

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

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Keywords:

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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, therefore become more popular and “welcome” as an alternative or even replacement of gasoline engines to reduce the emission of greenhouse and toxic gases. Another advantage in terms of environmental protection is the possibility to use non-fossil fuels such as long-chain alkyl esters (biodiesel) providing a lower carbon footprint than petrodiesel.^[1] The rapid increase of the share of new cars with diesel engine in the past 20 years in Western Europe is illustrated in Figure 1.^[2] This trend is expected to further increase within the next few years^[3] until the development of cheap and competitive hybrid technology is expected to bring the share of diesel and gasoline down to 15–35%, respectively, in 2030.^[4]

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 in their exhaust. 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 pyrolyzes to finally turn into a carbon deposit leading to the formation of soot. The presence of aromatics in the diesel fuel typically enhances the soot emission via the facile condensation of aromatic units to form larger polyaromatic hydrocarbons (PAHs), **whereas aliphatic compounds pass the growth mechanism via H-abstraction and consecutive (poly)acetylene addition**. There are two ways to eliminate or at least to decrease the amount of the particulate matter emitted from diesel engines: optimizing the combustion of diesel fuel in the engine and the after-treatment by installing particulate filters. The huge efforts made in these two directions are driven by the increasing awareness of the public on the potential cytotoxicity of soot particulate as recently confirmed by the World Health Organization WHO.^[5] As a consequence the legislation organ has imposed increasingly more strict emission levels.

A substantial decrease of the particulate emission rate by more than 95% (from 140 to 5 mg km⁻¹) can only be achieved by an essential improvement of the motor engineering. This

includes the construction of the engine as well as the combustion process of the diesel fuel. Among many modifications of the diesel engine, its equipment with a turbocharger or a supercharger greatly assists in increasing fuel economy and power output by relaxing the fuel-air intake speed limit. High injection pressures not only increase

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the amount of oxygen in the cylinders to favour complete combustion of the fuel but also improve its dispersion into smaller droplets, while the electronic control can adjust both the timing and the length of the injection process to optimise the combustion process at all speeds and temperatures.

However, from the chemical point of view a complete combustion (total oxidation) of the diesel fuel requires stoichiometric conditions with regard to the diesel/air ratio or an excess of oxygen at 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 heavy emission of black smoke (BS).

What are the structural and chemical differences of conventional and low-emission soot particles on the nanoscale? In general, the particulates are agglomerates of more or less spherical primary particles forming a secondary chain-like structure with final dimensions of up to 500 nm. The most evident change is in the size of primary soot particles as can be seen by transmission electron microscopy (TEM) of the samples collected directly from the exhaust gas of the engines (Figs. 1 a and b).^[6] Those emitted from a Euro IV engine exhibit a much smaller diameter than the BS particles from the older engine. The size distributions obtained from statistical analysis of primary soot particles are compared in Fig. 1 c. Euro IV soot is characterized by an average primary particle diameter of 10–15 nm combined with a very narrow size distribution. Instead, the soot of the older engine 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 as compared to 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 the modification of the diesel engine is the bulk and surface structure as well as surface functionalization 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, however, more bended, 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 hybridization within the 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 charge localization in the π -system of conjugated electrons on graphitic surfaces and those positions are potential and favoured anchoring points for surface functional groups by reaction with water or oxygen.^[10] The number of defects is smaller in the BS soot as indicated by the more flat BSU appearance (Fig. 1 a). Due to this highly defective structure, Euro IV soot contains more oxygen in the form of surface functional groups than conventional soot. Here, by means of infrared spectroscopy, the most abundant oxygen containing surface species were identified to be OH groups as well as a broad variety of C-O single and double bonds in agreement with a recent study pointing at the carboxylic groups being the dominant surface oxygen groups on diesel exhaust particulate.^{[11]-[13]} Their presence drastically increases the chemical reactivity of the carbon surface as indicated by a significant shift of maximum temperature in the CO_2 profiles of temperature-programmed oxidation of these soot samples.

A structural comparison of the Euro IV and the most recent Euro VI soot emission standards reveals a different response to a thermal treatment aimed to simulate 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 Euro IV and VI soot as depicted in Figure 3 and Table 1.

