

---

# **Plasma Enhanced Selective Catalytic Reduction: Kinetics of NO<sub>x</sub>-Removal and Byproduct Formation**

**Thomas Hammer and Tetsuo Kishimoto**  
Siemens AG

**Hans Miessner and Rolf Rudolph**  
Institut für Umwelttechnologien GmbH

Reprinted From: **Non-Thermal Plasma for Exhaust Emission Control:  
NO<sub>x</sub>, HC, and Particulates  
(SP-1483)**

The appearance of this ISSN code at the bottom of this page indicates SAE's consent that copies of the paper may be made for personal or internal use of specific clients. This consent is given on the condition, however, that the copier pay a \$7.00 per article copy fee through the Copyright Clearance Center, Inc. Operations Center, 222 Rosewood Drive, Danvers, MA 01923 for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. This consent does not extend to other kinds of copying such as copying for general distribution, for advertising or promotional purposes, for creating new collective works, or for resale.

SAE routinely stocks printed papers for a period of three years following date of publication. Direct your orders to SAE Customer Sales and Satisfaction Department.

Quantity reprint rates can be obtained from the Customer Sales and Satisfaction Department.

To request permission to reprint a technical paper or permission to use copyrighted SAE publications in other works, contact the SAE Publications Group.



**GLOBAL MOBILITY** DATABASE

*All SAE papers, standards, and selected books are abstracted and indexed in the Global Mobility Database*

No part of this publication may be reproduced in any form, in an electronic retrieval system or otherwise, without the prior written permission of the publisher.

**ISSN 0148-7191**

**Copyright 1999 Society of Automotive Engineers, Inc.**

Positions and opinions advanced in this paper are those of the author(s) and not necessarily those of SAE. The author is solely responsible for the content of the paper. A process is available by which discussions will be printed with the paper if it is published in SAE Transactions. For permission to publish this paper in full or in part, contact the SAE Publications Group.

Persons wishing to submit papers to be considered for presentation or publication through SAE should send the manuscript or a 300 word abstract of a proposed manuscript to: Secretary, Engineering Meetings Board, SAE.

**Printed in USA**

# Plasma Enhanced Selective Catalytic Reduction: Kinetics of NO<sub>x</sub>-Removal and Byproduct Formation

Thomas Hammer and Tetsuo Kishimoto  
Siemens AG

Hans Miessner and Rolf Rudolph  
Institut für Umwelttechnologien GmbH

Copyright © 1999 Society of Automotive Engineers, Inc.

## ABSTRACT

The mechanisms of plasma enhanced selective catalytic reduction of NO<sub>x</sub> on a V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-catalyst were investigated for temperatures between 100 °C and 200 °C by applying various analytical methods.

In experiments with synthetic gas mixtures containing Ar instead of N<sub>2</sub> as a carrier gas the formation of N<sub>2</sub> as a main product and thus catalytic reduction of NO<sub>x</sub> in reactions with NH<sub>3</sub> has been proven using mass spectroscopy. More detailed information on the reaction kinetics of NO-formation and removal induced by non-thermal plasmas has been obtained from experiments in gas mixtures containing isotopically marked <sup>15</sup>NO. FTIR-absorption spectroscopy was applied to measure the concentrations of <sup>14</sup>N- and <sup>15</sup>N-containing molecules.

Particles formed by the combined plasma- and catalytic treatment of Diesel exhaust with NH<sub>3</sub> as reducing agent were analyzed by energy dispersive X-ray scattering. The spectra indicate, that mainly sulfur containing particles were formed. Formation of NH<sub>4</sub>NO<sub>3</sub> plays a minor role. Non-thermal plasma treatment did not show a strong influence on catalytic removal of unburned hydrocarbons, but increased CO-emission was observed.

In all experiments plasma induced conversion of NO to NO<sub>2</sub> increased NO<sub>x</sub>-reduction rates.

