Selective Catalytic Reduction of Nitric Oxide with Acetaldehyde over NaY Zeolite Catalyst in Lean Exhaust Feed

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Introduction
Efficient reduction of NOx emissions (>90%) from diesel exhaust is critical to meeting future emission standards and improving vehicle fuel economy. In an effort to achieve this goal, the steady-state selective catalytic reduction (SCR) of nitric oxide (NO) was investigated under simulated lean-burn conditions using acetaldehyde (CH3CHO) as the reductant. Previous plasma-assisted lean NOx catalysis efforts identified acetaldehyde as the plasma-generated species necessary for the SCR of NOx over a sodium Y (NaY) zeolite catalyst and determined that the plasma-assisted oxidation of NO to NO2 was not required for efficient NOx reduction [1]. This work quantifies the influence of catalyst space velocity and the impact of nitric oxide, acetaldehyde, oxygen, sulfur dioxide, and water on NOx reduction activity using a laboratory flow reactor system and Fourier transform infrared (FTIR) measurements. Testing was carried out over a temperature range (150°C to 350°C) typical of light-duty diesel exhaust. The results of this study provide useful guidance in the design and operation of diesel NOx emission control systems.

Results and Discussion
Nitric oxide and acetaldehyde react over a NaY zeolite catalyst to form N2, HCN, and CO2, with N2 formation favored at temperatures below 225°C and peak HCN production at 300°C. Previous work revealed that HCN could easily be removed with a Pt/Al2O3 oxidation catalyst, although primarily N2O, a greenhouse gas, is formed [1]. Results shown in figure 1 indicate that with sufficient catalyst volume and acetaldehyde used as the reductant, 90% NOx conversion can be achieved at 200°C under steady-state conditions in simulated light-duty diesel exhaust. Initial NOx conversion is very high; however, the NOx conversion steadily declined with time due to catalytic oxidation of some of the stored (adsorbed) NO to NO2. This effect can have a significant impact on steady-state NOx conversion levels, particularly at low inlet NO concentrations and low temperatures (≤250°C). The NO conversion level in figure 1 is independent of the NO concentration in the feed. On the other hand, at high temperature (≥300°C) the inability of acetaldehyde to displace the adsorbed NOx species as NO2 results in a constant NOx conversion over the entire NO concentration range (0-400 ppm) examined in this study. Figure 2 specifies the catalyst selectivity, defined as the amount of acetaldehyde consumed as a function of the amount of NOx converted. Since the stoichiometry of the reduction reaction over this catalyst is unknown, it is not possible to determine the exact amount of acetaldehyde that is used only for NOx reduction. In order to put boundaries on the competition between HC as a NOx reductant (N2, HCN, CO2, H2O)
and HC combustion (CO, HCHO, CH₃OH, CH₃CH₂OH, CH₃COOH), we assume that the acetaldehyde oxidation/decomposition products that are not necessary for NOₓ reduction represent the most favorable HC utilization. The solid line in figure 2 is derived from the space velocity data in figure 1 with 242 ppm NO in the feed, while the dashed line represents the same data with the acetaldehyde oxidation/decomposition products removed. As the regression lines point out, under these conditions the CH₃CHO/NO consumption ratio ranges from 1.0 to 1.8. With 250 ppm NO in the exhaust feed stream, a maximum NOₓ conversion at 200°C can be achieved with ~400 ppm of acetaldehyde, with higher acetaldehyde concentrations resulting in production of acetic acid and breakthrough of NO₂ causing lower NOₓ conversion levels. Less acetaldehyde is necessary at lower NO concentrations, while more acetaldehyde is required at higher temperatures.

Oxygen is necessary in the exhaust feed stream to oxidize NO to NO₂ over the catalyst prior to reduction, and water is required to prevent catalyst deactivation. Sulfur in the exhaust feed stream as SO₂ can cause slow deactivation of the catalyst by poisoning the adsorption and subsequent reaction of nitric oxide and acetaldehyde. While only a minor effect at high temperature, this sulfur poisoning effect becomes more pronounced at low temperature. The addition of 400 ppm CO, 7% CO₂, and 135 ppm H₂, constituents that are also present in real diesel exhaust, has no effect on NOₓ conversion. These results are consistent with the reaction of adsorbed nitrate and acetate species to form an organic nitro/nitrite compound, leading to the production of N₂, HCN, and CO₂, possibly through a reaction involving an isocyanate (NCO) intermediate.

**Figure 1.** Impact of space velocity on NOₓ and NO conversions over NaY catalyst.

**Figure 2.** Acetaldehyde consumed as a function of NOₓ converted.

**References**