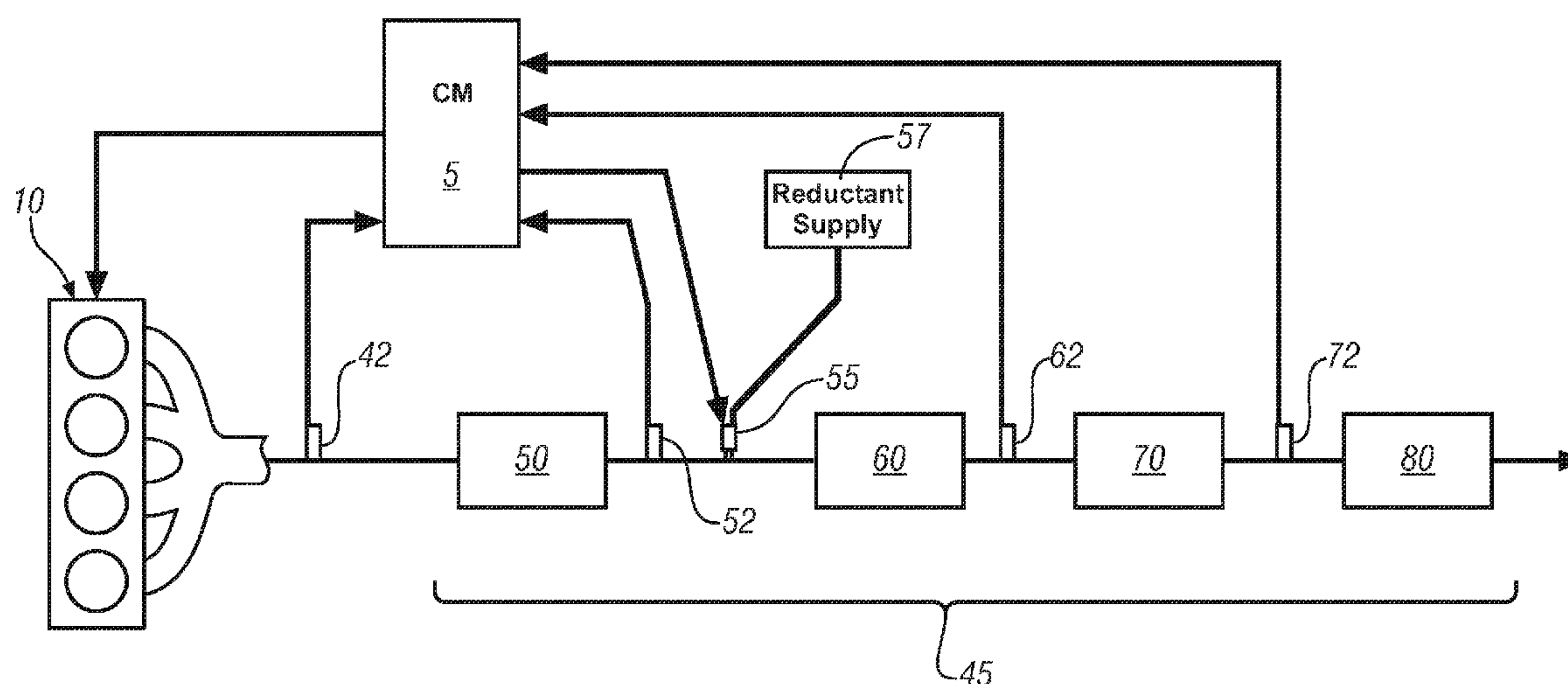


US 20100192545A1

(19) **United States**(12) **Patent Application Publication**  
**Schmieg et al.**(10) **Pub. No.: US 2010/0192545 A1**(43) **Pub. Date: Aug. 5, 2010**(54) **EXHAUST AFTERTREATMENT SYSTEM****Publication Classification**(75) Inventors: **Steven J. Schmieg**, Troy, MI (US);  
**Thompson M. Sloane**, Oxford, MI (US)(51) **Int. Cl.**  
**F01N 9/00** (2006.01)  
**F01N 3/10** (2006.01)Correspondence Address:  
**CICHOSZ & CICHOSZ, PLLC**  
**129 E. COMMERCE**  
**MILFORD, MI 48381 (US)**(52) **U.S. Cl. .... 60/286; 60/299; 60/297**(73) Assignee: **GM GLOBAL TECHNOLOGY OPERATIONS, INC.**, Detroit, MI (US)(57) **ABSTRACT**

An exhaust aftertreatment system connected to an internal combustion engine operative lean of stoichiometry includes first and second selective catalytic reactor devices. A preferred ratio of hydrocarbon:NO<sub>x</sub> to achieve a preferred concentration of ammonia immediately downstream of the first selective catalytic reactor device is determined. An ethanol-based reductant is dispensed upstream of the first selective catalytic reactor device.

