

Study of On-Board Ammonia (NH₃) Generation for SCR Operation

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ABSTRACT

Mechanisms of NH₃ generation using LNT-like catalysts have been studied in a bench reactor over a wide range of temperatures, flow rates, reformer catalyst types and synthetic exhaust-gas compositions. The experiments showed that the on board production of sufficient quantities of ammonia on board for SCR operation appeared feasible, and the results identified the range of conditions for the efficient generation of ammonia. In addition, the effects of reformer catalysts using the water-gas-shift reaction as an in-situ source of the required hydrogen for the reactions are also illustrated. Computations of the NH₃ and NO_x kinetics have also been carried out and are presented. Design and impregnation of the SCR catalyst in proximity to the ammonia source is the next logical step.

A heated synthetic-exhaust gas flow bench was used for the experiments under carefully controlled simulated exhaust compositions. Operating conditions include rich-lean cycles so that the transient production of NH₃ and the reduction of NO_x could be monitored. The bench offered significant flexibility and separate control over the wide ranges of temperatures, flow rates, and the compositions of the mixture. Gas concentrations were measured by Fourier Transform Infrared (FT-IR) Spectroscopy.

INTRODUCTION

Improvement of the fuel economy in internal combustion engines is important in confronting the problem of global warming. Using diesel engine is an obvious and reasonable way of improving the fuel economy of vehicles and industrial machines. However, containing the harmful emissions such

as particulate matter (PM) and the oxides of nitrogen (NO_x) from diesel engines remains as a major challenge. To reduce these emissions, aftertreatment devices are effective solutions. Diesel Particulate Filter (DPF) technology is the dominant technology to reduce PM, while multiple options of NO_x reduction techniques are making their way to the market, which depend very much on engine application. Unlike the gasoline engine, the exhaust gases from a diesel engine produce an oxygen-rich environment, making it difficult to use the Three Way Catalyst (TWC) to reduce NO_x.

The two leading technologies to reduce NO_x are Lean NO_x Trap (LNT) and ammonia Selective Catalytic Reduction (SCR). LNT technology has already been commercialized in some pick-up trucks in the US market, for instance [1]. However, the LNT catalysts are relatively expensive compared with SCR catalysts, because the LNT catalysts include precious metals such as platinum, palladium and rhodium. On the other hand, SCR is another promising technology which can reduce NO_x with little precious metals and better fuel consumption compared to the LNT [2]. SCR technology is currently used in on-road truck engines in US, Europe and Japan. However, the urea (or ammonia) injection system and infrastructures are needed for the SCR technology. Freeze protection of urea also needs to be considered.

An LNT and SCR combined system has been investigated to overcome some of these difficulties in recent years. The concept involves two types of catalysts. One catalyst similar to that in LNT converts NO_x into N₂ and NH₃ with reductants such as CO and/or H₂. The other catalyst is an SCR-type catalyst which can store ammonia produced by the

former catalyst and reduce NO_x with the stored ammonia. This LNT-SCR system can achieve high NO_x conversion efficiency with a small amount of precious metals and without an external source of urea.

Lambert [3] described an LNT and SCR combined system for automotive diesel NO_x reduction. The system uses LNT and SCR catalysts in series to utilize the NH₃ generated by the LNT during regeneration to further reduce NO_x emissions by the SCR catalysts. In 2007, the first commercial application of a composite LNT-SCR system in a passenger vehicle appeared in the US [4]. The car meets Tier2 Bin5 emission standards and the emission control system includes a close-coupled diesel oxidation catalyst, followed by an NO_x adsorber catalyst, a diesel particulate filter, and an SCR catalyst (without urea injection). Morita et al [5] have reported a two-layer LNT-SCR system. The lower layer promotes adsorption of NO_x in a lean-mixture condition and the conversion of NO_x to NH₃ in a rich mixture. The upper layer ensures NH₃ storage in the rich-mixture condition and the NH₃ SCR reaction in the lean. Hu et al [6] have also presented an LNT-SCR system which includes a fuel dozer and a fuel reformer catalyst. The fuel reformer catalyst works to convert injected diesel fuel to H₂ and CO as a reductant. Stanglmaier et al [7] also studied a commercial LNT as a possible H₂ reformer in SCR operation in series with the LNT but provided limited data or analysis.

