Reducing NO_x in Diesel Exhausts by SCR Technique: Experiments and Simulations

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Results of experiments are compared to simulations of the performance of V_2O_5/γ-alumina SCR catalyst used to remove nitrogen oxides from diesel exhausts. The kinetic model is based on Eley-Rideal kinetics. Temperature programmed desorption (TPD) of the ammonia is used to evaluate adsorption/desorption parameters. Stationary experiments on a 3.6-dm^3 engine with a 4.8-dm^3 honeycomb catalyst is used to evaluate kinetic rate parameters for the reduction of NO with NH_3. The desorption activation energy, $E_{a,des}$, is best fitted as a function of surface coverage yielding $E_{a,des} = 240 * (1 - 0.44 * \theta_{NH3}^{0.36})$ kJ/mol. A dynamic test (FTP) with a 12-dm^3 engine and 24.8-dm^3 honeycomb catalyst is done with a stoichiometric injection of ammonia. The NO_x conversion is 52%, but during the freeway traffic the conversion reached 72%. The prediction of NO_x conversion is good, but there are some deviations for temperature and ammonia slip.

Introduction

Cleaning exhaust from diesel vehicles is of great environmental and economic importance. Nitrogen oxides (NO_x) is one of the most difficult groups of compounds to remove from the exhaust. NO_x contributes to the formation of photochemical smog and to the acidification and fertilization of soil and lakes. When inhaled, nitrogen oxides have an acute toxic effect on humans. For Otto cycle engine vehicles, the reduction of NO_x has been accomplished by using the three-way catalyst. It catalyzes the redox reaction between nitric oxide and carbon monoxide, which is also present in the exhaust gas. In addition, nitric oxide reacts with hydrogen which is produced from hydrocarbons or from the water gas shift reaction. The three-way catalyst demands that the engine operates under stoichiometric conditions to keep the levels of pollutants low. However, it is not possible to use the three-way catalyst on a diesel engine vehicle due to the high partial pressure of oxygen in the exhaust gases, the low concentrations of carbon monoxide and hydrocarbons, and the low temperature.

There are ways to reduce the emissions of nitrogen oxides from diesel vehicles without catalytic treatment, for example, technical adjustments of the engine. These adjustments tend to reduce the efficiency of the engine and also to increase the particle emission. Lower fuel efficiency leads to raised costs and also to higher carbon dioxide emissions. By reducing the nitrogen oxides with a catalyst, it is possible to run the engine at the best fuel efficiency with low particle emissions and lower carbon dioxide emissions.

The selective catalytic reduction (SCR) of NO_x with ammonia or urea as the reducing agent is now a well-established technique for stationary applications in the cleaning of flue gases. In recent decades it has been installed in power plants for pollution control all over the world, mainly in Japan, Germany, and the USA (Bosch and Jansen, 1988). In recent years, the SCR technique for cleaning diesel engine exhaust has been a topic of increasing interest (Saito and Ichihara, 1991). It has also been commercially implemented on at least one ferry (Ingvarson, 1992) and at some diesel power plants in Sweden. The diesel engines in those implementations are normally run with several parallel engines and each is either operated with full (or nearly full) load or without any load. This method of operation makes it possible to have steady operation as a criterion in the design of the SCR catalyst and the reducing agent injection method. An investigation has also been made of the SCR reaction in the exhaust gas from a truck

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diesel engine, and it was reported as successful (Saito and Ichihara, 1991). This test was, however, done in some stationary points on the engine.

To use a SCR reactor on a diesel truck is not a simple task. A great variation of mass flow, temperatures, and nitrogen oxides concentrations create many difficulties. As a device for measuring the total mass flow, ammonia and NO_x flows with a short lag time (fractions of a second) do not exist at present, it is essential to predict those variables. For the same reasons it is also essential to have an appropriate kinetic model for the reaction and for the adsorption and desorption phenomena on the catalyst surface. The reaction model can then be the base for the calculation of the amount of ammonia or urea to be injected into the exhaust stream.

However, research on ammonia sensors with fast response time are progressing. In the future sensors could be used to measure the ammonia slip downstream from the catalyst. However, even if the ammonia slip can be measured, a model is needed to control the ammonia injection into the system. This need is caused by the fact that the catalyst can store large amounts of ammonia, which can be released when the temperature is raised by an increase of the engine load.

Special attention must be paid to the catalyst material. When the truck runs at full load for a long time, exhaust temperatures as high as 600°C can be reached. This temperature can cause some catalysts to sinter, for example, the vanadia on titania catalyst, which are used frequently in commercial flue-gas SCR plants. On the other hand, in operations at low loads the temperature in the exhaust decreases to about 200°C (and under idle conditions to below 100°C). This means that the catalyst must be able to achieve a high conversion of NO_x within a wide temperature range. In this article we present results from stationary experiments, which were obtained on a pilot system with a SCR reactor applied to a diesel engine. We also present results from full-scale experiments where the engine was operated dynamically (simulating a driving scheme for a truck). The results from the full-scale experiment are compared with the prediction from a dynamic reactor-model whose parameters were estimated from the pilot reactor and TPD experiments.

Experimental

Pilot reactor

The pilot reactor system is shown in Figure 1. The SCR reactor contains two cylindrical 5 2/3 in. × 6 in. corderite monoliths with 400 channels per in. from Corning Glasswork. The channel walls of the monoliths are covered with a wash coat consisting of 16% V_2O_5 on γ-Al_2O_3. The BET surface area of the washcoat was 110 m^2/g. The washcoat was prepared by impregnation of the γ-Al_2O_3 with NH_4VO_3 dissolved in oxalic acid as described elsewhere (Odenbrand et al., 1985). The total amount of washcoat was 360 g. The reactor was connected to a 3.58 liter VOLVO TD 40 diesel engine. The engine was connected to a brake which made it possible to

