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Differential kinetic analysis of diesel particulate matter (soot) oxidation by oxygen using a step–response technique

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Abstract

The effects of a catalytic coating on the oxidation of captured soot over diesel particulate filters (DPF) is debated in the literature, since a catalyzed filter wall appears to lack sufficiently tight contact with soot deposits to exercise direct catalytic action. The topology of soot–catalyst contact may change with progressive oxidation of the soot layer; hence, a technique capable of probing catalytic action via detailed kinetic analysis at different stages of oxidation is required to conclusively resolve this problem. A novel step–response technique was developed in this work as a methodological foundation for such study. Using this technique, various aspects of the oxidation process can be probed while consuming only differential amounts of carbon, and the impact of the reaction heat on the measured rates can be minimized. This technique was applied to soot oxidation by O_2 and showed that, after decoupling effects due to the sample history, carbon oxidation by O_2 in the absence of H_2O can be well-described by an unmodified Arrhenius equation, with similar activation energy values for diesel and model soot samples (137 ± 8.7 and 132 ± 5.1 kJ/mol, respectively). The reaction order in O_2 for these samples was found to be 0.61 ± 0.03 and 0.71 ± 0.03, respectively, and was remarkably independent of the temperature, suggesting that the fractional order is not due to mixed kinetic control. The reaction mechanism was also found to be independent of carbon conversion. The density of the reaction sites, however, appeared to increase with oxidation. This increase could not be accounted for by the changes in the specific surface area, either directly measured or derived from such simplified models as the shrinking-core formalism. The entire set of obtained experimental results can be described using a kinetically uncomplicated model in a broad range of temperatures, partial pressures of oxygen and degrees of soot oxidation.

Keywords: Diesel particulate matter; Soot; Carbon oxidation; Experimental methodology; Reaction kinetics

1. Introduction

Compression–ignition (diesel) engines have traditionally been the major source of propulsion for heavy-duty transportation and off-road applications, such as construction, mining and agriculture. They are also becoming increasingly popular for passenger vehicles, due to a combination of valuable consumer features. These include high torque at low speed, excellent durability and reliability, higher tolerance to fuel properties and, very importantly, a 15–25% fuel efficiency advantage over their gasoline counterparts [1,2]. Better fuel efficiency also translates into lower power-specific emissions of the greenhouse gas CO_2.

A broader introduction of diesel engines, particularly, in the United States, is limited by exhaust emissions, primarily of nitrogen oxides (NO_x) and diesel particulate matter (soot). The latter is specific to the diesel combustion process, where oxidation of fuel occurs under locally oxygen-starved conditions in the diffusion flame ‘‘plume’’, despite the net ‘‘lean’’ stoichiometry of diesel combustion. Diesel soot emissions are strictly regulated in most of the world. Upcoming regulations, for example, the 2007–2010 emissions regulations in the USA, will represent essentially a 10-fold reduction from the current level and a reduction of several orders of magnitude compared to 10 years ago [3].

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Soot can be effectively removed from the exhaust using diesel particulate filters (DPFs), however, DPFs need to be regenerated periodically by oxidizing the accumulated soot. Oxidation of soot by NO_2 present in the exhaust, albeit facile, becomes less feasible for the newer vintage of engines, since they have low NO_x emissions. The temperatures required for rapid oxidation of soot by O_2 are not attained in typical duty cycles. A number of facilitating catalytic technologies have been studied over the years, including the use of various fuel-borne catalysts, which become incorporated in the soot particles after passing through the combustion chamber; upstream oxidation catalysts, primarily to enhance oxidation of NO to NO_2 and oxidize hydrocarbons injected to raise the DPF's temperature; various catalytic coatings on the DPF itself, including low-temperature melting salts. Some of these applications are successfully commercialized.