The LNT-SCR system includes two types of catalysts with significant interactions between the catalysts. This complexity makes the system operation more intricate. The mechanisms of the overall NO_x conversion have not been fully illustrated. While NO_x reduction in SCR catalysts has been widely investigated by many researchers, the NH₃ generation in an LNT-type catalyst is very important in the composite system, but the detailed processes have not been widely elucidated nor published. This paper aims at exploring and discussing the in-situ ammonia generation for on board SCR operation in lieu of urea.

This study focuses mainly on investigating the mechanisms and the appropriate conditions and sensitivities of NH₃ generation in the LNT catalyst. The effects of environmental factors and the catalysts on NH₃ generation are investigated through the experiments. The catalyst modeling is carried out in conjunction with the experimental results to gain a deeper understanding of the NH₃ generation mechanisms.

EXPERIMENTAL SETUP

A synthetic exhaust gas flow bench was used in this study because it was necessary to specify precise test conditions not easily achievable in a real diesel engine. The test bench allows flexible independent control of the temperature, flow rate, and the composition of the mixture. The catalyst

samples were cut into a small piece from a catalyst brick. Gas concentrations were measured by a Fourier Transform Infrared (FT-IR) spectrometer.

SYNTHETIC EXHAUST GAS FLOW BENCH

The system is composed of gas sources, flow controllers, mixing chamber, in-line heaters, catalyst, and gas analyzers, shown in Figure 1.

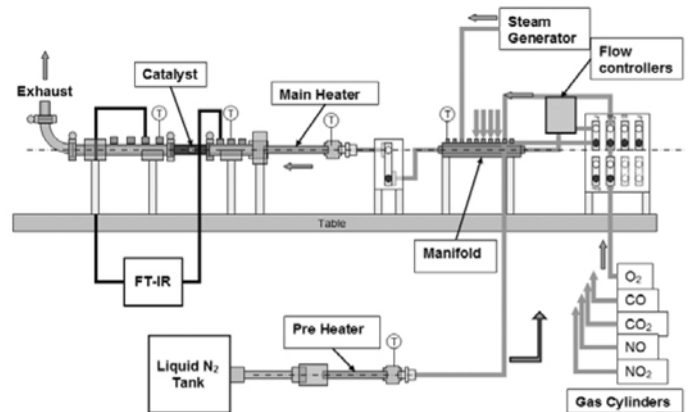


Figure 1. Synthetic exhaust gas flow bench

Liquid nitrogen is used as a source of carrier gas. The nitrogen gas passes through an in-line heater which is controlled by a PID controller. The in-line heater brings the cold N₂ up to room temperature, if necessary. N₂ and other gases are led through flow meters, mass flow controllers or solenoid valves which precisely meter the mixture flow that goes into the catalyst. The solenoid valves and mass flow controllers are controlled by a Labview system and deliver flexible flow rates as specified. The solenoid valves and mass flow controllers are programmed to produce periodic lean and rich conditions which are needed in the LNT-SCR system.

SYNTHETIC DIESEL EXHAUST GAS

Synthetic gas mixtures resembling diesel exhaust were used in the experiments. The synthetic gas was composed of O₂, CO, CO₂, NO, NO₂, H₂, water and the balance N₂. Each gas was provided by individual gas cylinders. Appropriate gas-composition ranges reflect those in typical real diesel engine operation. The LNT-SCR principle requires periodic lean-rich regeneration cycles. The lean-rich cycles used for these tests were a 45-second lean condition followed by a 5-second rich condition repeated cyclically, except when the cycle duration was the test parameter. The temperature of the synthetic gas was selectable from 50 °C to 500 °C. These gases were well mixed in the mixing chamber downstream of the flow meters. The flow of the mixture was metered and controlled by a large rotameter. Next, the mixture was heated up to the target temperature by an in-line heater. The heated

mixture then entered the catalyst. Temperatures, pressures and gas compositions were measured at the inlet and the outlet of the catalyst. The catalyst was covered by a heat-resistant mat and placed in the tube. The temperature of the catalyst was assumed to be the average between the mixture temperatures at 50 mm upstream and at 50mm downstream of the catalyst, which differ typically by about 30 °C.

CATALYSTS

Three core catalyst samples, all on monolith supports, were used in this study. One sample was an off-the-shelf LNT, which was tested as an ammonia generation catalyst. The other two samples were reformer catalysts, intended to provide some LNT function with enhanced in-situ hydrogen generation. The standard LNT was taken from a vehicle. The reformer catalysts were custom formulated and were supplied by a catalyst manufacturer per our request. The reformer catalysts were used to produce hydrogen from water and carbon monoxide to help ammonia generation. The catalyst configurations are provided in [Table 1](#).

