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Nitrogen release from a NO_x storage and reduction catalyst

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Abstract

In a NO_x storage and reduction (NSR) catalyst, the release and reduction of NO_x occurs over a very short period. The speed of the NO_x release and reduction creates difficulties in analyzing the chemistry using normal analytical techniques, which are typically better suited to slower, steady-state studies. We have investigated the time dependence of NO, NO_2, NH_3, N_2O and N_2 released by an NSR catalyst using a combination of FT-IR and gas chromatographic techniques. Nitrogen was detected with the GC by using He rather than N_2 as the background gas. The FT-IR was used not only to monitor NO, NO_2, NH_3 and N_2O, but also to establish cycle-to-cycle reproducibility. Under these conditions we used the GC to sample the effluent at multiple times over many lean–rich cycles. To the extent that the chemistry was truly periodic and reproducible, we obtained the time dependence of the release of nitrogen after the lean-to-rich transition. Similar information was obtained for O_2, H_2 and N_2O. Combining the FT-IR and GC data, we obtained good cycle averaged nitrogen balances, indicating that all the major products were accounted for.
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Keywords: NO_x trap; Storage/reduction; Nitrogen balance; Lean–rich cycling; Diesel emissions

1. Introduction

Due to their inherently higher fuel efficiency, the expanded use of diesel engines in automobiles and light duty trucks would result in a significant reduction in CO_2 emissions [1]. Unfortunately it has proven quite a challenge to reduce the NO_x emissions from diesel engines to acceptable levels. The strongly oxidative environment of lean-burn engine exhaust is a difficult one in which to chemically reduce NO and NO_2 to N_2. One promising approach is the use of NO_x storage and reduction (NSR) catalysts, often also called lean-NO_x trap (LNT) catalysts [2–4]. These catalysts very efficiently store NO_x under lean conditions, typically as a nitrate. Under rich conditions, the nitrate is readily reduced to N_2 leaving the catalyst ready to store NO_x again once lean conditions are re-established. One strategy for utilizing the NSR approach is to periodically operate the engine under both lean (i.e., excess oxygen) and rich (i.e., excess fuel) conditions. The lean operation period should be much longer than the rich one in order to take advantage of the natural ''lean-burn'' condition of a diesel engine.

The lean–rich cycling times are dictated by the lean cycle NO_x storage capacity and the rich cycle reduction rate. Careful optimization of the timing and length of the rich period will be necessary in order to minimize the fuel penalty while maintaining the requisite NO_x conversion efficiency. In practice the engine management will likely be very complicated, given the wide range of operating conditions to be expected for everyday driving. One important piece of information is the time evolution of nitrogen-containing species during the lean and especially the rich cycle. How this depends on variables such as the temperature, reductant identity, humidity, CO_2 concentration, and the space velocity is vital information required to develop any engine management strategy.

During the rich cycle, there is a very short burst of activity accompanied by large composition changes that make the chemistry difficult to follow. Furthermore, because nitrogen is the majority species in air, it is virtually impossible to detect and quantify N_2 formation during ordinary operation. Generally, nitrogen formation is inferred by the loss of NO_x and the inability to detect other logical nitrogen-containing products [5–7]. However, this type of inference is not completely satisfying, and gives little or no time-dependent information. Our approach to this problem is to synthesize simplified synthetic exhaust in which He has replaced atmospheric N_2. In addition, we take advantage of the periodic nature of NSR catalyst operation to sample the exhaust gases at many points

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over a series of cycles. As long as the chemistry is truly periodic, under these conditions the time dependence of the formation of N_2 can readily be established.

For the initial experiments reported here, we simplified the chemistry as much as possible, adding only NO_x, H_2 and O_2 to the background He flow. As has been pointed out [8], the lack of CO_2 and excess water is an unrealistic condition for diesel exhaust. However, both the storage and reduction chemistry of NSR catalysts is qualitatively, if not quantitatively, quite similar with or without these components. In future experiments, the effects of H_2O and CO_2 will be examined.

2. Experimental

Our experimental apparatus contains a gas handling system, a temperature controlled quartz reactor containing our monolith catalyst, and an FT-IR and micro-GC for effluent gas analysis. The gas handling system uses pure or mixed gases (i.e., He, O_2, H_2, and 0.5% NO or NO_2 in He) to form three separate gas streams, labeled the main, lean and rich flows. For the experiments described here, the main flow consisted of a fixed concentration of NO or NO_2 in helium. Other gases (e.g., CO_2, SO_2, and/or H_2O) could be added to this flow as well, but were not included for our first experiments reported here. The lean and rich flows consisted of either oxygen or hydrogen mixed with helium at the appropriate concentration. Two computer controlled three-way solenoid valves were simultaneously switched such that one of these mixtures was added to the main flow upstream of the catalytic reactor while the other was directed to the exhaust. Therefore, during the rich period no oxygen was present and during the lean period no hydrogen was present. By using equal volumetric flow rates of the rich and lean gases, the inlet NO_x concentration remained constant throughout the experiment. The gas manifold included a manual bypass valve used to set up and check the inlet gas concentrations.

