

# Dual SCR Aftertreatment for Lean NO<sub>x</sub> Reduction

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## ABSTRACT

Low-cost lean NO<sub>x</sub> aftertreatment is one of the main challenges facing high-efficiency gasoline and diesel engines operating with lean mixtures. While there are many candidate technologies, they all offer tradeoffs. We have investigated a multi-component Dual SCR aftertreatment system that is capable of obtaining NO<sub>x</sub> reduction efficiencies of greater than 90% under lean conditions, without the use of precious metals or urea injection into the exhaust. The Dual SCR approach here uses an Ag HC-SCR catalyst followed by an NH<sub>3</sub>-SCR catalyst. In bench reactor studies from 150 °C to 500 °C, we have found, for modest C/N ratios, that NO<sub>x</sub> reacts over the first catalyst to predominantly form nitrogen. In addition, it also forms ammonia in sufficient quantities to react on the second NH<sub>3</sub>-SCR catalyst to improve system performance. The operational window and the formation of NH<sub>3</sub> are improved in the presence of small quantities of hydrogen (0.1-1.0%). The response of the system to other factors such as exhaust oxygen content and space velocity has been explored. The system does not appear to be poisoned by heavy hydrocarbons. It is shown that this approach to lean NO<sub>x</sub> reduction is well matched to low-temperature diesel combustion, and is a potential enabler to satisfy Tier2/Bin5 and Tier2/Bin2 emissions standards.

## INTRODUCTION

Since the pioneering work of Iwamoto et al. (1) and Held et al. (2), extensive research has been done on hydrocarbon selective catalytic reduction (HC-SCR) of NO<sub>x</sub> to N<sub>2</sub>. While the early work focused on a range of metals and washcoat materials, recently the most progress has been made in studies of Ag/Al<sub>2</sub>O<sub>3</sub> catalyst systems (3,4). In particular, work done by members of

the EU KNOWNOX consortium has led to an advance in understanding of this reaction on silver (5). This research has shown that a wide range of hydrocarbons will react well on silver. Testing has included work with diesel fuel in diesel engine testing (6). However, in much of this work, high activity is often limited to temperatures above 350 °C. These catalysts perform much more poorly in the 150 °C to 300 °C range often found in the lean exhausts of diesel engines.

In 1999 to 2000 studies have shown that small amounts of hydrogen in the feedstream improve the low temperature performance of silver-based HC-SCR catalysts (7,8). Since that time a great amount of the effort on Ag systems has focused on understanding the role of hydrogen. The enhancement by hydrogen appears to be limited to silver-based catalysts that are also supported on alumina or silica-alumina zeolites. In addition, the effect of hydrogen is reversible. Usually, H<sub>2</sub> impacts the reaction beneficially upon introduction, while under some conditions its benefits decay with a longer time constant upon its removal, indicating the possible storage of a surface species (9).

More recently Ag/Al<sub>2</sub>O<sub>3</sub>-based catalysts emerged as the most active catalysts in a high throughput study of more than 8,000 catalytic combinations for HC-SCR under diesel conditions (10,11). Studies of these catalysts on a bench reactor (10) and on an engine (11) showed the best conditions for using these Ag/Al<sub>2</sub>O<sub>3</sub> catalysts

The mechanism of the HC-SCR reaction in general, and the "hydrogen effect" in particular, has also been studied intensively. Many papers have explored the effect of silver particle size and the oxidation state of silver. Recent papers (9) have focused on the role of an NCO intermediate in the pathway of the reaction that leads to N<sub>2</sub> as well as other species, such as ammonia. That

same pathway includes the transformation of an  $\text{Ag}^+\text{CN}$  species into the  $\text{Ag-NCO}$  species.

In actual use it has been noted, as mentioned above, that other nitrogen-containing species are formed over the silver catalyst during HC-SCR -- species that may need to be removed from the exhaust. This issue has been addressed by Miyadera and others (12,13), who use one or more catalysts to remove these species. A later study of a combined catalyst system by Arve et al. (14) also examined the effect of a second catalyst on improving low and high temperature  $\text{NO}_x$  removal. One reaction that can remove ammonia-containing species is the selective catalytic reduction of  $\text{NO}_x$  by ammonia. This is an extremely well studied reaction, particularly when the ammonia results from the thermolysis and hydrolysis of urea in commercial systems, the SCR reaction. This work has been reviewed in many locations and the reactions are well understood (15).