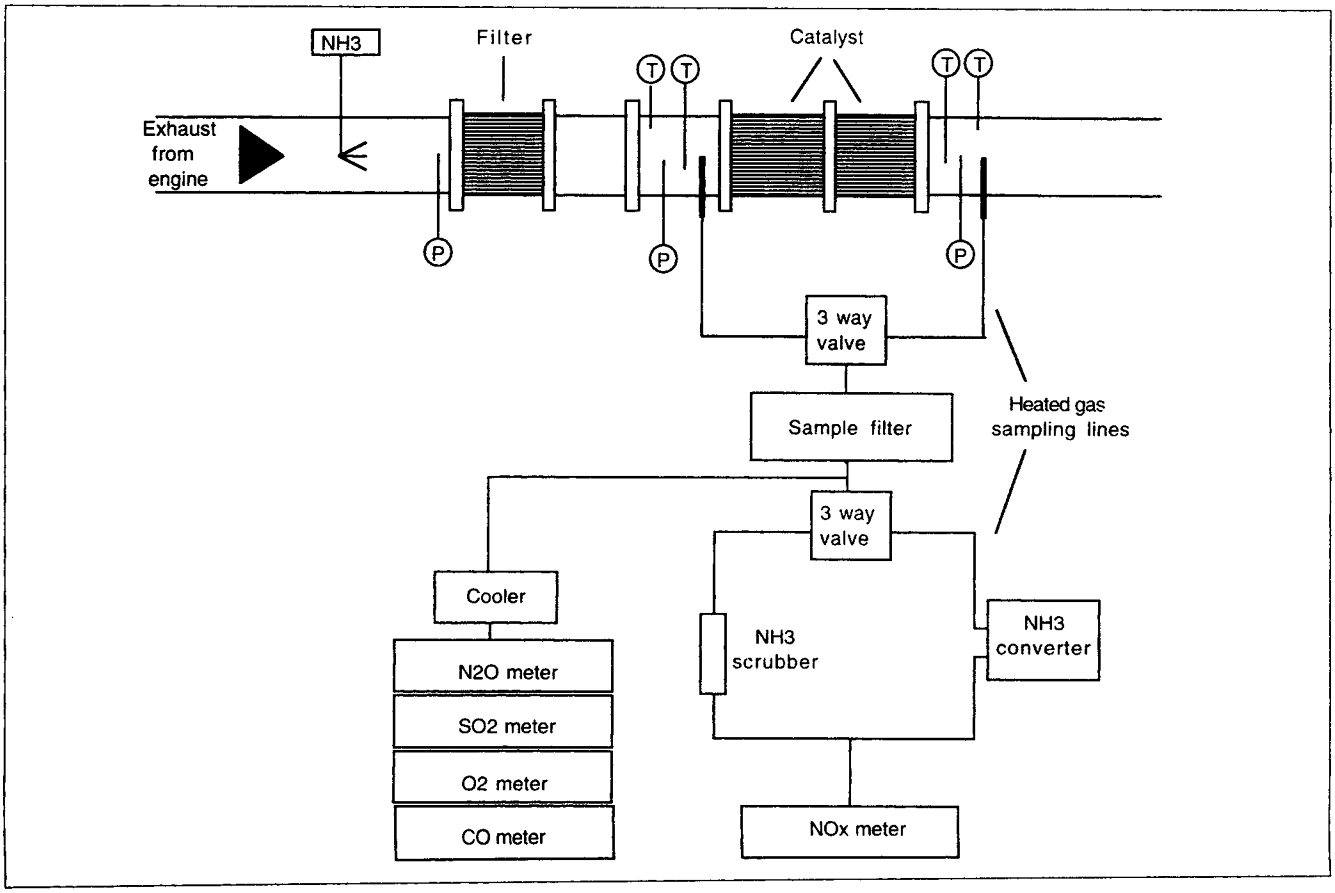

Figure 1. System setup for pilot-scale experiment.

vary the load and the engine speed. Ammonia was injected into the exhaust as a 20% aqueous solution premixed with air.

The exhaust was analyzed for NO and NO_x contents with a TECAN CLD 700 El ht chemiluminescence instrument. Before entering the analyzer the exhaust was cleaned from soot by means of a heated filter (from J.U.M. Engineering). Ammonia was removed by means of a scrubber with phosphoric acid supported on silica. In a separate sample line, a converter containing a 1% Pt/Al_2O_3 catalyst operated at 700°C was used to oxidize ammonia to NO_x. The total amount of NO_x and ammonia was thus measured on the same NO_x instrument after bypassing the scrubber with the aid of switching valves. The ammonia concentration was then calculated as the difference between the signals in NO_x mode and in the ammonia plus NO_x mode. Nitrous oxide was measured with a Siemens Ultramat 5E nondispersive IR instrument. The instrument was equipped with a gas container with a compensation gas mixture to decrease the cross sensitivity for hydrocarbons and carbon dioxide. Teflon or stainless steel tubing heated to 140°C was used to connect all devices to prevent the condensation of water and the formation of ammonium salts. Stationary measurements were carried out by varying the load at three different engine speeds, 1,200, 1,500 and 2,000 rpm. The data obtained represent three different mass flows and were used in the parameter estimations.

TPD

The TPD experiments were conducted in an equipment consisting of a reactor made of quartz with a 4 mm inner diameter. A two-hundred mg washcoat was placed on a fritted glass filter in the reactor. The heating of the reactor was accomplished by a gold-lined quartz tubular oven from Trans. Temp. Co. (U.S.A.). The temperature was increased linearly by a Eurotherm 902 electronic controller. The effluent gases were analyzed using a VG Pegasus SC mass spectrometer. The inlet system to the MS consisted of a stainless steel capillary leaking sample gas from a flow of 50 cm^3 gas per min through the reactor. All lines after the reactor were made of stainless steel tubing with an inner diameter of 2 mm and were heated to 150°C. The mass spectrometer was calibrated regularly with standard gases of known composition (from Alfax AB). The adsorption gas contained 1.5% NH_3 in helium with 3,000 ppm Ar. The ProcessSoft program (from VG) was used during both the calibration and the measurement sequences. The following masses (m/e) were used: 44 (N_2O), 32 (O_2), 30 (NO), 28 (N_2), 18 (H_2O) and 17 (NH_3). During the calibration sequence both the sensitivity factors and the splitting factors were determined automatically by the program yielding quantitative analysis of the composition of the gas phase.

