

Preface

It is widely recognized that Diesel vehicles are sure to significantly increase their worldwide penetration, particularly in countries like the United States where the present market share is not remarkable in comparison to that of vehicles with gasoline engines. This is mainly due to Diesel engines being inherently more thermodynamically efficient than spark-ignition engines, thus offering the prospect of reducing emissions of carbon dioxide.

Diesels produce, however, higher emissions of nitrogen oxides (NO_x) and particulate matter (PM). The emissions levels which can be achieved depend on both the engine-out emissions and the performance of the emissions control system. For the engine-out emissions, there is a well-known trade-off between PM and NO_x. Such a trade-off is not, however, a constant relationship between the two pollutants. Developments in combustion systems, fuel injection equipment, turbocharging, and associated control systems have allowed and continue to allow the trade-off curve to move to lower values of both NO_x and PM. The trade-off thus gives engine developers the opportunity to combine the optimization of 'raw' emissions and fuel economy with the optimization of the emissions control system.

Improvements in combustion and/or alternative fuels can lead to lower NO_x emissions, but it is generally recognized by now that, in order to meet the current and forthcoming legislative emissions standards both in Europe and in the USA, the application of after treatment systems is required. Indeed, Diesel particulate filters (DPFs) are 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 is also dictated by the upcoming regulations, are forcing a drastic decrease in the average temperature profile of the exhaust gases; in such conditions, the catalytic removal of NO_x becomes extremely challenging. In fact, a significant portion of the present test cycles (e.g., the NEDC, New European Driving Cycle, and the WHTC, World Harmonized Transient Cycle) is characterized by very low exhaust temperatures. This makes very difficult the fulfillment of NO_x emission limits.

Currently, the major deNO_x after-treatment technologies under consideration include the so-called Lean-NO_x Traps (LNT), which are used with direct injection gasoline and Diesel engines, and the Selective Catalytic Reduction (urea-SCR) process.

Urea-SCR was the European motor industry's technology of choice to meet Euro 4 and Euro 5 emissions requirements for heavy-duty Diesel engines and more recently was also applied to light-duty vehicles and passenger cars in the USA and in Europe, as well. An SCR system is designed to catalytically reduce NO_x emissions in the oxygen-rich environment of Diesel exhausts. To this purpose, the SCR system needs a chemical reagent, or reductant, to help convert the NO_x to nitrogen: in mobile applications, the preferred reductant is typically an aqueous solution of nontoxic urea, which is used as an ammonia source. In fact, the so-called Adblue[®] solution (or DEF, Diesel Emission Fluid) is injected into the exhaust system where it is decomposed to NH₃.

Usually, a Diesel Oxidation Catalyst is also present in the system configuration, upstream of the SCR converter, to partially convert NO to NO₂; this enriches the stream entering the SCR reactor with significant amounts of NO₂ in addition to NO, and thus enables the onset of the SCR deNO_x reactions at lower temperature in comparison to the case where most of the NO_x is composed of NO alone.

Urea-SCR was first brought to the market in 2005 for heavy-duty vehicle applications by Daimler AG (DaimlerChrysler at the time) under the trade mark BLUETEC[®], based on the use of extruded honeycomb monolith catalysts consisting of V₂O₅-WO₃-TiO₂, similar to those extensively used worldwide for the control of NO_x emissions from power stations and other stationary sources. Subsequently, we have seen a trend in the automobile industry to replace Vanadium-based SCR catalysts with a new generation of metal-exchanged zeolite-based systems in order to expand the operating temperature window and to solve the high temperature deactivation problems typical of the anatase-rutile TiO₂ transition. A variety of zeolites have been proposed for this purpose (e.g., ZSM-5, mordenite, beta, ferrierite, Y-zeolite, and more recently chabazite). Zeolites are generally promoted by transition metals, such as iron and copper: the resulting catalytic systems are associated with an excellent deNO_x activity, particularly in the case of the Cu-zeolites. Indeed, metal-promoted zeolites have rapidly become the class of automotive SCR catalysts of choice, making urea-SCR the leading deNO_x technology nowadays. In the last few years, the improvement of the critical low-temperature deNO_x activity has been impressive, primarily due to the development of a new generation of Cu-promoted catalysts based on small pore zeolites, which also exhibit unparalleled stability with time-on-stream. The fundamental reasons for such enhanced performance, however, are not fully understood yet: they currently represent the objective of many academic and industrial research efforts.

There are several additional complications in using urea-SCR, including for example. The need for efficient ammonia release from the urea solution, and the related risks of deposits in the exhaust system due to by-products formation. Another issue is the accurate ammonia dosage: there should be enough ammonia present on the catalyst to reduce all NO_x, but at the same time there must be no excess of ammonia, to prevent its slippage from the vehicle. In order to realize this balance, a deep understanding of the influence of the operating conditions on the amount of ammonia stored on the catalyst, and on the rates of ammonia

adsorption/desorption, is crucial for the design and particularly for the control of SCR catalytic converters for vehicles. Ammonia slip catalysts represent a recent development in this area. Another area of current development is related to the fact that the SCR catalyst is often placed downstream of the Diesel Particulate Filter (DPF), in order to meet the requirements on soot particle emissions. On one hand, this configuration exposes the SCR catalyst to very high temperatures during DPF regeneration, so that its hydrothermal stability is a major concern. On the other hand, the multifunctional combination of DPF and SCR in a single device (SCR catalyst coated onto the DPF) presents several advantages, and is receiving considerable attention.

Finally, mathematical modeling has been recognized since the early days as a critical tool for timely and cost-effective development of urea-SCR technology for vehicles. This has resulted in a significant evolution, wherein the initial simple empirical models have been progressively replaced by the present sophisticated, chemically and physically consistent models, used in many companies to generate reliable simulations of NO_x emissions in highly transient test cycles for a wide range of conditions and parameters. Further efforts are being devoted to incorporate more details of the SCR catalytic chemistry, and to relate them to the catalytic features.

Several years after its first commercial applications, the development of urea-SCR has now clearly turned into a success story, with positive and promising perspectives and still many opportunities for further improvements and breakthroughs in a number of areas. So now, it is probably a good time to review the status of the technology, and highlight the next challenges.

This book provides a complete overview of the selective catalytic reduction of NO_x by ammonia/urea (urea-SCR), drawing from the know-how of many leading experts in the field. The book begins with a discussion of the technology in the framework of the current context (legislation, market, system configurations), covers the fundamental aspects of the SCR process (catalysts, chemistry, mechanism, and kinetics) and eventually analyses its application to the real scale (modeling of full scale monolith catalysts, control aspects, ammonia/urea delivery systems and strategies, integration with other devices for combined removal of pollutants). The book concludes with case histories presented by two companies which have greatly and creatively contributed to make urea-SCR a well-established and crucial technology for the automotive industry.

The book is aimed primarily at researchers in industry and academia working on exhaust gas aftertreatment systems. Several chapters however provide reference material that will be useful for teaching general courses on catalytic processes for environmental protection, or dedicated courses on the Selective Catalytic Reduction of NO_x.

Finally, this book is the result of the work of a number of industrial and academic experts: all of these persons are to be congratulated for devoting their time and effort to the present volume.

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Diesel Exhausts

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