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Multi-catalytic soot filtration in automotive and marine applications

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ABSTRACT

The emission of particulate matter (PM) and NO_x from diesel engines has proven to have a negative influence on health, and future regulations will require more than 90% PM and NO_x removal. For land-based trucks using low-sulfur fuels, a sequential catalyst system is foreseen consisting of an upstream diesel oxidation catalyst (DOC), a catalyzed diesel particulate filter (cDPF), and a downstream SCR NO_x removal catalyst together with an ammonia slip catalyst (ASC). Urea is injected as a precursor for ammonia: engine → DOC → cDPF → $Urea_{inj}$ → SCR → ASC → out. The SCR function can with process advantage be integrated into the filter and reduce volume. The trapped soot in the cDPF must currently be combusted away. Three different soot combustion mechanisms are used: (1) passive soot regeneration by NO_2, (2) combustion by direct catalyst soot contact, and (3) active soot regeneration with O_2 at around 600 °C. Full soot combustion by direct catalyst soot contact is not needed in a system as soot combustion by NO_2 and O_2 gases plays major roles. For marine vessels, no PM emission regulation exists today. The emission problem is especially severe for vessels using heavy-fuel oil (HFO) with up to 3.5% sulfur and high (heavy) metal content, fuel properties that until now have prevented a reliable PM removal process. Recently, however, a catalyst-assisted passive soot regeneration process above 350 °C was developed including an "in situ" ash removal. This new process was validated on a ship using a sulfur-resistant Pd,V_2O_5 filter catalyst that combusts soot, CO, and HC including PAHs, and it is well suited as front end for an SO_x scrubber.

1. Introduction

Today, diesel engines all over the world play an important role in the modern society, as they are used widespread in trucks, buses, ships and passenger cars due to their relatively low fuel consumption and great reliability. Emission of particulate matter (PM) in combination with NO_x from engines has proven to have a negative influence on health such as lung diseases with premature death, on local climate such as smog formation in cities, and further on global warming such as black carbon. Regulations in combination with catalyzed filter processes have in some parts of the world largely reduced PM emissions; however, in other parts of the world and for seagoing ships, the implementation of known catalyzed solutions or the development of new PM reduction processes is still a compelling problem. In the near future, engine development alone does not seem to be able to reduce the engine-out particulate matter, particle number, or NO_x to meet present and future emission regulations. This implies that today catalyzed filter processes must play an environmental key role and, in the future, will be even more intensified in the abatement of the PM and NO_x emission problem. It furthermore means that improved PM filtering catalysts and processes that can also reduce NO_x are needed and will be developed on the basis of catalyst science and innovation. This paper gives an overview of the present catalytic standing for PM removal process systems for land- and marine-based diesel engines.

2. PM filtration involves multi-catalyst reactions

For removal of diesel particulate matter (PM), a number of filter types have been developed and tested over the years, but today the

Abbreviations: ASC, ammonia slip catalyst; cDPF, catalyzed diesel particulate filter; CRT, continuously regenerating trap; CSF, catalyzed soot filter, same as cDPF; Cu-DPF, Cu-SAPO-34 SCR catalyst integrated in DPF; Cu-ft, Cu-SAPO-34 SCR flow-through catalyst coated on cordierite; DPF, diesel particulate filter; DOC, diesel oxidation catalyst; FBC, fuel-borne catalyst; GWP, global warming potential; HC, hydrocarbons; HDV, heavy-duty vehicle; HFO, heavy-fuel oil; LSMGO, low-sulfur marine gas oil (below 0.1% S and made from distillate); MDO, marine diesel oil (a blend of heavy gasoil); PAH, polyaromatic hydrocarbon; PAH_{Phe}, polyaromatic hydrocarbons measured as phenanthrene equivalent as ppb; PGM, precious group metals; PM, particulate matter; REO_x, oxides of rare earth elements; SAPO, silica alumina phosphate; SCR, selective catalytic reduction; SECA, sulfur emission controlled areas; SOF, soluble organic fraction. Hydrocarbon fraction of soot; V-DPF, $V_2O_5/WO_3/TiO_2/SiO_2$ SCR catalyst integrated in DPF; V-ft, $V_2O_5/WO_3/TiO_2/SiO_2$ SCR flow-through catalyst coated on cordierite; VSCR, vanadium-based SCR catalyst; WHTC, world harmonized transient cycle; ZSCR, zeolite type SCR catalyst.

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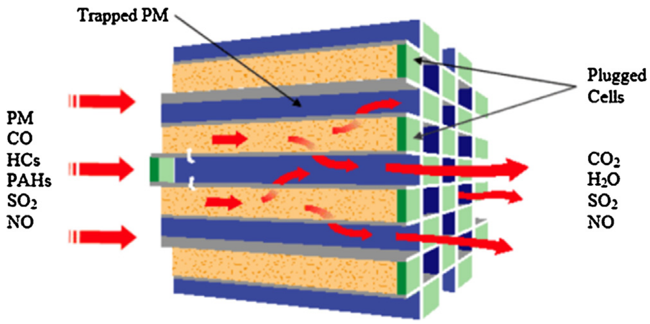

Fig. 1. Function of a catalyzed wall flow filter [1].

preferred PM trapping technology is the use of a ceramic wall flow filter. The preferred ceramic filter materials are cordierite, silicon carbide, aluminum titanate, and mullite. The PM trapping principle and main reactions of a catalyst-coated wall flow filter are shown in Fig. 1 from MECA [1].

