Angewandte International Edition Chemie

Exhaust Emission

DOI: 10.1002/anie.201206093

Emission of Highly Activated Soot Particulate—The Other Side of the Coin with Modern Diesel Engines**

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combustion · diesel engines · heterogeneous catalysis · nanoparticles · soot emission

Diesel engines are characterized by high fuel efficiency and high reliability due to the absence of an electrical ignition system. They produce only a small amount of carbon monoxide as they burn the fuel in excess air, even under full load conditions, and therefore they have become more popular and "welcome" as an alternative to or even replacement for gasoline engines to reduce the emission of greenhouse and toxic gases. Another advantage in terms of environmental protection is the possibility of using nonfossil fuels such as long-chain alkyl esters (biodiesel) that can have a lower carbon footprint than petrodiesel.[1] The rapid increase in the proportion of new cars with diesel engines in the past 20 years in Western Europe is illustrated in Figure 1.[2] This trend is expected to further increase over the next few years[3] until the development of cheap and competitive hybrid technology brings the share of diesel and gasoline motors down to an expected 15–35 % in 2030.[4]

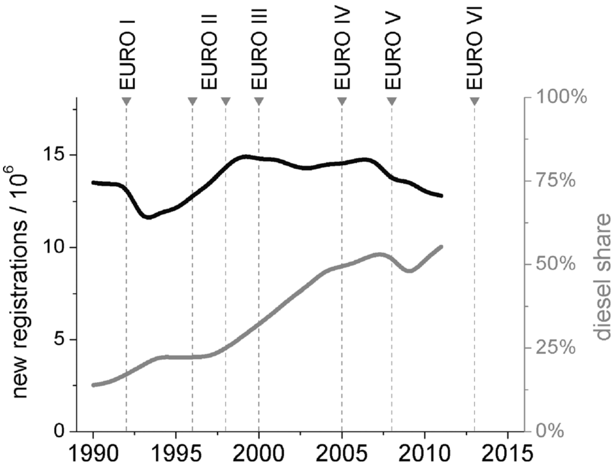

Figure 1. Proportion of new registrations of diesel cars in Western Europe. Data adapted from ACEA.[2].

The major disadvantage of diesel engines with regard to environmental and health protection is the typically enhanced production of black soot (more specifically: diesel particulate matter), which consists of unburned carbonaceous compounds. This is mainly caused by local cold spots, where the fuel is not fully oxidized. Relatively low temperatures appear at the walls of the combustion chamber and at the outside of poorly vaporized large fuel droplets. The surface of condensed fuel has less air to burn and partly pyrolizes to finally turn into a carbon deposit, which leads to the formation of soot. The presence of aromatic compounds in the diesel fuel typically enhances the soot emission through the facile condensation of aromatic units to form larger polyaromatic hydrocarbons (PAHs), whereas aliphatic compounds favor the growth mechanism through hydrogen abstraction and consecutive addition of (poly)acetylene. There are two ways to eliminate or at least to decrease the amount of particulate matter emitted from diesel engines: optimizing the combustion of diesel fuel in the engine and through the after-treatment by installing particulate filters. The huge efforts made in these two directions are driven by the increasing awareness of the public of the potential cytotoxicity of soot particulates, as recently confirmed by the World Health Organization (WHO).[5] As a consequence, the legislative body has imposed increasingly more strict emission levels.

A substantial decrease of more than 95 % in the rate of particulate emission (from 140 to 5 mg km^{-1}) can only be achieved by an improvement in motor engineering. This includes the construction of the engine as well as the combustion of the diesel fuel. Among the many possible modifications to a diesel engine, the addition of a turbocharger or a supercharger greatly assists in increasing the fuel economy and power output by increasing the fuel–air intake. High injection pressures not only increase the amount of oxygen in the cylinders to favor complete combustion of the fuel but also improve its dispersion into smaller droplets, while electronic control can adjust both the timing and the

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[**] This work is part of the project "Katalytisches System zur filterlosen kontinuierlichen Rußpartikelverminderung für Fahrzeugdieselmotoren" supported by the Bavarian Research Foundation.

length of the injection process to optimize the combustion process at all speeds and temperatures.