The TPD experiments were conducted as follows. The washcoat was degassed at 400°C for one hour under a flow of 50 cm^3 per min of helium. The sample was then cooled in a helium flow to 150°C during one hour. Ammonia was thereafter adsorbed on the sample at 150°C for 20 min. The physisorbed ammonia was desorbed at the same temperature by a flow of helium during one hour. Another adsorption/desorption sequence was then performed as above. The TPD was then started by increasing the temperature at a specified rate. The TPD experiments were done with the rates 15, 20 and 25 K/min. The outlet gases were analyzed with the mass spectrometer.

Full-scale experiments

The full-scale tests were carried out on a VOLVO TD 123 E, 12-L heavy-duty, six-cylinder in-line, turbo charged and charge air-cooled diesel engine. The engine was installed in a motor laboratory with facilities to operate an engine under transient conditions with a very high reproducibility. The system is shown in Figure 2. The full-scale reactor contained three cylindrical 10 1/2 × 6 in. monoliths from Corning Glassworks with a 2,042-g washcoat. The washcoat came from the same batch as that used for the pilot reactor. The gas analysis in this experiment was extended compared to the pilot experiments. An extra NO_x instrument of the same type as mentioned above was installed which made it possible to measure ammonia and NO_x simultaneously. The amount of ammonia injected into the system was measured continuously by weighing the loss of ammonia solution from a tank placed on a balance.

A constant velocity sampling (CVS) system was also used (see, for example, Lox et al., 1991). The diluted stream was analyzed for its NO_x, CO, and hydrocarbon contents with chemiluminescence, infrared spectroscopy (IR), and flame ionization detector (FID), respectively. The instrumentation consisted of standard instruments from Horiba.

In order to inject the right amount of ammonia into the system, the total mass flow and the NO_x concentrations were calculated from the throttle valve adjustment and the engine speed. In the experiments presented here the NH_3:NO_x ratio was 1:1.

The driving cycle used in this test was the FTP cycle (see, for example, Lox et al., 1991) which is divided into four parts: New York nonfreeway traffic, Los Angeles nonfreeway traffic, Los Angeles freeway traffic. New York nonfreeway traffic is then repeated again. Each part lasted 5 min. This driving cycle is used by the truck manufacturers when engines are certified for the U.S. market.

Modeling

In the modeling we treat NO_x as if it is NO. This is done to keep the number of equations down and is justified by the fact that more than 95% of the NO_x is in the form of NO and that the rest is mainly in the NO_2 form.

Reaction kinetics

The mechanism for the SCR reaction has been established as a direct reaction between gas-phase nitric oxide and ammonia adsorbed in different states, or a reaction between adsorbed nitric oxide and adsorbed ammonia (Odenbrand et al., 1989). The Eley-Rideal model has been the most used, due to the fact that no adsorbed nitric oxide had been detected during the reaction by FTIR, and as to pulse experiments no reaction occurred there when NO was preadsorbed (Inomata et al., 1980). The ambition in this modeling is to keep the model as simple as possible. Thus the model we adopted for the NO reduction follows the mechanism suggested by Miyamoto et al. (1982). The rate of adsorption of ammonia is given by:

$$NH_3(g) + *_f \rightarrow *_{NH_3} \quad r_{ads} = k_{ads} \exp\left(\frac{-E_{a,ads}}{RT}\right) c_{NH_3}(1 - \theta_{NH_3}) \tag{1}$$

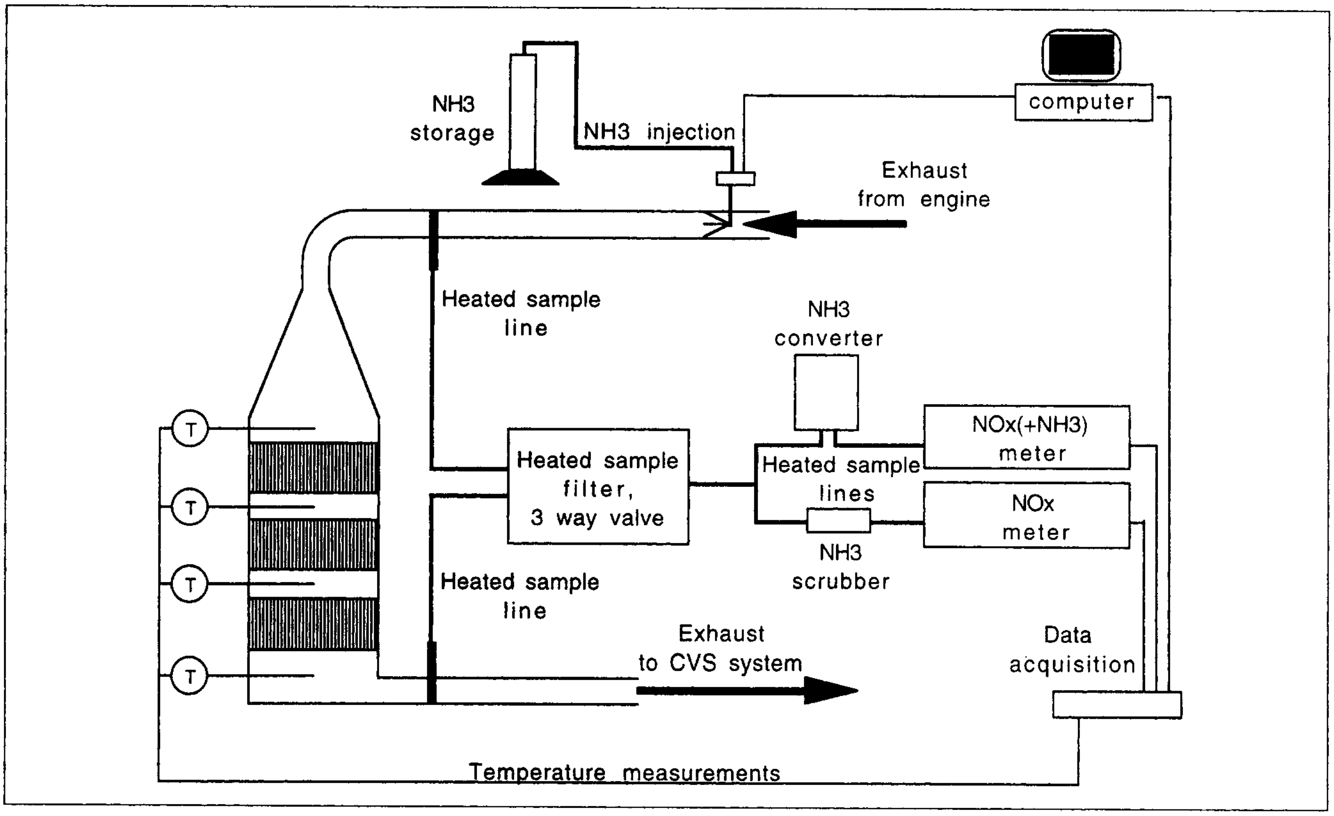

Figure 2. System setup for full-scale experiment.