## INTRODUCTION

Selective catalytic reduction of NO<sub>x</sub> on V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-catalysts using urea as a reducing agent has the potential for a more than 70 % NO<sub>x</sub>-reduction in diesel exhausts of heavy-duty trucks. Such vehicles normally have exhaust gas temperatures well above 200-°C [1]. In recent experiments the plasma enhanced selective catalytic reduction (PE-SCR) of nitric oxides NO and NO<sub>2</sub> using ammonia as a reducing agent was demonstrated in

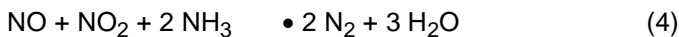
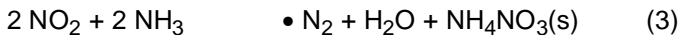
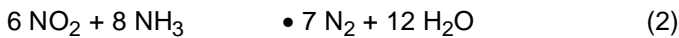
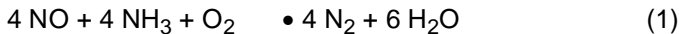
synthetic exhaust gases at temperatures as low as 60 °C [2]. It was shown that the most important reason for this low-temperature removal of NO<sub>x</sub> is the plasma induced partial conversion of NO to NO<sub>2</sub>. Nevertheless, no proof was given that the removal of NO<sub>x</sub> is mainly caused by chemical reduction. The NO<sub>x</sub> could also have been removed by formation of ammonium nitrate aerosol (NH<sub>4</sub>NO<sub>3</sub>(s)), which may occur at low temperatures either in catalytic surface reactions or in volume reactions. Diesel cars run with exhaust temperatures well below 200 °C in city driving cycles and during the first few minutes after start-up. For the practical application of the PE-SCR process it is necessary to avoid aerosol formation, because this would contribute to the unwanted emission of particulate matter (PM). Thus the low temperature kinetics of selective catalytic reduction on a V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-catalyst was investigated measuring the formation of molecular nitrogen N<sub>2</sub> in synthetic gas mixtures using mass spectroscopy. From these measurements upper limits for the contribution of PM forming reactions to the NO<sub>x</sub> removal were determined.

Another question related with the PE-SCR process is which by-products are formed in real diesel engine exhausts. These contain unburned hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), and sulfur dioxide (SO<sub>2</sub>), which were not part of the synthetic gas mixtures used in the mass spectroscopic measurements. To answer this question, the removal of HC and the formation of CO were investigated in a combination of a non-thermal plasma (NTP) reactor and a catalytic reactor. The formation of PM from NO<sub>x</sub> and SO<sub>x</sub> was investigated qualitatively.

More detailed experimental investigations of the chemical kinetics of the PE-SCR process were performed at the Institut für Umwelttechnologien (IUT) using isotopically marked nitric oxide <sup>15</sup>NO. These experiments gave insights into N<sub>x</sub>O<sub>y</sub> generation, conversion and reduction mechanisms.

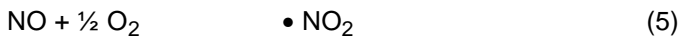
## LOW TEMPERATURE SCR PROCESS

In [2] a set of reactions of  $\text{NO}_x$  with ammonia ( $\text{NH}_3$ ) was suggested, which may remove  $\text{NO}_x$  either by reduction on a  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ -catalyst or by formation of  $\text{NH}_4\text{NO}_3$ .



The fraction of  $\text{NO}_x$  removed by reduction according to (1,2,4) could not be given.

**EXPERIMENTAL PROCEDURE** – Experiments with synthetic gas mixtures at atmospheric pressure were performed, in which Ar instead of  $\text{N}_2$  was used as a carrier gas and the concentration of  $\text{N}_2$  formed by reactions of  $\text{NO}_x$  with  $\text{NH}_3$  was measured mass spectroscopically (Figure 1). Initial concentrations of about 230 ppm NO and 430 ppm  $\text{NO}_2$  (measured after bypass) were obtained by premixing NO and  $\text{O}_2$ , which react according to



The bottled NO was delivered in a mixture containing 50 %  $\text{N}_2$ . In all experiments the mass flows were adjusted such, that the initial  $\text{NH}_3$ -concentration was equal to the initial total  $\text{NO}_x$ -concentration. The  $\text{O}_2$ -concentration was set to 4 %. In foregoing experiments only a small influence of the water content on  $\text{NO}_x$ -removal was observed. Thus for simplicity water was not added to the gas mixture. Total gas flows were varied from 5 liters (STP) to 15 liters (STP) per minute. Catalytic reactor and bypass were thermostatically heated to temperatures between 100 °C and 200 °C. A monolithic  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ -catalyst with a cell density of 100 cps (cells per square inch) and a volume of 27  $\text{cm}^3$  was used.

