# Two-stage Catalytic Exhaust Treatment for Lean-Burn Natural Gas Engines

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#### Introduction

Natural gas engines operating in the lean regime are widely implemented as stationary power generation sources due to the high fuel efficiency that could be obtained by operating in high oxygen concentrations. Although these engines produce cleaner exhausts, the effluent streams still contain significant levels of carbon monoxide, unburned hydrocarbons, and nitrogen oxides. A two-stage system that would employ methane, which is available in the exhaust stream, as the reducing agent for the catalytic reduction of NO has been developed [1]. The use of methane as a reducing agent poses significant challenges since methane combustion with oxygen proceeds with a higher selectivity under lean burn conditions and tends to deplete the reducing agent. However, the two stage mechanism is capable of overcoming this by the use of an NO oxidation catalyst to help the NO reduction reaction proceed with greater selectivity by converting the NO to NO<sub>2</sub>, which is a more easily reduced species than NO [2] and a reduction catalyst for the reduction of NO<sub>2</sub> with CH<sub>4</sub>. The oxidation catalyst formulation developed for the two-catalyst scheme has been shown to achieve equilibrium conversions of above 90% at 250°C [3]. Initial catalyst formulations for the reduction component have shown promising results [1]. This contribution discusses the effect of water vapor, which is a significant component of exhaust streams, on the activity of the dual-catalyst system composed of a physical mixture of these catalysts.

### Materials and Methods

Preparation and characterization of the NO oxidation catalyst (Co/ZrO<sub>2</sub>) has been reported earlier. [3]. The NO<sub>2</sub> reduction catalyst (Pd/SZ) was prepared through a single-step sol-gel procedure. The effect of water vapor on NO reduction activity of the mixed catalyst bed was investigated by cycling between dry and water vapor containing feed at 500°C at steadystate after allowing 50 minutes for stabilization. The feed for this experiment constituted of 400 ppm NO, 1700 ppm CH<sub>4</sub>, 200 ppm C<sub>2</sub>H<sub>6</sub>, 100 ppm C<sub>3</sub>H<sub>8</sub>, 10% O<sub>2</sub> and 0-6% H<sub>2</sub>O in He at a GHSV of 20,000 h<sup>-1</sup>. Gases were analyzed using gas chromatography and chemiluminescent NOx analysis. The thermal transformation of water over Pd/SZ was studied with *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) following adsorption at 50°C.

## **Results and Discussion**

Studies on individual components of the mixed bed have shown that water vapor had no significant effect on the oxidation catalyst [3] whereas it had a detrimental effect on the reduction catalyst (not shown). In order to investigate the effect of water vapor on the mixedcatalyst bed, the activity was monitored during NO reduction with hydrocarbon mixture while alternating between dry and 6% water vapor containing feed streams. 90% N<sub>2</sub> yield was achieved during simulated lean exhaust treatment over the mixed catalyst bed under dry conditions. The N<sub>2</sub> yield decreased to 67% upon introduction of water vapor (Figure 1a). However, complete recovery of the activity was observed when water vapor was switched off. Additional steady-state activity tests suggested that, although completely oxidized,  $C_2H_6$  and  $C_3H_8$  were not involved in NO reduction (not shown), demonstrating that the dual-catalyst system is also very active for the elimination these species. Figure 1b shows that adsorption of water resulted in the hydration of sulfate species as observed from bands at 1053, 1140 and 1224 cm<sup>-1</sup> which were assigned to bidentate  $SO_4^{2-}$ . Transformation into  $H_2SO_4$  at 150°C was observed through a band at 1265cm<sup>-1</sup>. The negative band at 1398 cm<sup>-1</sup> corresponds to S=O stretch of sulfate species and a band at 1650 cm<sup>-1</sup> has been associated with adsorbed  $H_2O$ . Both bands recover with temperature and no bands are observed in the IR spectrum at 600°C.

Presented results suggest that the effect of water vapor is reversible and cannot be associated with deactivation of the Pd/SZ through removal of acid sites, but rather with a competitive adsorption phenomenon. Further reaction and characterization studies including temperature-programmed experiments, X-ray photoelectron spectroscopy and laser Raman spectroscopy have been conducted for investigating the nature and interactions of the adsorbed species and the state of the catalysts under operating conditions.



Figure 1. (a) NO( $\bullet$ )/NOx (O) conversions as a function of time while switching water vapor on/off. Inset shows N<sub>2</sub> yield. (b) DRIFT spectra from 50-600°C following H<sub>2</sub>O adsorption.

# Significance

An aftertreatment system which is capable of eliminating atmospheric contaminants and achieving high  $N_2$  yields by eliminating fuel penalty would find widespread use in lean burn natural gas engines for stationary power generation sources.

#### References

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