The majority of 2007–2010 on-road diesel applications will require some strategy for forcing more active soot regeneration by increasing the exhaust temperature to achieve soot oxidation by O_2. Therefore, a detailed quantitative understanding of this reaction is required for the development of active DPF systems and in particular for the development of control algorithms capable of tracking the amount of soot in the filter.

The literature information regarding soot oxidation kinetics by oxygen, under conditions typical for diesel exhaust, is quite limited and often contradictory [5,6]. A very broad range of kinetic parameters including activation energy and reaction order with respect to O_2, H_2O and carbon can be found in the literature [7]. This can be partially attributed to the differences in composition, morphology and chemical properties of the soot samples, resulting from the differences in combustion conditions, fuel, lubricating oil and sampling conditions [5,7–11]. The understanding linking the microscopic properties of diesel soot and its reactivity is only now emerging [12–15].

Furthermore, the effect of catalytic coating of the DPF on the oxidation of captured soot by O_2 is debated in the literature, since a catalyzed filter wall appears to lack sufficiently tight contact with the soot deposits to exercise direct catalytic action [4]. Since the topology of soot–catalyst contact may change with progressive oxidation of the soot layer, a technique capable of probing catalytic action via detailed kinetic analysis at different stages of oxidation is required to conclusively resolve this problem. It should be noted that coating the DPF with a redox catalyst undoubtedly provides a number of secondary advantages for the practical application of the DPF system, including oxidation of hydrocarbons and CO slipping from the engine, as well as CO produced in the process of soot oxidation. Oxidation of NO to NO_2 over the catalyzed DPF wall can also assist soot regeneration. However, contribution of this factor appears to be fairly limited, since in the conventional DPF, NO_2 produced inside the catalyzed wall would need to diffuse against the convective flow of the exhaust gas in order to react with the soot deposits located on the inlet side of the wall.

The limited amount of kinetically relevant information on catalyzed and uncatalyzed soot oxidation is, at least in part, due to the experimental difficulties associated with studies of carbon reactivity. Thermogravimetric analyzers (TGA) are often used for such studies, since weight loss can be directly translated into carbon conversion. Unfortunately, in a conventional TGA, heat transfer and the external mass-transfer limitations can be very substantial, as quantitatively shown by the groups from Delft University and Universite de Haute Alsace [16,17]. In our earlier work, we have found that an acceptable agreement can be achieved between the TGA and fixed-bed reactor data in a lower temperature range, when the oxidation rates were sufficiently low to minimize the impact of the above limitations [18]. Fixed-bed reactors provide much better contact between the gas flow and the soot particles than TGA. However, as shown in this work, even at high levels of sample dilution by an inert material, dissipation of the reaction heat may remain a problem. It was reported by the group from the University of Minnesota that limitations typical for the fixed-bed reactors have been successfully resolved using the in-flight oxidation technique [19]; however, application of the developed technique is limited to very high temperatures, in excess of 800 °C.

The objective of this work was to develop an experimental methodology for soot oxidation studies, capable of probing various kinetic aspects of soot oxidation with differential consumption of soot. In the current study, such methodology was applied to the oxidation of diesel and model soot samples; future studies will be focused on determining the impact of the DPF catalytic redox coating on this kinetics.

2. Experimental

2.1.1. Soot samples

Two samples of soot were studied in this work: diesel particulate matter (diesel soot) and a commercial carbon black sample. The diesel soot sample studied in this work was collected using a Cummins ISB diesel engine, running on Phillips ultra-low sulfur fuel (<15 ppm). The soot was accumulated on a commercial diesel particulate filter (NGK cordierite C-558, 100 cpsi) for ~10 h under low-temperature exhaust conditions (less than 270 °C), to minimize sample loss due to its oxidation. Subsequently, the sample was removed from the filter using a reversed flow of compressed air and then stored in a closed container under ambient conditions.

The carbon black sample studied in this work – Printex-U^{TM} (Degussa) – represents a synthetic flame soot. Use of this compound as a model for diesel soot was pioneered by the group at Delft University a decade ago [20], and it is