However, from a chemical point of view, complete combustion (total oxidation) of the diesel fuel requires stochiometric conditions in terms of the diesel/air ratio or an excess of oxygen on an infinite time scale. This is not the case at full throttle conditions for maximum power output, when the diesel fuel is continuously injected into the compressed cylinders. This regime is usually characterized by the heavy emission of black smoke (BS).

What are the structural and chemical differences between conventional and low-emission soot particles on the nanoscale? In general, the particulates are agglomerates of more or less spherical primary particles that form a secondary chainlike structure with final dimensions of up to 500 nm. The most evident change is in the size of the primary soot particles, as can be seen by transmission electron microscopy (TEM) images of the samples collected directly from the exhaust gas of the engines (Figure 2a and b).[6] Those emitted from a Euro IV engine have a much smaller diameter than the BS particles from the older engines. The size distributions obtained from statistical analysis of primary soot particles are compared in Figure 2c. Soot from Euro IV engines is characterized by an average primary particle diameter of 10–15 nm combined with a very narrow size distribution. In contrast, the soot from the older engines comprises large spheres with diameters ranging from 30 to 40 nm and a broad size distribution.[7] This shows quite plainly the important effect of the Euro IV standard compared to the previous measures applied to reduce soot emission from diesel engines, which had little influence on the size distribution of the emitted particulate, and only reduced its quantity.[8]

The second significant change in the soot samples induced by modification of the diesel engine is in the bulk and surface structure as well as the functionalization of the surfaces with oxygen-containing groups. The basic structural unit (BSU) of graphitic carbon materials is a section of a single-layer graphene sheet with edge defects and a curvature induced by non-six-membered carbon rings.[9] High-resolution TEM analyses show that these BSUs in Euro IV soot are smaller than in BS soot, but are less flat, thus exhibiting a fullerene-like structure. The more pronounced bending of the carbon sheets in Euro IV soot indicates a high fraction of sp^3-hybridized carbon atoms and/or is a result of topological defects induced into the soot structure by alteration of the diesel combustion process. Both lead to an enhanced localization of charge in the π system of the conjugated electrons on the graphitic surfaces, and these positions are potential and favored anchoring points for surface functional groups on reaction with water or oxygen.[10] The number of defects is smaller in the BS soot, as indicated by the flatter appearance of the BSU (Figure 2a). In contrast, the highly defective structure in Euro IV soot contains more oxygen in the form of surface functional groups than does conventional soot. The most-abundant oxygen-containing surface species were identified by means of infrared spectroscopy to be OH groups as well as a broad variety of species with C−O single and double bonds; this finding is in agreement with a recent study that indicates that carboxylic groups are the dominant surface oxygen groups on diesel exhaust particulate.[11–13] Their

