19 Ceramic Catalysts, Supports, and Filters for Diesel Exhaust After-Treatment

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19.1 INTRODUCTION

19.1.1 DIESEL SOOT FORMATION

Since the invention by Rudolf Diesel in 1893, the application of the diesel engine has become very widespread across the world. The popularity of the diesel engine is a result of its attractive characteristics, such as fuel economy, durability, low maintenance requirements, and large indifference to fuel specification. Fuel efficiency for a diesel engine is 30 to 50% higher than that for a gasoline engine with comparable power. In other words the CO_2 emission will be 30 to 50% lower for a diesel engine for the same amount of generated power. CO_2 is one of the main greenhouse gases and contributes to global warning. If one wants to reduce the emission of CO_2 and at the same time maintain mobility via transportation, a transition from gasoline-powered engines to diesel-powered engines is a logical choice. Diesel engines are used in various fields. Transport applications of the diesel engine can be found in light passenger cars, trucks, construction equipment, and ships. Another large field of application is that of stationary power sources. Many electricity and hydraulic power plants are equipped with diesel engines.

Unfortunately, the reality of most combustion engines, including diesel engines, is that they encounter the problem of incomplete combustion, which leads to the emission of severe diesel pollutants.

During operation diesel fuel is injected into the cylinder. The liquid atomizes into small droplets, which vaporize and mix with air under pressure and burn. Fuel distribution is nonuniform, and the generation of unwanted emissions is highly dependent on the degree of nonuniformity. Carbonaceous soot is formed in the center of the fuel spray where the air/fuel ratio is low. Nonideal mixing of fuel and air creates small pockets of excess fuel where the solid carbonaceous soot particles (a solid and a soluble organic fraction, SOF) are formed [1–3].

Associated with carbonaceous soot, adsorbed hydrocarbons and small amounts of sulfates, nitrates, metals, trace elements, water, and unidentified compounds make up the diesel particulate matter (PM). A transmission electron microscopy (TEM) image and a schematic of the structure and composition of PM are shown in Figure 19.1 and Figure 19.2, respectively. Figure 19.3 illustrates the process of soot formation.

Adsorbed hydrocarbon, sulfate, and water act as "glue," causing multiple particles to agglomerate and shift the particle size and mass distribution upward [5]. PM is typically composed of more than 50% to approximately 75% elemental carbon (EC) depending on the age of the engine, deterioration, heavy duty versus light duty, fuel characteristics, and driving conditions. The hydrocarbon portion of PM originates from unburned fuel, engine lubrication oil, low levels of partial combustion, and pyrolysis products, and typically ranges from approximately 19 to 43%, although the range can be broader depending on many of the same factors that influence the EC content of PM. Polyaromatic hydrocarbons generally constitute less than 1% of the PM mass. Metal compounds and other elements in the fuel and engine lubrication oil are emitted as ash and typically make up 1 to 5% of the PM mass. Elements and metals detected in diesel emissions include barium, calcium, chlorine, chromium, copper, iron, lead, manganese, mercury, nickel, phosphorus, sodium, silicon, and zinc [4,5,8].

Together with particulate emissions, CO, hydrocarbon (HC), and NO_x are emitted as diesel exhaust gaseous pollutants. As with the formation of soot, CO and HC are the results of incomplete combustion. In contrast with soot formation, NO_x is created where the air/fuel ratio approaches stoichiometry and high temperatures are generated [9].

The output range of basic toxic material, the temperature, and the exhaust mass flow rate are summarized in Table 19.1. For gas and PM emissions, the lower values can be

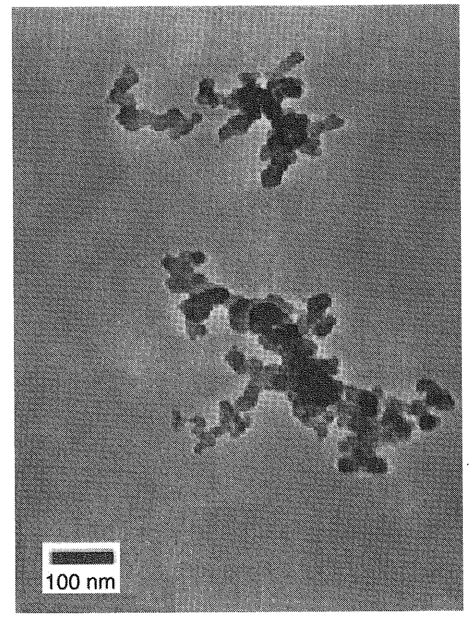

FIGURE 19.1 TEM image of PM < 10 μm (PM10) collected by impaction for 30 sec. (After Bérubé, K.A., Jones, T.P., Williamson, B.J., Winters, C., Morgan, A.J., and Richards, R.J., *Atmos. Environ.*, 33, 1599–1614, 1999.)