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		Onion-like carbon ^[14]
		(20°C)	(500°C)	(20°C)	(500°C)	(517 °C) ^[a]
529.8	Fe _x O _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 in Ref. ^[14] and in Ref. ^[15] was 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 to the preferential gasification of defective carbon atoms inside the particle leading to an apparent increase in their structural order, i.e., graphitization. This is accompanied by the formation of micropores to initiate the breakup of the soot particle into smaller particles and/or shrinking of the particle as a whole.^[16]

The Euro VI sample does not undergo changes in the particle size distribution, which would mean, according to the core-shell particle concept, that the outer shell hinders the oxidation/combustion. This would mean that the particles are not combusted at all, or if

combustion starts, the Euro VI particles combust completely, due to the higher reactivity of oxygen functional groups in the Euro VI sample than in the Euro IV sample.

Important to mention is the fact that the Euro VI sample does not only reduce the oxygen content but it changes the distribution of functional groups. Less stable oxygen groups are removed during the oxidation treatment or converted into more stable ones, as shown by the depth profile study.^[15] Thus, the oxygen species on the carbon surface of the soot particles is the most determining factor 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 probed by some heterogeneously catalyzed chemical reactions. Based on our expertise we 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 excess of steam, respectively. The initial productivity of the untreated Euro IV soot used as the catalyst in these reactions exceeds the data of well performing other carbonaceous materials compiled from literature (Fig. 4). However, due to the fragile and disordered nanostructure the soot catalyst is unstable under reaction conditions applied and the productivity collapses within hours, whereas the data for the other (nano)carbon catalysts shown in Fig. 4 could be obtained at steady-state conditions. Nevertheless, the pronounced chemical potential of fresh Euro IV soot in the form of highly activated oxygen surface groups, which correspond to the active state of high-performance heterogeneous catalysts, is impressively evidenced in these experiments.

The modifications performed on the diesel engine to fulfil the low emission standard have essentially changed the morphology and surface functionalization. In a recent study onion-like carbon with a related structural motif as observed for the soot particles (Fig. 2) was furthermore shown to successfully catalyze the ODH of *n*-butane to butenes and butadiene.^[22] It was concluded that especially the curvature of the outermost carbon shells, which is more pronounced the smaller the spherical carbon particles are, promotes the activation of molecular oxygen. **Carbon materials can be considered as bi-functional 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 an increased cytotoxicity and inflammatory potential of Euro IV soot toward human peripheral blood monocyted-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 an old diesel engine 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 of the cells, as revealed by the appearance of numerous apoptotic and necrotic cells (Fig. 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. Also the Euro IV soot particles were internalized by MDMs in a much larger number than the bigger aggregates of BS nanoparticles. **In a recent study, these results were confirmed 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 exposition to diesel exhaust particles.**^[23] Here it was found that the soot particulate penetrates into all the cell types and also in co-culture. The formation of reactive oxygen species (ROS) was observed in all cases except for MDDC monoculture. The key finding of

this study is, however, a synergistic effect between the different cell types, owing to their interaction to modulate the levels of total antioxidant capacity as well as the release of cytokines and chemokines. It means 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*. Like airway epithelial cells, the epidermal cells are among the first cell populations exposed to chemical pollutants and are an important source of pro-inflammatory mediators. In recent experiments with human skin cells^[24] it was observed that soot nanoparticles were spontaneously internalized by keratinocytes and distributed mostly around the cell nucleus. Also in these experiments Euro IV soot particles 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 proceed. Recently, it was shown that the heterogeneous reactions of aerosol particles with ozone, which is ubiquitously formed 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 and adverse health effects of toxic and allergenic air-particulate matter, such as soot, polycyclic aromatic hydrocarbons and proteins. These post-activation, however, could also affect larger and less defective diesel soot particulate.