Concentrations were measured using a differential pumped quadrupole mass spectrometer ( $\text{N}_2$ , NO,  $\text{O}_2$ , Ar), an FTIR absorption spectrometer with 1m-White cell heated to 180 °C ( $\text{NH}_3$ , NO,  $\text{N}_2\text{O}$ ,  $\text{NO}_2$ ), and a flue gas analyzer with electrochemical sensors for monitoring concentrations of  $\text{O}_2$ , NO, and  $\text{NO}_2$ . The MS was calibrated for  $\text{N}_2$  using gas mixtures containing  $\text{N}_2$ -concentrations between 500 ppm and 1500 ppm. Because concentrations in the 100 ppm range were at the lower detection limit of the MS, differential measurements were performed by switching the gas flow between catalytic reactor and bypass 5 times, subtracting the concentration values obtained from each pair of measurements, and averaging the concentration differences. The uncertainty of the  $\text{N}_2$ -concentration values obtained in this way was about 25 %. Due to this procedure no temperature programmed reaction experiments could be performed. However, experiments for different gas flows were started at 100 °C, and the temperature was increased from experiment to experiment.

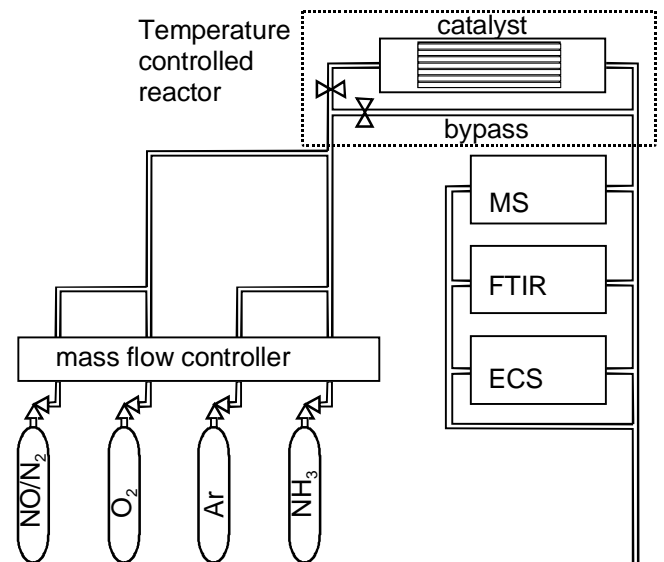


Figure 1. Schematic of the experimental setup for the investigation of the SCR-process. MS – differential pumped quadrupole mass spectrometer, FTIR – Fourier transform infrared absorption spectrometer, ECS – electrochemical sensors for  $\text{O}_2$ - and  $\text{NO}_x$ -concentration measurement.

**$\text{N}_2$ -FORMATION AND  $\text{NO}_x$ -REMOVAL** – The temperature dependency of  $\text{NO}_x$ -removal and  $\text{N}_2$ -formation is shown in Figure 2.

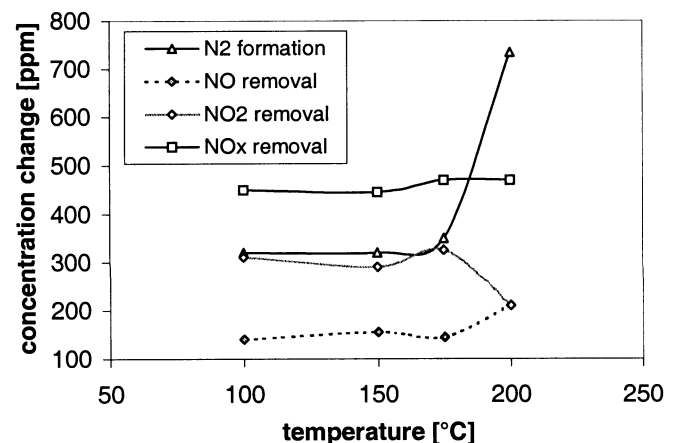


Figure 2. Concentration change of  $\text{NO}_x$  (removal) and  $\text{N}_2$  (formation) caused by catalytic reactions at a space velocity of 11,000/h.

