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Nanolubricants for diesel engines: Related emissions and compatibility with the after-treatment catalysts

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ABSTRACT

The effect of the lubricant oil additivated with MoS_2 nanopowders was assessed through a set of full-scale tests on a real diesel engine – several engine points and cooling water temperatures were investigated for both a reference oil and a MoS_2-additivated one. The emission abetment efficiency of the DOC and DPF reduces the gas and solid pollutants obtained with the MoS_2-additivated oil to levels equivalent to the ones reached with the reference oil. An endurance test of 100 h (equivalent to 10,000 km) proved the stability of the catalytic system and the suitability of commercial after-treatment catalysts to cope with the emission modifications induced by the inclusion of nanoadditives in the oil matrix.

1. Introduction

Fluid lubricants are used in almost every field of human technological activity and their purpose is multi-fold – they reduce frictional resistance, protect the contacting surfaces of engines against wear, remove wear debris, reduce heat and contribute to cooling, improve fuel economy and reduce emissions.

Advanced nanomaterials have shown some promise because of their contribution to reducing friction and enhancing protection against wear [1–3]. When incorporated in full lubricant formulations in a stable way, and if their performance benefits can be sustained under those circumstances, they offer the possibility of some performance breakthroughs which have not been witnessed since the development of the now ubiquitous anti-wear additives, zinc dialkyl dithiophosphate (ZDDP) and molybdenum dithiocarbamate (MoDTC). It has been demonstrated that ZDDP and MoDTC used together improve the friction and anti-wear performances by the formation of a molybdenum disulfide layer on the rubbing surfaces [4–6]. The developments brought by nanomaterials can contribute to a substantial energy saving, reduce equipment maintenance and lengthen the life of the machines. In the case of engine oil (crankcase) applications, these nanomaterials can help increase the durability and performance of exhaust-treatments and reduce harmful emissions – in fact, exhaust catalysts tend to become poisoned by sulfur and phosphorus that are present in conventional lubricant additives. As a matter of fact, the stability of the nanomaterials, coupled to the reduction of the content of ash-giving metal additives in the lubricant oil formulation, can lead to an overall reduction of ash emissions and longer life of diesel particulate filters.

Nanostructured transition metal dichalcogenides, with the generic formula MX_2 (M=W, Mo; X=S, Se), whose synthesis was first demonstrated at the Weizmann Institute by Tenne and co-workers [7–9], seem to be very promising materials to be dispersed as nanoparticles in the oil matrix. They involve a reaction between MO_3 and H_2S, in reducing atmosphere at high temperatures, and the corresponding sulfide (WS_2 or MoS_2) is obtained. Many other synthetic routes have also been followed to obtain these kinds of nanostructured materials [10–12].

The specific lubrication mechanism ascribed to these metal sulfides, often called inorganic fullerenes due to their peculiar structure of spherical concentric layers, is currently debated; however, several studies clearly indicate that an exfoliation process of these layers, and the consequent liberation of nanosheets directly inside the surface contact area, is the prevalent lubricating mechanism for these systems [13,14]. This is very interesting because the lubrication additive is brought directly in the contact area without any prior chemical reaction, avoiding the transient period characteristic of the current additives. It was also hypothesized that these nanoparticles behave as nanoball bearings, due to their spherical shape, ultra-hardness and nanosize, at least temporarily until they gradually deform and start to exfoliate giving rise to the observed low friction coefficients – investigations involving direct visualization of the nanoparticle behavior in the contact area, over a broad pressure range, were attempted by combining Transmission Electron Microscope (TEM) and Atomic Force Microscopy (AFM) [15].

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The present study focuses on MoS_2 nanoparticles which have to be incorporated in engine lubricant oils. A wet synthesis technique has been devised within our group [16], which is based on the preparation of an aqueous solution of citric acid and ammonium molybdate to form a complex of molybdenum(IV) with citric acid, to which a suitable amount of ammonium sulfide was added to obtain MoS_2. This technique resorts to a simple and scalable process, and involves low cost reagents, instead of other more complex reaction methods. An example of the MoS_2 particles obtained with this technique is depicted in Fig. 1. Moreover, this synthesis route is extremely versatile since it can be adapted for continuous MoS_2 particle production, in specific devices that allow to control the particle diameter and obtain reproducible results in terms of particle size distribution [17,18].

As previously mentioned, a progressive poisoning of after-treatment catalysts occurs due to the presence of species that were originally present in the lubricant oil as additives, and which are then released into the flue gases after in-cylinder combustion. One major requirement for the application of these nanoparticles as lubricant oil additives, in substitution to the currently adopted ones, is their complete compatibility with the catalytic substrates present in the after-treatment line, whose lifetime operation should not be affected to any great extent. This analysis is crucial for the introduction of such nanosized additives for lubricant oils on the market, and in this work was applied to EURO V-compliant catalysts for DOC, DPF and SCR systems.

