

CARBONACEOUS PARTICLES FORMATION IN COMBUSTION CONDITIONS

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Introduction

The processes involved in soot precursor formation exhibit a wide range of time scales, spanning pico- or nanoseconds for intramolecular processes to milliseconds for the formation of the first soot precursors. In order to accurately describe this process, it is important to model reactions occurring at different time scales and at the same time to characterize these particles in terms of chemical structure/components. The growth of nanostructures in combustion conditions has been described using two atomistic models, Kinetic Monte Carlo (KMC) and Molecular Dynamic (MD), in order to provide atomistic scale structure as the compound evolves into a three-dimensional structure [1-2].

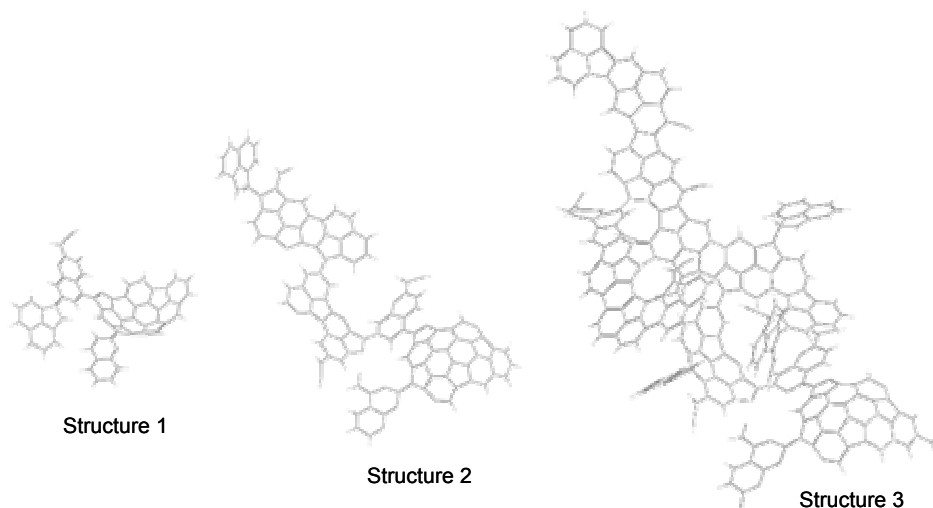


Figure 1: Structural evolution of nanoparticles

The KMC/MD code applies the two methodologies sequentially, allowing the extension of the accessible time scale by orders of magnitude relative to direct MD, while retaining full atomistic detail. As input to the KMC/MD code a list of possible reactions is prepared that includes addition of hydrocarbons and their radicals to the growing structure. Microscopic reversibility and fragmentation reactions, where a radical breaks a part to form either a stable species and a new radical or two radicals, are included too

[2]. Figure 1 shows the evolution in time of structures produced with the KMC/MD code in a low pressure benzene flame [3].

The molecular weight growth process for the formation of nanostructures involves both the addition of low molecular species, such as acetylene, to radical sites on aromatic compounds and the radical recombination of aromatic molecules. Together with the gas phase molecular weight growth-type mechanism is one that involves the structural rearrangement of carbon. Given sufficient residence time in a high energy environment, nanoparticles can undergo bond rearrangement. The aim of this work is to look at rearrangement reactions that can occur at a microscopic time scale during the MD module of the KMC/MD code.

Results

As example we chose *Structure 1*, produced through the KMC/MD code, whose enlargement is reported in Fig.2 as *Structure a*. The latter is produced by KMC that has chosen as random escape path the abstraction of H from site 1. During the MD time, that follows the KMC step, the site where the reaction has been lastly performed undergoes rearrangements that lead to a more stable structure. The MD module is used for relaxation of the molecules towards thermal equilibrium. Within the MD method, the potential used to describe hydrocarbon interactions is the adaptive intermolecular reactive bond order (AIREBO) [4] and it is based on the reactive empirical bond-order potential of Brenner [5]. Figure 2 illustrates one multi-step rearrangement that takes place during the MD time.

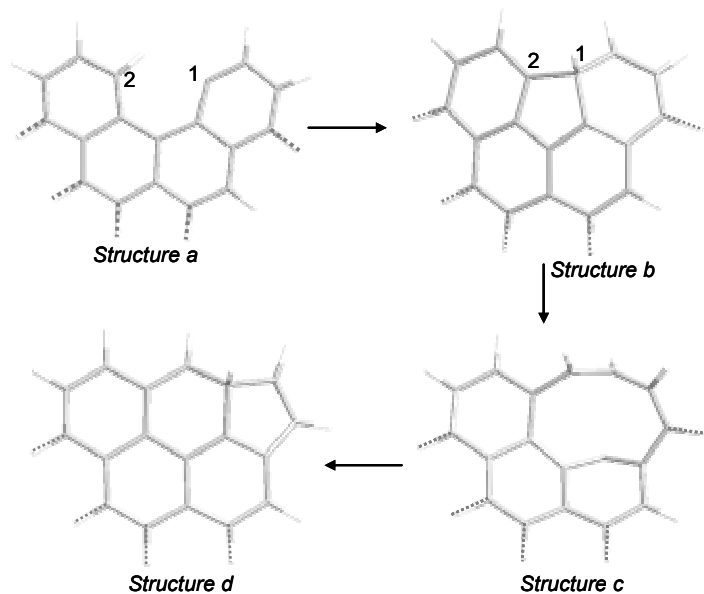


Figure 2: Multi-step rearrangement reaction

The first modification is represented by a cyclodehydrogenation reaction: a new five-membered ring is formed between C1 and C2. Then the H atom presents on C2 migrates to C1. At this point there is a transposition of five and six-member rings and

the final structure is reported in Fig.2 as Structure d. The pathway identified by the MD run, that involves the transposition of 5- and 6-membered rings, can be conceptually viewed as the migration of a five-membered ring from one position in the network to another. Under high-energy conditions five-membered rings should be able to migrate throughout the polycyclic network of carbon atoms until the most stable compound is reached. The motion of a thermodynamically driven “annealing” was introduced very early in the fullerene literature [6]. The similarities of sub-structures *b* and *d* and benzo[ghi]fluoranthene and cyclopenta[cd]pyrene are evident. Studies of the isomerization of these two compounds show that cyclopenta[cd]pyrene is thermodynamically favored over benzo[ghi]fluoranthene at temperature above 1000K. For example, the equilibrium constant is 5.2 at 2000K. Thermodynamic equilibrium predicts that PAH with internal five-membered rings are less favored at flame temperature than their isomers.

Conclusions

The use of the KMC/MD approach enables the inclusion of reactions that can occur at different time scales. The possibility of taking into account rearrangement reactions that can occur on the time scale of pico- or nanoseconds, allows us to characterize the carbonaceous particles formation in terms of chemical structure/components. Structure-pathways and structure-property relationships may lead to a deeper understanding of surface reactivity and hence growth mechanisms. Rearrangement reactions that can lead to the formation of surface defects needs to be taken into account and they may be responsible for the loss of reactivity of soot particle surface to growth.

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