(21) Appl. No.: **12/363,054**(22) Filed: **Jan. 30, 2009**

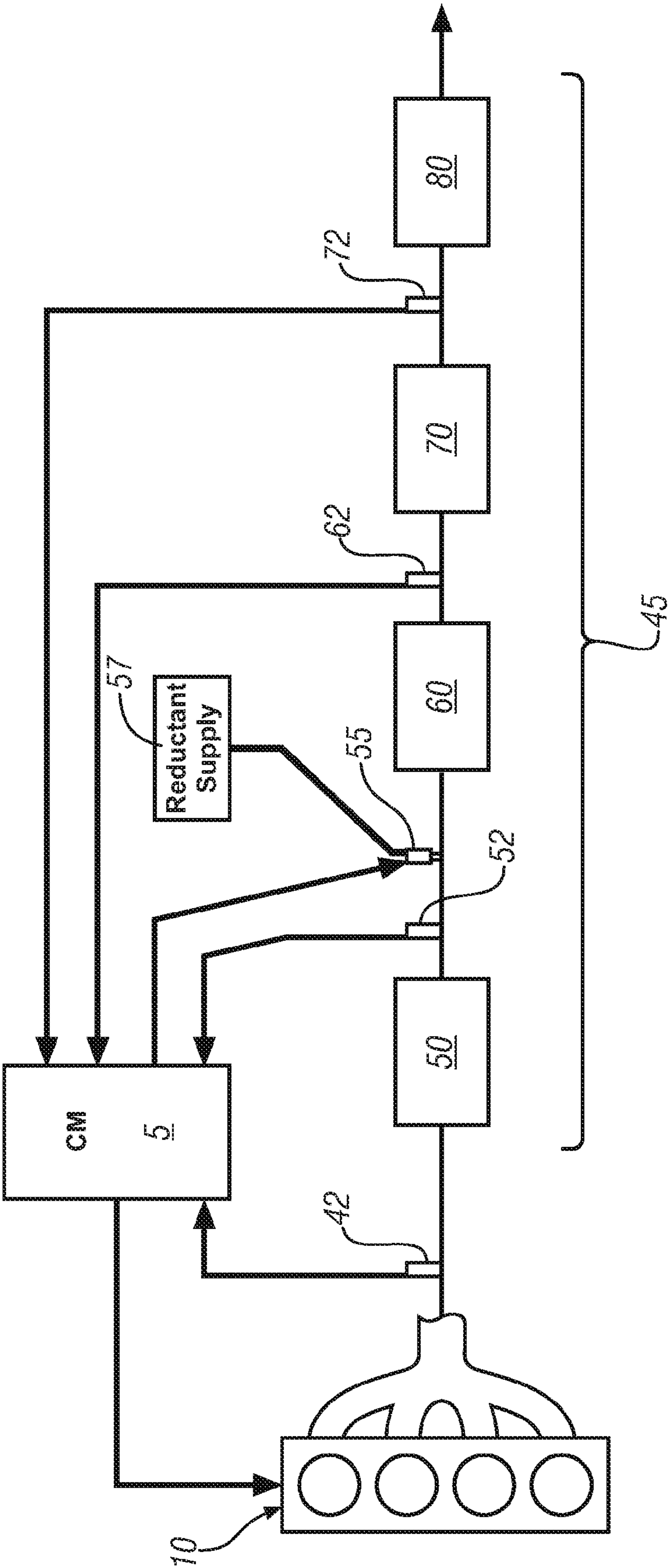


FIG. 1

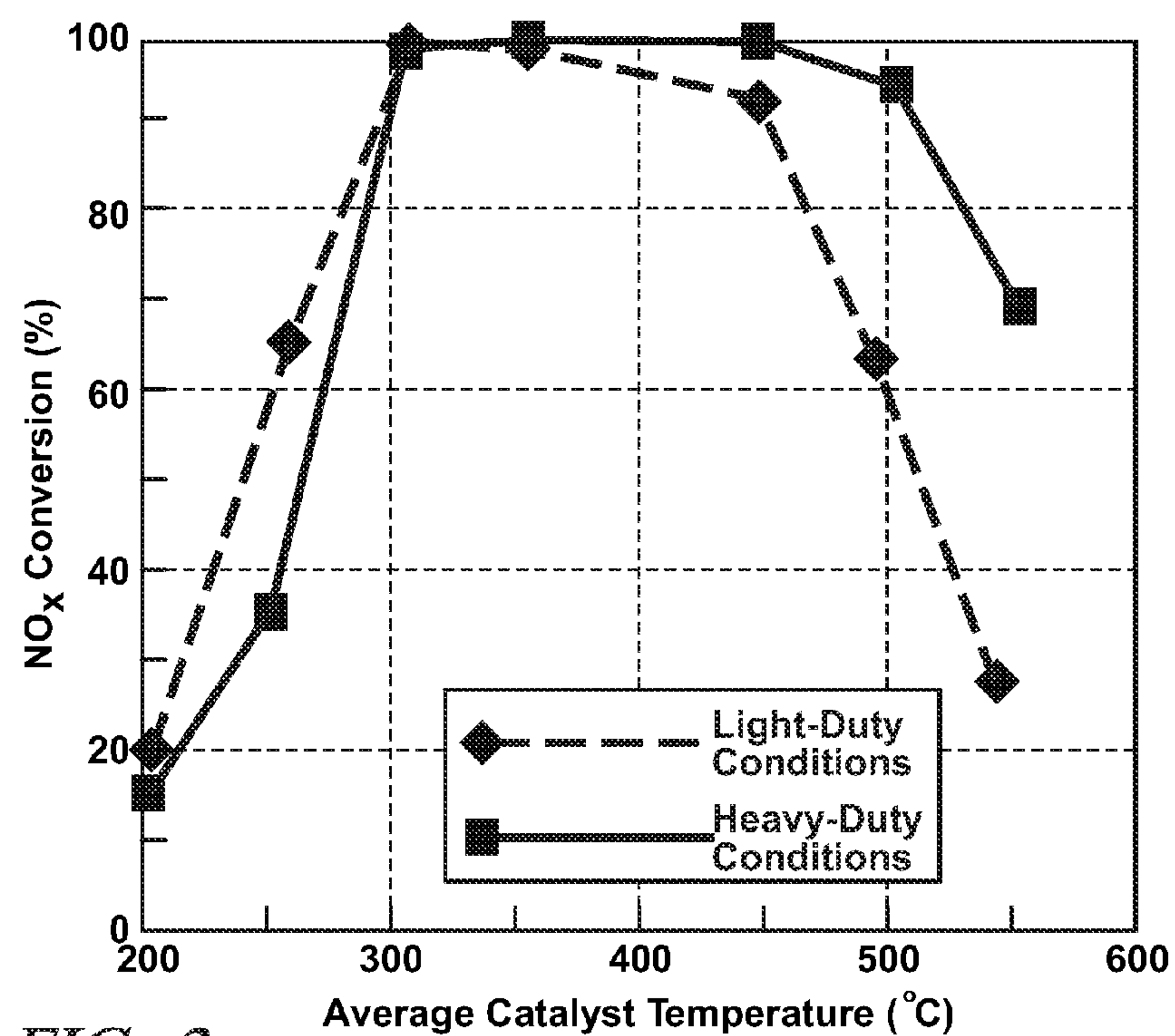


FIG. 2

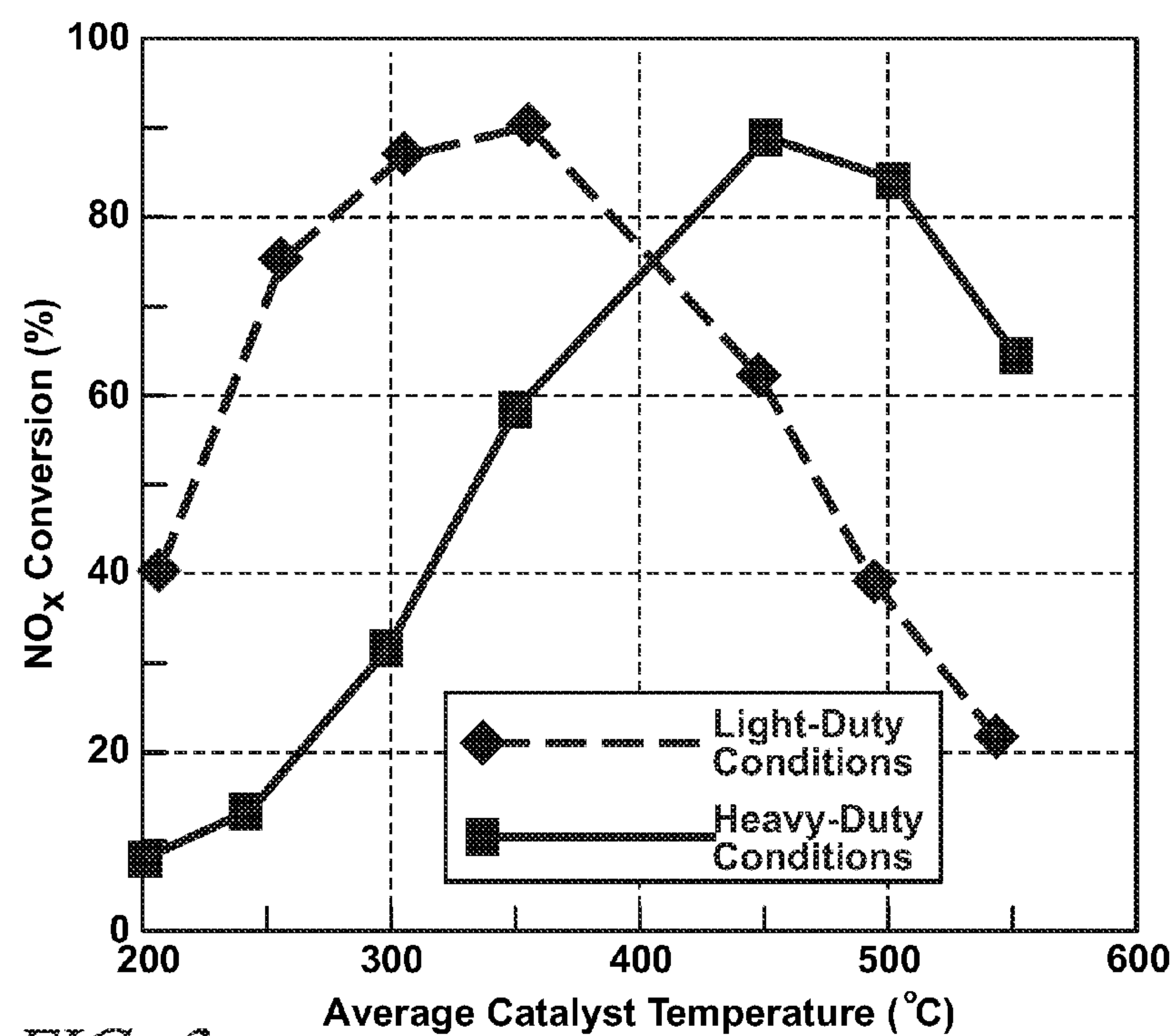


FIG. 3

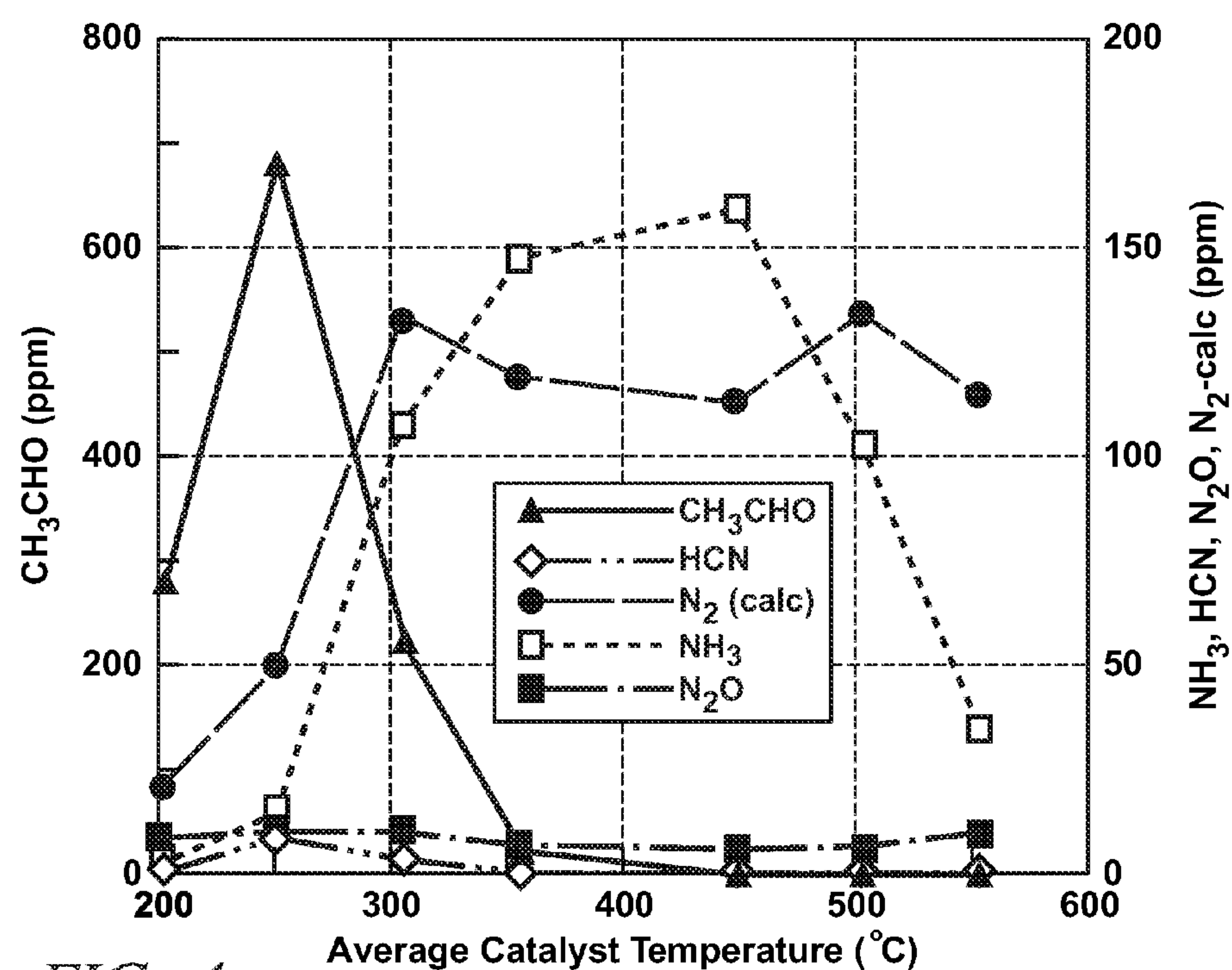


FIG. 4

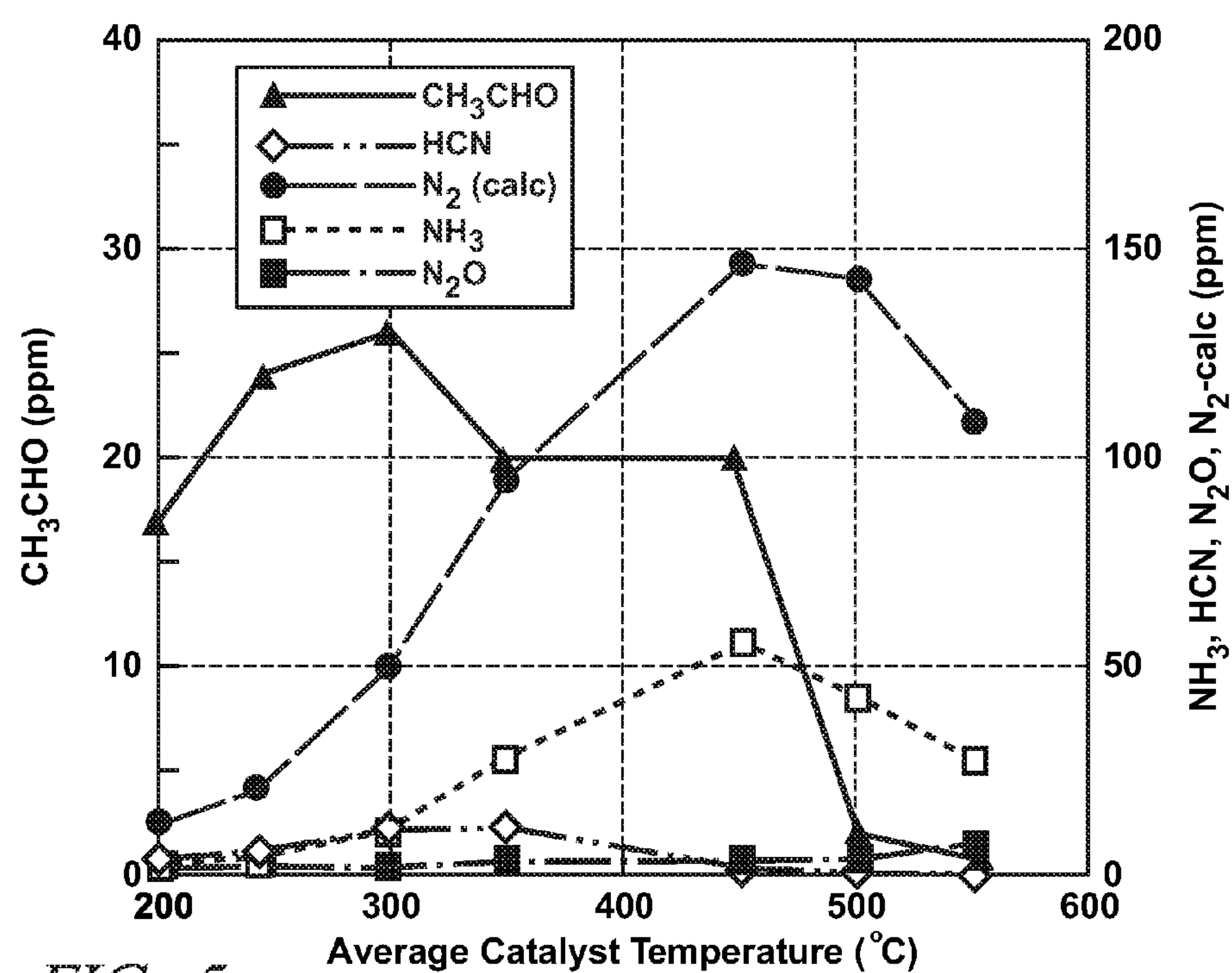


FIG. 5



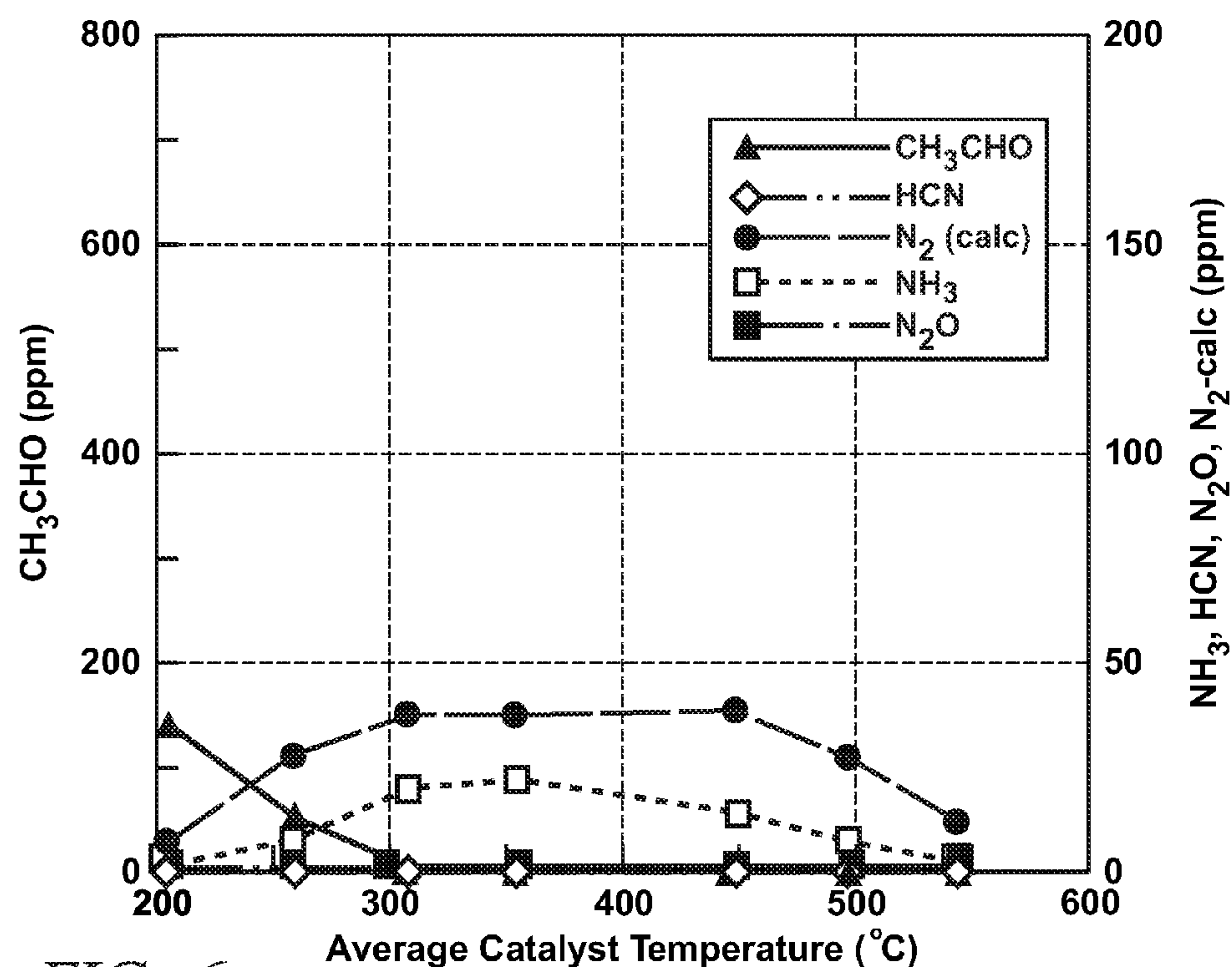


FIG. 6

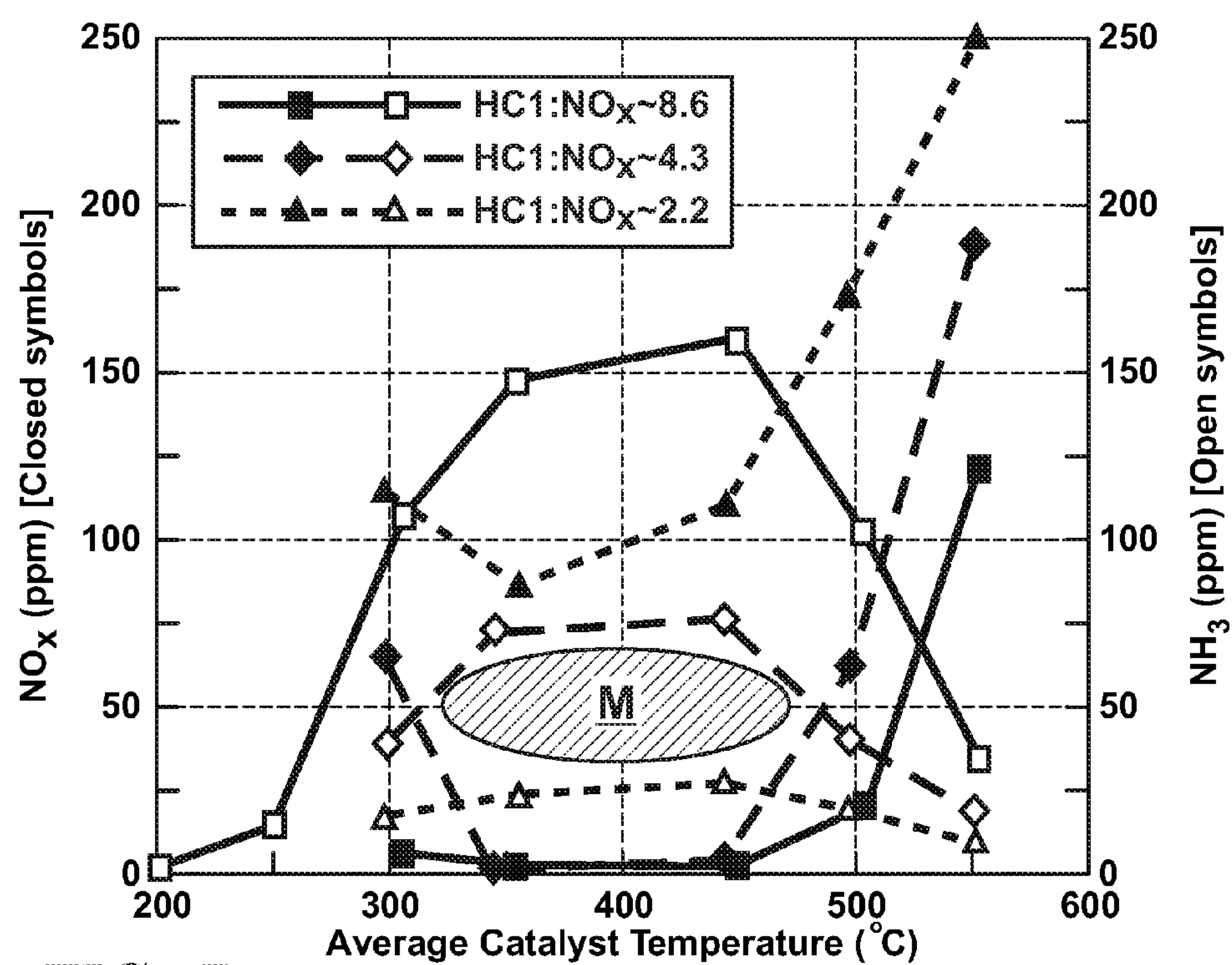


FIG. 7

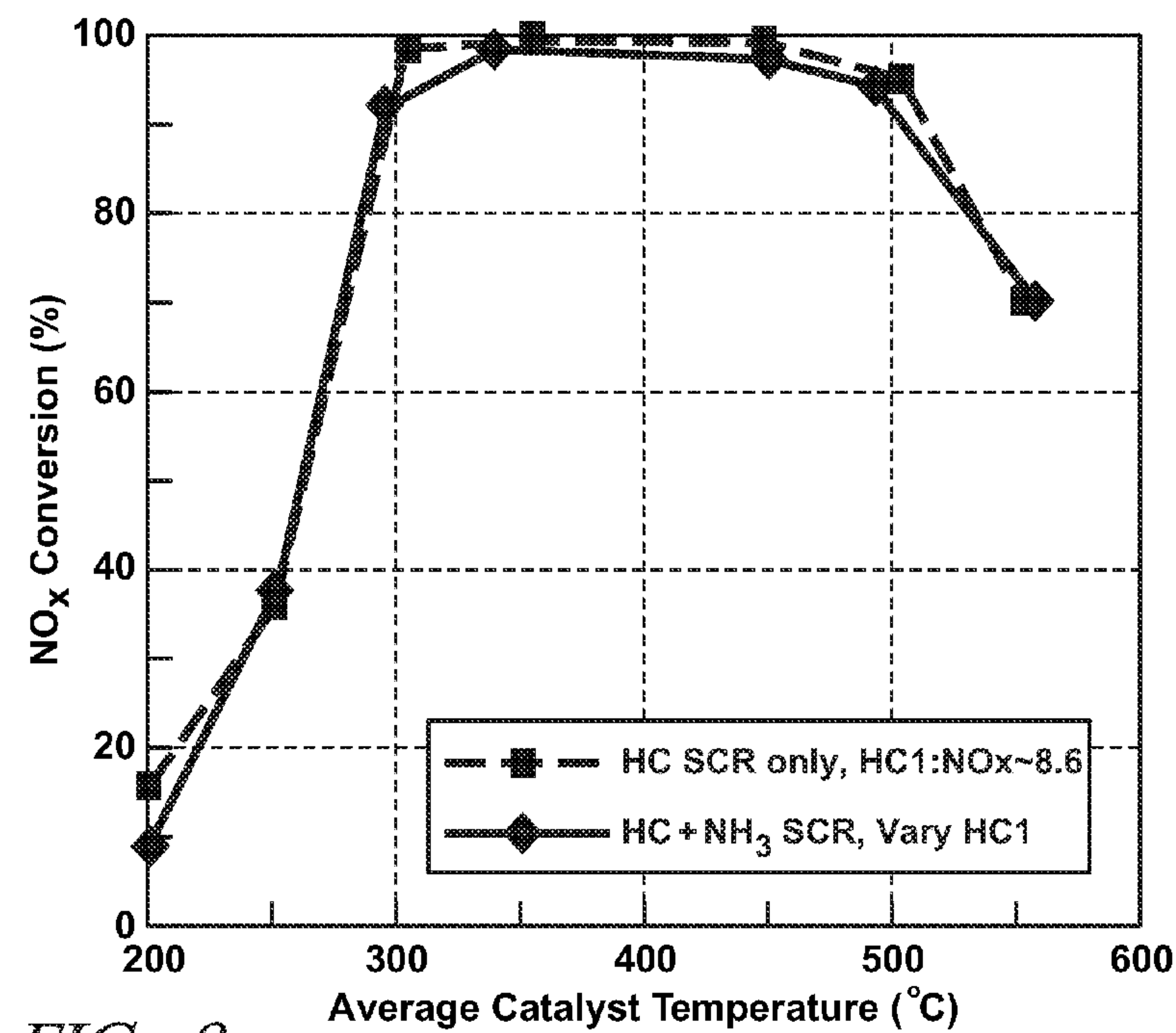


FIG. 8

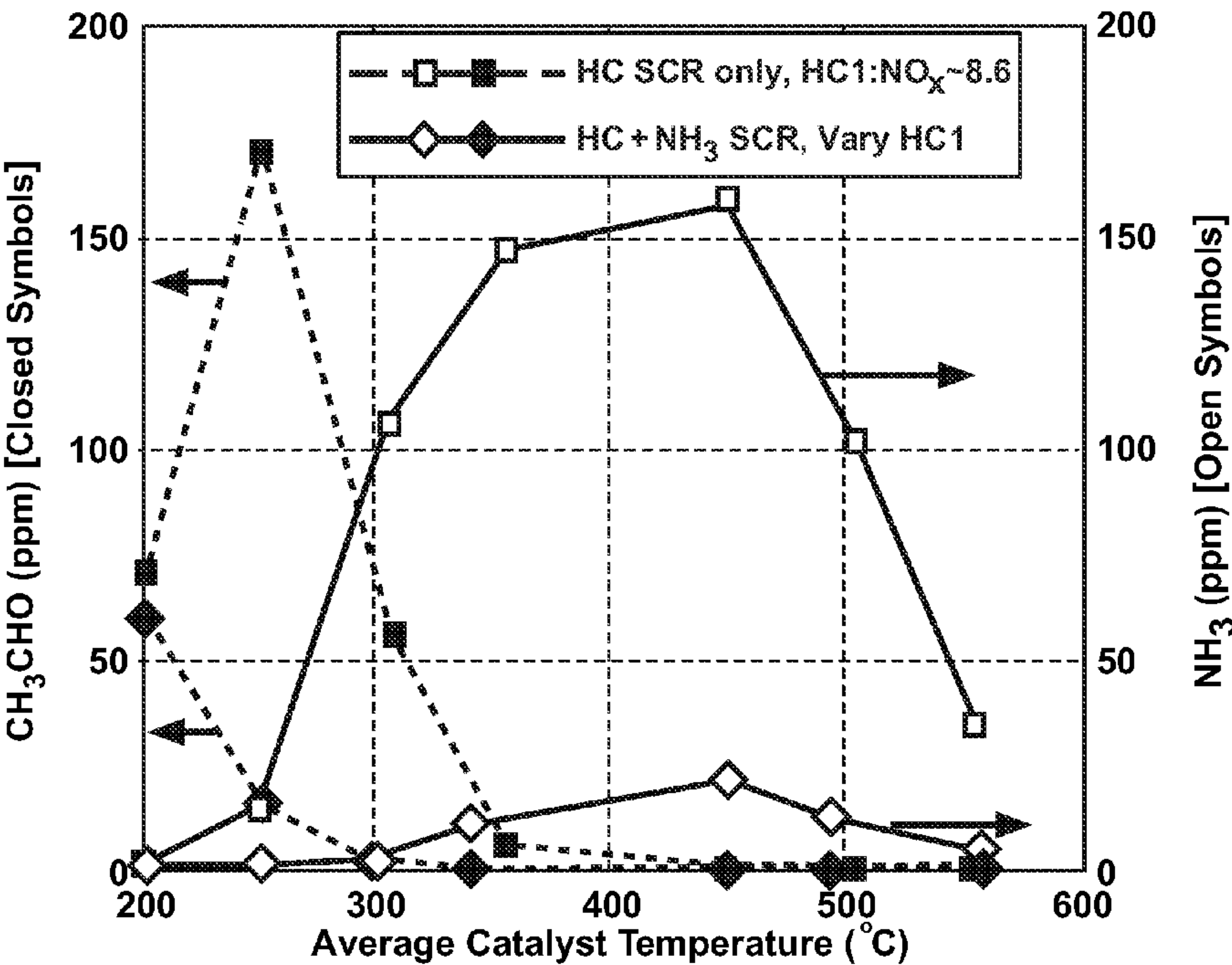


FIG. 9



## EXHAUST AFTERTREATMENT SYSTEM

### GOVERNMENT CONTRACT RIGHTS

**[0001]** The U.S. Government has a paid-up license in this invention and the right in limited circumstances to require the patent owner to license others on reasonable terms as provided for by the terms of DE-FC26-02NT41218 awarded by the U.S. Department of Energy.

