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Surface reactivity of polycyclic aromatic hydrocarbon clusters

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Abstract

A scheme to characterise surface atoms is proposed to probe molecular representations of homogenous pyrene and coronene clusters. The concept of solvent-excluded surface, which is widely used for proteins, forms the basis of this scheme. The scheme is used to provide insights into the surface reactivity in terms of the surface availability of active atoms and sites for different gaseous species. It was found that the surface availability of active sites varies with gaseous species, system temperature and particle size. The number of active sites available for a small gaseous species is always greater than that for a large species. Surface exposure increases with an increase in temperature and an obvious enhancement exists when transforming to liquid-like configurations. The surface availability decreases with increasing particle size following a linear relation with reciprocal size. The parameter α , which is used in the soot literature to empirically quantify surface reactivity, was further estimated in the context of HACA mechanism and was approximately 0.8~0.9 for reactions between soot particles and acetylene. By exploring one particular pocket on the surface of a coronene cluster with 100 molecules, it was noted that it is feasible for both oxygen and acetylene molecules to penetrate inside the cluster in principle. However, the lifetime of individual pockets was found to be very short compared to the time-scale of a surface reaction, thus ruling out the possibility that surface reactions can take place in regions beyond the boundary by means of surface pockets.

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1. Introduction

Surface reactions play an important role in the mass growth of soot, and have been the subject of intense experimental and theoretical investigation [1–6]. However, these investigations are limited by poor understanding of the microscopic structure

of soot. A surface reaction of a soot particle is defined as a reaction between a small gaseous species and an individual active site on the surface of soot particle [7–9]. Usually, the aromatic sites in a particle are not always available for reaction [10–12]. A few reactive sites are “buried” inside the particle structure and not exposed to the gaseous species. This should be necessarily taken into account otherwise it will lead to overestimation of the surface availability of the sites and thus the rate of surface reaction. Experimentally, it is

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extremely difficult to probe this phenomenon because soot particles are structurally heterogeneous [13]. By contrast, Frenklach and Wang [14] proposed an empirical parameter, α , to account the availability of active sites which can react with gaseous species via the HACA mechanism. The main pathway of the HACA mechanism proceeds via the creation of surface radical sites by hydrogen abstraction, and later, the reaction of acetylene molecules with these sites to form 5- or 6-member rings. The growth processes can occur on the free-edge (FE), zig-zag (ZZ) and armchair sites of an individual PAH [15]. Surface oxidation reactions are also initialised by hydrogen abstraction at FE and armchair sites [11,16].

Following Frenklach and Wang's initial investigation, more recent numerical studies have investigated the parameter α and applied it to understand the surface reactions of soot particles in laminar premixed flames [3,16–18] and non-premixed co-flow flames [19,20]. Likewise, a free model parameter known as growth factor g , is included in some population balance models to adjust the rate of surface reaction of PAHs in large soot particles [8,9]. In nature, both parameters α and g represent a steric phenomenon that should be dependent on the microscopic arrangement of a soot particle. However, no one has yet estimated these parameters numerically due to the lack of a satisfactory microscopic representation. Recently, Chen and coworkers studied the thermostability of homogenous pyrene and coronene clusters as analogues for nascent soot particles [21] and demonstrated a phase change due to the addition of mass [22]. These studies provide a representation of these particles that enables the theoretical investigation of their surface reactivity.

To enable the probing of a surface representation, Richards [23] first described a solvent-accessible surface (SAS) as the surface was traced out by the center of a spherical probe representing a solvent molecule of a defined size using a “rolling

ball” algorithm [23] (see the dashed black line on Fig. 1). Later, a more appropriate concept, the solvent-excluded surface (SES), was proposed to represent the actual surface of a configuration [24] (see the orange solid line on Fig. 1). This surface contains the parts of the van der Waals surface of the atoms that are “touched” by the probe and linked by a series of concave and saddle-shaped surfaces between the atoms. In practice, the SES can be computed using a “rolling ball” algorithm [25–27]. Using the SES representation, reactive regions known as “pockets” can be identified inside a configuration [28]. Technically, a pocket inside a configuration is defined as an empty concavity on the surface of the configuration into which bulk gaseous or solvent atoms can gain access [29,30]. In other words, a pocket represents a mouth-type opening connecting the interior with the outside atmosphere or solution. Obviously, pocket detection can geometrically characterise the surface porosity of a target configuration and thus we can investigate whether gaseous or solvent atoms can penetrate inside a configuration and react with the active sites via individual pockets.

In this work, the surface properties of homogenous pyrene and coronene clusters, including the surface availabilities of hydrogen atoms, FE and ZZ sites, are investigated microscopically using geometric analysis. For the first time, we can examine the surface reactivity of small PAH clusters directly from their molecular arrangements. We study the dependence of the surface availability on the gaseous species, system temperature and molecular size. We also identify surface pockets located on a particular particle and investigate whether gas-phase species can access regions beyond the boundary of the configuration of a coronene cluster via individual pockets.

2. Computational method

2.1. Molecular cluster

The current work investigates the surface reactivities of a number of clusters, P_N . N denotes the number of molecules and varies from 50 to 500. P represents either pyrene or coronene. All the clusters were taken from previous work [21] in which the detailed microscopic representations were assembled and equilibrated using conventional Molecular Dynamics (MD). For each size, 100 different configurations have been extracted from a trajectory of 1 ns which is considered to represent an equilibrium state. The reported surface properties are computed by averaging over these configurations and the standard deviations are used to build the error bars.

The main concerns of this work are the surface availabilities of hydrogen atoms, FE and ZZ sites

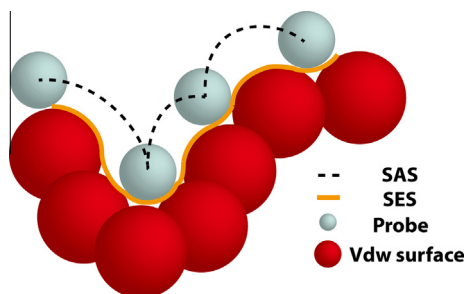


Fig. 1. Illustration of the “rolling ball” algorithm and the definition of the solvent accessible surface (SAS), the solvent-excluded surface (SES), and the van der Waals (Vdw) surface.

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