

The Effect of Hydrocarbons on the Selective Catalyzed Reduction of NO_x over Low and High Temperature Catalyst Formulations

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ABSTRACT

Selective Catalytic Reduction of NO_x is a promising technology to enable diesel engines to meet certification under Tier 2 Bin 5 emissions requirements. SCR catalysts for vehicle use are typically zeolitic materials known to store both hydrocarbons and ammonia. Ammonia storage on the zeolite has a beneficial effect on NO_x conversion; hydrocarbons however, compete with ammonia for storage sites and may also block access to the interior of the zeolites where the bulk of the catalytic processes take place.

This paper presents the results of laboratory studies utilizing surrogate hydrocarbon species to simulate engine-out exhaust over catalysts formulated to operate in both low (≈ 175 -500°C) and high temperature (≈ 250 -600°C) regimes. The effects of hydrocarbon exposure of these individual species on the SCR reaction are examined and observations are made as to necessary conditions for the recovery of SCR activity. An evolution of SCR catalysts is observed, culminating in nearly complete resistance to hydrocarbon inhibition for the low temperature formulations. Further improvement is needed for the high temperature versions.

incorporating various base metal ions. These zeolites are known to store both hydrocarbons and ammonia. Ammonia storage on the zeolite has a beneficial effect on NO_x conversion, particularly during transient events during which it is difficult to inject sufficient urea to titrate NO_x. Hydrocarbons however, compete with ammonia for storage sites and therefore have a detrimental effect on NO_x conversion, especially at the low temperatures typical of the light-duty FTP-75 cycle [7,8]. In addition, hydrocarbons may block access to the interior of the zeolites where the bulk of the catalytic processes take place.

In this study, surrogate hydrocarbons were used to simulate engine-out exhaust over different zeolite-based SCR catalysts. Hydrocarbon species and concentrations were based upon analytical speciation of engine-out cold start bag samples. Surrogates for engine-out olefins, aromatics and paraffins were employed; the effects of hydrocarbon exposure of these individual species on the SCR reaction are examined and observations are made as to hydrocarbon resistance and necessary conditions for the recovery of SCR activity.

EXPERIMENTAL SETUP

Flow Reactor System

Catalyst testing was carried out in an integral quartz flow reactor. The reactor consists of three segments. The front segment is a gas preheater containing a heat exchanger composed of a honeycomb section of silicon carbide. The center section is a "Tee" arrangement which allows injection of gases just upstream of the catalyst sample. The final tube contains the catalyst sample, usually a core 1.0" D x 1.5" L, wrapped with a mineral wool (Fiberfrax) to prevent gases from leaking past the edges. The entire system is heated by placement within clamshell type furnaces. In all tests described in this report, the overall space velocity was 30,000 hr⁻¹, based on the total geometric volume of the catalyst core. Inlet temperatures were measured by an

INTRODUCTION

One promising technology to enable diesel engines to meet certification under Tier 2 Bin 5 emissions requirements for NO_x is urea based SCR. The Selective Catalytic Reduction (SCR) of NO_x is achieved by injection of urea into the exhaust system upstream of an appropriate catalyst, thereby providing NH₃ (through the thermal decomposition of urea) as the chemical reductant for a number of reactions which collectively result in the reduction of NO_x. To date, this technology has been used primarily for the reduction of NO_x from stationary sources [1], though feasibility for vehicle on-board use has been proven by work at multiple vehicle manufacturers [2-6]. SCR catalysts envisioned for vehicle use are typically composed of zeolitic materials

open bead 0.032" D Type K thermocouple, which was positioned through a central monolith channel with the bead protruding 1/8" in front of the catalyst face.

Sample gases were blended by means of mass flow controllers into a mixing manifold. CO₂, in a parallel stream, was routed through a steam generation system and mixed with the water vapor in the correct proportions to simulate the level of water in diesel exhaust. The CO₂/steam mixture was then mixed with the remaining manifold gases. At this point, the gases were either routed through a by-pass line to be analyzed, or were routed through the catalyst system and thence to the analytical system.

Certain reaction gases were introduced in a somewhat different fashion. To analyze by-pass values, ammonia was introduced into the mixing manifold with the other gases in the normal manner. However, for catalyst testing, the ammonia was introduced by means of the Tee arrangement a few inches upstream of the catalyst. This was done for three reasons; in order to minimize possible homogeneous reactions, to duplicate the on-vehicle injection of urea upstream of the SCR catalyst and to save time insofar as NH₃ is a "sticky" gas and takes a significant amount of time to reach equilibration values. Mixing characteristics of the ammonia injection were determined under various flow and temperature conditions using O₂ as an injected tracer gas and analyzing at various points at the front face of an uncoated cordierite sample. Mixing was determined to be complete and uniform under all conditions examined. In the case of the hydrocarbons employed, those which are liquids at room temperatures (benzene-decane) were introduced by means of a high precision syringe pump into a heated zone which was swept through by gases leaving the mixing manifold.