Our work here has been carried out to explore how a silver-based HC-SCR catalyst followed by an  $\text{NH}_3$ -SCR catalyst can increase the efficiency of  $\text{NO}_x$  removal. We have found that inducing the HC-SCR catalyst to generate ammonia for subsequent reaction with the  $\text{NH}_3$ -SCR catalyst can significantly increase this efficiency and provide low cost  $\text{NO}_x$  conversion under a range of lean exhaust conditions.

### $\text{NH}_3$ GENERATION WITHIN THE DUAL SCR SYSTEM

In the Dual SCR system the Ag HC-SCR is the initial catalyst. Its function in this method is two-fold. First, as many have shown, it catalyzes the reaction of hydrocarbons, especially heavy straight chain HCs such as  $\text{C}_8\text{H}_{18}$  and  $\text{C}_{12}\text{H}_{26}$ , together with  $\text{NO}_x$ , to produce  $\text{N}_2$ . Large quantities of the saturated, long chain HCs are not needed to effectively reduce  $\text{NO}_x$ . In fact, a C/N ratio of only 3 to 6 is capable of easily achieving up to 75% conversion of  $\text{NO}_x$  to  $\text{N}_2$ . With  $\text{H}_2$  present, further improvements in the Ag HC-SCR catalyst's activity at low temperature are observed. Secondly, in addition to  $\text{N}_2$ , both  $\text{NH}_3$  and  $\text{NO}$  (from unreacted  $\text{NO}_x$ ) can be produced under a range of conditions. Their concentrations and relative ratios are controlled by a variety of factors that include both  $\text{H}_2$  concentration and C/N ratio. As shown in Figure 1a, at 300 °C,  $\text{H}_2$  helps promote the formation of  $\text{NH}_3$ . At a C/N ratio of 3, in the presence of 1%  $\text{H}_2$ , an  $\text{NH}_3/\text{NO}_x$  ratio of ~1 is produced -- an ideal mix for an  $\text{NH}_3$ -SCR catalyst.

The graph also shows that various levels of  $\text{NH}_3$  can be produced as a function of HC concentration. By tuning the quantity of HC and/or  $\text{H}_2$  present, the  $\text{NH}_3$  and  $\text{NO}$  levels exiting the HC-SCR catalyst can be adjusted to provide the ideal  $\text{NH}_3:\text{NO}$  ratio of 1:1 which would be preferred by the  $\text{NH}_3$ -SCR catalyst that follows (16). The Dual SCR concept is shown schematically in Figure 1b, with only the N-containing species of interest shown. As we will show, the overall  $\text{NO}_x$  conversion efficiency achieved by the combination of these two catalysts can be as high as 95% over a range of exhaust conditions.

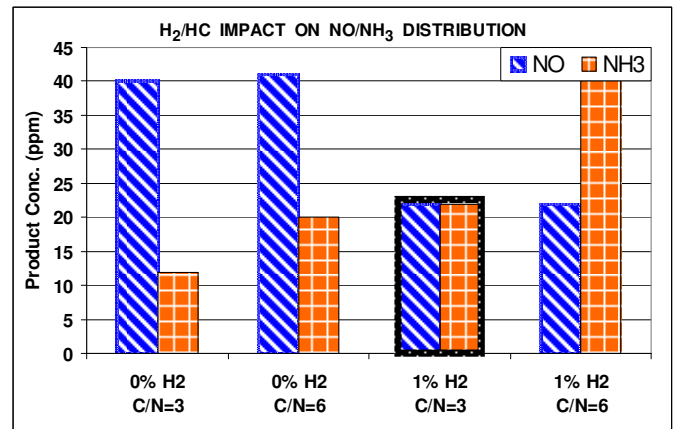


Fig.1a. Ag HC-SCR  $\text{NH}_3$  and  $\text{NO}$  product distribution. 300 °C, 27,000  $\text{h}^{-1}$ , 8%  $\text{O}_2$ , 4%  $\text{CO}_2$ , 6%  $\text{H}_2\text{O}$ , 140ppm  $\text{C}_3\text{H}_8$ , 200ppm  $\text{NO}/\text{NO}_2(1:1)$