### TECHNICAL FIELD

**[0002]** This disclosure relates to exhaust aftertreatment systems.

### BACKGROUND

**[0003]** The statements in this section merely provide background information related to the present disclosure and may not constitute prior art.

**[0004]** It is known that operating an internal combustion engine at an air/fuel ratio that is lean of stoichiometry can improve fuel economy but can increase some exhaust emissions, including oxides of nitrogen (NOx). Known aftertreatment systems for internal combustion engines operating lean of stoichiometry can include an oxidation catalytic converter followed by other exhaust aftertreatment devices, including a lean-NOx reduction catalyst, also referred to as a lean NOx adsorber and a selective catalytic reduction (SCR) catalytic device. Known three-way oxidation-reduction catalytic converters (TWC) function to reduce engine-out hydrocarbons (HC), carbon monoxide (CO), and NOx emissions during stoichiometric engine operation and HC and CO emissions during lean operation. Known SCR devices include catalyst material(s) that promotes the reaction of NOx with a reductant, such as ammonia (NH<sub>3</sub>) or urea, to produce nitrogen and water. The reductants may be dispensed into an exhaust gas feedstream upstream of the SCR device, requiring dispensing systems, tanks and control schemes. The tanks may require periodic refilling and can freeze in cold climates requiring additional heaters and insulation.

