

NO_x REDUCTION BY FAST LEAN-RICH CYCLING ON PLATINUM CONTAINING MONOLITH CATALYSTS: IMPACT OF STORAGE COMPONENTS

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Abstract

NO_x reduction under net lean or stoichiometric conditions was studied under fast lean/rich cycling using Pt/Al₂O₃, Pt/CeO₂/Al₂O₃ and Pt/BaO/Al₂O₃ washcoated monolith catalysts. We investigated the impact of storage components BaO (NO_x storage) and CeO₂ (oxygen storage) on the NO_x conversion and product distribution over a range of conditions. The findings elucidate the working mechanism and provide insights about impacts of storage materials on NO_x storage and reduction (NSR) under fast cycling. NO_x storage functionality is essential for lean NO_x reduction while oxygen storage functionality only promotes NO_x reduction for net stoichiometric and rich feeds. Lean NO_x conversion by H₂ over each of the three catalysts follows the NO_x storage capacity. The addition of O₂ exhibits a complex impact on NO_x reduction over Pt/CeO₂/Al₂O₃ due to the storage of NO_x and O₂ by ceria. Enhanced NO_x conversion is achieved with fast cycling and/or with C₃H₆ as reductant over Pt/BaO/Al₂O₃ for a lean feed or over Pt/CeO₂/Al₂O₃ for a stoichiometric feed.

Keywords

NO_x reduction, Fast Cycling, NO_x/oxygen storage.

Introduction

The effective removal of NO_x remains an on-going challenge due to increasingly stringent regulations. Several years ago Toyota researchers (Bisaiji et al. 2012) proposed a new deNO_x system, Di-Air (diesel NO_x aftertreatment by adsorbed intermediate reductants), which involves fast periodic injection of fuels into the exhaust upstream of a NSR converter. The Di-Air system is notably more effective than transitional NSR at high temperatures and space velocities. The Di-Air working mechanism remains under debate. Three possible working mechanistic pathways have been proposed; namely, hydrocarbon intermediate (Bisaiji et al. 2012), conventional with improved NO_x storage utilization (Ting et al. 2018), and redox (Wang et al. 2018).

The first two require the participation of a NO_x storage material (e.g. BaO). In contrast, the redox pathway is realized by incorporation of oxygen storage material (e.g. CeO₂). We investigate the role of NO_x and oxygen storage materials in the Di-Air system, using three catalysts, Pt/Al₂O₃ (denoted by PA), Pt/CeO₂/Al₂O₃ (PCA) and Pt/BaO/Al₂O₃ (PBA) having the same Pt loading (1 wt.%) over a range of feed conditions.

Fig. 1a compares the cycle-averaged NO_x conversion under lean conditions with H₂ as reductant. PCA and PBA exhibit the highest cycle-average NO_x conversion below or above 300°C, respectively. The impact of the catalyst

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formulation on NO_x conversion (Fig. 1a) parallels that of the NO_x storage capacity (data not shown here). Over the entire feed temperature range, PCA and PBA give a higher NO_x conversion than PA, showing the beneficial impact of both BaO and CeO₂. Above 450 °C, the cycle-averaged NO_x conversion over PCA and PA drops to ~14% (rich duty fraction), suggesting that the effective NO_x reduction is confined in the rich phase. As PCA has negligible NO_x storage capacity, its limited conversion (~14%) indicates that NO decomposition over reduced ceria or Pt sites contribute little to NO_x reduction under lean conditions.

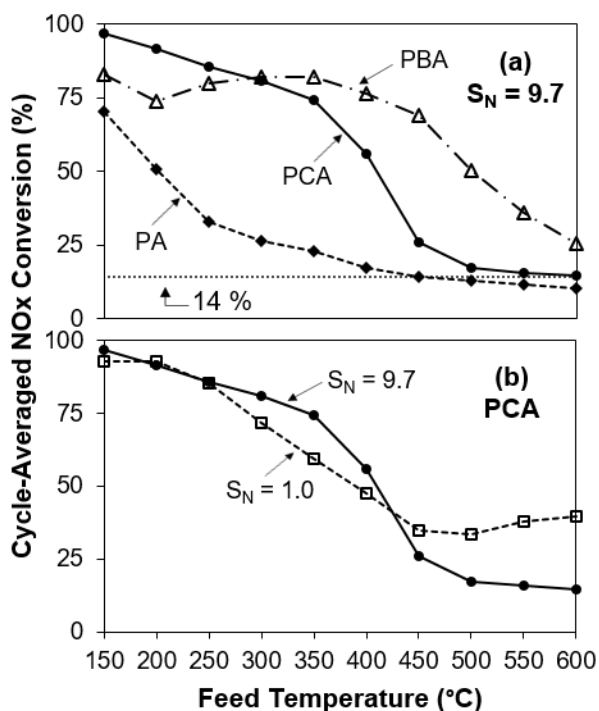


Figure 1. Cycle-averaged NO_x conversion as a function of feed temperature. [Conditions: lean/rich switching frequency: 6/1s; lean: 300 ppm NO, 5% O₂ ($S_N = 9.7$) or 0.5% O₂ ($S_N = 1.0$); rich: 300 ppm NO, 6.21% H₂].

Fig. 1b compares the cycle-average NO_x conversion over PCA under net lean ($S_N = 9.7$) and stoichiometric ($S_N = 1.0$) conditions. Excess O₂ enhances NO_x conversion below 400 °C but inhibits NO_x reduction above 400 °C. The non-monotonic dependence of NO_x conversion on O₂ concentration for PCA can be ascribed to the inherent NO_x and oxygen storage capacity of ceria. PCA has oxygen storage capacity over the entire feed temperature range but only exhibits NO_x storage capacity at low temperatures (i.e. <400 °C). Below 400 °C, the NO_x stored on PCA in the lean phase can be reduced in the rich phase. Excess O₂ promotes NO_x storage on PCA and thus the overall NO_x reduction. Above 450 °C, NO can only be reduced via reduced ceria and/or Pt sites. O₂ is a better oxidant than NO and thus it hinders NO reduction to N₂ or NH₃.

Fast cycling enhances NO_x conversion over PBA for $S_N = 9.7$ or over PCA for $S_N = 1.0$. The promotion by fast cycling may be attributed to the more efficient utilization of “fast” NO_x or oxygen storage sites. The “fast” NO_x and oxygen storage sites include the NO_x and oxygen storage sites proximal to Pt particles and surface oxygen sites on ceria (Zhou et al. 2019). Compared to H₂, C₃H₆ gives a higher NO_x conversion over PBA for $S_N = 9.7$ or over PCA for $S_N = 1.0$ under fast cycling (e.g. 6/1s). The use of C₃H₆ as reductant for PBA or PCA increases the degree of reduction, with involvement of hydrocarbon surface species on Pt and/or ceria. The additional deposited hydrocarbon intermediates may account for the elevated NO_x conversion by C₃H₆.

Conclusions

This study confirms the traditional NSR mechanism and the hydrocarbon intermediate pathways in Di-Air system. The redox pathway is validated but proven to only extend considerable impact in near stoichiometric cases. The enhancement by fast cycling over PBA and/or PCA arises from the more efficient utilization of fast NO_x and/or oxygen storage sites. Compared to H₂, C₃H₆ promotes NO_x reduction over PBA and/or PCA, thanks to the additional reduction of Pt and/or ceria by C₃H₆.

Acknowledgments

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