The rate of desorption of ammonia is given by:

$$*_{NH_3} \rightarrow NH_3(g) + *_f \quad r_{des} = k_{des} \exp\left(\frac{-E_{a,des}}{RT}\right)\theta_{NH_3} \quad (2)$$

The rate of reduction of nitric oxide is given by:

$$NO(g) + *_{NH_3} \rightarrow N_2(g) + H_2O(g) + *_H$$

$$r_{re} = k_{re} \exp\left(\frac{-E_{a,re}}{RT}\right) c_{NO}\theta_{NH_3} \quad (3)$$

This step leaves one hydrogen on a site, which needs to be oxidized according to:

$$\tfrac{1}{4}O_2(g) + *_H \rightarrow *_f + \tfrac{1}{2}H_2O(g)$$

$$r_{reox} = k_{reox} \exp\left(\frac{-E_{a,reox}}{RT}\right)\theta_H \quad (4)$$

The oxidation of ammonia to nitric oxide on a similar catalyst has been reported (Odenbrand et al., 1991) and is of great significance in the high temperature region. This reaction is included in the model as:

$$1\tfrac{1}{4}O_2(g) + *_{NH_3} \rightarrow NO(g) + 1\tfrac{1}{2}H_2O(g) + *_H$$

$$r_{ox} = k_{ox} \exp\left(\frac{-E_{a,ox}}{RT}\right)\theta_{NH_3} \quad (5)$$

The incorporation of oxygen in reactions 4 and 5 is probably a multistep mechanism involving bulk oxygen ions. In this study the oxygen is present in large excess since the diesel engines are run in a very lean mode. Thus we assume a zero-order dependence to the oxygen concentration in the kinetic expressions. Furthermore we assume that reaction 4 is very fast compared to reaction 3. Hence, reactions 3 and 4 could be combined to form:

$$NO(g) + \tfrac{1}{4}O_2(g) + *_{NH_3} \rightarrow N_2(g) + 1\tfrac{1}{2}H_2O(g) + *_f$$

$$r_{red} = k_{red} \exp\left(\frac{-E_{a,red}}{RT}\right) c_{NO}\theta_{NH_3} \quad (6)$$

Equations 1, 2, 5 and 6 are then used as heat and mass sources in the balances for heat and mass described below.

Balance equations of heat and mass

An ideal plug-flow model for the channels in the monolith with a film model for the heat and mass transfer between the solid and fluid was used. The heat- and mass-transfer coefficients were taken from the correlations given by Tronconi and Forzatti (1992). To simplify the mathematical model some assumptions were made. The axial conduction was neglected because of the rather high Peclet number. The accumulation terms for heat and mass in the gas phase were neglected because of the low capacities. These assumptions lead to the following equation for the solid phase temperature:

$$\rho_s C_{p,s} \frac{\partial T_s}{\partial t} = ha(T_g - T_s) + \frac{\lambda_{\text{eff}}}{r}\left[\frac{\partial}{\partial r} r\left(\frac{\partial T_s}{\partial r}\right)\right] + \sum_{i=1}^{n}[(-\Delta H)_i r_i] \quad (7)$$

The assumptions given above regarding the gas-phase temperature show that the radial heat transfer to the washcoat is equal to the axial convective heat transport:

$$0 = ha(T_g - T_s) - v_z \frac{\partial}{\partial z}(\rho_g C_{p,g} T_g) \quad (8)$$

The mass balance for nitric oxide in the gas bulk is similar to the last balance:

$$0 = k_c a(c_{\text{NO},g} - c_{\text{NO},wc}) - v_z \frac{\partial c_{\text{NO},g}}{\partial z} \quad (9)$$

In the gas phase within the washcoat the mass transfer of NO from the gas bulk flow equals the rate of disappearance by the redox reaction and rate of formation by the ammonia oxidation reaction:

$$0 = k_c a(c_{\text{NO},g} - c_{\text{NO},wc}) - r_{\text{red}} + r_{\text{ox}} \quad (10)$$

The balances for ammonia in the gas stream and in the gas phase within the washcoat are similar to the balances for nitric oxide:

$$0 = k_c a(c_{\text{NH}_3,g} - c_{\text{NH}_3,wc}) - v_z \frac{\partial c_{\text{NH}_3,g}}{\partial z} \quad (11)$$

$$0 = k_c a(c_{\text{NH}_3,g} - c_{\text{NH}_3,wc}) - r_{\text{ads}} + r_{\text{des}} \quad (12)$$

Then in the balance for adsorbed ammonia the accumulation term is equal to the rate of appearance due to adsorption minus the rate of disappearance due to desorption, the redox reaction and the oxidation reaction. This can be written as:

$$n_V \frac{\partial \theta_{\text{NH}_3}}{\partial t} = r_{\text{ads}} - r_{\text{des}} - r_{\text{red}} - r_{\text{ox}} \quad (13)$$

A control volume method was used for the discretization. The resulting differential equations were parabolic and solved explicitly. The variables in Eqs. 1, 2, 5, 6 and 9–12 were treated as constant during each time step. Equation 8 gives (after space discretization) the gas-phase temperature as a linear function of the solid temperature. This is used in the balance for solid temperature. The heat differential equations (Eq. 7) is then solved by using the analytical solution for the time step in every control volume. The differential equation for adsorbed ammonia (Eq. 13) is solved by using a Taylor series including the first and second derivatives. The second derivative is approximated by a backward difference.