**[0005]** Known aftertreatment systems include dispensing a NOx reductant, e.g., urea, upstream of an urea-SCR catalyst device to reduce NOx to N<sub>2</sub>. Use of urea as a reductant necessitates a urea distribution infrastructure and an on-vehicle monitoring system for the urea, and can have problems in cold weather climates due to a relatively high freezing point of the urea solution. Systems using NOx storage catalysts can require large catalyst volumes and large amounts of platinum-group metals, coupled with use of low sulfur fuel to operate efficiently. Known NOx storage systems require periodic catalyst regeneration that can include injecting fuel into the exhaust gas feedstream to generate high exhaust gas temperatures along with dispensing reductants to regenerate the storage material of the catalyst.

**[0006]** Selective catalytic reduction of NOx using hydrocarbons (HC-SCR) is a known method for reducing NOx emissions under oxygen-rich conditions. Ion-exchanged base metal zeolite catalysts, e.g., Cu-ZSM5, are not sufficiently active under many vehicle operating conditions and are susceptible to degradation by sulfur dioxide and water exposure. Catalysts employing platinum-group metals, e.g., Pt/Al<sub>2</sub>O<sub>3</sub>, operate over a narrow temperature window and are highly selective towards N<sub>2</sub>O production.

**[0007]** Catalytic devices using alumina-supported silver, e.g., Ag/Al<sub>2</sub>O<sub>3</sub>, can selectively reduce NOx under lean

exhaust conditions with various hydrocarbon species as reductants. It is known to use reductants including light hydrocarbons (e.g., propene, propane) and heavier fuel-component hydrocarbons (e.g., octane, decane) on HC-SCR devices using Ag/Al<sub>2</sub>O<sub>3</sub> catalysts to reduce NOx emissions. NOx reduction using lighter hydrocarbons present in engine exhaust as the combustion products are known to be effective at converting NOx emissions at higher temperatures. NOx reduction using heavier hydrocarbons (e.g., octane, decane) and oxygenated hydrocarbons (e.g., ethanol) are known to be effective at converting NOx emissions at lower temperatures.

**[0008]** A known exhaust aftertreatment system for reducing NOx emissions in lean exhaust gas feedstream includes using a HC-SCR catalyst coupled to a NOx storage catalyst coupled to an ammonia-SCR catalyst. In such systems the HC-SCR catalyst reduces some fraction of the NOx emissions when a reductant (e.g., HC, CO, or H<sub>2</sub>) is dispensed into the exhaust feedstream, thereby decreasing the frequency of regenerating the NOx storage catalyst, i.e., increasing periods of operation at lean air/fuel ratios. The NOx storage catalyst adsorbs NOx molecules during lean engine operation and produces ammonia and nitrogen during rich regeneration, while the ammonia-SCR catalyst utilizes the ammonia formed during the aforementioned regeneration to further reduce NOx in the lean exhaust. Known catalyst materials used in SCR devices have included vanadium (V) and tungsten (W) on titanium (Ti). Mobile applications include base metals including iron (Fe) or copper (Cu) with a zeolite washcoat as catalyst materials. Material concerns for catalyst materials include temperature operating ranges, thermal durability, and reductant storage efficiency. For mobile applications, SCR devices have a preferred operating temperature range of 200° C. to 600° C., and may vary depending on the selected catalyst material(s). The operating temperature range can increase during or after higher load operations. Temperatures greater than 600° C. may cause NOx and reductants to breakthrough and degrade the SCR catalysts, and effectiveness of NOx reduction can decrease at temperatures lower than 200° C.

### SUMMARY

**[0009]** An internal combustion engine is operative lean of stoichiometry and provides an exhaust gas feedstream fluidly connected to an exhaust aftertreatment system which includes a first selective catalytic reactor device fluidly connected upstream to an ammonia-selective catalytic reactor device. A method for operating the internal combustion engine includes monitoring operation of the internal combustion engine and the exhaust gas feedstream upstream of the first selective catalytic reactor device. The method further includes determining a preferred ratio of hydrocarbon:NOx for the exhaust gas feedstream upstream of the first selective catalytic reactor device effective to achieve a preferred concentration of ammonia immediately downstream of the first selective catalytic reactor device based upon the operation of the internal combustion engine and the exhaust gas feedstream upstream of the first selective catalytic reactor device. An ethanol-based reductant is dispensed upstream of the first selective catalytic reactor device to achieve the preferred ratio of hydrocarbon:NOx in the exhaust gas feedstream upstream of the first selective catalytic reactor device.

### BRIEF DESCRIPTION OF THE DRAWINGS

**[0010]** One or more embodiments will now be described, by way of example, with reference to the accompanying drawings, in which:



[0011] FIG. 1 is a schematic drawing of an engine and exhaust aftertreatment system, in accordance with the present disclosure; and

[0012] FIGS. 2-9 are data graphs, in accordance with the present disclosure.

#### DETAILED DESCRIPTION

[0013] Referring now to the drawings, wherein the showings are for the purpose of illustrating certain exemplary embodiments only and not for the purpose of limiting the same, FIG. 1 schematically illustrates an internal combustion engine 10, an aftertreatment system 45, and an accompanying control system including a control module 5 (CM) that have been constructed in accordance with an embodiment of the disclosure. The engine 10 comprises a multi-cylinder direct-injection four-stroke internal combustion engine that is operative at a lean air/fuel ratio. The exemplary engine 10 can comprise a compression-ignition engine, a spark-ignition direct-injection engine, and other engine configurations that operate using a combustion cycle that includes lean operation.

[0014] The engine 10 is equipped with various sensing devices for monitoring engine operation, including an exhaust gas sensor 42 configured to monitor the exhaust gas feedstream. The exhaust gas sensor preferably comprises a device operative to generate an electrical signal correlatable to air/fuel ratio of the exhaust gas feedstream, from which oxygen content can be determined. The exhaust gas sensor 42 can further comprise a device operative to generate an electrical signal correlatable to a parametric state of NO<sub>x</sub> concentration in the exhaust gas feedstream. Alternatively, a virtual sensing device executed as an algorithm in the control module 5 can be used as a substitute for the exhaust gas sensor, wherein NO<sub>x</sub> concentration in the exhaust gas feedstream is determined based upon engine operating conditions monitored using other sensing devices (not shown). The engine 10 is preferably equipped with a mass air flow sensor (not shown) to measure intake air flow, and thus exhaust mass air flow. Alternatively or in combination, an algorithm can be executed to determine mass air flow through the engine 10 based upon engine rotational speed, displacement, and volumetric efficiency.

[0015] The control system includes the control module 5 that is signally connected to a plurality of sensing devices operative to monitor the engine 10, the exhaust gas feedstream, and the exhaust aftertreatment system 45. The control module 5 is operatively connected to actuators of the engine 10 and the exhaust aftertreatment system 45, many of which are not shown. The control system executes control schemes, preferably comprising a set of control algorithms in the control module 5, to control the engine 10 and the exhaust aftertreatment system 45. In operation the control system monitors operation of the internal combustion engine 10 and the exhaust aftertreatment system 45 and controls a reductant dispensing device 55 as described herein.

[0016] The control module 5 preferably comprises a general-purpose digital computer including a microprocessor or central processing unit, storage mediums comprising non-volatile memory including read only memory and electrically programmable read only memory, random access memory, a high speed clock, analog to digital conversion circuitry and digital to analog circuitry, and input/output circuitry and devices, and appropriate signal conditioning and buffer circuitry. The control module 5 executes the control algorithms

to control operation of the engine 10. The control algorithms comprise resident program instructions and calibrations stored in the non-volatile memory which are executed to provide the desired functions. The algorithms are executed during preset loop cycles such that each algorithm is executed at least once each loop cycle. Algorithms are executed by the central processing unit to monitor inputs from the aforementioned sensing devices and execute control routines and diagnostic routines to control and monitor operation of the engine 10, the aftertreatment system 45, and the actuators, including using preset calibrations. Loop cycles are executed at regular intervals, for example each 3.125, 6.25, 12.5, 25 and 100 milliseconds during ongoing engine and vehicle operation. Alternatively, algorithms may be executed in response to occurrence of an event. The engine 10 is controlled to operate at a preferred air-fuel ratio to achieve performance parameters related to operator requests, fuel consumption, emissions, and driveability, with the intake air flow controlled to achieve the preferred air-fuel ratio.

[0017] The exhaust aftertreatment system 45 is fluidly coupled to an exhaust manifold of the engine 10 to manage and treat the exhaust gas feedstream. The exhaust aftertreatment system 45 comprises a plurality of aftertreatment devices fluidly connected in series. Preferably, the exhaust aftertreatment system 45 includes a first selective catalytic reactor device fluidly connected in series with a second selective catalytic reactor device. In one embodiment, shown in FIG. 1, there are first, second, third and fourth aftertreatment devices 50, 60, 70 and 80. In the embodiment shown in FIG. 1, the first aftertreatment device 50 comprises an oxidation catalyst, the second aftertreatment device 60 comprises the first selective catalytic reactor device, the third aftertreatment device 70 comprises the second selective catalytic reactor device, and the fourth aftertreatment device 80 comprises a catalyzed particulate filter, although the concepts described herein are not so limited. The first, second, third and fourth aftertreatment devices 50, 60, 70 and 80 can be assembled into individual structures that are fluidly connected and assembled in an engine compartment and a vehicle underbody with one or more sensing devices placed therebetween. Alternatively, the first and second aftertreatment devices 50 and 60 can be assembled into a first structure and the third and fourth aftertreatment devices 70 and 80 can be placed into a second structure. One having ordinary skill in the art can conceive of other assembly configurations.

[0018] A first sensing device 52 is upstream of the second aftertreatment device 60, preferably operative to monitor temperature of the exhaust gas feedstream downstream of the first aftertreatment device 50. The first sensing device 52 generates a signal correlatable to temperature of the exhaust gas feedstream entering the second aftertreatment device 60, i.e., entering the first selective catalytic reactor device.