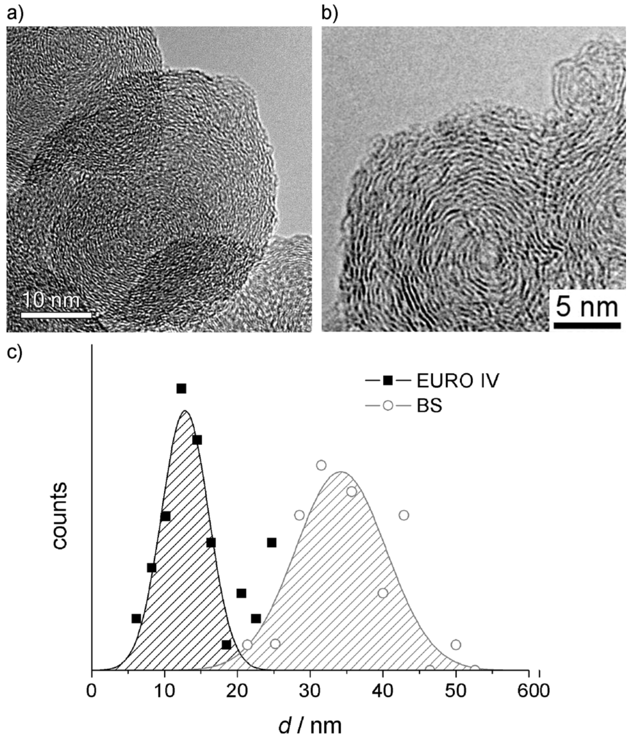

Figure 2. TEM images of a) BS soot showing almost spherical soot particles, b) Euro IV soot consisting of core–shell primary particles with defective bulk and surface structures. Reprinted with permission from Ref. [6]. Copyright 2008, American Chemical Society. c) Size distributions of soot particles emitted by Euro IV and Euro III diesel engines run under black smoke conditions. Data adapted from Ref. [7]. With kind permission from Springer Science + Business Media. Copyright 2004.

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presence drastically increases the chemical reactivity of the carbon surface, as indicated by a significant shift of the maximum temperature in the CO_2 profiles of the temperature-programmed oxidation of these soot samples.

A structural comparison of the Euro IV soot and Euro VI soot, which complies with the most recent soot emission standards for engines, reveals a different response to a thermal treatment aimed at simulating the combustion process in the exhaust system. Electron energy loss spectroscopic (EELS) analysis of the π*/σ* bonding states shows a rehybridization of the Euro IV soot upon oxidation, while the graphitic character of the Euro VI soot was not affected. X-ray photoemission spectroscopy (XPS) reveals a different composition and temperature stability of the oxygen functional groups on the surface of the Euro IV and VI soot, as depicted in Figure 3 and Table 1.

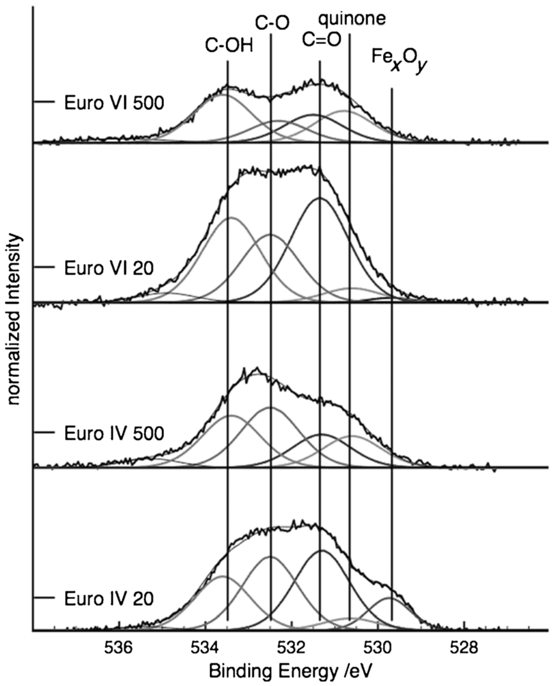

Figure 3. XPS analysis of oxygen functional groups on fresh (20°C) and heat-treated (500°C) soot samples (Euro IV and VI). Reprinted from Ref. [15] with permission. Copyright 2008, American Chemical Society.

Table 1: Absolute oxygen abundance (at.%) for the individual contributions in the Euro IV and Euro VI samples.

E_b [eV]		Euro IV		Euro VI		Onionlike carbon[14]
		(20°C)	(500°C)	(20°C)	(500°C)	(517°C)[a]
529.8	Fe_xO_y	0.04	0.02	0.15	0.19	–
530.6	quinone	0.04	0.32	0.22	0.84	1.01
531.4	C=O	1.56	1.46	4.07	2.46	–[b]
532.5	C-O	1.62	1.37	3.05	2.13	2.56
533.7	C-OH	2.60	2.56	4.04	3.00	2.99

[a] Used as a catalyst in the oxidative dehydrogenation of ethylbenzene. [b] Data from Refs. [14] and [15] were fitted with different contributions and curve shapes.