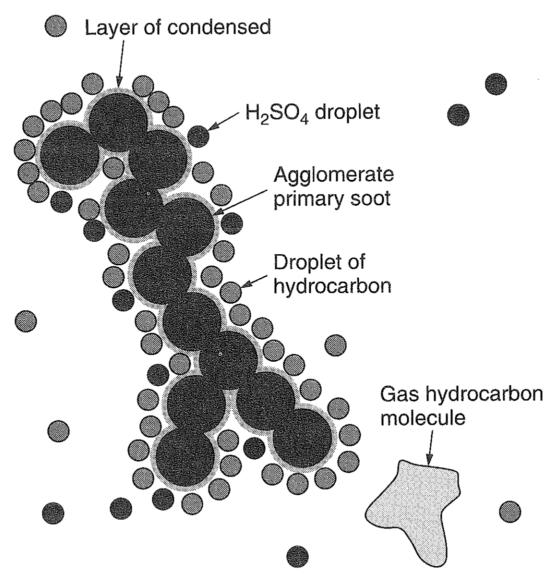

FIGURE 19.2 Schematic of diesel soot and its adsorbed species. (After Mark, J. and Morey, C., *Diesel Passenger Vehicles and the Environment*, Union of Concerned Scientists, Berkeley, CA, 1999, pp. 6–15 and Johnson, J.H., Bagley, S.T., Gratz, L.D., Leddy, D.G., SAE paper 940233, 1994.)

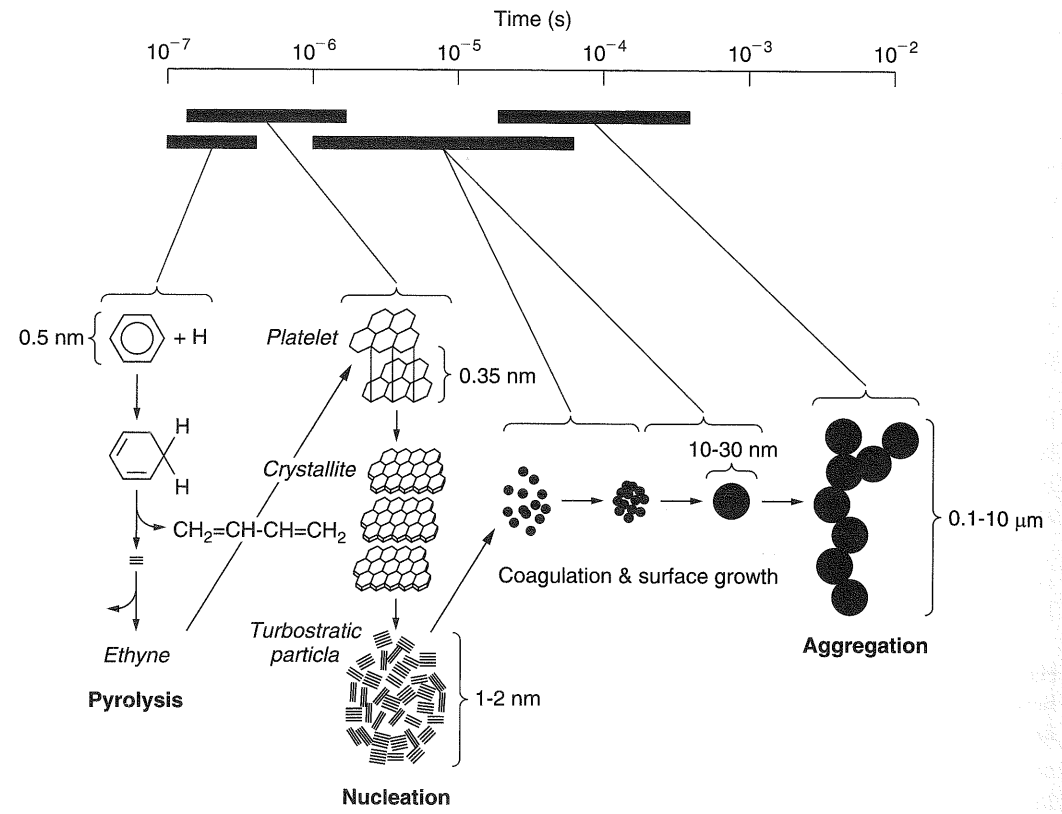

FIGURE 19.3 Formation of soot particle; a schematic mechanism [7].

