Driving the Selectivity of NO Reduction to N₂, NH₃ or N₂O during Lean/Rich Cycling of a Lean NO₂ Trap Catalyst

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Introduction
During LNT regeneration, N₂ and NO products are formed concurrently in two peaks. The primary peaks appear immediately after the rich-phase inception, and tail off with the breakthrough of the reduc tant front accompanied by NH₃ product (Fig. 1a). N₂ is the main and desired product, while NH₃ is a by-product that can be utilized for further NO₂ reduction over an SCR catalyst. NO₂ is, however, a chemically stable gas with a high global warming potential. Our previous work [1,2] suggested that local NO₂ reduction selectivity on the rich regeneration front is determined by the ratio between the rates of NO₂ release and Pt group metal (PGM) reduction. The latter depends on the individual “light-off” characteristics of different reductants with a maximum NO₂ selectivity obtained at the light-off temperature of each reductant. In the present study, we analyzed the spatiotemporal evolution of all relevant gas-phase species and key surface intermediates as a function of reductant type, temperature and regeneration length to identify the mechanisms and operating parameters driving the selectivity of NO₂ reduction under lean/rich cycling conditions.

Materials and Methods
The dynamics and selectivity of N₂, NH₃ and NO₂ formation during and after the regeneration of a commercial NO₂ storage catalyst containing Pt, Pd, Rh, Ba on Ce/Zr, Mg/Al and Al oxides were studied with high-speed FTIR and SpaciMS analyzers. The lean/rich cycling experiments (60s/5s and 60s/3s) were performed in temperature range 200–400°C, and Al oxides were studied with high-speed FTIR and SpaciMS analyzers. The lean/rich regeneration of a commercial NO₂ trap catalyst containing Pt, Pd, Rh, Ba on Ce/Zr, Mg/Al and Al oxides were studied with high-speed FTIR and SpaciMS analyzers. The lean/rich cycling experiments (60s/5s and 60s/3s) were performed in temperature range 200–400°C.

Results and Discussion
The primary N₂ peak exhibited a broadening shoulder aligned with the movement of reduction front from the zone where both NO₂ and oxygen were stored to NO₂-free zone where only oxygen storage capacity was saturated (Fig. 1b). The N₂ formed in the NO₂-free zone originated from the reaction of NH₃ with stored oxygen, but NO₂ formation in this zone was very low.

The secondary N₂ and NO₂ peaks appeared at the rich-to-lean transition as a result of reactions between surface-deposited reductants/intermediates (CO, HC, NH₃, -NCO) and residual stored NO₂. At 200–300°C, up to 30% of N₂ and 50% of NO₂ products originated from secondary peaks. The NO₂/N₂ selectivity ratio as well as the magnitude of secondary peaks decreased with temperature and duration of the rich phase. This suggests that the magnitude of secondary peaks depended on the amount of residual stored NO₂ and adsorbed reductants/intermediates. Furthermore, the N-products selectivity in secondary peaks was influenced by the rate of PGM sites transition back to high NO₂ and oxygen coverage.

Based on this finding, a novel strategy is proposed for minimization of secondary N₂O peaks. It consists of applying a slightly lean (near stoichiometric) phase between the rich and lean phases. During this intermittent slightly lean phase, the adsorbed reductants/intermediates and residual stored NO₂ can continue to react over well reduced PGM sites even beyond the rich regeneration phase, preventing NO₂ formation (Fig. 1). The strategy also allows additional NH₃ formation while minimizing CO or HC breakthrough, which is highly desirable for the coupled LNT-SCR applications.

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References