[0019] A second sensing device 62 is upstream of the third aftertreatment device 70, preferably operative to monitor constituent elements of the exhaust gas feedstream, e.g., NO<sub>x</sub> concentration. The second sensing device 62 generates a signal correlatable to NO<sub>x</sub> concentration of the exhaust gas feedstream, or another parameter (e.g., NH<sub>3</sub>). Alternatively, the second sensing device 62 can comprise a virtual sensing device executed as an algorithm in the control module 5 and used as a substitute for the exhaust gas sensor, wherein NO<sub>x</sub> concentration in the exhaust gas feedstream is determined based upon engine operating conditions monitored using other sensing devices (not shown).



[0020] There is a third sensing device **72** downstream of the third aftertreatment device **70**, preferably operative to monitor constituent elements of the exhaust gas feedstream, e.g., NO<sub>x</sub> concentration. The third sensing device **72** generates a signal correlatable to NO<sub>x</sub> concentration or another exhaust gas constituent in the exhaust gas feedstream. Each of the first, second, and third sensing devices **52**, **62**, and **72** are signally connected to the control module **5**.

[0021] The exhaust aftertreatment system **45** includes the reductant dispensing device **55** having an dispensing mechanism and a nozzle (not shown) that are fluidly connected to a reductant supply system (Reductant Supply) **57** that preferably contains an ethanol-based reductant. In one embodiment, the reductant supply system can include a reservoir (not shown) that stores reductant materials for dispensing into the exhaust gas feedstream via the reductant dispensing device **55**. In one embodiment, supply of the ethanol-based reductant can originate with a fuel tank (not shown) that contains ethanol-based fuel for powering the internal combustion engine **10**. The nozzle of the reductant dispensing device **55** is inserted into the exhaust system **45** upstream of the second aftertreatment device **60**, i.e., upstream of the first selective catalytic reactor device. The reductant dispensing device **55** is controlled by the control module **5** to dispense a mass flow-rate of the ethanol-based reductant into the exhaust gas feedstream. Alternatively, in a system wherein the first selective catalytic reactor device is directly fluidly connected to the engine **10** without an intervening oxidation catalytic device, the reductant dispensing device **55** can be omitted and the ethanol-based reductant can be dispensed by controlling engine fuel injectors to inject fuel into the combustion chambers during the exhaust stroke of the engine cycle, none of which is shown.

[0022] Each of the exhaust aftertreatment devices **50**, **60**, **70**, and **80** comprises a device which employs technologies having various capabilities for treating the constituent elements of the exhaust gas feedstream, including oxidation, selective catalytic reduction, reductant dosing, and particulate filtering. Design features for each of the aftertreatment devices **50**, **60**, **70**, and **80**, e.g., volume, space velocity, cell density, washcoat density, and metal loading can be determined for specific applications and are determinable by a person having ordinary skill in the art. The aftertreatment devices **50**, **60**, **70**, and **80** are fluidly connected in series using known pipes and connectors.

[0023] The first aftertreatment device **50** preferably comprises an oxidation catalytic device, preferably comprising a cordierite substrate including a multiplicity of flow-through channels coated with an alumina-based washcoat containing one or more platinum-group metals, e.g., platinum or palladium. In one embodiment (not shown) the first aftertreatment device **50** may be omitted.

[0024] The second aftertreatment device **60** comprises the first, ethanol-selective catalytic reactor device in one embodiment, preferably a cordierite substrate including a multiplicity of flow-through channels coated with a washcoat. The preferred washcoat uses silver-alumina (Ag—Al) as the catalytic material and comprises 3 wt. % Ag<sub>2</sub>O supported on alumina in one embodiment.

[0025] The third aftertreatment device **70** comprises the second, ammonia-selective catalytic reactor device in one embodiment, preferably a cordierite substrate including a multiplicity of flow-through channels coated with a washcoat. The preferred washcoat comprises a zeolite-based washcoat containing one or more metals, e.g., iron (Fe), copper (Cu), vanadium (V), tungsten (W) and titanium (Ti).

[0026] The fourth aftertreatment device **80** preferably comprises an ammonia slip catalytic device, preferably a cordierite substrate including a multiplicity of flow-through channels coated with an alumina-based washcoat containing one or more platinum-group metals, e.g., Pt, Pd, and Rh, operative to oxidize ammonia and other exhaust gas feedstream constituents. The fourth aftertreatment device **80** can comprise a second oxidation catalyst combined with a particulate filter. It is understood the fourth aftertreatment device **80** can include, singly or in combination, other exhaust aftertreatment devices, including catalyzed or uncatalyzed particulate filters, air pumps, external heating devices, sulfur traps, phosphorous traps, selective reduction devices, and others, according to specifications and operating characteristics of a specific application.

[0027] The preferred reductant comprises an ethanol-based reductant, which includes partially oxidized hydrocarbons, e.g., alcohols. The ethanol-based reductant can reduce NO<sub>x</sub> emissions in the presence of Ag/Al<sub>2</sub>O<sub>3</sub> at low exhaust gas feedstream temperatures. The ethanol-SCR can also convert some of the NO<sub>x</sub> emissions into ammonia. The ethanol-based reductant can be obtained from on-board fuels, e.g., ethanol-containing fuels such as E85 which is an ethanol/gasoline mixture containing 70-85% ethanol.

[0028] The control system preferentially operates the internal combustion engine **10** at an air/fuel ratio that is lean of stoichiometry while monitoring operation of the internal combustion engine and the exhaust gas feedstream. The monitored parameters of the exhaust gas feedstream preferably comprise an inlet temperature to the first selective catalytic reactor device, a mass flow rate of the exhaust gas feedstream, and NO<sub>x</sub> and ammonia and oxygen concentrations in the exhaust gas feedstream. The parameters are preferably used by the control system to calculate an optimum HC<sub>1</sub>/NO<sub>x</sub> ratio for the NO<sub>x</sub> reduction under specific operating conditions. The HC<sub>1</sub>/NO<sub>x</sub> ratio is defined as an amount of dispensed fuel on a C<sub>1</sub> basis divided by the inlet NO<sub>x</sub> concentration. By way of example, a reductant comprising 1 part per million (ppm) evaporated diesel fuel has approximately 14 carbon atoms. Thus a HC<sub>1</sub>:NO<sub>x</sub> ratio of 10:1 with 100 ppm inlet NO<sub>x</sub> in the exhaust feedstream requires dispensing of  $10 \times 100 / 14 = 71$  ppm diesel fuel. By way of example, a reductant comprising 1 ppm evaporated ethanol has 2 carbon atoms. Thus a HC<sub>1</sub>:NO<sub>x</sub> ratio of 10 with 100 ppm inlet NO<sub>x</sub> in the exhaust feedstream requires dispensing of  $10 \times 100 / 2 = 500$  ppm ethanol. A preferred ratio of HC<sub>1</sub>:NO<sub>x</sub> in the exhaust gas feedstream can be determined that achieves a preferred concentration of ammonia downstream of the first selective catalytic reactor device, i.e., the second aftertreatment device **60**. The preferred ratio of HC<sub>1</sub>:NO<sub>x</sub> is determined based upon the operation of the internal combustion engine **10** and the exhaust gas feedstream. The reductant dispensing device **55** is controlled by the control module **5** to dispense a mass flow-rate of the ethanol-based reductant into the exhaust gas feedstream upstream of the first selective catalytic reactor device that corresponds to the preferred ratio of HC<sub>1</sub>:NO<sub>x</sub> in the exhaust gas feedstream. Thus there can be real-time and simultaneous NO<sub>x</sub> reduction over the first and second selective catalytic reactor devices, i.e., the second and third aftertreatment devices **60** and **70**. The NO<sub>x</sub> reduction can occur under lean exhaust conditions without operating with a rich exhaust gas feedstream to generate the ammonia and without the use of platinum-group metals. Preferably, there is sufficient NO<sub>x</sub> reduction in the first selective catalytic reactor



device, i.e., the second aftertreatment device **60**, such that there are similar amounts of NOx and ammonia exiting the first selective catalytic reactor device comprising the silver-alumina catalytic reactor device. The preferred ammonia:NOx ratio exiting the first selective catalytic reactor device is preferably near a stoichiometric ammonia:NOx ratio to achieve NOx reduction with minimal or no ammonia slip.

**[0029]** FIGS. 2-9 illustrate data graphs that depict results indicative of operating an embodiment of the engine and aftertreatment system constructed in accordance with the system depicted and described with reference to FIG. 1. The embodiment of the aftertreatment system **45** included a first selective catalytic reactor device comprising an ethanol-selective catalytic reactor device using silver alumina as the catalytic material and comprising 3 wt. % Ag<sub>2</sub>O supported on alumina. The second selective catalytic reactor device comprised an ammonia-selective catalytic reactor device using Cu-zeolite as the catalytic material. The catalytic material was supported on a 400 cell per square inch cordierite monolith substrate. The selective catalytic reactor devices were hydro-thermally aged employing air and 10% water at 650° C. for 16 hours prior to testing. The data graphs comprise results achieved by selectively dispensing the ethanol-based reductant upstream of the first selective catalytic reactor device and by selectively dispensing a simulated diesel fuel reductant upstream of the first selective catalytic reactor device. The results described in the data graphs were developed using a laboratory reactor to flow a simulated exhaust gas feedstream through the first and second selective catalytic reactor devices. The aftertreatment system was instrumented with appropriate sensors, including a magneto-pneumatic exhaust gas analyzer to determine O<sub>2</sub> concentration in the exhaust, a Fourier transform infrared spectrometer to determine NOx and ammonia concentration levels entering and exiting the first and second selective catalytic reactor devices, and a flow meter to determine exhaust flow rate translatable to catalyst space velocity (SV). Space velocity represents a rate of feed of exhaust gas, in volume, per unit volume of one of the first and second selective catalytic reactor devices, and has a unit of inverse hour (h<sup>-1</sup>).

**[0030]** Baseline laboratory conditions included the following standard gases in the simulated exhaust feedstream: 6% O<sub>2</sub>, 5% CO<sub>2</sub>, 5% H<sub>2</sub>O, 750 ppm CO, 250 ppm H<sub>2</sub>, and 400 ppm NO. Ethanol and a simulated diesel fuel mixture consisting of a volumetric mixture of n-dodecane (67 vol. %, long-chain alkane) and m-xylene (33 vol. %, aromatic) were used as the NOx reductants. The effect of space velocity and concentration effects of O<sub>2</sub>, NOx, and HC were evaluated as a function of catalyst inlet temperature.