Analytical system

Gas species were analyzed using a Midac Model I1701 FTIR, operating at a resolution of 0.5 cm⁻¹ and having a pathlength of approximately 3.3m. The gas cell was heated to 121°C and all sample lines downstream of the catalyst test system were heated, eliminating the necessity of separating water from the system with the possible loss of water soluble species (NO₂, NH₃ etc.).

Blank Runs

Prior to catalyst testing, blank runs, i.e. with an empty sample tube, were carried out utilizing a full complement of gases in addition to the individual hydrocarbons to be employed. Upper bound temperatures were ascertained at which reactions occurred homogeneously (cracking etc.) or possibly heterogeneously on the silicon carbide preheater section, upstream of the SCR catalyst. Conditions used for determining the blank reactions are given in Table 1. Note that blank runs contained only single hydrocarbons, not combinations.

Table 1:
Gas concentrations for blank runs

Component	Concentration
Oxygen (O ₂)	14%
Nitric Oxide (NO)	350 ppm
Ammonia (NH ₃)	350 ppm
Carbon Dioxide (CO ₂)	5%
Water (H ₂ O)	4.6%
Ethylene (C ₂ H ₄)	1100 ppm
Propylene (C ₃ H ₆)	700 ppm
Benzene (C ₆ H ₆)	130 ppm
Decane (C ₁₀ H ₂₂)	110 ppm
Nitrogen (N ₂)	Balance

Decane and ethylene were found to be reactive under these test conditions as illustrated in Figures 1 and 2.

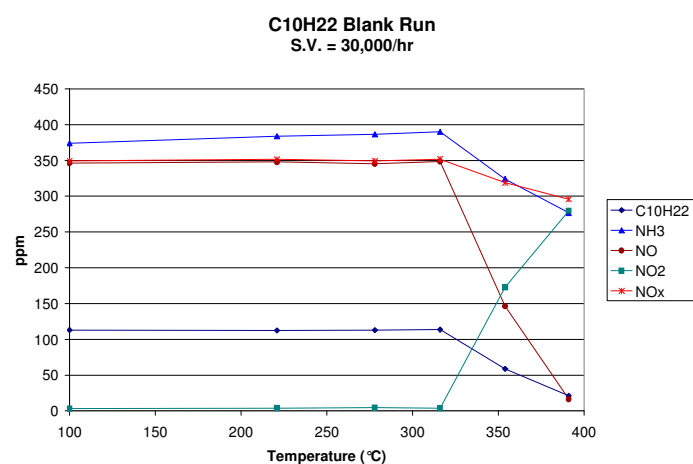


Figure 1: Conversions of gas species in an empty reactor tube using decane as the surrogate hydrocarbon.

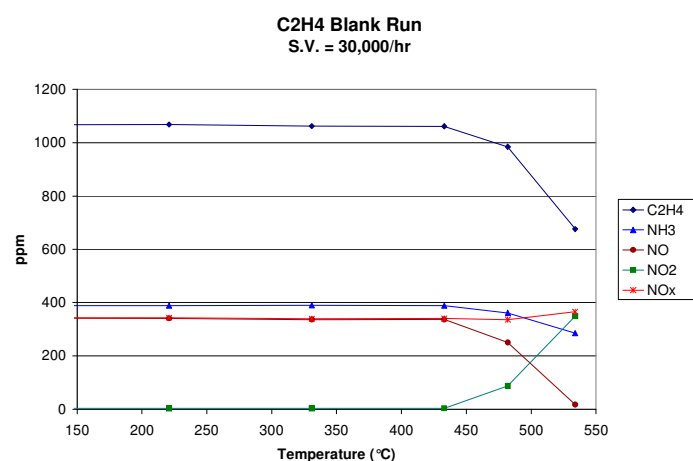


Figure 2: Conversions of gas species in an empty reactor tube using ethylene as the surrogate hydrocarbon.

Figure 1 (e.g.), the decane blank, shows that decane is non-reactive at temperatures up to 315°C, with

homogeneous reactions occurring at about 350°C. Decane, NO and NO_x were lost, with production of NO₂ taking place. In all cases, catalyst test temperatures were kept below the point at which any discernible homogeneous reactions took place. For this reason, any tests involving decane were run to a maximum temperature of 300°C and tests involving ethylene were limited to 400°C.