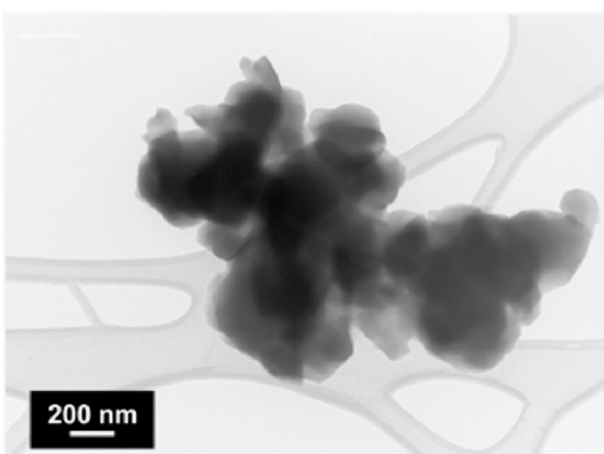

Fig. 1. TEM micrograph of MoS_2 nanoparticles.

2. Experimental

One important requirement for the application of these nanoparticles as lubricant oil additives is their compatibility with the catalytic substrates present in the after-treatment line – therefore, an assessment was carried out about a possible interaction between the MoS_2 nanopowders and some commercial catalysts, representative of EURO V-compliant catalytic converters present in the after-treatment line of light-duty diesel engine vehicles, for which a diesel engine bench (OPEL 1900 cm^3 JTD common Rail) connected to a dynamometer (AVL Alpha 240 kW) with a maximum rpm/torque of 10,000 rpm/600 Nm, was used (schematically depicted in Fig. 2).

The experimental campaign was carried out in different steps – initially, the engine was conditioned with a commercial synthetic oil (multi-grade SAE 5W-30 provided by Fuchs Lubricants), through a standardized procedure for internal oil circulation before the test was started. Then, five different engine points were tested in order to reproduce the different operation conditions of the car (engine frequency in rpm and bpme in bar: 1500×1, 2000×2, 2500×3, 3000×4 and 3500×5, all with 0% EGR), and for each engine point four different cooling water temperatures of the engine were fixed (40, 60, 80 and 95 °C). The exhaust gas recirculation was fixed to zero in all operating conditions. These settings were operated through a dedicated AVL PUMA program, by monitoring all engine conditions with INCA software connected to the Electronic Control Unit (ECU) integrated with ETAS and BOSCH instrumentation – the temperature of the cooling water, of the engine outlet exhaust gases and of the lubricant oil were measured with K-type thermocouples.

The same procedure was adopted for the MoS_2 nanoparticle-additivated oil, whose concentration was 0.5 wt%.

The tests consisted in monitoring and measuring the gas composition, particle size distribution, the temperature and pressure, at each engine point and in each cooling water temperature in the engine on steady state. In particular, the gas composition was continuously monitored before and after both the Diesel Oxidation Catalyst converter (DOC) and the Diesel Particulate Filter (DPF), with an ABB gas analyzer, equipped with two Uras26 analyzers for N_2O, NO, CO_2, CO and SO_2, and a Magnos206 analyzer to measure O_2. The HCs were measured with a Multifid14 analyzer Hartmann&Braun. The smoke number was measured with a Variable Sampling Smoke Meter AVL 415S G002. The soot particle size distribution was recorded using a Scanning Mobility Particle Sizer 3080 (SMPS), which consists of an impactor (type 0.0508 cm), a neutralizer, a differential mobility analyzer, and a condensation particle counter, with the sheath and aerosol flows set to 6 and

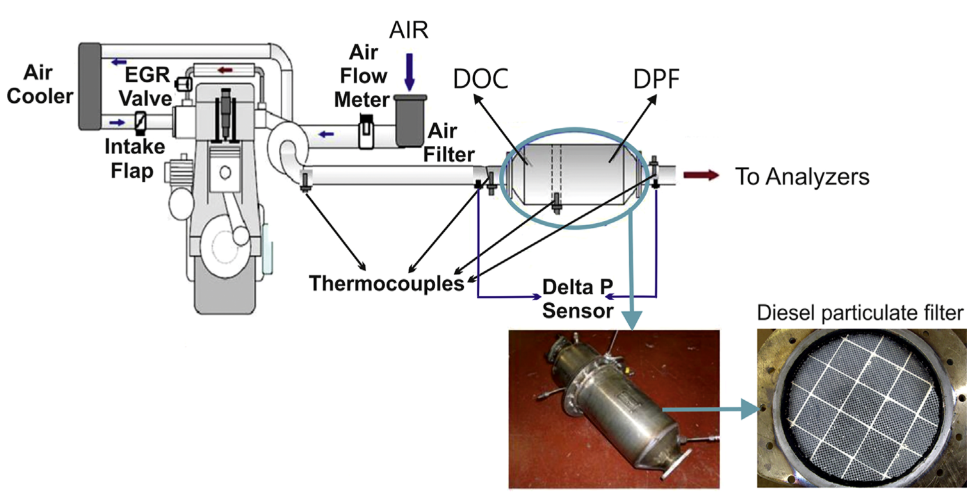

Fig. 2. Schematic of the diesel engine bench.