Ammonia and Nitrous Oxide Formation During NOx Storage and Reduction on Pt/Ba Monolith Catalysts

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Introduction

Lean burn engines are more fuel efficient than stoichiometrically operated gasoline engines. The unconverted oxygen in the exhaust prevents the use of three-way catalysts to reduce NO_X to N_2. During the past decade there has been a vigorous development of exhaust after-treatment systems for lean NOx reduction. NO_X Storage and Reduction (NSR) has been shown to be an effective technology in achieving high NO_X conversion, but NSR requires periodic operation to sequentially store and reduce NOx. Moreover, the NSR chemistry involves multiple reaction pathways and products that are complicated by thermal, feed composition, and transient effects. Elucidation of the selectivity of NOx reduction to desired product N_2 and byproducts NH_3 and N_2O is paramount in optimizing the lean NOx trap or hybrid LNT/SCR systems. The objective of this study is to identify the byproduct pathways and to quantify conversions and selectivities over a wide range of feed compositions and temperatures, and cycle timing parameters for Pt/Ba, Pt, and Ba catalysts.

Materials and Methods

A benchscale monolith reactor system was employed to evaluate NOx storage and reduction, using H_2 and CO as reductants. The monolith catalysts contained 0-2.2% Pt and 0-16.3% BaO on a γ-Al_2O_3 washcoated cordierite base material. The outlet gases were analyzed by a FTIR spectrometer and an O_2 analyzer. Steady-state data were obtained over a wide range of feed temperature and NO/H_2 feed ratios. For the lean/rich cycling experiments, both instantaneous and time-averaged data were obtained for different lean and rich feed compositions and durations.

Results and Discussion

Steady state data for several reaction systems were obtained, which provided critical information about reaction pathways and rates that are helpful in elucidating the behavior during cycling. Some key findings are as follows:

- Similar steady-state behavior is exhibited by the Pt and Pt/BaO catalysts. Light-off behavior was observed for the H_2 oxidation and NH_3 oxidation reaction systems.
- The BaO exhibited a non-negligible but lower activity and different product distribution than the Pt- and Pt/Ba catalysts.
- The oxidation of H_2 is inhibited by NO, which increases the light-off temperature.
- Ammonia oxidation produced a complex mixture of N_2O, NO, and N_2. The selectivities are a sensitive function of the NH_3/O_2 feed ratio and catalyst temperature.
- Ammonia decomposition was important at temperatures exceeding 350 ºC and was inhibited by H_2 and N_2.
- The anaerobic NO + H_2 reaction produced a mixture of N_2O, NH_3, and N_2. The main N-containing product was dictated by the NO/H_2 feed ratio and catalyst temperature. The aerobic NO + H_2 reaction is affected by the oxidation of reactant H_2 and product NH_3.

Cycle-averaged results show high NOx conversion and N_2 selectivity exceeding 80% and 70%, respectively, over a range of conditions (Figure 1). The NOx conversion maximum occurs in the 300 to 350 ºC temperature window, although conversions exceeding 60% can be sustained at temperatures as low as 150 ºC with H_2 as the reductant. The NH_3 formation and consumption is complex and dependent on the amount of NOx stored, stoichiometric number ($S_N = (2[O_2] + [NO]) /[H_2]$), H_2/NO ratio, temperature, and mass transfer. Regeneration with H_2 produces significant NH_3 over a wide range of temperatures while N_2O is only important at lower temperatures (< 200 ºC) and $S_{N,p} > 0.9$. Instantaneous effluent composition data reveal N_2O is produce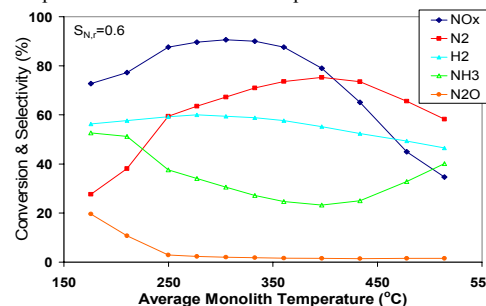d at the onset of the rich pulse while NH_3 is formed during the latter part of the rich cycle. The cycle-averaged NH_3 selectivity exhibits a minimum at an intermediate temperature. This counterintuitive trend is shown to be a result in part from the kinetic inhibition of NH_3 decomposition by unreacted H_2, as well as thermodynamic inhibition by H_2 and the N_2 carrier.

Storage effects are observed to be one of the main contributing factors to NOx conversion and selectivity to N_2, NH_3, and N_2O. The Pt-only catalyst is shown to be an effective catalyst at lower temperatures in which NOx storage on alumina occurs. While NOx storage capacity determines the maximum attainable conversion, the ratio of H_2 fed to NOx stored has an important effect on selectivity to N_2O and NH_3. Figure 2 shows the product distribution as a function of the NOx stored. The selectivity is dictated largely by the NO/H_2 feed ratio during the latter part of the rich pulse, and is consistent with the findings from the steady-state NO/H_2 experiments. A high effective NO/H_2 is achieved at reduced NOx storage and/or rich pulse conditions.

A phenomenological reaction system will be presented that explains the steady-state and transient trends.

Figure 1. Time averaged conversion and selectivity vs. monolith temperature. Feed: (lean) 500 ppm NO and 5% O_2 and (rich) 500 ppm NO, 1.5% O_2, 5.1% H_2.
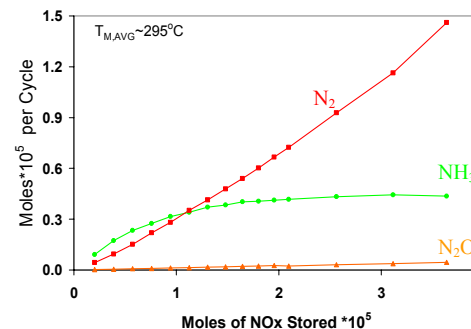

Figure 2. Time averaged production of N_2, NH_3, and N_2O vs. moles of NOx stored. Feed: (lean) 500 ppm NO and 5% O_2 and (rich) 2% H_2.