At temperatures below 175 °C the  $\text{NO}_x$  removal exceeds the  $\text{N}_2$  formation. This may be caused by reaction (3), which does not reduce  $\text{NO}_x$  but forms  $\text{NH}_4\text{NO}_3$  aerosol. Using FTIR-absorption spectroscopy substantial amounts of IR-active byproducts could not be detected. Surprisingly, at 200 °C  $\text{N}_2$  formation exceeds  $\text{NO}_x$  removal. Thus another explanation of the observed behavior may be, that at temperatures below 200 °C a part of the  $\text{NO}_x$  is adsorbed on the catalyst but does not react with  $\text{NH}_3$  to gaseous products until the temperature is increased to 200 °C. Adsorption-desorption effects

were observed in the experiment performed at the IUT, too.

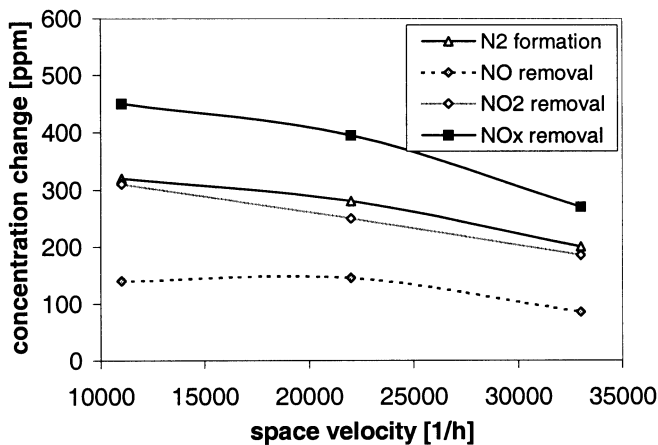


Figure 3. Concentration change of  $\text{NO}_x$  (removal) and  $\text{N}_2$  (formation) caused by catalytic reactions at a temperature of  $100\text{ }^\circ\text{C}$ .

The concentration changes obtained for different gas flows indicate (Figure 3), that the catalytic reaction begins to get transport limited at space velocities above about  $20,000/\text{h}$ . This is well above the maximum space velocity of  $11,000/\text{h}$ , for which this catalyst (normally used for  $\text{NO}$ -reduction in power plants at  $T > 200\text{ }^\circ\text{C}$ ) is designed.

To get deeper insight into reaction kinetics, more sophisticated experiments including surface analysis for the investigation of adsorption, formation of adsorbed intermediates and desorption effects are necessary. Nevertheless, the  $\text{NO}$ -removal is consistent with the  $\text{N}_2$ -formation observed according to (4) within the error limits of the concentration measurements:

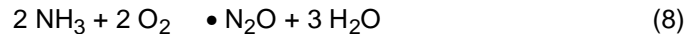
$$d[\text{N}_2] \bullet -2 d[\text{NO}] \quad (6)$$

This means, that all the  $\text{NO}$  loss can be attributed to reaction (4). Since this reaction consumes an equivalent amount of  $\text{NO}_2$ , an upper limit for the ratio of  $\text{NH}_4\text{NO}_3$  formed by reaction (3) to the total removed  $\text{NO}_x$  of about 18 % could be estimated for these experiments:

$$d[\text{NH}_4\text{NO}_3]/d[\text{NO}_x] < \frac{1}{2} (d[\text{NO}_2] - d[\text{NO}])/d[\text{NO}_x] \quad (7)$$

The fraction of  $\text{NO}_2$  spent in reaction (3) to the total removed  $\text{NO}_2$  was estimated to be below 50 %. Because in the PE-SCR-process  $\text{NO}_2$  is formed by plasma induced oxidation of  $\text{NO}$ , optimum conditions for  $\text{NO}_x$ -reduction in Diesel exhaust according to reaction (4) can be obtained by converting only half of the  $\text{NO}$  to  $\text{NO}_2$ .