The particle size is reduced due to the oxidation and combustion processes, which occur from the outside to the inside of the soot particles. Most significant, however, is that the rate of the combustion process is clearly influenced by the structure of the particles. The shell-by-shell "burning" occurs in parallel with the preferential gasification of defective carbon atoms inside the particle, thereby leading to an apparent increase in their structural order (namely, graphitization). This is accompanied by the formation of micropores to initiate the breakup of the soot particles into smaller particles and/or shrinking of the particles as a whole.[16]

The Euro VI sample does not undergo changes in the particle-size distribution, which means, according to the core–shell particle concept, that the outer shell hinders the oxidation/combustion. This means that the particles are not combusted at all, or if combustion starts, the particles from the Euro VI engine combust completely, because of the higher reactivity of the oxygen functional groups in the Euro VI sample than in the Euro IV sample.

It is important to mention the fact that the oxygen content in the Euro VI sample is not only reduced but the distribution of functional groups changes. Less-stable oxygen groups are removed during the oxidation treatment or converted into more stable ones, as shown by a study of the depth profile.[15] Thus, the oxygen species on the carbon surface of the soot particles is the most determining factor of their reactivity.

The chemical activation of the soot particulate originating from low-emission Euro IV diesel engines is extreme. The carbon surface in its initially defective, hence highly functionalized, state shows an outstanding activity, as evident by some heterogeneously catalyzed chemical reactions. We thus tested the particulate in two reactions which were already proven to be successfully catalyzed by the nanostructured carbon materials, namely the oxidative dehydrogenation (ODH) of ethylbenzene to styrene[17] and the selective oxidation of acrolein to acrylic acid.[18] The syntheses of these chemicals are very important chemical processes and are catalyzed by highly developed promoted (mixed) oxides with an excess of steam. The initial productivity of the untreated Euro IV soot used as the catalyst in these reactions exceeds the data of other well-performing carbonaceous materials compiled from the literature (Figure 4). However, as a consequence of its fragile and disordered nanostructure, the soot catalyst is unstable under the reaction conditions applied and the productivity collapses within hours, whereas the data for the other (nano)carbon catalysts shown in Figure 4 could be obtained under steady-state conditions. Nevertheless, the pronounced chemical potential of fresh Euro IV soot in the form of highly activated oxygen surface groups, which corresponds to the active state of high-performance heterogeneous catalysts, is impressively evidenced in these experiments.

The modifications made to the diesel engine to fulfill the low emission standard have essentially changed the morphology and surface functionalization of the soot. In a recent study, onionlike carbon with a structural motif related to that observed for the soot particles (Figure 2) was furthermore shown to successfully catalyze the ODH of *n*-butane to butenes and butadiene.[22] It was concluded that, in particular,

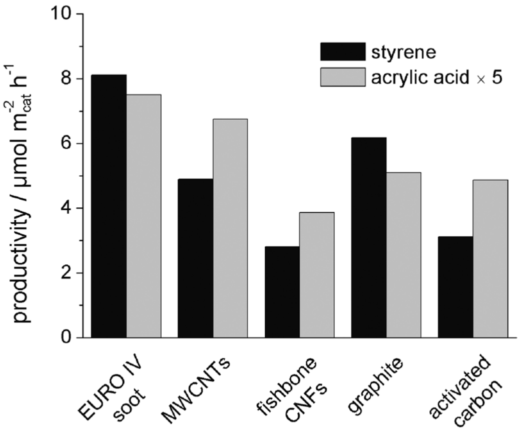

Figure 4. Catalytic activities of carbonaceous materials in the ODH of ethylbenzene to styrene (2 vol% EB/2 vol% O_2/He, 623 K) and in the selective oxidation of acrolein to acrylic acid (5 vol% C_3H_4O/10 vol% O_2/He, 573 K). Data compiled from the literature[17–21] and, if necessary, corrected with respect to the reaction conditions according to reported kinetic data.[17]