Our catalytic reactor consisted of a 2.5 cm OD × 2.2 cm ID × 40 cm long quartz tube adapted to 0.64 cm diameter glass tubing on both the inlet and outlet ends. We added a coarse glass frit near the inlet end so that loosely packed glass beads could be inserted upstream of the catalyst to enhance gas mixing and temperature equilibration. The reactor's large open end was adapted to a threaded glass connector, and a threaded Teflon plug used to seal the reactor. The plug was removed to load or unload the catalyst, and had a centered, threaded hole used to insert a type-K thermocouple into the reactor right up against the downstream end of the catalyst. A small monolithic piece (∼2.1 cm diameter × 2.1 cm long, ∼7 cm^3) of a degreened (16 h in air at 700 °C in 10% H_2O) commercial lean NO_x trap catalyst manufactured by Umicore was sealed against the walls of the reactor by wrapping with fiberglass string and then placed near the outlet end of the reactor. The entire reactor was housed inside a 12 in. temperature programmable horizontal furnace (Lindberg/Blue). The furnace was temperature controlled using its own external thermocouple, but we report here the actual temperatures recorded inside the reactor at the outlet end of the catalyst.

The Umicore catalyst in many ways resembles a three-way catalyst with added barium for storage. This catalyst was supplied to us by Oak Ridge National Laboratory and is being used in several laboratories as a benchmark NSR catalyst. It contains the precious metals Pt, Pd and Rh (in descending quantities), added ceria and zirconia (for oxygen storage) and BaO for NO_x storage. The barium loading is 20 wt.% as BaO on Al_2O_3, and the targeted precious metal loading was 100 g/ft.^{3} of Pt/Pd/Rh in a 9:3:1 ratio.

After exiting the reactor, the gas flow was directed through mildly heated stainless steel tubing (∼50 °C) to the FT-IR or the micro-GC for analysis. The FT-IR (Nicolet Magna 560) was equipped with a 2 m gas cell held at 50 °C and a liquid nitrogen cooled MCT detector. The gas cell had a volume of 200 cm^3, which was equal to approximately 5 s of flow at 2 standard liters per minute. The ultimate time response of the FT-IR was therefore limited by the gas turnover time in the cell. We utilized the OMNIC software package to obtain and quantify spectra (2–3 scans at 0.5 cm^{-1} resolution) every 3–4 s. For most gases, we obtained standard calibration spectra on site using gas mixtures with known concentrations. For ammonia, we obtained a 1 ppm-meter standard spectrum, also taken at 50 °C, from the PNNL spectral library [9]. Based on calibration experiments using He dilution, we can say that the relative accuracy of our method is quite good. The absolute accuracy is harder to quantify due to the combined effects of errors in the calibration standards, the various flow rates, and any interference effects not correctly compensated for. However, the consistent and nearly complete nitrogen balances we obtained under a number of different conditions suggests the absolute accuracies were acceptable.

Our micro-GC (MTI analytical Quad series) was equipped with both a 10 m 5 Å molecular sieve column held at 60 °C and a 6 m Poroplot U column held at 50 °C. The former was used to detect H_2, O_2, and N_2, while the latter was utilized to measure N_2O. Under these conditions, approximately 65 s was required to elute all the gases present, which determined the shortest possible time between injections. Since the GC sampled the flow at only one instant during a cycle, it was necessary to control the lean-to-rich transition with respect to the GC injection over a series of identical cycles. This was accomplished by letting the GC free run at a predetermined injection rate and adjusting the lean-to-rich transition time accordingly. Although we did not control the injection time externally, we were able to record the injection time for comparison with the computer controlled lean-to-rich transition. By programming the total lean–rich cycle period to be slightly shorter than the GC repeat time, we were able to sample gas over the entire rich period. The number of sample points (i.e., lean–rich cycles) required to measure through the entire rich period was determined by the length of the rich period in combination with the difference between the lean–rich cycle time and the GC repeat time. Once we knew the transit time from the solenoid valve to the GC inlet (approximately 6 s) we could adjust the initial parameters such that the first few injections sampled gas from late in the

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