Elucidating Lean NO_x Trap Regeneration and Degradation Chemistry: Insights from Intra-Catalyst Spatiotemporally Resolved Measurements

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Lean NO_x trap (LNT) catalysts are inherently complex transient integral devices whose local chemistry and state is continuously changing along their length during both NO_x-trapping and regeneration phases. These devices are also susceptible to sulfur and thermal degradation which can further modify the LNT transient chemistry distributions. This spatiotemporally dynamic nature complicates detailed understanding of how these devices function in practical lean-rich cycling conditions. We have used intra-catalyst spatiotemporally resolved measurements to better understand the nature of LNTs with respect to NO_x storage and regeneration, and performance degradation. The resulting insights have broad applied and fundamental implications including device control and state assessment, actual chemistry modeling, fundamental understanding of LNT chemistry such as nature of sulfation and desulfation, and roles of ammonia and water-gas-shift reaction (WGSR) to LNT regeneration. The presentation will focus on our work to understand NH_3 and WGSR during LNT regeneration and the resulting insights to LNT chemistry.

Recently, ammonia has been recognized as an intermediate in LNT regeneration with H_2. Our intra-LNT measurements clearly support the intermediate role of NH_3 in regeneration. Temporal NH_3 and N_2 profiles at different locations indicate that NH_3 was formed on a similar time scale as N_2 and consumed as aggressively as H_2 by downstream oxidants. This trend was observed consistently at different temperatures, but the apparent NH_3 contribution was greater at lower temperature. The intermediate role of NH_3 being clearly confirmed, a remaining question is how important the intrinsic contribution of the NH_3 route is. Due to the integral nature of the LNT, and even with intra-LNT measurements, the true partitioning of NH_3-route/H_2-route is difficult to extract. Such information could be obtained by improving the measurement spatial resolution to obtain gas composition near the very front of the catalyst where the integral impact was minimal, and by virtual experiments using predictive models

The WGSR occurs during LNT regeneration. WGSR can contribute to regeneration reactions and be used in catalyst-system control strategies as a means to indirectly assess catalyst performance. Exhaust sulfur can limit the overall LNT performance, but its impact on specific LNT reactions, including WGSR, varies. For example we have found that sulfation inhibits NO_x storage/reduction (NSR) function in a plug-like manner, while it only partially inhibitsa oxygen storage capacity (OSC) function. Sulfation progressively degrades WGSR in a plug-like manner; however, this dramatic impact is broader compared to that of sulfation on the NO_x storage distribution. Furthermore, intermittent lean-purges mitigate the S impact on WGSR performance, suggesting that surface S could be mobile and reversibly poison Pt sites ($2Pt\text{-}S + 3O_2 = 2Pt\text{-}O + 2SO_2$). However, sulfation appears to impact the nature of the active sites relevant to WGSR rather than the number of Pt sites, based on detailed site titration and probing. Apparently in sulfated conditions, a zone where surface S levels sufficient to degrade WGSR but not NO_x storage, exists immediately downstream of the NSR poisoned zone at the catalyst front, and causing broadening of the WGSR-zone affected by sulfation.

This work has implications on conceptual understanding of NO_x storage sites, regeneration chemistry, the impact of sulfation, and device control and state assessment.