the curvature of the outermost carbon shells—which becomes more pronounced the smaller the spherical carbon particles are—promotes the activation of molecular oxygen. Carbon materials can be considered as bifunctional catalysts with two different surface properties, metallic and oxidic, associated to two different surface phases.[14]

Some of the environmental consequences and health effects are seen in the increased cytotoxicity and inflammatory potential of Euro IV soot toward human peripheral blood monocyte-derived macrophage cells (MDM). At the same mass concentration, soot particles produced under low-emission conditions (Euro IV) exhibit a much higher toxic and inflammatory potential than particles from old diesel engines operating under BS conditions.[6] BS soot particles did not induce significant signs of necrosis or apoptosis, whereas Euro IV soot particles produced extensive damage to the cells, as revealed by the appearance of numerous apoptotic and necrotic cells (Figure 5). The Euro IV soot particles were found to be more homogeneously distributed than the BS soot particles, which were found to aggregate into bigger clusters. Furthermore, the Euro IV soot particles were internalized by MDMs in a much larger number than the larger aggregates of BS nanoparticles. These results were confirmed in a recent study for several types of human lung cells, that is, monocultures of A549 human epithelial lung cells, human monocyte-derived macrophages, and monocyte-derived dendritic cells (MDDCs) as well as triple cell co-cultures consisting of all three cell types, after exposure to diesel exhaust particles.[23] It was found that the soot particulate penetrates into all the cell types and also in the co-culture. The formation of reactive oxygen species (ROS) was observed in all cases except for the MDDC monoculture. The key finding of this study is, however, that there is a synergistic effect between the different cell types, which interact to modulate the levels of total antioxidant capacity as well as the release of cytokines and chemokines. This means

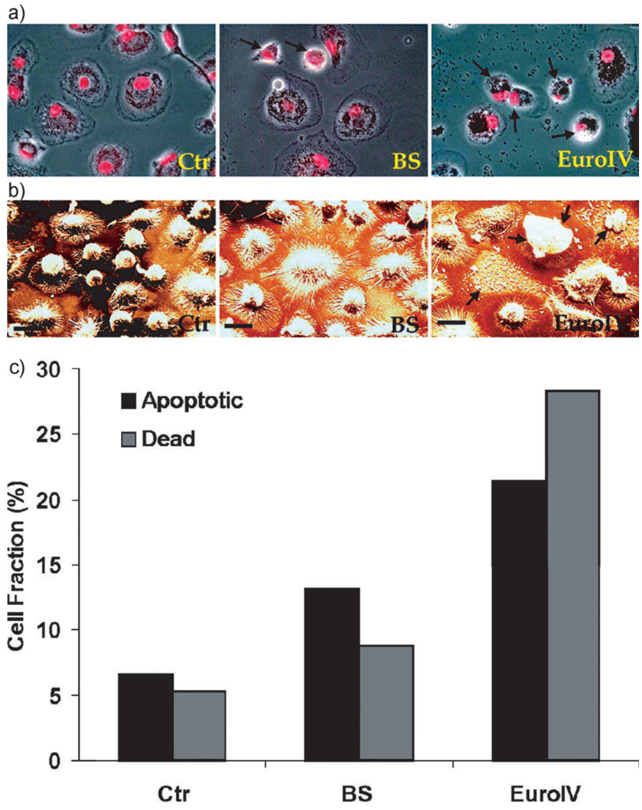

Figure 5. Untreated (control, Ctr) and particle-treated MDM cultures (BS or Euro IV soot). a) Phase contrast and fluorescence microscopy after staining the nuclei with propidium iodide (PI;red hue). Black arrows indicate apoptotic/necrotic cells. b) Scanning electron microscopy views of cells. c) Evaluation of dead cells by a live/dead cell vitality assay and of apoptotic MDM cells. Reprinted from Ref. [6] with permission. Copyright 2008, American Chemical Society.

that co-cultures are essential to evaluate the cytotoxicity and inflammatory potential of diesel particulate matter.