Table 1. Catalyst configurations

Catalyst	LNT	Reformer No.1	Reformer No.2
Cells/in2	400	400	400
Diameter (mm)	30.5	30.5	30.5
Length (mm)	12.7 – 50.4	38.1	38.1
Formulation	Ba-based Pt/Pd/Rh Total 3g/L	-	-

GAS COMPOSITION ANALYSIS

A MultiGas 2030 (MKS inc.) analyzer was used in this study. The analyzer is a Fourier Transform Infrared (FTIR) based analyzer that is capable of ppb to ppm sensitivity for multiple gas species in a variety of applications, such as in stack emissions monitoring, ambient air, automobile and diesel exhaust, and SCR monitoring. In addition, the analyzer has a built-in O₂ sensor. The gas concentration data were averaged over 4 cycles under stabilized condition.

TYPICAL CONCENTRATION TRANSIENT PROFILES

FTIR measurements of the transient behavior of NO_x, N₂O and NH₃ for the baseline condition at 160 °C (details apparent in subsequent sections) are shown in [Figure 2](#). The test used 45 seconds of a lean cycle followed by 5 seconds of a rich cycle, as recorded and shown in the dashed rich-lean signal in the figure. As expected, the gaseous concentrations downstream of the catalyst are periodic in time. As the lean cycle starts, NO_x begins to be adsorbed by the catalyst with decreasing NO_x for a portion of the lean cycle. Then NO_x

risers when NO_x conversion (delayed from the previous rich cycle) diminishes or when the stored NO_x reaches the storage capacity of the catalyst. Next, rich condition starts. After a short delay, NH₃ is generated, which would not have been present in the absence of the rich cycle. NO_x and N₂O are also released from the catalyst during the rich cycle, but NO_x quickly reduces again as NO_x reduction starts due to the rich condition or when absorption on the storage catalyst resumes when the lean cycle re-starts. It is a primary objective in this study to explore the sensitivity of the ammonia generation and the transient gaseous behavior to a range of parameters.

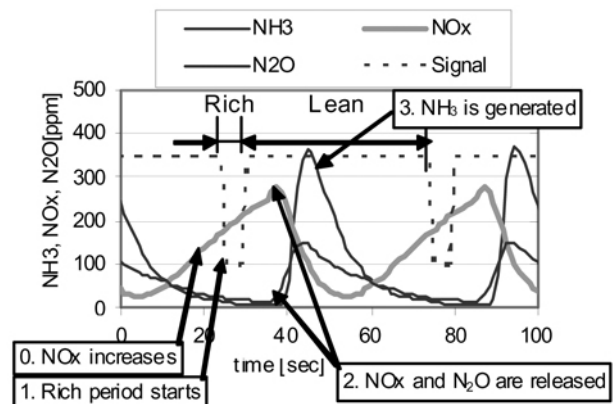


Figure 2. Typical concentration curves during cycling

EXPERIMENTAL RESULTS AND DISCUSSIONS

NH₃ OXIDATION TEST

To better understand the NH₃ kinetics in subsequent NH₃ generation tests, NH₃ oxidation as a function of temperature in O₂ and N₂ only was first measured to determine the temperature range of NH₃ oxidation. Gas compositions of the mixture are listed in [Table 2](#). The mixture was fed into the catalyst at preset temperatures. The flow rate was constant without lean-rich cycling.

Table 2. Testing Conditions for NH₃ Oxidation Study

O ₂	6 %
NH ₃	1100 ppm
N ₂	(Balance)
Temperature	100 - 350 °C
SV	50000 h ⁻¹

The results of the NH₃ oxidation test are shown in [Figure 3](#). NH₃ oxidation and NO_x and N₂O formation were observed at high temperatures. NH₃ after the catalyst was almost completely oxidized above 250 °C in the presence of O₂. In contrast, NO_x was generated above 250 °C and continued to

increase with temperature. N_2O was also observed at high temperatures, however, peak generation was observed at 280 °C and N_2O generation dropped again above 300 °C. According to the results, high temperature promotes NH_3 oxidation and accelerates NOx and N_2O generation. These results are related to the oxidation ability of the catalyst. Therefore, in interpreting the following NH_3 generation results, it should be noted that some ammonia could have been oxidized at the higher temperatures.

