crystallite A using random numbers ranging from 0 to 100. At every gasification time, the specific rate simulated using the random numbers from 0 to 100 was exactly one-tenth of the rate simulated using the random numbers from 0 to 10. However, the reactivity profile itself did not change. This indicates that the selected range of random numbers influences only the computer calculation time, or the rate. If the range is too small, too many carbon atoms will be gasified in one gasification loop. If it is too large, the calculation time would become impractically long. The chosen range (0–10) is a compromise between these conflicting requirements.

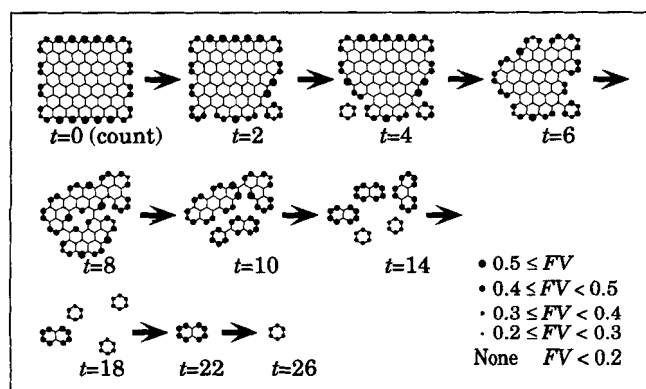Figure 5 illustrates the gasification of model A crystallite

Figure 5. Gasification process for model crystallite A.

The size of solid circle corresponds to the value of FV and t corresponds to uncalibrated gasification time.
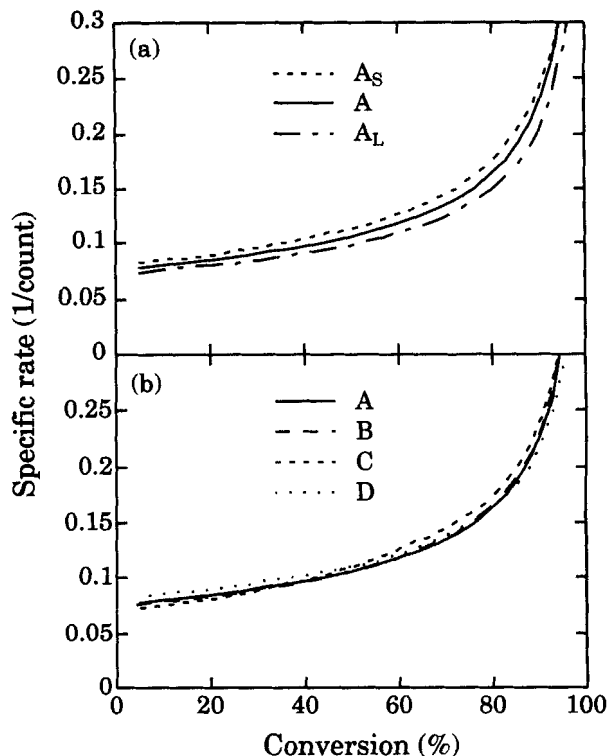

Figure 6. Effect of molecular size (a) and shape (b) on the gasification reactivity profiles (specific rate vs. conversion).

during one simulation experiment. The actual reactivity profile is close to the average one shown in Figure 4. The size of the solid circles indicates the value of FV; the larger it is, the greater the site reactivity is expected to be. In agreement with well-established experimental facts (Thomas, 1965; Henning, 1966), gasification starts at the periphery of carbon crystallites. The reactivity order zigzag > armchair > basal is maintained during gasification, despite the significant changes in crystallite size and shape as gasification proceeds.

Figure 6 shows the reactivity profiles for all the model crystallites studied. The profiles are the result of an average of 50 simulation experiments for each model crystallite. In all cases, the specific rate increases monotonically with conversion. This is in agreement with commonly observed phenomena in actual carbon gasification (Lizzio et al., 1990). Figure 6a presents the reactivity profiles for the rectangular crystallites of different sizes. Over the entire conversion range, the rate for the smallest crystallite A_s is the highest. On the other hand, there is no meaningful difference in Figure 6b, where the reactivity profiles are shown for the model crystallites of different shape. We can conclude that the specific rate depends on crystallite size, but is independent of its shape. The former conclusion is easily deduced from the fact that the ratio of the number of reactive edge atoms to the total number of atoms is smaller for larger crystallites. This factor outweighs the small increase in FV values with increasing crystallite size (see Table 1). The latter conclusion is not straightforward. Although the averages of FV values at edge atoms in model crystallites A and B are initially larger than those in models C and D, this difference was not sufficient to influence the specific rate appreciably.
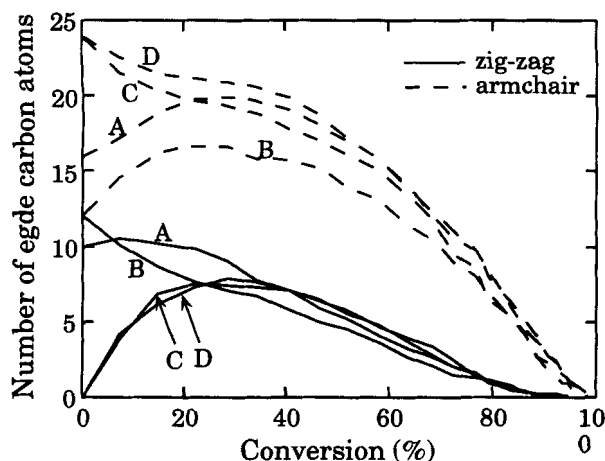
Figure 7. Variations in the number of zigzag and armchair atoms with conversion for model crystallites A, B, C, and D.

Figure 7 shows the variations in the number of zigzag and armchair atoms during gasification of model crystallites $A-D$. Before gasification (at $X = 0$), the numbers of zigzag and armchair sites differ appreciably among the various structures, as shown in Table 1. The relative numbers change with conversion and the curves for both zigzag and armchair sites exhibit a tendency to converge. This implies that there is no large difference in the course of gasification even if the starting crystallites have different shapes. It explains why the reactivity profiles were independent of crystallite shapes (see Figure 6b).

Conclusions

The entire course of carbon gasification, from 0 to 100% conversion, was simulated for the first time using molecular orbital theory. This method could simulate the following commonly observed features in actual gasification: (1) gasification starts at edge carbon atoms; (2) zigzag sites are more reactive than armchair sites; (3) specific rate increases monotonically with conversion. Furthermore, this simulation predicted that the specific rate depends on crystallite size, but is insensitive to crystallite shape.

The advantages in this approach over the conventional simulation methods are to make it possible to visualize how the carbon model molecule is gasified and to give fundamental insights into the gasification mechanism. The present work is now in a very primitive stage, but the introduction of more sophisticated molecular orbital theory and further development of computer hardware would allow us to simulate gasification more accurately. The factors affecting actual gasifica-

tion, such as temperature and type of gaseous reactant, should be incorporated in the next step of simulation. Furthermore, the introduction of surface oxygen-containing compounds into the model would also be necessary, because actual gasification takes place via the formation and the desorption of such compounds.

Acknowledgment

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