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Structural effects on the oxidation of soot particles by O_2: Experimental and theoretical study

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ABSTRACT

Soot particles are composed of polycyclic aromatic hydrocarbons (PAHs), which have either planar or curved structures. The oxidation behaviors of soot particles differ depending on their structures, arrangement of PAHs, and the type of surface functional groups. The oxidation rate of curved PAHs in soot is thought to be higher than that of planar ones. To understand the role that PAH structure plays in soot reactivity towards O_2, experimental studies are conducted on two types of commercially produced soot, Printex-U and Fullerene soot, using high resolution transmission electron microscopy, electron energy loss spectroscopy, thermo-gravimetric analysis and elemental analysis. The relative concentrations of active sites, oxygenated functional groups, aliphatics and aromatics present in soots are evaluated. The activation energies for soot oxidation at different conversion levels are determined. The average activation energies of the two soots are found to differ by 26 kJ/mol. To understand the reason for this difference, quantum calculations using density functional (B3LYP) and Hartree–Fock theories are conducted to study the reaction pathways of the oxidation by O_2 of planar and curved PAHs using 4-pyrenyl and 1-corannulenyl as their model molecules, respectively. The energetically preferred channels for curved PAH oxidation differ from the planar one. The addition of O_2 on a radical site of a six-membered ring to form a peroxyl radical is found to be barrierless for both the model PAHs. For peroxyl decomposition, three pathways are suggested, each of which involve the activation energies of 108, 170 and 121 kJ/mol to form stable molecules in the case of planar PAH, and 94, 155 and 125 kJ/mol in the case of curved PAH. During the oxidation of a five-membered ring, to form stable molecules, the activation energies of 90 kJ/mol for the curved PAH and 169 kJ/mol for the planar PAH relative to the energy of the peroxyl radical are required. The low activation barriers of preferred pathways for the oxidation of six and five-membered rings present on curved PAH (as compared to the planar one) explain and support its experimentally observed high reactivity.

1. Introduction

Soot particles and polycyclic aromatic hydrocarbons (PAHs) result from incomplete combustion of hydrocarbons and are readily found in emissions from engines and furnaces. In engines, the poor mixing of fuel and air creates fuel-rich zones that support soot formation at high temperatures. They are harmful to human health when inhaled and may cause cancer, asthma and cardiac problems [1]. Soot particles are the second largest contributor to global warming (after CO_2), and are involved in increasing regional temperatures and accelerating the melting of polar icecaps [2,3]. It is, therefore, important to reduce the formation or at least the emission of soot and PAHs to the environment by oxidizing them to meet stringent air quality standards.

To reduce the emission of soot particles to the environment, particulate filters are used in engine exhaust pipelines for capture. However, frequent regeneration of the filter bed is required to avoid pressure buildup in the exhaust system. This is done by oxidizing soot at high temperatures (above 400 °C). The rate of soot oxidation is clearly important in determining the frequency and the rate of filter regeneration.

A large number of theoretical and experimental studies have focused on the oxidation of soot and PAHs by O_2, NO_2 and NO with and without the use of catalysts to gain an understanding of the oxidation kinetics and to develop emission control technologies [4–17]. Soot oxidation by O_2 is particularly desirable for the regen-

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eration of particulate filters due to high concentrations of O_2 (around 10%) in diesel engine exhaust [18]. The experimental studies have been conducted either on soot particles generated from engines and captured using particulate filters or using commercial soot such as carbon black. Oxidation catalysts reduce the soot burn-off temperature by about 300 °C, but their high costs limit their usage in developing countries, and make the non-catalytic oxidation of soot preferable [4]. Some additives such as fuel-borne catalysts have also been suggested in the literature to accelerate soot oxidation inside engines or in particulate filters to reduce their emission [19]. However, the loss of such catalysts to the environment poses health risks [20]. While research works are ongoing in the search of an inexpensive catalyst for soot oxidation [21,22], and to physically modify engines or their operating parameters to improve fuel–air mixing for soot reduction [23–27], it is equally important to work towards the development of fuel additives that can enhance the reactivity of soot particles for faster oxidation in filters or inside a given combustion chamber. In engines, increasing the rate of in-cylinder soot oxidation (through enhanced reactivity) would also ensure that less number of particles are emitted to the environment in the absence of particulate filters. Such work requires knowledge of the factors on which soot reactivity may depend.