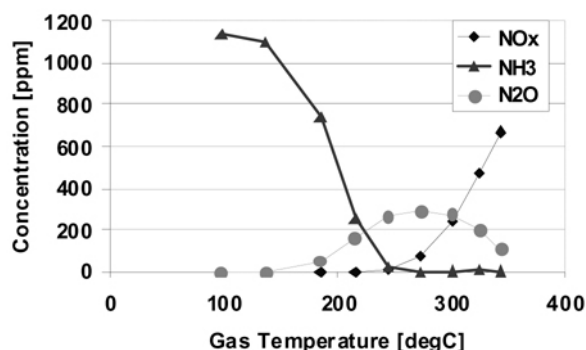


Figure 3. NH_3 conversion to NOx and N_2O

THE EFFECT OF TEMPERATURE ON NH_3 GENERATION

The generation of NH_3 and the reduction of NOx as a function of temperature were measured. The synthetic exhaust gas included lean and rich cycle. The lean and rich cycles used for the test were 45 seconds and 5 seconds respectively. Hydrogen was used as a reductant in the rich mixture. The test conditions are listed in Table 3.

Table 3. Testing condition for NH_3 generation as a function of temperature

		Lean	Rich
N_2	%	(Balance)	
O_2	%	6	0
H_2	ppm	0	20000
NO	ppm	500	
Temperature	°C	50 – 350	
Catalyst size	mm	D 30.5 x 38.1	
Flow rate	SLPM	23	
SV	h^{-1}	50000	

Figure 4 shows the time-averaged NH_3 and N_2O generation from the LNT as a function of temperature. NH_3 generation was observed only between 100 and 200 °C. As expected, no appreciable NH_3 is formed above 250 °C. NOx reduction was high between 120 °C and 220 °C.

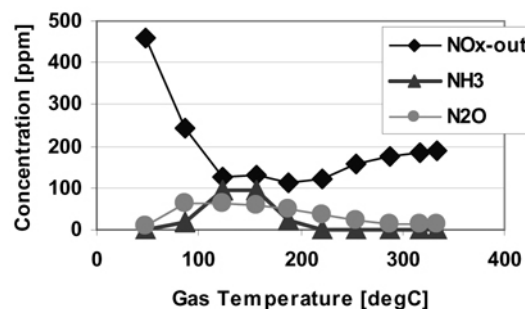


Figure 4. NH_3 generation and N_2O generation as a function of temperature

A number of reasons can be given for the result of a temperature range for NH_3 generation. Below 100 °C, NOx desorption and NOx reduction are minimal due to low catalyst activity. The catalyst starts to increase NOx desorption and reduction around 100 °C, however, the activity of reductant would still be low at that temperature. The NOx desorption and reducing ability of the catalyst and the activity of reductant become higher above 120 °C. Therefore, high NH_3 generation is observed. At still higher temperatures above 180 °C, NH_3 oxidation begins to become significant, thereby limiting the net amount of NH_3 produced above 180 °C. NOx reduction is high between 120 °C and 220 °C. Corresponding to the NH_3 formation rate, the highest NOx conversion efficiency is observed at about 150 °C.

The apparent existence of an effective temperature window in the 100-200 °C range suggests both a constraint and an opportunity in the design and control of the catalyst operation. The results imply that NOx reduction via the intermediate step of NH_3 can improve NOx conversion efficiency even at low temperatures in the actual LNT-SCR system. In the full composite system operation, the SCR catalyst “downstream” of the LNT would further reduce NOx with the NH_3 generated from the LNT. The downstream SCR catalyst location could physically be in close proximity to the LNT catalyst.

THE EFFECT OF FLOW RATE

Flow speed and Space Velocity (SV) are important in determining optimum catalyst configurations. The generation of NH_3 and reduction of NOx as a function of flow rate were measured at constant catalyst size, in the first series of tests. The lean and rich gas compositions are the same as those described in the temperature sweep test. The flow rate used ranged from 13 to 37 SLPM; so for the same catalyst the corresponding SV ranged from 30,000 to 80,000 h^{-1} , as shown in Table 4. In the second series of tests, flow rate was kept constant while the catalyst size was changed, resulting in different space velocities.