In summary the major question arises whether the emissions of modern diesel engines are characterized by a potentially greater threat to human being. The answer is not straightforward. The reduction of the emission rate of soot nano-particulate does not automatically lead to a reduction of the toxic effects toward humans if, concurrently, the

structure and functionality of the soot changes and therefore its biological, cytotoxic and inflammatory potential, increase. Clearly, on a basis of exposed unit 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 fulfil the emission criteria of the Euro VI standard to be introduced in 2013, are characterized by even smaller particles, higher defect density, and increased degree of oxygen functionalization as compared to the Euro IV soot.^[26] Thus, future analyses of such soot samples can be expected to bring up an even higher threat to environment and human health. An additional question still under debate is the impact of biodiesel (blends) on DPM nanostructure and bioactive properties. However, a critical review of recent studies^[27] tentatively indicates that the amount of soot and PAH emitted is equal or reduced with biodiesel and so is the general health effect. In any case, *in vitro* cytotoxicity studies cannot exactly reflect the *in vivo* conditions due to the unknown concentrations of *in vivo* exposition. What would be needed is the definition of a dose of carbon surface exposed to a living system. The current use of biological effect per mass applied is inappropriate in estimating the biological potential of carbons. 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 for the older generations of diesel engines. Within the past 20 years the DPM emission level for HD diesel engines was decreased by almost two orders of magnitude rendering an evaluation, which combines qualitative and quantitative aspects, difficult. Although the development of improved particle filters and novel methods for particulate removal in diesel cars is an ongoing task for industry the ultimate answer could be given by the future statistical analysis of mortality due to soot exposition. For 2003 in Germany, an interval of 10.000 to 19.000 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 of the diesel engine technology.

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Figure Captions:

Figure 1. Share of diesel in new car registrations in Western Europe. Data adapted from ACEA.^[2]

Figure 2. High-resolution TEM images of (a) BS soot showing almost spherical soot particles, (b) Euro IV soot with core–shelled primary particles showing defective bulk and surface structure. Reprinted with permission from Ref.^[6]. © 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, © 2004.

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

Figure 4. Catalytic activities of carbonaceous materials in the ODH of ethylbenzene to styrene (2 vol.% EB/2 vol.% O₂/He, 623 K) and in the selective oxidation of acrolein to acrylic acid (5 vol.% C₃H₄O/10 vol.% O₂/He, 573 K). Data compiled from literature^{[17][18][19][20][21]} and, if necessary, corrected with respect to the reaction conditions according to kinetic data reported in literature.^[17]

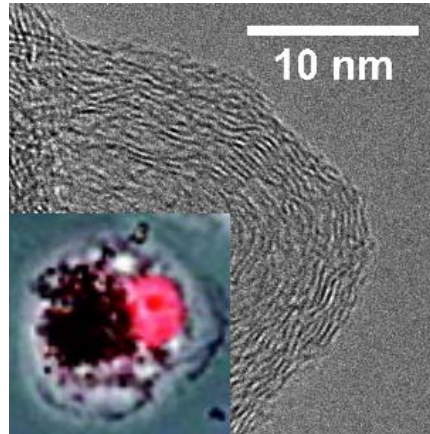
Figure 5. Untreated (control, Ctr) and particle-treated MDM cultures (BS or Euro IV soot). (a) Phase contrast and fluorescence microscopy after PI staining of nuclei (red hue). Black arrows indicate apoptotic/ necrotic cells. (b) Scanning electron microscopy views of cells. (c) Evaluation of dead cells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

Exhaust Emission

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Emission of Highly Activated Soot
Particulate – the Other Side of the Coin
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Soot toxification. The increasing chemical activity induced on the emitted soot particulate, which is produced by modern diesel engines is an unwanted side-effect of a modified motor engineering. This makes Euro IV and VI soots chemically and biologically highly active and hazardous. Taking these factors into consideration, the question arises whether the induced micro- and nanostructure overcompensates for the reduced net mass of diesel soot particulate emitted.

Benjamin Frank completed his PhD at the Technical University of Berlin (Germany) in 2007, and then moved to the Fritz Haber Institute (FHI) of the Max Planck Society as a post-doctoral fellow in the Department of Inorganic Chemistry. His research is focused on heterogeneously catalyzed selective hydrogenation and oxidation reactions and the application and design of nanostructured carbon materials in heterogeneous catalysis. Since 2011 he coordinates the carbon-related activities within the department.



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