

Actively Controlled Catalytic Systems With a “Memory” For Diesel Exhaust Emissions Reduction

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The 2007/2010 US EPA diesel exhaust emissions regulations are associated with a number of fundamental challenges, primarily selective reduction of NO_x in the net lean environment across a very broad range of conditions and poor reactivity of diesel soot towards oxidation under typical diesel exhaust conditions. Further challenge is associated with the need to actively control the aftertreatment systems, either continuously or in a periodic manner, based on the catalyst short-term history, long-term degradation factors, or driving conditions. This effectively leads to a need for sophisticated, often kinetic models-based control. Implementation of such systems therefore requires detailed quantitative understanding of their performance and degradation and often drives development of the nontrivial analytical approaches, especially for the inherently non-steady-state, periodically operated systems.

Lean NO_x Trap catalyst (LNT) technology is among the key candidates for meeting the unprecedented challenge of these US EPA regulations [1]. Operation of LNTs is inherently complex, encompassing oxidative storage of NO_x on the catalyst surface under the net oxidizing conditions typical for diesel exhaust; periodic transition to the artificially induced net reducing conditions, which involves reductant transformation processes such as steam reforming and water-gas shift (WGS), as well as reduction of the catalyst surface; and finally release and reduction of NO_x to N₂ or other products. Such operation requires LNT catalyst to contain a combination of red-ox and acid-base components, serving a variety of functions depending on the operation mode. The NO_x storage-reduction cycle, usually occurring with a periodicity on the order of minutes, is superimposed with another, much slower cycle, related to accumulation of SO_x on the catalyst surface and its periodic removal to maintain high efficiency. The sulfur removal occurs under a net reducing, high temperature environment, substantially outside the range of conditions typically found in diesel exhaust. Such exposures are largely responsible for the progressive aging of the catalyst, which affect various LNT functions to different extent. Thus, at any point in time, instantaneous efficiency of NO_x removal by LNT is not a “state function” of the reaction conditions alone, but is affected by the LNT history with regards to these three life cycles – thermal age, amount (as well as form and distribution) of sulfur, and NO_x saturation.

Furthermore, cyclic trapping operation results in massive changes in chemical composition and structure of the LNT catalyst surface. Common practice in heterogeneous catalysis is to operate a catalyst at temperatures substantially below the Tamman temperature of its individual components, to prevent their mobility and preserve catalyst structure and function over time. In contrast, LNTs routinely operate at temperatures which even exceed the melting point of its components, for example when bulk alkali or alkaline-earth nitrates are formed during the NO_x trapping phase. Indeed, it was recently demonstrated [2] that cyclic storage and release of NO_x from a model LNT catalyst results in massive migration of the NO_x storage component. In our work we have further explored the hysteresis behaviors resulting from this unique feature of

LNTs, using response to sulfur poisoning and recovery as probe process. Overall, the above combination of functions and life cycles renders optimization of LNT catalyst composition and operation conditions very nontrivial, when required to maintain very high catalyst activity and selectivity across a broad range of operating conditions.

Rapidly evolving understanding of the LNT functions resulted in some novel approaches to improving their efficiency. For example, the step including NO_x release and conversion can yield substantial quantities of NH₃, depending on the catalyst formulation and NO_x regeneration conditions. It was recently demonstrated that this otherwise undesirable byproduct can be stored on downstream or adjacent selective catalytic reduction (SCR) catalyst, aiding NO_x reduction during the subsequent lean operation cycle [3]. While conceptually elegant, hybrid LNT-SCR system requires close coordination between NH₃ generation function of the LNT, NH₃ storage and NO_x reduction functions of the SCR catalyst. Better understanding of the factors controlling NH₃ production [4] and its role in the LNT regeneration process [5], provide a foundation for analytical, rather than empirical optimization of such systems.

The “memory” challenge is not unique to LNTs alone, but to some extent is inherent to the SCR technology and very important to diesel soot oxidation. As mentioned above, some SCR catalysts, in particular zeolite-based, possess substantial NH₃ storage capacity which on one hand can serve as a buffer during transient operation, but on the other hand complicates control of its instantaneous NO_x reduction efficiency. Removal of diesel soot via filtration, followed by periodic or continuous oxidation, also entails a number of history-dependent aspects, including reversible changes in surface functional coverage [5] and progressive changes in gross morphology [6], arguably arising from its nano-structure [7].

Finally, reaction engineering factors, as well as facilitating and enabling devices (such as oxidation and clean-up catalysts) play a very important, yet often underestimated role in the diesel exhaust emissions removal systems.

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