Table 4. Testing condition for NH₃ generation as a function of flow speed at constant catalyst length

		Lean	Rich
N ₂	%	(Balance)	
O ₂	%	6	0
H ₂	ppm	0	20000
NO	ppm	500	
Temperature	°C	50 – 350	
Catalyst size	mm	D 30.5 x 38.1	
Flow rate	SLPM	13, 23, 37	
SV	h ⁻¹	30K, 50K, 80K	

Figure 5 and Figure 6 show NH₃ generation and NOx reduction as a function of flow rate. High NH₃ generation and high NOx conversion efficiency were observed at high flow rate (high SV) conditions. Usually high NOx conversion efficiency to N₂ has been observed at low flow rates (low SV). One reason why there is a different trend with NOx to NH₃ conversion is that the kinetics of the reduction mechanisms could be so different to the extent that ammonia generation would be dependent on diffusion rates of bulk gas species to the active catalyst surface. The diffusion rate to the surface increases at high flow rates. In addition, fresh catalysts were used in this study, which provided ample NOx adsorption sites on the catalyst for even the high SV conditions. The next section addresses NH₃ generation at various space velocities at a constant flow rate.

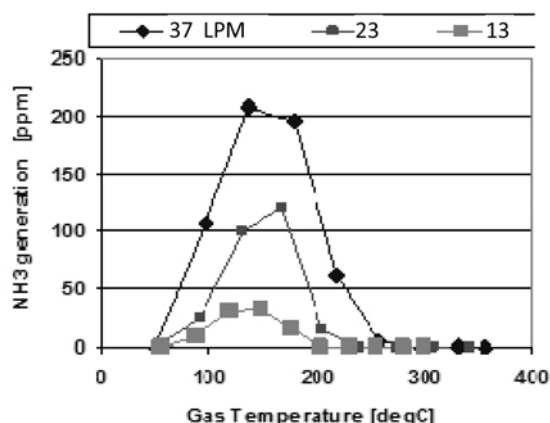


Figure 5. NH₃ generation as a function of flow speed

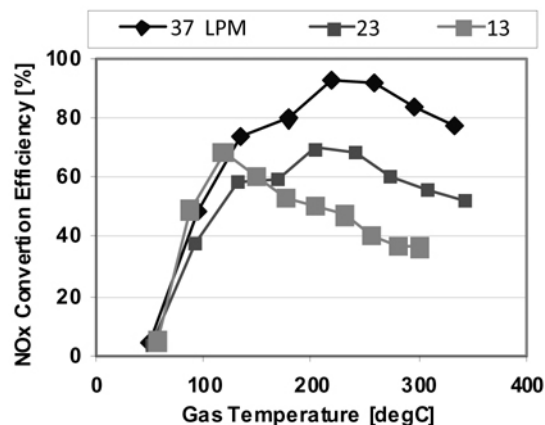


Figure 6. NOx conversion as a function of flow speed

THE EFFECT OF CATALYST LENGTH

The effect of catalyst length was investigated. The lean and rich gas compositions were the same as those in the previous test and the flow rate was maintained constant (23SLPM) through the tests. The length of the catalyst samples varied from 12.7 mm to 50.8 mm with the same diameter (30.5mm). According to the sample length, SV was changed from 40,000 to 150,000 h⁻¹.

Figure 7 and Figure 8 show the effect of catalyst length on NH₃ generation and NOx conversion. The catalyst length did not have much effect on the NOx conversion efficiency. NH₃ generation was also at about the same level for most of the catalyst lengths except at the longest catalyst at 50.8 mm, where NH₃ generation actually dropped. These results show that flow speed is a more important factor for NOx conversion to NH₃ than catalyst length, and lend credence to the hypothesis that diffusion to and from the surfaces plays an important role in NOx conversion to ammonia, in contrast to that in conversion to nitrogen.

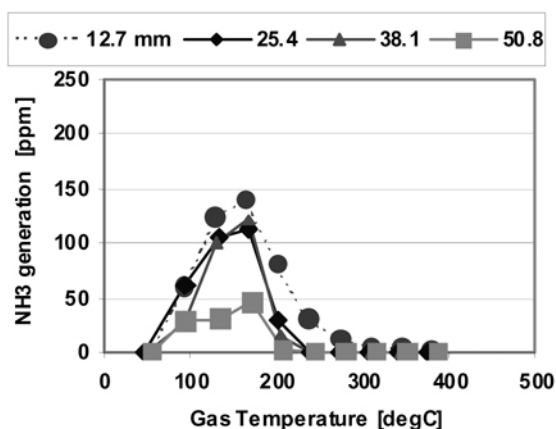


Figure 7. The effect of catalyst length on NH_3 generation as a function of catalyst length at constant flow speed