Diesel exhaust particulate is a major constituent of ambient air pollution and is associated with respiratory and cardiovascular diseases as well as skin cell alterations in vitro. Similar to airway epithelial cells, the epidermal cells are among the first cell populations to be exposed to chemical pollutants and are an important source of proinflammatory mediators. It was observed in recent experiments with human skin cells[24] that soot nanoparticles were spontaneously internalized by keratinocytes and distributed mostly around the cell nucleus. In these experiments the Euro IV soot particles also exhibited a much higher oxidative, profibrotic, and toxic potential on these cell types than BS soot particles collected from an older diesel engine.

In addition to these alarming effects of as-produced soot samples, a fatal post-activation can also occur. Recently, it was shown that the heterogeneous reactions of aerosol particles with ozone, which is formed ubiquitously in traffic zones by UV radiation induced reactions of nitric oxide with molecular oxygen, are of central importance to air quality.[25] Reactive oxygen intermediates with a lifetime greater than 100 s can play a key role in the chemical transformations as well as the adverse health effects of toxic and allergenic air-particulate matter, such as soot, polycyclic aromatic hydrocarbons, and proteins. This post-activation, however, could also affect larger and less defective diesel soot particulate.

In summary the major question arises whether the emissions from modern diesel engines are characterized by a potentially greater threat to humans. The answer is not straightforward. The reduction of the emission rate of soot nanoparticulate does not automatically lead to a reduction in the toxic effects toward humans if, concurrently, the structure and functionality of the soot changes and its biological, cytotoxic, and inflammatory potential increases. Clearly, on the basis of exposed units of surface area, the low-emission soots impose higher risks, as mentioned above. Moreover, ongoing structural analyses highlight that soot samples from diesel engines which already fulfill the emission criteria of the Euro VI standard, which will be introduced in 2013, are characterized by even smaller particles, higher defect density, and an increased degree of oxygen functionalization compared to the Euro IV soot.[26] Thus, future analyses of such soot samples can be expected to raise an even higher threat to environmental and human health. An additional question still under debate is the impact of biodiesel (blends) on the nanostructure and bioactive properties of the diesel particulates. However, a critical review of recent studies[27] tentatively indicates that the amount of soot and PAH emitted is equal to or reduced with biodiesel, and so is the general health effect. However, in vitro cytotoxicity studies cannot exactly reflect the in vivo conditions because of the unknown concentrations of in vivo exposure. What is needed is the definition of a dose of carbon surface exposed to a living system. The current use of biological effect per mass is inappropriate for estimating the biological potential of carbon materials. The highly reactive soot particulate is more susceptible to surface oxidation, even allowing its application as a heterogeneous catalyst in certain oxidation reactions. On the other hand, the total amount of emitted soot is substantially lower than that from older generations of diesel engines. Within the past 20 years the particulate emission level for heavy duty diesel engines decreased by almost two orders of magnitude, thus rendering an evaluation which combines qualitative and quantitative aspects difficult. Although the development of improved particle filters and novel methods for the removal of particulate in diesel cars is an ongoing task for industry, the ultimate answer might be provided by the future statistical analysis of mortality as a result of soot exposure. For 2003 in Germany, for example, 10000 to 19000 diesel soot related deaths, e.g., due to lung cancer, were estimated as a result of long-term effects.[28] The future course of this death rate will be the final benchmark for the appraisal of past and current efforts to overcome the environmental and health burden on diesel engine technology.

Received: July 30, 2012
Published online: January 10, 2013

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