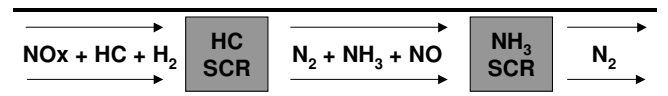


Fig 1b. Dual SCR Concept

## EXPERIMENTAL DESCRIPTION

The basic features of the bench gas reactor system used in this work, to characterize the Dual SCR catalyst system, have been previously described (17). However, the system, as it exists today, employs two separately heated sections (Fig. 2). The main reactor that thermally manages the gas flow to the catalyst is the same as in earlier designs. The secondary or side reactor serves as a heat exchanger to aid in mixing and vaporizing of liquid fuels, such as the dodecane or iso-octane used here. These liquid fuels are first injected and predominantly vaporized ahead of the secondary reactor by use of an MKS Direct Liquid Injection System. The vaporized fuel is carried by a nitrogen balance gas to blend down the fuel component concentration. The desired flow of fuel can then be added to the main reactor flow by use of a high temperature flow controller. At that point, all the components of the gas feed to the catalyst are present and blended as they pass through the main reactor furnace.

The space velocity of the gas feed is normally 27,000  $\text{h}^{-1}$ , but additional data was taken at 50,000  $\text{h}^{-1}$ . All of the gases are of research purity with their flow metered by calibrated flow controllers in a range chosen to selectively mimic light duty diesel exhaust. The lines used to transport the gas stream to the reactors and the sampling lines to the analyzers are heated to a minimum of 165 °C and are silica-passivated to inhibit unwanted reactions or loss of product. Standard components of our simulated exhaust feed include  $\text{NO}(0\text{-}800\text{ppm})$ ,  $\text{NO}_2(0\text{-}400\text{ppm})$ ,  $\text{O}_2(0\text{-}8\%)$ ,  $\text{CO}_2(4\%)$ ,  $\text{CO}(350\text{-}700\text{ppm})$ ,  $\text{C}_3\text{H}_8(140\text{ppm})$ ,  $\text{C}_7\text{H}_8(0\text{-}75\text{ppm})$ ,  $\text{C}_{12}\text{H}_{26}(0\text{-}200\text{ppm})$ ,  $\text{C}_8\text{H}_{18}(0\text{-}200\text{ppm})$ ,  $\text{H}_2\text{O}(6\%)$ , and balance  $\text{N}_2$ . For most of the work reported here, a C/ $\text{NO}_x$  ratio of 3:1 or 6:1 was used. The catalysts that were characterized in the system were placed at the end of the heated lines in the main reactor furnace. This allowed catalyst heating only

via heated gas and monitoring of catalyst temperature changes associated with reactions occurring on the catalysts. Temperatures were measured both before the first catalyst and after the first or second catalyst depending if one or both catalysts were used. These catalysts were also thermally isolated to minimize loss of heat through the walls of the transport tube. The catalyst samples used in this paper were made of proprietary formulations. The HC-SCR catalyst substrate was  $\text{Al}_2\text{O}_3$  and in bead form. This catalyst was washcoated with Ag to give an active surface for HC based  $\text{NO}_x$  reduction. Between this catalyst and the following  $\text{NH}_3$ -SCR catalyst was approximately 0.5" of quartz wool to physically separate the two catalysts. The second catalyst, as mentioned, was a  $\text{NH}_3$ -SCR catalyst based on an extruded zeolite monolith. The source and composition

of the catalyst is proprietary, but is believed to be a Fe-based zeolite. Activity data was generally taken between 150 °C and 500 °C with steady state data recorded at either 200 °C or 300 °C to compare with temperatures found in light-duty diesel vehicles. Typical experiments included slowly ramping the catalyst down in temperature and monitoring its  $\text{NO}_x$  products to obtain the  $\text{NO}_x$  reduction efficiency of the system under quasi steady state or isothermal conditions. This data will also be used for future modeling efforts of the dual catalyst behavior. Other experiments involved maintaining the catalyst or catalysts at a predefined temperature and measuring their response to different gas compositions. Catalyst cleaning, after long exposures to inlet gas