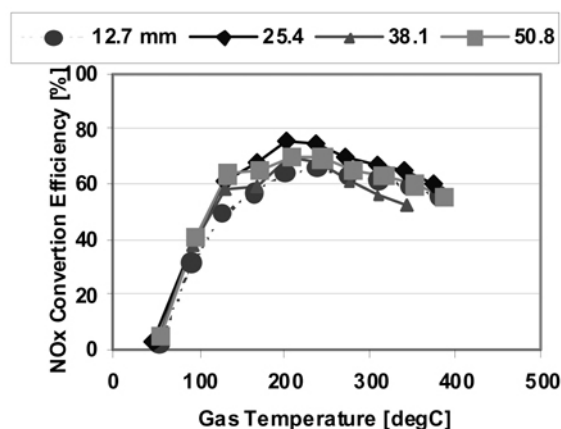


Figure 8. NO_x conversion efficiency as a function of catalyst length

Another possible reason why flow speed is important for NO_x conversion and NH_3 generation is axial mixing between the lean and rich mixtures. The mixing between lean and rich mixtures is depicted in [Figure 9](#). Lower flow speed provides a longer residence time of the mixtures prior to reaching the catalyst. The increased mixing between the rich and lean mixtures could have oxidized some of the hydrogen in the rich mixture [8], depriving the supply of the reductant for NO_x reduction. However, this effect should be small at real engine conditions because the flow speed in the real engine exhaust is much higher than at this test condition (bench 0.3 - 0.8 m/s, engine 1.5 - 6.0 m/s). The transit time from the engine to the aftertreatment system is so short that the effect of the rich-lean mixing would be small. Besides, two separate series of tests were conducted to illustrate the flow speed effect in the bench reactor. Hence axial mixing (and reductant depletion) could be a peripheral unintended cause for the observation that reduced flow speed decreased ammonia generation.

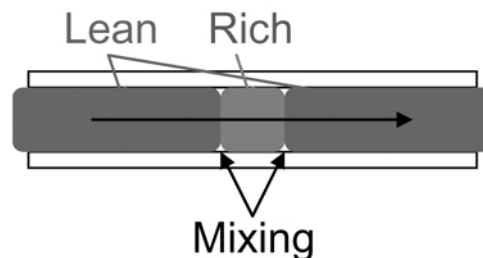


Figure 9. Mixing surface between lean and rich mixture

A similar argument that the higher SV for NH_3 generation (e.g. $150,000 \text{ h}^{-1}$; 12.7 mm catalyst) is preferable to low SV (e.g. $40,000 \text{ h}^{-1}$; 50.4 mm catalyst) can be ascribed to the effect of residence time of the gas mixture in the catalyst and the amount of stored O_2 in the Pt and ceria sites of the catalyst. The residence time in the short catalyst is shorter than in the long catalyst. The argument is applied to the ammonia oxidation kinetics rather than to the NO_x -to-nitrogen reduction kinetics. The long residence time of the gas mixture in the catalyst would accelerate NH_3 oxidation. In addition, the long catalyst contains a larger amount of O_2 in the Pt and ceria sites than the short catalyst. Long residence time and large amount of O_2 are considered to consume NH_3 in the long catalyst. However, there would be an upper limit of SV in high NH_3 generation, because once flow times become sufficiently short, chemical times, as that in the NO_x to NH_3 generation reaction, will begin to become the rate limiting factor. Fresh catalysts were used in this study, therefore, the NH_3 generation reaction would be very active even in the short catalyst.

THE EFFECT OF CYCLE DURATION

In this test, the effect of lean-rich cycle duration was investigated. The lean and rich gas compositions were the same as those in the previous test. The catalyst size was 30.5 mm diameter by 38.1 mm length and the temperature of the catalyst was about 200°C . The flow rate was 23 SLPM. The lean/rich cycle duration ranges from 18/2 sec to 180/20 sec, listed in [Table 5](#). The ratio of rich to lean duration was constant.

Table 5. Cycle duration test conditions

Lean [sec]	Rich [sec]	Cycle duration [sec]
18	2	20
45	5	50
90	10	100
180	20	200

The results in [Figure 10](#) and [Figure 11](#) show that long cycle duration (180/20) is preferable for high NH_3 generation and high NO_x conversion efficiency. Long cycle duration can