It is quite easy to filtrate the particulate matter (soot) from the engine exhaust by 90–99% for both PM mass and number; however, as the accumulated soot in the filter increases, the pressure drop will progressively influence the fuel consumption and, in the end, stop the engine if the soot is not frequently or constantly removed by combustion reactions. The soot-oxygen reaction rate is low at normal exhaust temperatures of 200–500 °C. Thus, PM trapping and removal reactions imply a number of catalyzed bricks for several catalytic reactions in a whole system. When also NO_x has to be converted, the catalyzed soot reactions must be compatible with these NO_x reactions.

Consequently, PM trapping and removal do not only involve one catalyst but several catalysts in a series involving several chemical reactions in a system—a sort of a “chemical plant”. Fig. 2 shows an example of such a system developed to meet EURO VI and US EPA 2010 regulations including both PM and NO_x removal. The important catalyst bricks for PM reactions are shown within the circle.

3. DPF catalyst formulations and reactions for automotive

The diesel filter exhaust catalyst system for only PM removal as indicated in the circle in Fig. 2 and, inter alia, used to meet Euro V or EPA 2007 truck regulations, is composed of an oxidation catalyst (DOC) and a catalyzed particulate filter, cDPF, as shown in Fig. 3 together with the main chemical reactions taking place on the single catalyzed bricks.

As the soot oxygen reaction rate is low at normal exhaust temperatures of 200–500 °C, the system in Fig. 3 has to be a combination of a diesel oxidation catalyst that can both generate NO_2 and increase temperature plus a catalyzed diesel particulate filter, cDPF, that facilitates soot combustion in the whole temperature range of 250–650 °C by the different mechanisms. The cDPF is typically coated with a catalyst combination of

1) base metal catalysts such as stabilized cerium oxide for decreasing the temperature of soot oxygen combustion by direct contact with soot, and

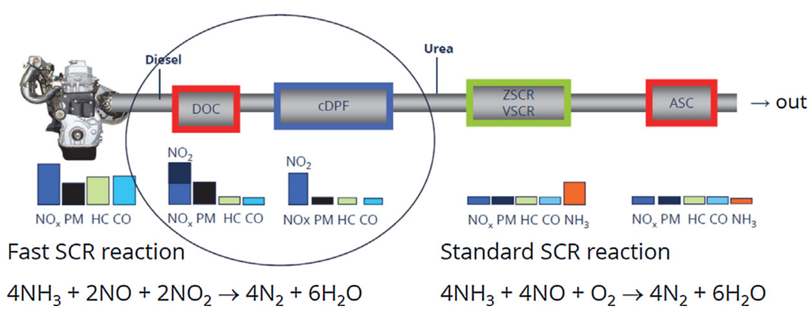

Fig. 2. Euro VI and EPA 2010 complicated PM after treatment system with additional NO_x reactions.

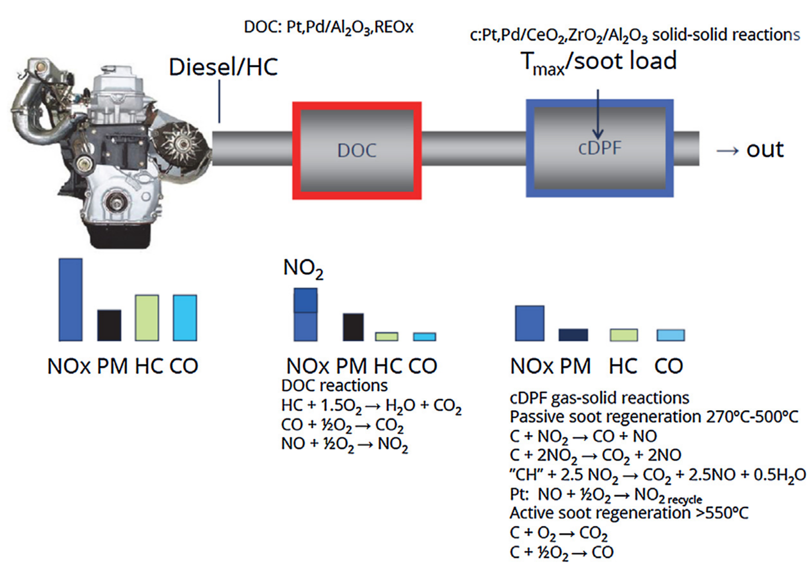

Fig. 3. PM catalysts with reactions to meet Euro V and US EP 2007. REO_x refers to rare earth element oxides.