Parameter estimation

The kinetic parameters were fitted by nonlinear regression using the above equations. The rate parameters for adsorption and desorption in Eqs. 1 and 2 were fitted by using the results from the TPDs and using Eqs. 1, 2, 11, 12 and 13. The rate parameters in Eqs. 5 and 6 were fitted to results from the pilot experiments using Eqs. 1–13 with the accumulation term set to zero in Eqs. 7 and 13.

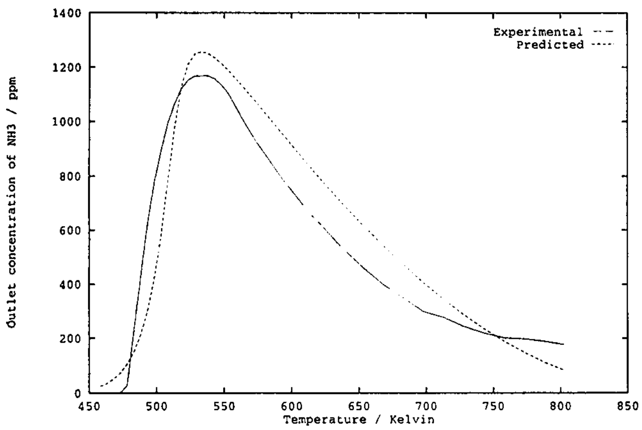

Figure 3. One example of TPD on V_2O_5/γ-Al_2O_3.

Temperature rate: 20 K/min; flow rate: 50 mL/min; simulation parameters are given in Table 1.

Results and Discussion

TPD

The result from the TPD of NH_3 is shown in Figure 3 and in Table 1. It can be concluded that the ammonia adsorption does not take place only on a single site or that the adsorption energy varies with coverage. During the TPD, N_2 was desorbed. However, the amount of N_2 was approximately 0.2% of the desorbed amount of NH_3, so the reaction of ammonia to nitrogen was not introduced into the model. To avoid introducing more than one site into the model it was assumed that the activation energy for desorption was a function of the surface coverage:

$$E_{a,\text{des}} = E_{a,\text{des0}} \cdot (1.0 + \alpha \cdot \theta_{\text{NH}_3}^{\beta}) \quad (14)$$

This new function was included in Eq. 2 in the computer program.

Table 1. Estimated Parameters from TPD and Pilot-Scale Experiments with the 95% Confidence Interval

Parameter	Value	95% Conf.	Units
k'_{ads}	120	±900	$m^3/(g \cdot s)$
k'_{des}	250	±1,000	$\mu mol/(g \cdot s)$
$E_{a,\text{ads}}$	25	±66	kJ/mol
$E^0_{a,\text{des}}$	240	±120	kJ/mol
α	−0.44	±0.015	
β	0.36	±0.33	
k'_{red}	4.1	±0.21	$dm^3/(g \cdot s)$
k'_{ox}	59	±81	$nmol/(g \cdot s)$
$E_{a,\text{red}}$	77	±3.2	kJ/mol
$E_{a,\text{ox}}$	220	±56	kJ/mol

Note that the regressions were done with the rate constant expressed as $k' \exp\{-E_a/R(1/T - 1/T_{\text{ref}})\}$. Hence $k = k' \exp\{E_a/(RT_{\text{ref}})\}$. $T_{\text{ref}} = 648$ K.

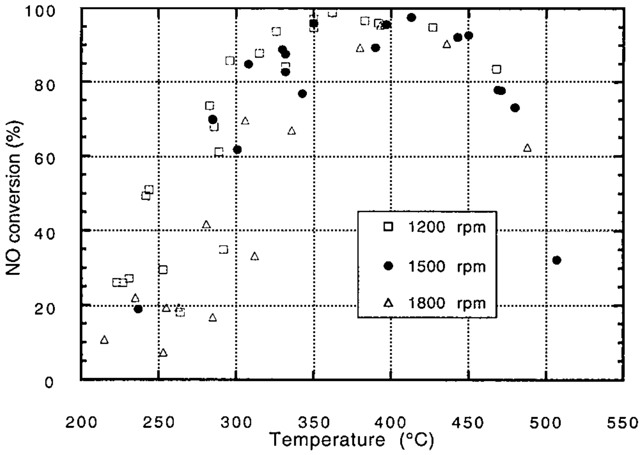

Figure 4. Conversion vs. temperature from the pilot-scale experiments.

There is a strong correlation between the adsorption and desorption parameters (for example, the correlation coefficient between k_{ads} and k_{des} was 0.91), indicating that the adsorption-desorption was close to equilibrium during the TPD. This is consistent with the low flow rate used. Nevertheless the regressions always gave a pre-exponential factor for adsorption within a magnitude from the collision frequency and an activation energy for adsorption between 15 and 35 kJ/mol. This simple model cannot explain the tailing which could be due to different sites and/or to the presence of a mixture of nondissociated and dissociated ammonia.

Pilot experiments

The conversions achieved at different space velocities and temperatures in the stationary pilot experiments are shown in Figure 4. As can be seen, the reaction is dependent on the space velocity in the low temperature region up to 400°C. At higher temperatures (>440°C) the rate of the NO_x reduction is not limited by the amount of catalyst but limited by the rate of the side reactions. The side reactions are in this case the oxidation of NH_3 to N_2 and NO. Even at high temperature, no N_2O was detected (detection limit 1 ppm). This is due to the high water content in the exhausts. A previous investigation (Odenbrand et al., 1991) shows that water hydrolyzes the N_2O-producing Lewis-acid sites leading to a blocking of this side reaction. Furthermore, it can be seen that there are rather large deviations between different experiments of the reaction rate in the low temperature region. This was found to be correlated with the prehistory of the catalyst, especially to the time the catalyst had been operated in temperatures below 350°C. A reversible deactivation, probably caused by soot and/or sulphur-dioxide can explain these findings.