TABLE 19.1
Typical Conditions of Diesel Exhaust [9–13]

	CO (vppm)	HC (vppm)	SO_2 (vppm)	NO_x (vppm)	PM (g/m^3)	Exhaust temp. (°C)	Exhaust flow rate (m^3/h)
Passenger car	150–1500	20–400	10–150	50–1400	0.01–0.1	100–360	40–50
Heavy-duty truck	n.q.	n.q.	n.q.	50–1600	0.05–0.25	100–450	15–125

n.q. = not quoted.

found in new clean diesel engines, while the higher numbers are characteristic of older engines [9–13].

19.1.2 Environmental and Health Effects of Diesel Particulate Emissions

Particulate matter from diesel engines emitted directly to the air is one of the origins of air pollution. Together with biomass combustion, fuel combustion contributes to the excess of soot particles at the lower troposphere level [14]. In urban areas, where exposure to diesel exhaust may be especially high, diesel engines will be a major source of particulates [15].

TABLE 19.2
U.S. Diesel Engine Emission Standards (g/kWh): Past, Present, and Future

Year	THC	CO	NO_x	PM (trucks)	PM (urban buses)
1974–1978	21.5	53.6			
1979–1984	2.0	33.5	13.4[a]		
1985[b]–1987	1.8	20.8	10.7		
1988–1989	1.8	20.8	10.7	0.8	0.8
1990	1.8	20.8	8.1	0.8	0.8
1991–1992	1.8	20.8	6.7	0.3	0.3
1993	1.8	20.8	6.7	0.34	0.13
1994–1995	1.8	20.8	6.7	0.13	0.09
1996–1997	1.8	20.8	6.7	0.13	0.07
1998–2003	1.8	20.8	5.4	0.13	0.07
2004	—	20.8	3.4[a]	0.13	0.07
2007	—	20.8	1.48[a]	0.014	0.014
2010	—	20.8	0.27[a]	0.014	0.014

[a]THC + NO_x (THC = total hydrocarbon).
[b]Test cycle changed from steady-state to transient operation.

The presence of soot as air pollutant has serious consequences for human health. In general, particles inhaled by humans are segregated by size during deposition within the respiratory system. Larger particles deposit in the upper respiratory tract while smaller inhalable particulates travel deeper into the lungs and are retained for longer periods of time. If the smaller particles are present in greater numbers, they have a greater total surface area than larger particles of the same mass. Therefore, the toxic material carried by small particles is more likely to interact with cells in the lungs than that carried by larger particles [16,17].

Diesel PM smaller than 10 μm, PM10, not only penetrates deeper and remains longer in the lungs than larger particles, but it also contains large quantities of organic materials that may have significant long-term health effects. Linear- and branched-chain hydrocarbons with 14 to 35 carbon atoms, polynuclear aromatic hydrocarbons (PAH), alkylated benzenes, nitro-PAHs, and a variety of polar, oxygenated PAH derivatives are common particulate-bound compounds. Several of them have the potential to be carcinogenic and mutagenic [18,19].

Diesel emission legislation applied in the past forced car manufacturers to comply and reflected levels of diesel emissions with time. In Table 19.2 the U.S. emissions regulations for heavy-duty trucks and urban buses are presented as an example.

19.1.3 Strategies in Diesel Engine Emissions Control

The emissions of diesel engines are greatly influenced by engine variables such as combustion chamber design, air/fuel ratio, rate of air/fuel mixing, and fuel injection timing and pressure. For a diesel engine the emissions of PM and NO_x have an inverse correlation. An effort to reduce soot particles is always associated with an increase in NO_x. This is called the trade-off of soot and NO_x. For example, so-called exhaust gas recirculation (EGR) and retarded injection can reduce the NO_x emission, but at the same time increase particulate emission (Figure 19.4, curve 1). However, high-pressure injection and cooled EGR can suppress the particulate emission but they increase NO_x emissions (Figure 19.4, curve 2)