Increased NH_3 and N_2O emissions from three-way catalytic converters

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Introduction

In an effort to decrease emissions from mobile sources to meet stricter standards and achieve low regulated emissions over the vehicle life-time, environmental regulations from many countries have targeted the sulfur content in gasoline [1]. Given the continuing reduction in the level of sulfur, it is important to understand how this could impact the performance of the three-way catalytic converter (TWC). Even in small amounts, sulfur in gasoline has multiple effects on the operation on the TWC once it emerges from the engine as sulfur dioxide. These effects, both undesirable and beneficial, are not widely appreciated and depend on the temperature, the redox potential of the exhaust and the composition of the catalyst [2].

A problem that has not received much attention is the emission of side products from the network of reactions that occur on the TWC as NH_3 and N_2O. Only a small numbers of reports have focused on the role of sulfur in the formation of side products from the TWC operating under practical conditions. Recently, we reported [3] that decreasing sulfur levels in gasoline activates the formation of NH_3 as it increases NO conversion under rich conditions. We also observed that under lean conditions N_2O is formed, and the presence of SO_2 has only a minor effect in that case. In order to understand how NH_3 and N_2O emissions are evolving and what will be their impact in the near future, in this work we report the effect of low-sulfur gasoline on the operation of commercial converters.

Materials and Methods

Two new commercial TWC were used. The loading of Pd in the first one (Pd-TWC) was 2.29×10^{-4} g/cm^3, whereas the second one contained Pt, Pd and Rh (3.28×10^{-4}, 7.06×10^{-6} and $8.12x^{-5}$ g/cm^3, respectively) labeled as Pt-Rh-TWC. Monolith samples were cut, having a total volume of 0.562 cm^3 for Pd-TWC and 0.306 cm^3 for Pt-Rh-TWC. They were tested in a quartz tubular reactor mounted in an electric furnace. The feed stream composition was: 2100 ppm of NO, 515 ppm of C_3H_8, 6700 ppm of CO, 2200 ppm of H_2 and 10% vol of water; SO_2 was varied in the 0-50 ppm range and the gas balance was N_2. The A/F ratio ranged between 14.3 (rich) and 14.8 (lean). The analysis of reactants and products was made by GC (HP 6890 and Shimadzu GC-12A) and also on line with an FTIR spectrophotometer (Bruker Tensor 27) equipped with a 0.75 m path length infrared gas cell heated at 120°C. Spectra were acquired at a 4 cm^{-1} resolution by averaging 64 scans.

Results and Discussion

Ours results show that at 500°C and rich conditions, NH_3 is the main by-product in absence of SO_2. The addition of SO_2 in the feed stream inhibits NH_3 formation but promotes generation of N_2O (Figure 1). N_2O appears to be formed during NO reduction by CO. NH_3 is generated by reduction by H_2 present in the exhaust or H_2 generated via steam reforming (SR) and water-gas shift (WGS) reactions [3,4], the latter occurring at high temperatures in the TWC. It has been reported [5] that SO_2 is adsorbed molecularly on CeO_2 and reacts with molecular O_2 from the gas phase or by reduction of ceria to produce sulfates. The presence of sulfate groups favors the reaction pathway to produce N_2O. Sulfate groups also hamper the oxidation-reduction of ceria, inhibiting the SR and WGS reactions to produce H_2, hence NH_3. As a result, lowering sulfur in fuels has a dual effect, because it activates the reaction pathway to NH_3 and inhibits N_2O formation, in agreement with our experimental results (Figure 1).

Significance

Our results show that the use of low sulfur fuel by vehicles equipped with TWC can be an important factor in lowering urban air quality and in promoting climate change. NH_3 reacts in the atmosphere with sulfuric and nitric acids to produce aerosol particles ($PM_{2.5}$) that may have adverse health effects and create visibility problems in urban areas. On the other hand, N_2O is one of the most potent greenhouse gases. Direct atmospheric measurements agree with our experimental results. The elucidation of the phenomena involved could be useful in designing better environmental regulations and in improving the performance of new generation TWC.

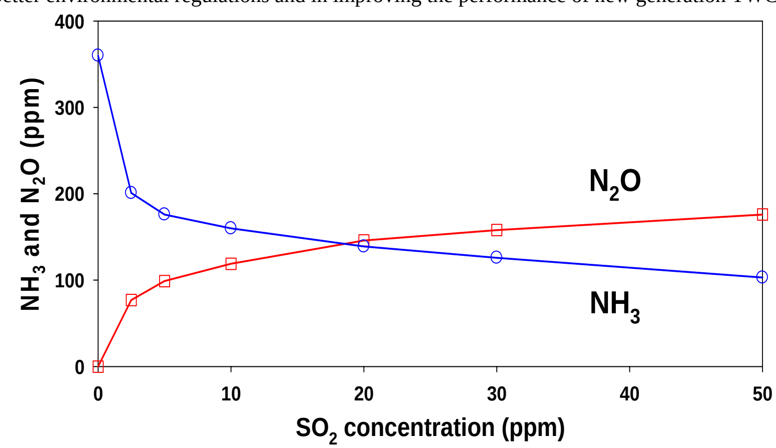

Figure 1. Effect of low sulfur gasoline upon NH_3 and N_2O emissions from commercial Pd-TWC under rich conditions (A/F = 14.5) at 500°C.

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