At a catalyst temperature of  $200\text{ }^\circ\text{C}$  the formation of  $\text{N}_2\text{O}$  was observed by FTIR-spectroscopic measurements. The measured concentration of 13 ppm corresponds to 3 % of the  $\text{NO}_x$ -removal for this temperature. In some other experiments with initial  $\text{NO}_x$ - and  $\text{NH}_3$ -concentrations up to 1750 ppm  $\text{N}_2\text{O}$ -concentrations up to 62 ppm were observed. It is known, that at higher temperatures  $\text{N}_2\text{O}$ -formation can occur due to oxidation of  $\text{NH}_3$



For this reaction a nonlinear dependency of the  $\text{N}_2\text{O}$ -concentration from the initial  $\text{NH}_3$ -concentration is expected, which is in qualitative agreement with experimental results.

## FORMATION OF BY-PRODUCTS IN DIESEL EXHAUST

To investigate the formation of  $\text{CO}$  and  $\text{PM}$  originating from  $\text{NO}_x$  and  $\text{SO}_2$  in real Diesel exhaust, experiments were performed using a 1-cylinder 4-cycle engine (Hatz 1 D 30,  $377\text{ cm}^3$ ,  $4.7\text{ kW}$ ) equipped with a soot filter (Corning EX 80, volume  $2.44\text{ liters}$ ).

As NTP converter a coaxial dielectric barrier discharge (DBD) reactor with a discharge cross section of about  $9\text{ cm}^2$  was used (Figure 4), which was made up of sharp edged stainless steel discs fed on a cylindrical electrode rod as inner electrode and a metal coated  $5\text{ mm}$  thick alumina tube with a diameter of  $55\text{ mm}$  as outer electrode. The inner electrode was connected to a high-voltage pulse generator (pulse duration  $100\text{ ns}$ ); the outer electrode was grounded [3].

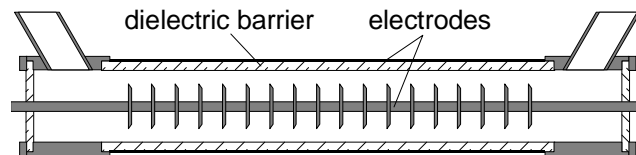


Figure 4. Schematic of the plasma converter.

The catalytic reactor, which was equipped with a monolithic  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ -catalyst with a cell density of 100 cpsi and a volume of 3.5 liters, was put immediately behind the DBD-reactor.

For the experiments reported the engine was running with 2900 rpm and an external load of 2 kW. An exhaust gas flow of about 530 liters (STP)/min was measured, the gas temperature in the plasma reactor was about  $220\text{ }^\circ\text{C}$ , and catalyst temperature was about  $170\text{ }^\circ\text{C}$ . Average plasma powers up to 150 W were applied, which correspond to specific energies of 17 J/liters (STP).

**REMOVAL OF  $\text{NO}_x$  AND HC** – Applying the *plasma only* (without the SCR-catalyst) to the diesel exhaust, HC was removed and  $\text{CO}$  was formed (Figure 5). The  $\text{CO}$ -formation can be attributed to HC-removal as well as to plasma induced reactions of  $\text{CO}_2$ . The SCR-catalyst not loaded with  $\text{NH}_3$  (*plasma & catalyst*, 0 W) worked as an oxidation catalyst for HC but not for  $\text{CO}$ . Mixing  $\text{NH}_3$  to the exhaust gas enhanced HC-removal slightly and reduced  $\text{CO}$ -formation significantly. Pretreatment of the exhaust gas by DBDs led to slightly reduced HC-emission and to enhanced  $\text{CO}$ -emission.