**[0031]** Table I shows numerical values of catalyst inlet temperature, NOx concentration, and space velocity that correspond to labeled low and high states for the experimental results described with reference to FIGS. 2-9 that were conducted with ethanol as the reductant. The numerical values are approximations.

TABLE I

	Low	High
Temperature, ° C.	300-375° C.	375-450° C.
Inlet NOx, ppm	100-250 ppm	250-400 ppm
Space Velocity, 1/h	5,000-12,000 1/h	12,000-20,000 1/h

**[0032]** The preferred inlet concentration of ethanol to the first selective catalytic reactor device, expressed as the catalyst inlet HC<sub>1</sub>:NOx ratio needed to achieve equal (i.e. stoichiometric) concentrations of NOx and ammonia at the exit of the first selective catalytic reactor device was then determined using a known model at combinations of low, medium, and high values of these variables. An exemplary operating strategy for controlling the inlet concentration of ethanol-based reductant to the first selective catalytic reactor device was constructed. This comprises a preferred range of HC<sub>1</sub>:NOx concentration for low and high ranges of the variables. For example, the range of low temperature operation is defined to be between 300 and 375° C., and the range of high temperature operation is defined to be between 375 and 450° C. for the embodiment. This exemplary operating strategy is shown in Tables IIA and IIB.

**[0033]** Tables IIA and IIB show preferred ranges of HC<sub>1</sub>/NOx to achieve equal (i.e. stoichiometric) NOx and ammonia concentrations after the first selective catalytic reactor device for combinations of low and high ranges of exhaust gas temperature, inlet NOx concentration, and space velocity of the first selective catalytic reactor device for the embodiment, as described with reference to Table I.

TABLE IIA

Temperature	Low	High	High	High
Inlet NOx	Low	Low	High	Low
Space Velocity	Low	Low	Low	High
HC <sub>1</sub> :NOx	5.0-9.2	5.0-14.7	4.2-7.6	5.0-12.7

TABLE IIB

Temperature	Low	Low	Low	High
Inlet NOx	Low	High	High	High
Space Velocity	High	Low	High	High
HC <sub>1</sub> :NOx	6.5-10.7	4.5-6.6	4.2-6.7	5.0-6.9

**[0034]** For example, when the inlet temperature of the first selective catalytic reactor device is in the range of 300 to 375° C., the inlet NOx concentration is in the range 100 to 250 ppm, and the space velocity is in the range 5000 to 12,000 h<sup>-1</sup>, the range of HC<sub>1</sub>:NOx needed to achieve equal (i.e. stoichiometric) concentrations of NOx and ammonia after the first selective catalytic reactor device is 5.0:1 to 9.2:1. These high and low ranges can be further subdivided as needed to determine the preferred HC<sub>1</sub>:NOx over as narrow a variable range as required for effective control and operation of an embodiment of the engine **10** and aftertreatment system **45** that is constructed to operate in accordance with the system described herein.

**[0035]** FIG. 2 graphically illustrates test results showing NOx conversion (%) across the first selective catalytic reactor device, i.e., the Ag—Al catalyst, plotted as a function of average catalyst temperature (C) wherein SV of the first selective catalytic reactor device was 12,750 h<sup>-1</sup> with an exhaust gas feedstream comprising 10% oxygen, 5% H<sub>2</sub>O, 5% CO<sub>2</sub>, 750 ppm CO, 250 ppm H<sub>2</sub>, and 100 ppm NO. A reductant flow rate of 431 ppm of the ethanol generates an HC<sub>1</sub>:NOx of approximately 8.6 for light-duty vehicle application test conditions. Additionally, an exhaust gas feedstream is shown wherein SV was 25,500 h<sup>-1</sup> comprising 6% oxygen, 5% H<sub>2</sub>O, 5% CO<sub>2</sub>, 750 ppm CO, 250 ppm H<sub>2</sub>, 400 ppm NO. A reductant flow rate of 1724 ppm of the ethanol



provides a range of HC<sub>1</sub>:NOx of approximately 8.6 for heavy-duty vehicle application test conditions.

**[0036]** FIG. 3 graphically illustrates test results showing NOx conversion (%) across the first selective catalytic reactor device, plotted as a function of average catalyst temperature (C) wherein SV was 12,750 h<sup>-1</sup> with an exhaust gas feedstream comprising 10% oxygen, 5% H<sub>2</sub>O, 5% CO<sub>2</sub>, 750 ppm CO, 250 ppm H<sub>2</sub>, and 100 ppm NO. A reductant flow rate of 79 ppm of the simulated diesel fuel provides a HC<sub>1</sub>:NOx ratio of approximately 8.4 for light-duty vehicle application test conditions. Additionally, an exhaust gas feedstream wherein SV was 25,500 h<sup>-1</sup> comprising 6% oxygen, 5% H<sub>2</sub>O, 5% CO<sub>2</sub>, 750 ppm CO, 250 ppm H<sub>2</sub>, and 400 ppm NO. A reductant flow rate of 316 ppm of the simulated diesel fuel reductant provides a HC<sub>1</sub>:NOx ratio of approximately 8.4 for heavy-duty vehicle application test conditions.

**[0037]** FIG. 4 graphically illustrates test results showing the production of CH<sub>3</sub>CHO, NH<sub>3</sub>, HCN, N<sub>2</sub>O, and N<sub>2</sub> {N<sub>2</sub> (calc)=[<sup>in</sup>NO-<sup>out</sup>(NO+NO<sub>2</sub>+NH<sub>3</sub>+HCN+2×N<sub>2</sub>O)]/2} (ppm) across the first selective catalytic reactor device, plotted as a function of average catalyst temperature (C) wherein SV was 25,500 h<sup>-1</sup> with an exhaust gas feedstream comprising 6% oxygen, 5% H<sub>2</sub>O, 5% CO<sub>2</sub>, 750 ppm CO, 250 ppm H<sub>2</sub>, and 400 ppm NO. A reductant flow rate of 1724 ppm of the ethanol reductant provides a HC<sub>1</sub>:NOx ratio of approximately 8.6.

**[0038]** FIG. 5 graphically illustrates test results showing the production of CH<sub>3</sub>CHO, NH<sub>3</sub>, HCN, N<sub>2</sub>O, and N<sub>2</sub> {N<sub>2</sub> (calc)=[<sup>in</sup>NO-<sup>out</sup>(NO++NO<sub>2</sub>+NH<sub>3</sub>+HCN+2×N<sub>2</sub>O)]/2} (ppm) across the first selective catalytic reactor device, plotted as a function of average catalyst temperature (C) wherein SV was 25,500 h<sup>-1</sup> with an exhaust gas feedstream comprising 6% oxygen, 5% H<sub>2</sub>O, 5% CO<sub>2</sub>, 750 ppm CO, 250 ppm H<sub>2</sub>, and 400 ppm NO. A reductant flow rate of 316 ppm of simulated diesel fuel reductant provides a HC<sub>1</sub>:NOx ratio of approximately 8.4.

**[0039]** FIG. 6 graphically illustrates test results showing the production of CH<sub>3</sub>CHO, NH<sub>3</sub>, HCN, N<sub>2</sub>O, and N<sub>2</sub> {N<sub>2</sub> (calc)=[<sup>in</sup>NO-<sup>out</sup>(NO+NO<sub>2</sub>+NH<sub>3</sub>+HCN+2×N<sub>2</sub>O)]/2} (ppm) across the first selective catalytic reactor device, plotted as a function of average catalyst temperature (C) wherein SV was 12,750 h<sup>-1</sup> with an exhaust gas feedstream comprising 10% oxygen, 5% H<sub>2</sub>O, 5% CO<sub>2</sub>, 750 ppm CO, 250 ppm H<sub>2</sub>, and 100 ppm NO. A reductant flow rate of 431 ppm of the ethanol reductant provides a HC<sub>1</sub>:NOx ratio of approximately 8.6.

**[0040]** FIG. 7 graphically illustrates test results showing the breakthrough of NOx (comprising NO+NO<sub>2</sub>) and NH<sub>3</sub> (ppm) across the first selective catalytic reactor device, plotted as a function of average catalyst temperature (C) wherein SV was 25,500 h<sup>-1</sup> with an exhaust gas feedstream comprising 6% oxygen, 5% H<sub>2</sub>O, 5% CO<sub>2</sub>, 750 ppm CO, 250 ppm H<sub>2</sub>, and 400 ppm NO. Reductant flow rates of variable amounts of the ethanol-based reductant provide HC<sub>1</sub>:NOx ratios of 2.2, 4.3, and 8.6. The hash-marked area (M) indicates the desired concentrations of NOx and NH<sub>3</sub> (ppm) entering the downstream ammonia-SCR catalyst, which is obtainable with a HC<sub>1</sub>:NOx ratio between 2.2 and 4.3.

**[0041]** FIG. 8 graphically illustrates test results showing NOx conversion (%) across the first selective catalytic reactor device (HC SCR only) plotted as a function of average catalyst temperature (C) wherein SV was 25,500 h<sup>-1</sup> with an exhaust gas feedstream comprising 6% oxygen, 5% H<sub>2</sub>O, 5% CO<sub>2</sub>, 750 ppm CO, 250 ppm H<sub>2</sub> and 400 ppm NO. A reductant flow rate of 1724 ppm of the ethanol reductant provides a

HC<sub>1</sub>:NOx ratio of approximately 8.6. Additionally, test results show NOx conversion (%) across the first and second selective catalytic reactor devices (HC+NH<sub>3</sub>SCR) plotted as a function of average catalyst temperature (C) wherein SV was 25,500 h<sup>-1</sup> across the first selective catalytic reactor device and 60,000 h<sup>-1</sup> across the second selective catalytic reactor device with an exhaust gas feedstream comprising 6% oxygen, 5% H<sub>2</sub>O, 5% CO<sub>2</sub>, 750 ppm CO, 250 ppm H<sub>2</sub> and 400 ppm NO. Reductant flow rates of variable amounts of the ethanol-based reductant providing equivalent NOx conversion levels to that observed across the first selective catalytic reactor device are shown.

