Elucidating Effects of Rh, CeO_2 and Feed Conditions During NOx Storage and Reduction on Pt/Rh/BaO/CeO_2 Monolith Catalysts

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Introduction

NO_X Storage and Reduction (NSR) is a periodically operated catalytic process for NO_X emission abatement in lean burn gasoline and diesel engines. The process involves two sequential steps of storage and reduction on a bifunctional catalyst in the lean NO_X trap (LNT). Optimization of the multi-functional catalyst is a crucial component of LNT design. This is complicated by the existence of H_2O and CO_2 in the feed and the large number of concurrent reactions during the regeneration step, including NO decomposition, NO reduction by various reductants (H_2, CO, HCs), water gas shift (WGS), and hydrocarbon steam reforming. For example, CO_2 is known to be detrimental to NOx storage and can consume feed H_2 by the reverse WGS reaction at higher temperatures [1, 2]. In this study, we employ a bench-scale reactor system to compare the performance of a family of Pt/Rh/BaO/CeO_2 monolith catalysts. The objective is to elucidate the roles of the precious metal and storage components, identify regeneration pathways, and provide performance data for LNT modeling and design.

Materials and Methods

The experimental system comprises a bench-scale reactor with synthetic feeds mimicking lean burn engine exhaust, utilizing both FTIR and mass spectrometers to measure transient effluent compositions. Monolith catalyst samples provided by BASF Catalysts LLC have different combinations of Pt, Rh, BaO, and CeO_2 loadings on alumina washcoat (Table 1). The catalyst samples were evaluated in terms of NOx storage, NO oxidation activity, and reduction activity, the latter of which included cycle-averaged NOx conversion and product selectivities. Typical cycling experiments involved 60 s storage feed containing 500 ppm NO, 5% O_2, 5% H_2O, and 5% CO_2 in diluent followed by a 3 to 30 s regeneration feed containing 0.5% H_2, 5% H_2O, and 5% CO_2 in diluent.

Table 1. Washcoat compositions of Pt/Rh/BaO/CeO_2/Al_2O_3 catalyst samples

	P/B	**P/BC**	**PR/B**	**PR/BC**
Pt (wt%)	2.36	2.36	2.36	2.36
Rh (wt%)	n/a	n/a	0.20	0.20
BaO (wt%)	13.0	13.0	13.0	13.0
CeO_2 (wt%)	n/a	13.0	n/a	13.0

Results and Discussion

The four catalysts enable a systematic comparison of NO oxidation activity relevant to NOx storage, the role of CeO_2 on storage, contributions of WGS reactions in affecting to NSR performance, of Rh and/or CeO_2 on WGS activity, among other salient issues. Typical cycling results are shown in Figure 1 which compares the cycle-averaged NOx conversion as a function of catalyst temperature for the four catalysts and for feeds without and with CO_2 during the lean and rich steps. The protracted reduction (30 s) ensures that most of the stored NOx is reduced. In the absence of feed H_2O and CO_2 all four catalysts have conversions exceeding 80% over the entire temperature range with the conversion approaching 100% between 300 and 350 ^oC. An adverse effect of feed CO_2 is evident for all catalysts which results from a reduction in NOx storage on alumina and/or barium phases primarily, and reduction in NO oxidation conversion secondarily. The addition of Rh reduces the CO_2 inhibition. This is due to the reverse water gas shift reaction ($H_2 + CO_2 \leftrightarrow CO + H_2O$) since the generated CO does not inhibit NO reduction on Rh to the extent it does on Pt. CeO_2 also increases the NOx conversion in the presence of CO_2, again, due to NOx storage enhancement.

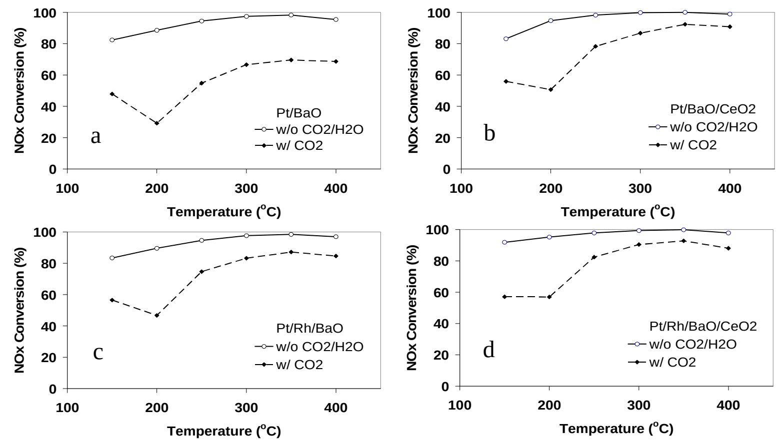

Figure 1. Cycle-averaged NOx conversion for feeds without and with CO_2 for catalysts P/B (a), P/BC (b), PR/B (c), and PR/BC (d).

The results of ongoing experiments will be presented which elucidate mechanistic issues associated with Rh and CeO_2 during the regeneration with regeneration times of 3-30 s. We will also identify operating conditions which optimize the NOx conversion to N_2 and minimize reductant consumption for each of the catalysts in the operating parameter space of catalyst temperature, cycle time, and regeneration feed composition and duty cycle.

Significance

NOx storage and reduction technology is an elegant approach to using lean burn vehicle exhaust species to reduce NOx. In this study systematic experiments are carried out to determine the roles of the different catalyst components and the contributions of regeneration feed constituents and cycle timing on the NOx conversion and product distribution.

References

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