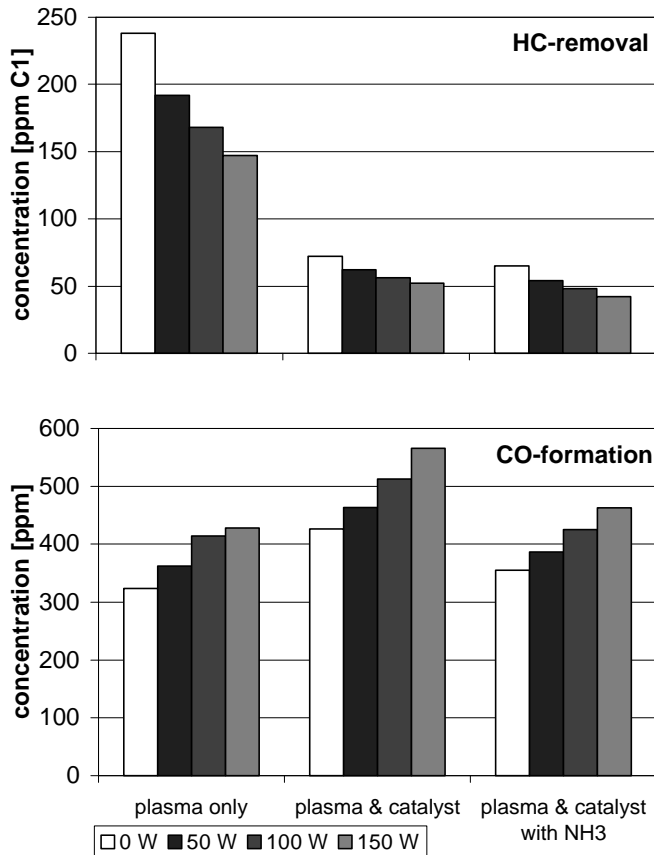


Figure 5. HC-removal and CO-formation in experiments with plasma only, plasma combined with an SCR-catalyst (without NH<sub>3</sub>), and with plasma combined with SCR-catalyst saturated with NH<sub>3</sub> (initial NH<sub>3</sub>-concentration 425 ppm).

DBD-induced NO-removal was mainly caused by oxidation to NO<sub>2</sub>, but obviously small amounts of an unknown byproduct originating from reactions of NO<sub>x</sub> with HC were formed, too (Figure 6): Similar to the observations reported in [4,5], most of the NO<sub>x</sub> removed by the DBDs was recovered on the SCR-catalyst. In experiments performed with synthetic gas mixtures not containing HC no NO<sub>x</sub>-recovery was observed on the SCR-catalyst. Another property of the catalyst is that it reduces NO<sub>2</sub> to NO. Again this reaction was only observed in Diesel exhaust but not in HC-free gas mixtures. Therefore it is concluded, that HCs work as reducing agent for NO<sub>2</sub> but not for NO. Only when NH<sub>3</sub> was mixed to the Diesel exhaust NO<sub>x</sub>-reduction was observed. As expected the degree of NO<sub>x</sub>-reduction increased when NO<sub>2</sub> was formed by NTP treatment. Thus the reduction in CO-formation may be explained by NO<sub>2</sub>-removal in reactions with NH<sub>3</sub>.