Table 2. Integrated Conversions of Some Pollutants in the Full-Scale Test (Percent)

Period	CO	HC	NO	Predicted NO
NY non-F	—	—	23	12
LA non-F	—	—	28	19
LA F	—	—	72	68
NY non-F	—	—	54	58
Total	0	50	52	48

NY≡New York, LA≡Los Angeles, and F≡freeway traffic.

The rate parameters obtained from the parameter estimation are summarized in Table 1. The engine to be used in the transient test was a low sooting engine and also a fuel with a low content of sulphur (<50 ppm) was used. Thus the data from experiments when the catalyst was the most deactivated were excluded in the estimation.

Full-scale experiments

Experimental Results from Transient Driving Tests. The results from this test are summarized in Table 2. In the freeway traffic (which produces more than 50% of the NO_x in this test) there is good conversion. By increasing the washcoat load from 80 to 130 g/L and using four honeycombs instead of three we would probably be able to reach a conversion between 85 and 90%. This catalyst would then be a very interesting one for trucks which operate mainly in high speed traffic, especially in Europe where the speed is a bit higher than in the U.S. It can also be seen that the activity of this catalyst is too low in city traffic. This is due to the low exhaust gas temperatures

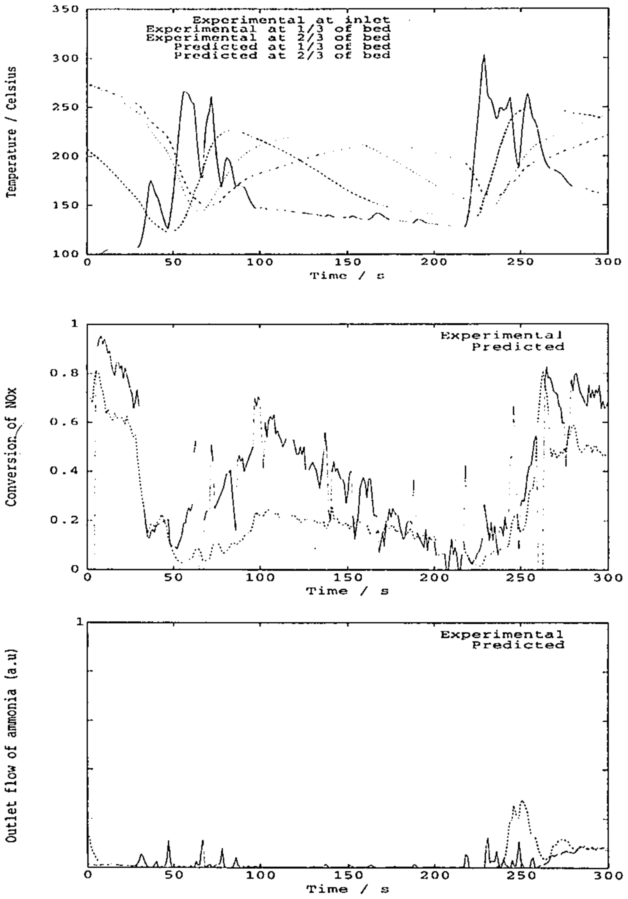

Figure 5. New York nonfreeway traffic period started after 20 min. nonoperation: experiment and prediction of (a) temperature, (b) NO_x conversion, and (c) relative ammonia flow at the outlet.

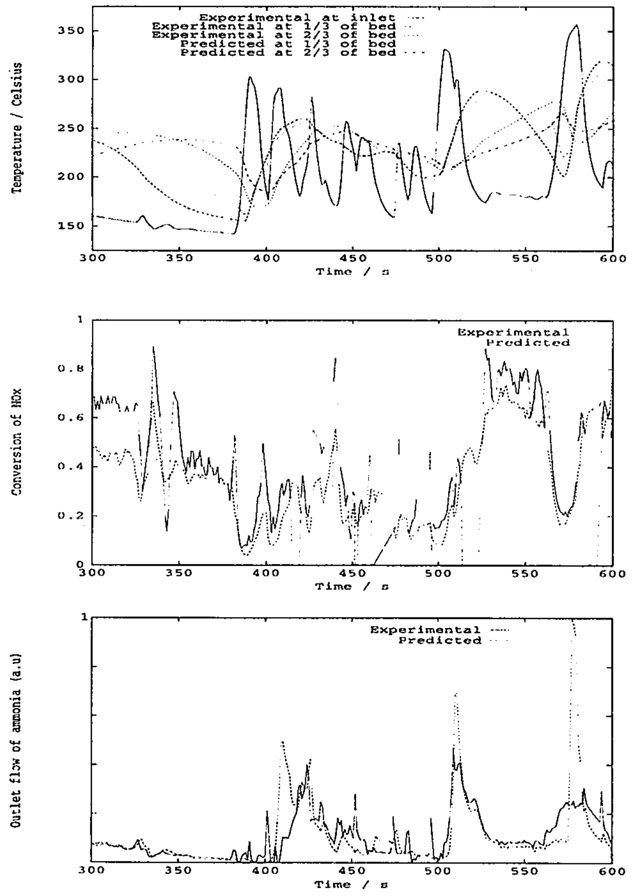

Figure 6. Los Angeles nonfreeway traffic period: experiment and prediction of (a) temperature, (b) NO_x conversion, and (c) relative ammonia flow at the outlet.