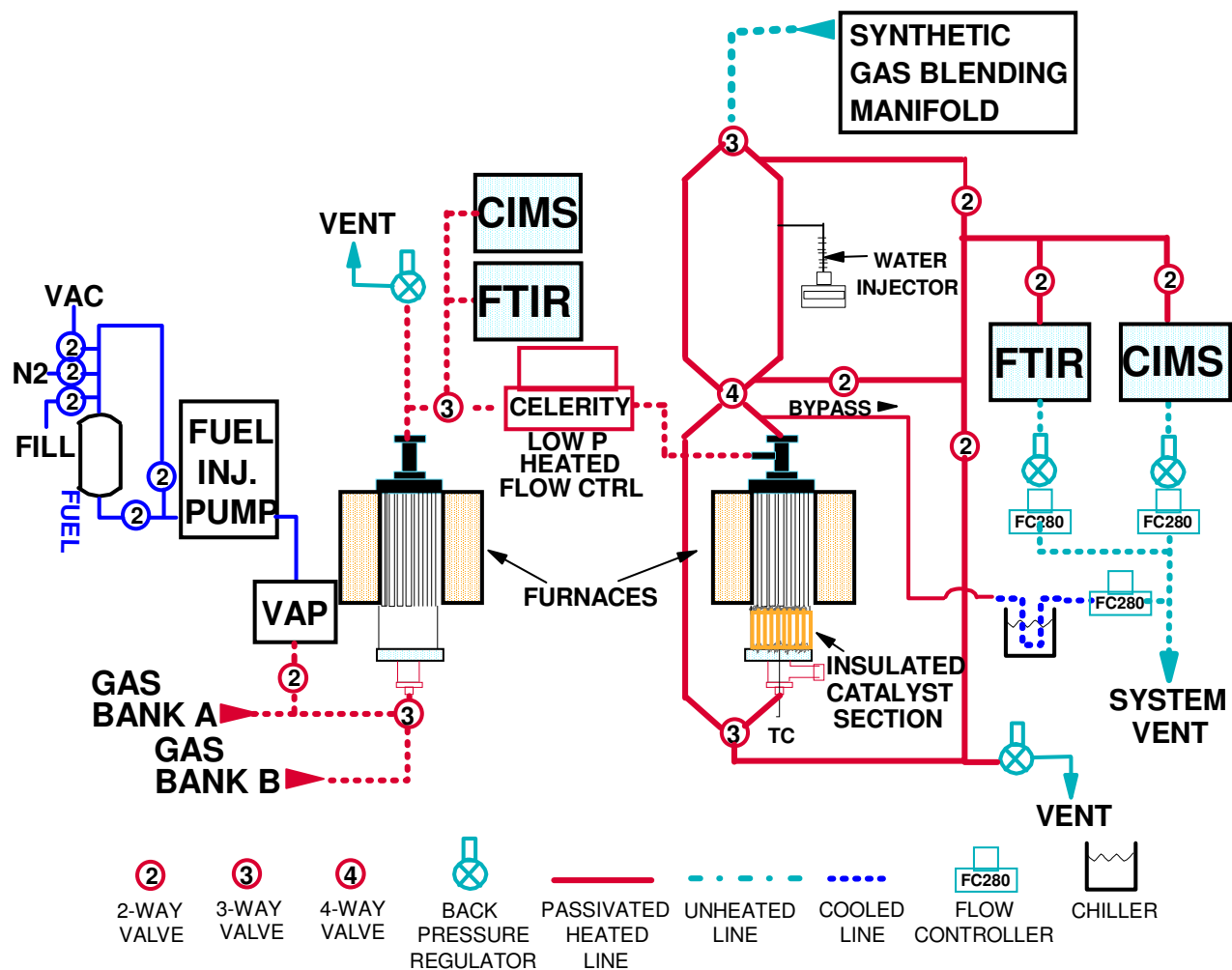


Fig 2. Emissions Characterization Bench Reactor System

feeds, was accomplished by heating the dual catalyst to 600 °C in the presence of 10%  $\text{O}_2$  and 6%  $\text{H}_2\text{O}$ .

The gas analysis components of this system include a Chemical-Ionization Mass Spectrometer (CIMS) and a Fourier Transform Infrared Spectrometer (FTIR). Together, these analyzers provided quantitative data on a wide range of HC- and N-containing species so that mass balances can be estimated. The system allows for

nearly second by second analysis of gases both before and after the catalysts to obtain conversion efficiencies.