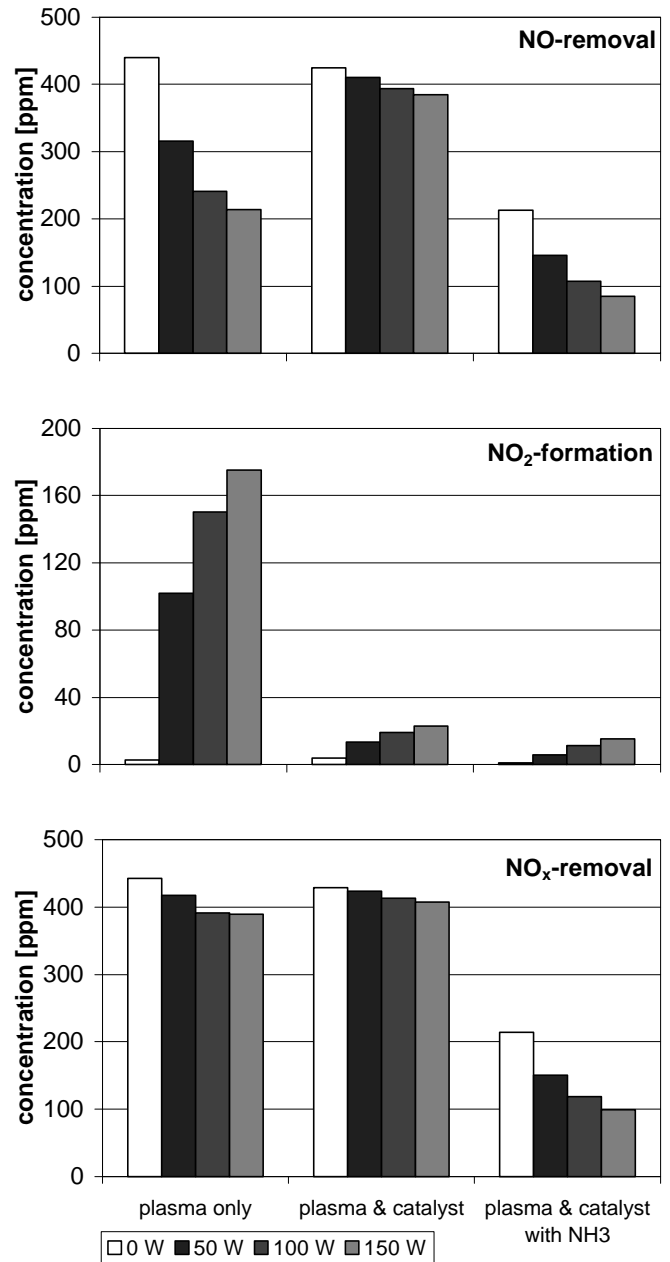


Figure 6. NO<sub>x</sub>-removal in experiments with plasma only, plasma combined with an SCR-catalyst (without NH<sub>3</sub>), and with plasma combined with SCR-catalyst saturated with NH<sub>3</sub> (initial NH<sub>3</sub>-concentration 425 ppm).

FORMATION OF PM – During these experiments small amounts of a light yellow powder were formed and precipitated on the walls of the tubing behind the catalytic reactor. The structure and the peaks marked with S (sulfur), N (nitrogen), C (carbon) and O (oxygen) obtained by energy dispersive X-ray (EDX) scattering indicated, that most of the PM consisted of sulfates (Figure 7) and not of nitrates. This result supports the assumption, that a much smaller fraction of NO<sub>2</sub> than that estimated above is used for NH<sub>4</sub>NO<sub>3</sub>(s) formation.

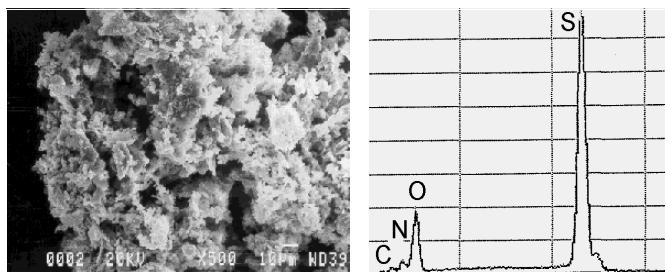


Figure 7. PM formed by the PE-SCR process in Diesel exhaust (a) electron microscopic picture (b) spectrum taken by EDX analysis.

## CHEMICAL KINETICS OF THE PE-SCR-PROCESS

**EXPERIMENTS USING ISOTOPICALLY MARKED  $^{15}\text{NO}$**  – Experiments using isotopically marked  $^{15}\text{NO}$  instead of  $^{14}\text{NO}$  were performed at the IUT to distinguish between reactions forming NO and reactions removing NO. The gas mixture supplied with a flow of 1 liter (STP)/min was prepared by mixing 500 ppm  $^{15}\text{NO}$  with  $\text{N}_2$  and 13 %  $\text{O}_2$ . In experiments with  $\text{NH}_3$  an initial concentration of 500 ppm was used. Reactor and gas mixture were thermostatically heated to temperatures between 100 °C and 240 °C.

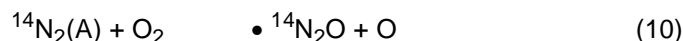
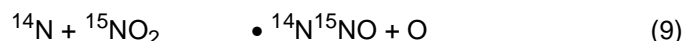
For the NTP treatment a DBD-reactor with a structured inner electrode like that described above but with a much smaller discharge gap of 0.5 mm was applied. A fused silica tube with an inner diameter of 20 mm was used as dielectric barrier, a metal mesh as grounded outer electrode. For electrical excitation slowly rising pulse voltages were applied with a pulse repetition frequency of about 40 Hz (rise time 10  $\mu\text{s}$ , a fixed amplitude of about 19 kV, maximum pulse repetition frequency 500 Hz) resulting in a specific energy of 90 J/liter (STP). A catalytic reactor with a volume of 3 ml containing the  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ -catalyst in granular form (sieve fraction 1-2 mm) was used for the SCR-process.