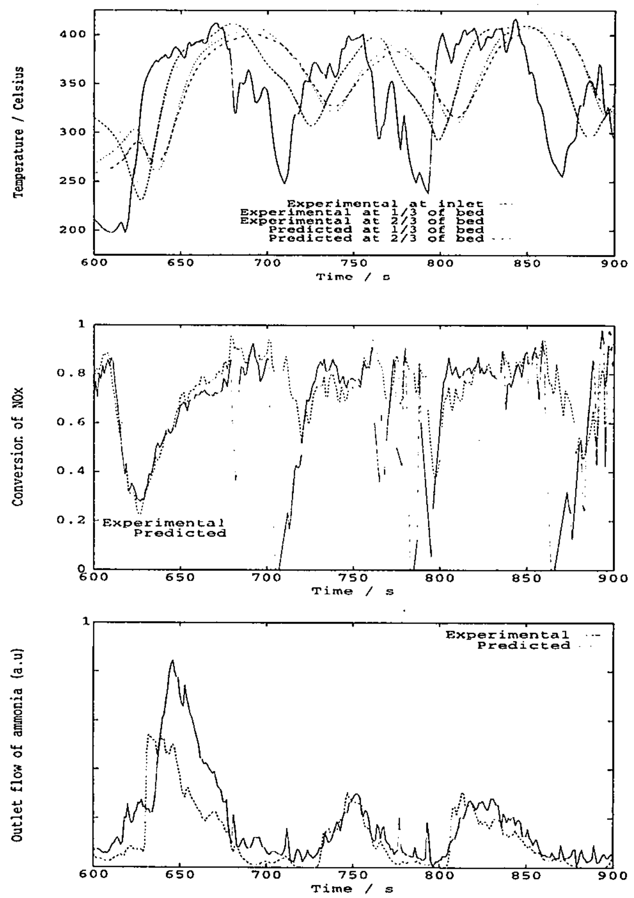

Figure 7. Los Angeles freeway traffic period: experiment and prediction of (a) temperature, (b) NO_x conversion, and (c) relative ammonia flow at the outlet.

reached in this kind of traffic, mainly below 250°C. During the first part of the experiment, the New York nonfreeway traffic period, the temperature was mainly between 140-200°C and this is probably too low for any catalyst used in the SCR technique. This can be seen in Figures 5 to 8 where the experimental and simulated temperature, NO_x conversion, and ammonia slip are shown as a function of time. It should be noted that the experimental time-dependent conversions shown in the Figures 5b to 8b are calculated from the NO_x concentration in the outlet relative to the concentration in the inlet measured in a previous run. Since the data points are collected once each second, a deviation of a half second could be obtained. Furthermore, the time delay between the inlet and outlet measuring points varies by 0.04 to 1 s due to the variation in space velocity during transient operation. This could sometimes make the conversion numbers false since the concentrations in the conversion calculation do not represent the same gas flow. Therefore, there are some unexpected "strange peaks" in the figures and even negative conversions, for example, at 1,060 s. There are also periods when the NO_x concentration in the inlet and in the outlet is below 15 ppm. These low concentrations are registered by the instrument as 10 ppm and hence the result is a zero conversion, for example, at 705 s.

In Figures 7a and 7b it can be seen that there are some low conversion periods due to short periods of low exhaust gas temperatures. This is caused by idling operation or engine brake operation producing low temperature gases with nearly no NO_x. This entails a period during high load when a rather large part of the catalyst is at temperatures which are too low for high conversions. If bypassing of cool gases from idle or engine brake operations is used, a higher total conversion would be obtained.

Figures 5c to 8c show that there are some large slips of ammonia, for example, at 520 s. This particular slip is the result of using a stoichiometric feed of ammonia even when the catalyst is too cold for any conversion to be expected. In a commercial application, a strategy based on the catalyst temperature and the amount of ammonia adsorbed on the catalyst is needed for the ammonia injection to avoid this slip.

In Table 2 it can be seen that the catalyst had no activity for carbon monoxide oxidation but converted hydrocarbons to the same level as it converted NO_x. By mass balance calculations we found that most of the hydrocarbons were oxidized by oxygen. This conclusion is somewhat uncertain since the hydrocarbon concentration was only a few percent of the NO_x concentration.

Predictions. Using 33 finite volumes and a 31-ms time step

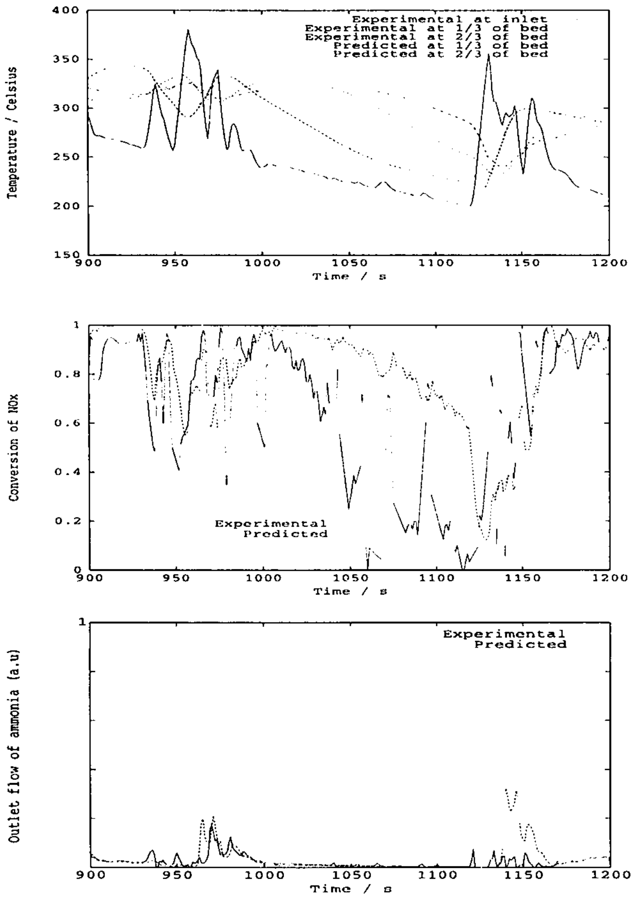

Figure 8. New York nonfreeway traffic period: experiment and prediction of (a) temperature, (b) NO_x conversion, and (c) relative ammonia flow at the outlet.

for the solid-phase temperature and a 8-ms time step for the adsorbed ammonia, it was found that the model can be run in parallel with the experiments. Approximately 70% of the CPU-time on a 33 MHz 486 PC was used for the model. In the prediction model a calculated mass flow, measured concentrations of NO_x and NH_3, and measured inlet temperatures were used as inlet conditions. The simulation stipulated that the $E_{a,\text{des}}$ should be $\geq 1.6 \times 10^5$ J/mol. The reason for this is explained below.