**[0042]** FIG. 9 graphically shows test results showing the production of CH<sub>3</sub>CHO and NH<sub>3</sub> (ppm) across the first selective catalytic reactor device (HC SCR only) plotted as a function of average catalyst temperature (C) wherein SV was 25,500 h<sup>-1</sup> with an exhaust gas feedstream comprising 6% oxygen, 5% H<sub>2</sub>O, 5% CO<sub>2</sub>, 750 ppm CO, 250 ppm H<sub>2</sub> and 400 ppm NO. A reductant flow rate of 1724 ppm of the ethanol reductant provides a HC<sub>1</sub>:NOx ratio of approximately 8.6. Additionally, test results show the production of CH<sub>3</sub>CHO and NH<sub>3</sub> (ppm) across the first and selective catalytic reactor devices (HC+NH<sub>3</sub>SCR) plotted as a function of average catalyst temperature (C) wherein SV was 25,500 h<sup>-1</sup> across the first selective catalytic reactor device and 60,000 h<sup>-1</sup> across the second selective catalytic reactor device with an exhaust gas feedstream comprising 6% oxygen, 5% H<sub>2</sub>O, 5% CO<sub>2</sub>, 750 ppm CO, 250 ppm H<sub>2</sub> and 400 ppm NO. Reductant flow rates of variable amounts of the ethanol-based reductant provide equivalent NOx conversion levels to that observed across the first selective catalytic reactor device are shown.

**[0043]** Results of the data presented with reference to FIGS. 2-9 indicate that NOx conversion for the exemplary first selective catalytic reactor device is affected by the type of reductant and the conditions under which the catalyst is tested. Under operating conditions for a light-duty vehicle application (i.e., lower SV, lower NO concentration, higher O<sub>2</sub> concentration) good low temperature (250-400° C.) NOx conversion performance is observed for both diesel fuel and ethanol as reductants. However, under operating conditions for a heavy-duty vehicle application (i.e., higher SV, higher NO concentration, lower O<sub>2</sub> concentration) only the ethanol-based reductant shows a wide temperature window for NOx conversion efficiency. However, preferred catalyst performance limits the production of undesired reaction by-products other than the desired product, nitrogen (N<sub>2</sub>). Under heavy-duty test conditions using an ethanol-based reductant (See FIG. 4) and diesel as a reductant (See FIG. 5), the production of ammonia (NH<sub>3</sub>) and acetaldehyde (CH<sub>3</sub>CHO) is significant, particularly when ethanol is used as the reductant. While lesser amounts of ammonia are formed when diesel fuel is used as the reductant, as shown in FIG. 5, and when ethanol is used as the reductant under operating conditions for a light-duty vehicle application, as shown in FIG. 6, the control scheme described herein still apply.

**[0044]** A further embodiment can include dispensing a mass of hydrogen into the exhaust gas feedstream upstream of the first selective catalytic reactor device. A further embodiment can include controlling oxygen in the exhaust gas feedstream upstream of the first selective catalytic reactor device.

**[0045]** Operating embodiments of the engine 10 and exhaust aftertreatment system 45 configured as described according to the control schemes as described can result in improved selectivity toward the desired reaction product, i.e.,



nitrogen. Results related to operating the engine and exhaust aftertreatment system provide design considerations for determining a preferred volume of the first, silver-alumina catalytic reactor device based upon maximum engine airflow and corresponding space velocity related to the maximum engine airflow. Usage of the ethanol-based reductant can be minimized for a selected engine and exhaust aftertreatment system.

[0046] The disclosure has described certain preferred embodiments and modifications thereto. Further modifications and alterations may occur to others upon reading and understanding the specification. Therefore, it is intended that the disclosure not be limited to the particular embodiment(s) disclosed as the best mode contemplated for carrying out this disclosure, but that the disclosure will include all embodiments falling within the scope of the appended claims.

1. Method for operating an internal combustion engine operative lean of stoichiometry and providing an exhaust gas feedstream fluidly connected to an exhaust aftertreatment system including a first selective catalytic reactor device fluidly connected upstream to an ammonia-selective catalytic reactor device, comprising:

monitoring operation of the internal combustion engine and the exhaust gas feedstream upstream of the first selective catalytic reactor device;

determining a preferred ratio of hydrocarbon:NOx for the exhaust gas feedstream upstream of the first selective catalytic reactor device effective to achieve a preferred concentration of ammonia immediately downstream of the first selective catalytic reactor device based upon the operation of the internal combustion engine and the exhaust gas feedstream upstream of the first selective catalytic reactor device; and

dispensing an ethanol-based reductant upstream of the first selective catalytic reactor device to achieve the preferred ratio of hydrocarbon:NOx in the exhaust gas feedstream upstream of the first selective catalytic reactor device.

2. The method of claim 1, wherein the preferred concentration of ammonia corresponds to a preferred ratio of ammonia:NOx upstream of the ammonia-selective catalytic reactor device.

3. The method of claim 2, wherein the preferred ratio of ammonia:NOx upstream of the ammonia-selective catalytic reactor device comprises substantially equal concentrations of NOx and ammonia.

4. The method of claim 1, wherein monitoring operation of the internal combustion engine and the exhaust gas feedstream upstream of the first selective catalytic reactor device comprises determining a concentration of NOx, a temperature, and a mass flow of the exhaust gas feedstream upstream of the first selective catalytic reactor device, the method further comprising:

determining a space velocity of the first selective catalytic reactor device; and

wherein dispensing an ethanol-based reductant upstream of the first selective catalytic reactor device comprises controlling a mass flow rate of the ethanol-based reductant upstream of the first selective catalytic reactor device based on the concentration of NOx and the temperature of the exhaust gas feedstream upstream of the first selective catalytic reactor device, and the space velocity of the first selective catalytic reactor device.

5. The method of claim 4, wherein determining the preferred ratio of hydrocarbon:NOx for the exhaust gas feed-

stream upstream of the first selective catalytic reactor device comprises determining the preferred ratio of hydrocarbon:NOx for the exhaust gas feedstream upstream of the first selective catalytic reactor device effective to achieve substantially equal concentrations of NOx and ammonia upstream of the ammonia-selective catalytic reactor device corresponding to the concentration of NOx, the temperature, and the mass flow of the exhaust gas feedstream upstream of the first selective catalytic reactor device.

6. Method for operating an internal combustion engine at a lean air/fuel ratio, comprising:

fluidly connecting an exhaust aftertreatment system to an exhaust gas feedstream of the internal combustion engine, the exhaust aftertreatment system including a silver-alumina catalytic reactor device fluidly connected upstream to an ammonia-selective catalytic reactor device;

determining a concentration of NOx in the exhaust gas feedstream upstream of the silver-alumina catalytic reactor device;

determining a preferred ratio of hydrocarbon:NOx for the exhaust gas feedstream upstream of the silver-alumina catalytic reactor device effective to achieve substantially equal concentrations of NOx and ammonia in the exhaust gas feedstream immediately downstream of the silver-alumina catalytic reactor device; and

dispensing a reductant upstream of the silver-alumina catalytic reactor device to achieve the preferred ratio for hydrocarbon:NOx in the exhaust gas feedstream upstream of the silver-alumina catalytic reactor device.

7. The method of claim 6, wherein dispensing a reductant upstream of the silver-alumina catalytic reactor device comprises dispensing an ethanol-based reductant.

8. The method of claim 6, further comprising:

monitoring the internal combustion engine and the exhaust gas feedstream upstream of the silver-alumina catalytic reactor device to determine the concentration of NOx in the exhaust gas feedstream upstream of the silver-alumina catalytic reactor device, a temperature of the exhaust gas feedstream upstream of the silver-alumina catalytic reactor device and a mass flow of the exhaust gas feedstream upstream of the silver-alumina catalytic reactor device,

determining a space velocity of the silver-alumina catalytic reactor device corresponding to the mass flow of the exhaust gas feedstream upstream of the silver-alumina catalytic reactor device; and

wherein dispensing a reductant upstream of the silver-alumina catalytic reactor device comprises controlling a mass flow rate of an ethanol-based reductant upstream of the silver-alumina catalytic reactor device based on the concentration of NOx and the temperature of the exhaust gas feedstream upstream of the silver-alumina catalytic reactor device, and the space velocity of the silver-alumina catalytic reactor device.

9. Apparatus, comprising

an internal combustion engine configured to operate lean of stoichiometry and provide an exhaust gas feedstream;

an exhaust aftertreatment system fluidly connected to the internal combustion engine to receive the exhaust gas feedstream, including an ethanol-selective catalytic reactor device fluidly connected upstream to an ammonia-selective catalytic reactor device and a reductant



dispensing system configured to dispense an ethanol-based reductant upstream of the ethanol-selective catalytic reactor device;

a control system signally and operatively connected to the internal combustion engine and the exhaust aftertreatment system, the control system configured to monitor the internal combustion engine and the exhaust aftertreatment system and control the reductant dispensing system to dispense the ethanol-based reductant upstream of the ethanol-selective catalytic reactor device to achieve a preferred ratio of ammonia:NOx downstream of the ethanol-selective catalytic reactor device and upstream of the ammonia-selective catalytic reactor device.

**10.** The apparatus of claim **9**, wherein the ethanol-selective catalytic reactor device comprises a flow-through substrate coated with a silver-alumina catalyst.

**11.** The apparatus of claim **10**, wherein the silver-alumina catalyst comprises a 3 wt. % Ag<sub>2</sub>O catalyst supported on an alumina washcoat.

**12.** The apparatus of claim **9**, wherein the ammonia-selective catalytic reactor device comprises a flow-through substrate coated with a copper-zeolite catalyst.

**13.** The apparatus of claim **9**, further comprising the reductant dispensing system operative to dispense the ethanol reductant into the exhaust gas feedstream at a HC1:NOx ratio that achieves substantially equal concentrations of NOx and ammonia in the exhaust gas feedstream downstream of the ethanol-selective catalytic reactor device and upstream of the ammonia-selective catalytic reactor device.

\* \* \* \* \*