## RESULTS FOR THE SILVER CATALYST

### A. $\text{NO}_x$ Reduction Activity of an Ag HC-SCR Catalyst: Role of Reductants

Before the  $\text{NO}_x$  reduction efficiency of the combined HC-SCR and  $\text{NH}_3$ -SCR system can be defined, we must first

determine the activity of the HC-SCR component. For the purpose of this paper, we will first examine the HC-SCR catalyst. As with other HC-SCR catalysts, the bulk of the NO<sub>x</sub> reduction activity of this catalyst comes from reactions between HC species and NO<sub>x</sub> components of the feed over the catalyst in the presence of oxygen.

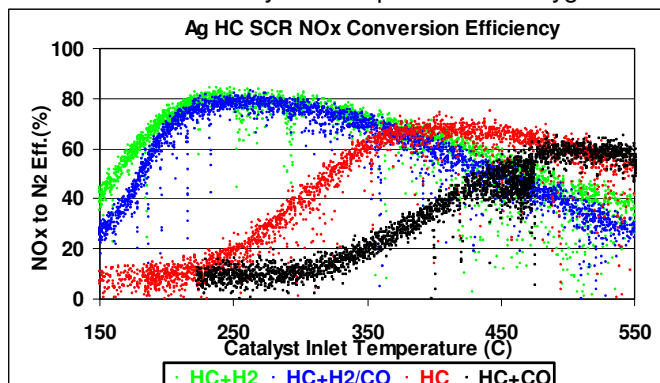


Fig. 3. Reductant Influence on Ag HC-SCR Efficiency. 27,000 h<sup>-1</sup>, 8% O<sub>2</sub>, 4% CO<sub>2</sub>, 6% H<sub>2</sub>O, C/N=4, 350ppm CO, 1% H<sub>2</sub>, 140ppm C<sub>3</sub>H<sub>8</sub>, 200ppm NO/NO<sub>2</sub>(1:1), 100ppm C<sub>8</sub>H<sub>18</sub>

Figure 3 shows that when C<sub>8</sub>H<sub>18</sub> is the only reductant present, NO<sub>x</sub> reduction begins to peak at about 350 °C with a NO<sub>x</sub> conversion efficiency of ~70% (18). The presence of other reducing agents such as CO actually shifts the lightoff to higher temperatures by ~100 °C and lowers the overall conversion efficiency to 60%. CO (350ppm) is essentially poisoning the HC + NO<sub>x</sub> reaction. Conversely, the presence of 1%H<sub>2</sub> dramatically lowers the lightoff temperature to 170 °C when C<sub>8</sub>H<sub>18</sub> is the only other reductant present, and improves the peak NO<sub>x</sub> reduction to 80%. The presence of both H<sub>2</sub> and CO, together with C<sub>8</sub>H<sub>18</sub>, shows only the synergistic effect of the H<sub>2</sub> and HC together. This indicates that H<sub>2</sub> is able to completely negate the interfering effects of CO and improve NO<sub>x</sub> reduction efficiency, especially at low temperatures.

A number of different mechanisms have been proposed to explain why H<sub>2</sub> improves the NO<sub>x</sub> activity of silver, in addition to that in Ref. 9. One group, led by Satsuma and Satokawa, has shown UV evidence that H<sub>2</sub> helps create reversible Ag clusters that support heavy HC reactions with NO<sub>x</sub> (8,19). Others have speculated that H<sub>2</sub> destabilizes surface nitrates (20) that tend to poison the surface reactions of Ag, and liberates the nitrates as NO<sub>2</sub> gas. In either case, the effect is readily visible and the activity of the catalyst in the presence of H<sub>2</sub> is stable.

## B. H<sub>2</sub> Concentration and NO<sub>x</sub> Reduction Products

The previous results show the importance of H<sub>2</sub> in aiding heavy HC reduction of NO<sub>x</sub>. In order to better quantify this effect, various concentrations of H<sub>2</sub> were used in the feed gas and the resulting NO<sub>x</sub> conversion efficiencies were measured. Figure 4 shows that as H<sub>2</sub> is removed from the reactant mixture, the low temperature NO<sub>x</sub> performance of the catalyst exhibits the most decline.