Temperature. The temperature of the gas phase in the experiment and the simulation are shown at various positions along the catalyst bed in Figures 5a–8a. Except during idle operation (for example, 90–220 s in Figure 5a), the calculated temperatures agree quite nicely with the measured ones with only some small errors. The small errors could be explained by a dispersion introduced by the lag time of the thermocouple used in the measurements of the inlet temperature. Small errors can also be due to numerical dispersions and errors in the heat capacity and heat-transfer coefficients, as well as errors in the predicted mass flow. The largest errors are probably caused by an error in the mass-flow prediction during idling operation. In the simulation it was also assumed that there was a uniform distribution of the flow in the monolith. It was planned that the flow distribution should be measured by a step-response of the temperature but a malfunction of two thermocouples made this impossible.

NO_x Conversion. The predicted and measured conversions were rather nicely correlated except for some periods (for example, 50–150 s in Figure 5b) where the prediction gives too low values. During these periods the catalyst is mainly below 250°C. This could be due to the fact that there were not so many stationary data below 250°C and the data used in the parameter estimations were from experiments when the catalyst was a little bit deactivated. There is one period (1,030–1,130 s in Figure 8b) when the predicted conversion is much greater than the experimental conversion; this is because of faulty prediction of the catalysts temperature (errors between 10 and 30 K).

Ammonia Slip. The predicted outlet flows of ammonia (Figures 5c–8c) did not agree with the experiment as well as the NO_x conversions did, especially during low temperature operation. During the period of a few and short idle operations (680–900 s in Figure 7c) when the temperature prediction is good, the ammonia outflow prediction was also quite good. The errors are mostly due to the bad temperature predictions and the simple model used for adsorption and desorption. Errors were also caused by the fact that the estimated parameters from the TPD were obtained from conditions at which the surface coverage was less than 0.52 and at temperatures above 200°C. In a preliminary simulation using the desorption parameters shown in Table 1 there were some large deviations between predicted and experimental outlet flows of ammonia. Due to the lack of information from the TPD in the low temperature range a limitation was introduced for the activation energy for desorption ($E_{a,\text{des}} \geq 1.6 \cdot 10^5$ J/mol).

Conclusions

The system for reducing NO_x emissions with the SCR technique seems promising and V_2O_5/γ-alumina as a catalyst could be used for trucks which drive mostly on freeways. However, for trucks in city traffic, a catalyst with a higher activity for temperatures below 300°C is needed. At the same time the catalyst needs to survive temperatures up to 600°C.

A relatively simple mathematical model with kinetic parameters estimated from TPD and stationary pilot-scale experiments can be used for predicting the efficiency of the catalyst system in real-time driving and therefore can be used for the ammonia injection strategy.

Acknowledgments

We thank Bengt Cyrén and Rolf Egnell at Aspen Utvecklings AB for programming and ideas for the ammonia injection system. Gunnar Lundholm at the Dept. of Heat and Power Engineering, Combustion Engineering, Lund Institute of Technology kindly supplied the pilot engine, and Jan Erik Everitt has been most helpful during the pilot testing. Volvo AB is acknowledged for the use of their engine laboratory, and Jan Eismark and Christer Eriksson for help with the transient experiments. Svenska Emissionsteknik AB kindly prepared and delivered the honeycomb catalysts. Without the financial support from NUTEK, the Swedish National Board for Industrial and Technological Development, this project would never have been possible.

Notation

a = wall area per volume honeycomb
c_{xx} = concentration of compound xx

C_p = heat capacity
$E_{a,xx}$ = activation energy for reaction *xx*
h = heat-transfer coefficient
k_c = mass-transfer coefficient
k_{xx} = preexponential factor in rate expressions for reaction *xx*
n = number of active sites per mass of washcoat
r = radius
r_{xx} = reaction rate for reaction *xx*
R = gas constant
T = temperature
v_z = velocity in axial direction
z = axial distance

Greek letters

α, β = parameters for the surface coverage dependence of the activation energy for desorption
$-\Delta H$ = heat of reaction
θ_{xx} = surface coverage of compound *xx*
λ_{eff} = effective heat diffusivity
ρ = density
$*$ = active site

Subscripts

f = nonoccupied site
g = gas phase
s = solid phase
wc = washcoat

Literature Cited

Bosch, H., and F. Janssen, "Catalytic Reduction of Nitrogen Oxides," *Catal. Today*, **2**, 369 (1988).

Ingvarson, A., "Katalysatorn går till sjöss," *Ny Teknik*, **15**, 26 (1992).

Inomata, M., A. Miyomata, and Y. Murakami, "Mechanism of the Reaction of NO and NH_3 on Vanadium Oxide Catalyst in the Presence of Oxygen under Dilute Gas Condition," *J. Catal.*, **62**, 140 (1980).

Lox, E. S., B. H. Engler, and E. Koberstein, "Diesel Emission Control," *Catalysis and Automotive Pollution Control II*, A. Crucq, ed., Elsevier, Amsterdam (1991).

Miyamoto, A., K. Kobayashi, M. Inomata, and Y. Murakami, "Nitrogen-15 Tracer Investigation of the Mechanism of the Reaction of NO with NH_3 on Vanadium Oxide Catalyst," *J. Phys. Chem.*, **86**, 2945 (1982).

Odenbrand, C. U. I., S. T. Lundin, and L. A. H. Andersson, "Catalytic Reduction of Nitrogen Oxides: 1. The Reduction of NO," *Appl. Catal.*, **18**, 335 (1985).

Odenbrand, C. U. I., R. Gabrielsson, R. Egnell, and F. Ahlström, "SCR-Tekniken i Automotiva Tillämpningar," Report for the Swedish National Board for Technological Development (1989).

Odenbrand, C. U. I., P. L. T. Gabrielsson, J. G. M. Brandin, and L. A. H. Andersson, "Effect of Water Vapor on the Selectivity in the Reduction of Nitric Oxide over Vanadia Supported on Silica-Titania," *Appl. Cat.*, **78**, 109 (1991).

Saito, K., and S. Ichihara, "Purification of Diesel Exhaust Gas," *Catal. Today*, **10**, 45 (1991).

Tronconi, E., and P. Forzatti, "Adequacy of Lumped Parameter Models for SCR Reactors with Monolith Structure," *AIChE J.*, **38**, 201 (1992).

Manuscript received Mar. 1, 1993, and revision received Nov. 10, 1993.