On a vehicle, we would expect these homogeneous reactions to occur, as in the laboratory. However, we are unaware of any vehicle testing which has been carried out on an uncatalyzed system employing urea injection. This is a gap which we hope will be filled in presently. As an aside, we do not claim to fully understand the myriad reactions taking place above the homogenous cracking points of these hydrocarbons, although one can speculate; e.g., we have observed a condensed red liquid downstream of the sample furnaces when utilizing hydrocarbons. IR analysis shows typical nitro and H-C absorbances, leading to the conclusion that nitrated hydrocarbons are being formed. At any rate, experimental conditions were confined to temperatures below these phenomena.

Propylene and benzene were unreactive to at least 525°C, with all additional species monitored (NO, NO₂ and NH₃) remaining constant; therefore these tests were carried out to 500°C.

RESULTS AND DISCUSSION

Initial Testing—First Generation Low Temperature SCR Catalyst

Hydrocarbon poisoning tests were first carried out on a low temperature formulation, SCR-LT#1, one of the earliest copper-zeolite SCR catalysts and quite typical of the offerings at that time. These were basic tests consisting of putting a hydrocarbon free simulated diesel exhaust reaction gas through the catalyst, attaining steady state conversions and then blending in a known amount of a **single** surrogate hydrocarbon.

The base test gas compositions used are shown in Table 2.

Table 2:
Base gas concentrations

Component	Concentration
O ₂	14%
NO	280 ppm
NO ₂	70 ppm
NH ₃	350 ppm
CO ₂	5%
H ₂ O	4.5%
N ₂	Balance

Note that the 70 ppm NO₂ was included based upon the assumption that an active oxidation catalyst, after aging, would produce 20% NO₂ on average.

Decane, ethylene and benzene were used as surrogates for the paraffinic, olefinic and aromatic components of diesel exhaust gas. From past experience, a heavier straight chain hydrocarbon such as C₁₅-C₁₈ would be more realistic, but experimental difficulties of constant injection of the heavier species made decane an attractive alternative. The relative ratios of the hydrocarbons used in this test series were based on speciation data generated from a light-duty diesel vehicle equipped with a production oxidation catalyst, run over the European MVEG test cycle [9]. The amount of hydrocarbons employed in these tests was based on an analysis of total hydrocarbons produced by a diesel Focus, equipped with a DOC and a 3.6l SCR catalyst, over an FTP test cycle. The amount was normalized for the size of the SCR catalyst sample (1.17in³) employed in the laboratory tests. Finally, the amounts injected were adjusted to simulate 100,000 miles of emissions over five days, i.e. 1 min = 13.8 mi of hydrocarbons.

The mass of injected hydrocarbons used was one of the following:

C₂H₄: 5.13mg/min/in³ catalyst
C₆H₆: 0.52mg/ min/in³ catalyst
C₁₀H₂₂: 0.62mg/ min/in³ catalyst

These tests were run at a temperature of 250°C, an average temperature observed for FTP tests. An example of the addition of decane is seen in Figure 3.

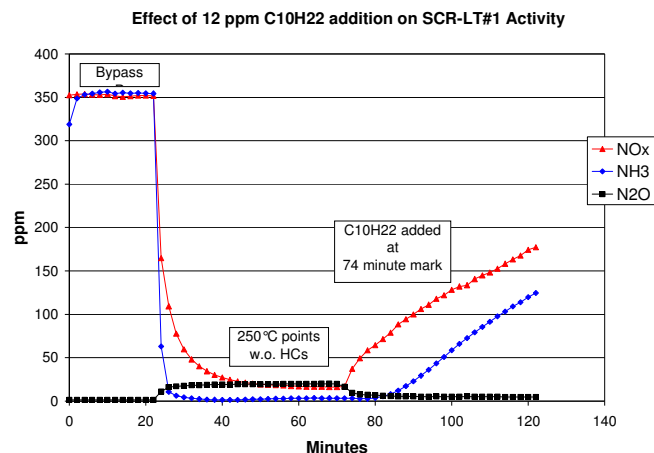


Figure 3: Effect of 12 ppm decane addition to NO_x activity over SCR-LT#1.

Upon addition of decane, there is an immediate loss of NO_x activity with an associated appearance of NH₃. The next figure, Figure 4, shows the effect of the various hydrocarbons employed, with each series representing approximately one hour of hydrocarbon injection.