The oxidation rate of soot particles can be affected by chemical as well as physical modifications in its nanostructures. Such chemical and physical modifications can be achieved by the following means. (a) Adding oxygenated functional groups to the soot surface. The presence of oxygenated compounds on soot particles enhances their oxidation rate by the desorption of CO and CO_2 on the application of heat [28,29]. (b) Increasing the concentrations of active sites on soot. Soot particles are believed to be mainly composed of PAHs [30–33], even though some complex structures such as aliphatic–aromatic-linked hydrocarbons and aromatic rings with long aliphatic chains may also be present in them [32,34]. The radicals present on PAHs comprising soot provide sites for the addition of oxidizing agents such as O_2 and OH. Thus, an increase in their concentration will directly enhance soot reactivity towards oxidants [4,35]. (c) Increasing the ratio of basal to edge C atom. The basal carbon atoms present in PAHs comprising soot are about 100–1000 times less reactive to oxidants than are the carbon atoms present on the edge [36]. If the size of the PAHs in soot is reduced, the ratio of edge-to-basal carbon atoms increases, thus enhancing their reactivity. (d) Increasing the concentration of reactive cyclic or acyclic aliphatic groups on soot surface. The presence of saturated aliphatics on soot surface, which have higher H/C ratios and higher reactivity than aromatics, can enhance the soot oxidation rate [37,38]. (e) Increasing the amorphous content of soot. PAHs present in soot are stacked together (forming nanocrystallites) and aligned along the edges of soot particles, thus providing some graphitic nature to soot particles. However, near the core, PAH molecules are generally randomly oriented and give rise to amorphous nature of soot [39–41]. At low temperatures, soot oxidation begins from the inner core towards the outer surface, possibly due to the higher reactivity and higher active surface area of the amorphous part rather than the graphitic part (though the presence of small and reactive PAHs in the core could also be responsible for the internal burning of soot) [42,43]. Therefore, by increasing the amorphous content of soot through the reduction of crystallite thickness, its reactivity can be increased. (f) Introducing curvatures in the structures of PAHs comprising soot. In [44,45], experiments on soot formation were conducted using low-pressure flames, where curved or fullerenic structures were observed in soot particles. It was concluded that the extent of curvatures in soot depends on the operating conditions. Some additives were suggested that could enhance the concentration of curved or fullerenic structures in soot particles. In [42], soot oxidation was carried out at low temperatures, and hollow core formation was observed due to internal burning. It was postulated that the presence of curved structures in the core of soot particles, which have higher oxidation rates than do planar ones, were responsible for the internal burning. Thus, increasing the concentration of curved PAHs in soot through the techniques discussed in [44,45] may enhance its reactivity.

The size, amount, structure, elemental composition and functional groups of PAHs comprising soot particles depend on the fuel along with the operating conditions of the combustion devices producing these particles [29,46–50]. Thus, for a given set of operating conditions, physical or chemical modifications in soot can be made by designing additives for real fuels that produce soot with desired properties (i.e., high reactivity). Thereafter, these highly reactive soot particles, when captured by particulate filters, can be easily oxidized to regenerate the filter bed.

Some studies have considered the role of the nanostructure of soot particles on their oxidative reactivity [51–56]. In [51], the oxidation rates for soot particles obtained from benzene, ethanol and acetylene were studied at different O_2 concentrations. The oxidation rates of soot particles from benzene and ethanol were found to be five times faster than those from acetylene. By comparing the high resolution transmission electron microscopy (HRTEM) images of soot particles, this difference in oxidation rates was attributed to the changes in soot nanostructures, but the changes in other physical and chemical properties of soot particles that can significantly affect their reactivity were not taken into account.

In [52,53,55], spark-discharge soot, diesel soot, furnace carbon black, Euro IV heavy-duty diesel engine soot and hexabenzocoronene were used to study the oxidation behaviors of different carbonaceous materials. Several experimental techniques such as Raman microspectroscopy, electron energy loss spectroscopy, HRTEM, thermogravimetric analysis and Fourier transform-infrared spectroscopy were used. In [53], the apparent activation energy for spark-discharge soot was found to be 130 kJ/mol, while that for diesel soot was found to be 160 kJ/mol. It was also observed in these studies that spark-discharge soot oxidizes faster than other soots. By comparing the HRTEM images of different soot samples, it was postulated that the presence of curved/fullerenoid structures in spark-discharge soot should be responsible for its high reactivity. However, no discussions were presented in terms of the concentrations of active sites on soot particles that can also affect soot reactivity. The reason for the difference in activation energies was not explained. Furthermore, no theoretical study on curved PAHs has been presented to demonstrate and quantify their higher reactivity towards O_2 compared with the planar PAHs.

The objective of this study is to investigate and quantify the difference in the reactivity of curved and planar PAHs comprising soot particles towards O_2. Experimental studies were conducted to compare the oxidative properties of soot particles composed primarily of planar PAHs with those composed primarily of curved PAHs, and to determine the effects of the type of functional groups, active sites, chemical bonding, and PAH size and structure on the observed reactivities of soot particles. The difference in the reactivities were quantified at different conversion levels of soot in terms of activation energies.

To understand the experimental observations, quantum calculation were conducted using the density functional theory (DFT) and the Hartree–Fock (HF) theory to develop detailed reaction mechanisms for the oxidation of planar and curved PAHs. For the first time, the mechanistic differences between their oxidation mechanisms along with the changes in the activation energies of the important elementary reactions involved in oxidation and their effect on reaction rate constants at different temperatures is highlighted.