

Diesel NO_x aftertreatment catalytic technologies: towards a convergence of the catalytic chemistry?

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It is widely recognised that diesel engine vehicles are fated to significantly increase their worldwide market penetration, even in countries like the United States where the present market share is not as significant as that of gasoline engines. This is mainly due to the fact that diesel engines are inherently more thermodynamically efficient than petrol engines and thus they offer the prospect of reducing emissions of carbon dioxide as well [1,2].

However, diesels produce higher emissions of nitrogen oxides (NO_x) and particulates.

The tail-pipe emissions levels that can be achieved depend upon both the engine-out emissions and the performance of the emissions control system. Improvements in combustion and/or alternative fuels can lead to lower NO_x emissions, but it is widely accepted that in order to meet future legislative emissions standards (Euro6 for light duty vehicles and EuroVI for Heavy Duty engines, as well as the US 2010 Bin5), the employment of after treatment systems will be required [1,2]. Indeed, diesel particulate filters (DPFs) will be needed to achieve the PM emission levels regardless of the system used to reduce NO_x. But, most importantly, the significant CO₂ reduction (i.e. the improved fuel consumptions) that will be also dictated by future regulations will imply a drastic decrease in the average temperature profile of the exhaust gases; in such conditions, the catalytic removal of NO_x is extremely challenging. In fact, a significant portion of the new test cycles (both the NEDC, New European Driving Cycle, and the WHTC, World Harmonized Transient Cycle), is characterized by a very low exhaust temperature profile [2].

Currently, there are two main after-treatment technologies under consideration as potentially compliant with such strict limits: the Lean NO_x Trap systems, which are used with direct injection gasoline and diesel engines, and the NH₃/urea Selective Catalytic Reduction (SCR) for diesel engines.

Lean NO_x Traps were first developed and put into the market by Toyota to remove NO_x from vehicles equipped with lean burn engines [3]. NO_x are stored under lean conditions in the form of nitrites and nitrates that are reduced to nitrogen during a short rich excursion. LNT materials typically consist of a NO_x storage component, such as an alkaline earth metal oxide (e.g. Ba), and of a noble metal (e.g. Pt) that catalyzes the oxidation of NO_x, CO and of hydrocarbons and the reduction of stored NO_x as well. In spite of the fact that these catalysts are being used at the commercial scale, common agreement on the mechanisms of the storage of NO_x and of their subsequent reduction is still lacking [3].

SCR was the European motor industry's main technology of choice to meet Euro4 and Euro5 emissions requirements for heavy-duty diesel engines and during the last year it has been announced by some manufacturers for light-duty applications in the US and more recently in Europe, as well [1]. An SCR system is designed to catalytically reduce NO_x emissions in the oxygen rich environment of diesel exhaust by injecting urea as reducing agent [4]. A Diesel Oxidation Catalyst is also present in the system configuration, upstream of the SCR converter,

to partially convert NO to NO₂; this permits the flow entering the SCR reactor to contain significant amounts of NO₂ in addition to NO, and thus the onset of the SCR deNO_x reactions can occur at lower temperature, in comparison to the case where most of NO_x is made of NO alone.

During the last few years, both LNT and SCR catalytic processes have been widely investigated in our labs: this paper will report on the main results of these studies and in particular it will analyse the chemistry and the reaction pathways operating for the reduction of NO_x in both the processes, in order to highlight the similarities/differences between them.

A systematic study of the reduction by hydrogen under near isothermal conditions of NO_x species adsorbed on model Pt-Ba/Al₂O₃ LNT catalysts was performed: it was found that the reduction process is not initiated by the thermal decomposition of the stored NO_x ad-species, but a catalytic pathway involving Pt is instead operating. It was also shown that such a catalytic pathway is composed of two consecutive steps in which NH₃ is formed as an intermediate upon reaction of nitrates with H₂, and further reacts with nitrates to produce selectively N₂ [5,6].

The reactions involved in the NH₃-NO/NO₂ SCR reacting system were investigated by an extensive set of various unsteady state experiments performed over both vanadium based and zeolite based commercial catalysts: the bulk of results led to the proposal of an original global mechanistic scheme of the different reactions that compose the complete NH₃-NO/NO₂ SCR reacting system. In such a scheme, a key role is played by nitrate species, which are formed by NO₂ disproportion onto the catalyst surface and are then reduced by NO to nitrites. These species lead then to nitrogen upon reaction with ammonia [7,8].

Accordingly, in both LNT and SCR chemistries, the reduction of NO_x involves nitrite and nitrate surface species, which are selectively reduced to nitrogen by ammonia, either formed as intermediate or supplied as a reactant.

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