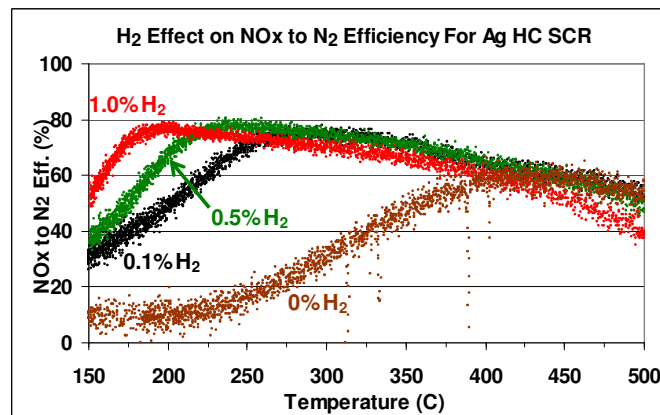


Fig. 4. H<sub>2</sub> Influence on Ag HC-SCR NO<sub>x</sub> Efficiency. 27,000 h<sup>-1</sup>, 8% O<sub>2</sub>, 4% CO<sub>2</sub>, 6% H<sub>2</sub>O, C/N=3, 140ppm C<sub>3</sub>H<sub>8</sub>, 200ppm NO/NO<sub>2</sub>(1:1)

This is represented by a shift in lightoff temperature for NO<sub>x</sub> reduction to progressively higher temperatures. The temperature for peak NO<sub>x</sub> reduction is also shifted higher as H<sub>2</sub> is removed. However, the peak NO<sub>x</sub> conversion efficiency is relatively unaffected at ~75%. The data also indicates relatively low levels of H<sub>2</sub> in the feed (0.1-1.0%) are able to aid NO<sub>x</sub> reduction in three ways. First, the temperature window for NO<sub>x</sub> reduction is substantially widened. Second, the peak in NO<sub>x</sub> activity is lowered from 400 °C (0% H<sub>2</sub>) to 250 °C (0.1% H<sub>2</sub>) to 180 °C (1% H<sub>2</sub>). Lastly, the overall NO<sub>x</sub> activity is boosted by 15% in the presence of H<sub>2</sub>.

Thus far, only NO<sub>x</sub> conversion to N<sub>2</sub> has been discussed. However, other nitrogen containing species are also represented in the product distribution. We have observed, under most conditions studied here, that those species are mainly NO and NH<sub>3</sub>. No other species were verified in any significant concentration other than unreacted NO<sub>2</sub>. The relative concentrations of these species are important because of their ability in the dual catalyst system to react (NO<sub>x</sub> + NH<sub>3</sub> → N<sub>2</sub>) over a NH<sub>3</sub>-SCR Catalyst to increase the overall NO<sub>x</sub> conversion to N<sub>2</sub>. To gain additional insight into the role of H<sub>2</sub> in this process, the concentrations of NO and NH<sub>3</sub> evolved from the HC-SCR catalyst, were also measured as a function of H<sub>2</sub> concentration. Figure 5 demonstrates, at 300 °C,

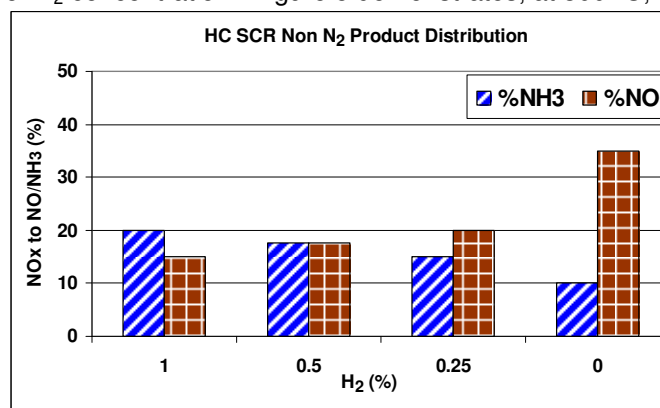


Fig. 5. Ag HC-SCR H<sub>2</sub> Effect on NO/NH<sub>3</sub> distribution. 300 °C, 27,000 h<sup>-1</sup>, 8% O<sub>2</sub>, 4% CO<sub>2</sub>, 6% H<sub>2</sub>O, C/N=3, 140ppm C<sub>3</sub>H<sub>8</sub>, 200ppm NO/NO<sub>2</sub>(1:1)