Analysis of the gaseous products was performed by an FTIR spectrometer with a heated 20.25 m absorption cell (volume 5 liters). Because of differences in molecular mass and inertial moment there is an isotope shift between the ro-vibrational spectra of  $^{14}\text{N}_x\text{O}_y$  and  $^{15}\text{N}_x\text{O}_y$ , which was used to measure the concentrations of products formed from  $^{15}\text{NO}$  and  $^{14}\text{N}_2$ ,  $\text{O}_2$  and  $^{14}\text{NH}_3$ . A problem occurred with the measurement of NO- and  $\text{NO}_2$ -concentrations: Due to the long residence time of gases in the absorption cell about 20 % of the NO was converted to  $\text{NO}_2$  in these experiments (checked by measurements with a chemoluminescence detector having a much smaller gas volume). Thus all results regarding NO- or  $\text{NO}_2$ -concentrations have a systematic error, but total  $\text{NO}_x$ -concentrations are measured correctly.

## RESULTS

### DBD-Treatment of NO in Nitrogen-Oxygen Mixtures

The main effect observed for the DBD-treatment of the gas mixture not containing  $\text{NH}_3$  was oxidation of NO to  $\text{NO}_2$ . The ratio of the  $^{15}\text{NO}$ -concentration to the  $^{15}\text{NO}_2$ -concentration increased with temperature (Figure 8). This temperature dependency is well known [6,7] and can be explained by the temperature dependency of the reactions of NO and  $\text{NO}_2$  with plasma-generated O-radicals. Nearly independent of the temperature about 42 ppm  $^{14}\text{NO}_x$  was formed and 61 ppm of the  $^{15}\text{NO}_x$  were removed by reduction. The formation of  $^{14}\text{NO}$  and the reduction of  $^{15}\text{NO}$  both are caused by reactions with N-radicals, which seem to have similar temperature dependencies. A part of the  $^{14}\text{NO}$  was oxidized to  $^{14}\text{NO}_2$ . Because the ratio  $[\text{NO}]/[\text{NO}_2]$  did not differ significantly from  $[\text{NO}]/[\text{NO}_2]$  it is concluded that the oxidation of NO occurred with a much larger rate than the formation or the reduction. Another reaction connected with the formation of N-radicals or electronically excited  $\text{N}_2(\text{A})$  is the formation of  $\text{N}_2\text{O}$ :



$^{14}\text{N}^{15}\text{NO}$  and  $^{14}\text{N}_2\text{O}$  were formed with the same concentration of about 2 ppm each, which decreased with increasing temperature.

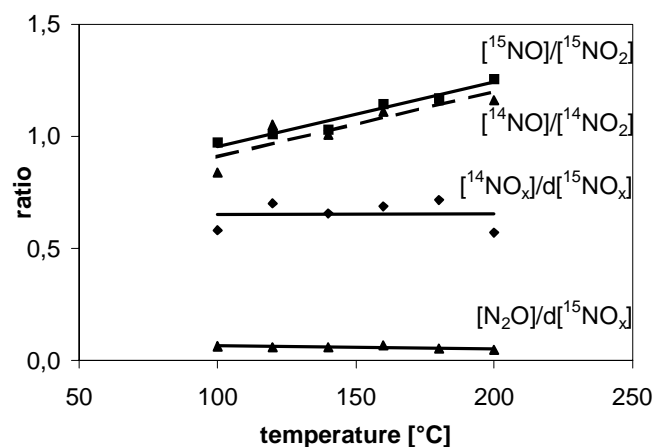


Figure 8. Concentration ratios of  $\text{N}_x\text{O}_y$  formed/removed by the application of DBDs to NO in  $\text{N}_2$  with 13 %  $\text{O}_2$ .

When  $\text{NH}_3$  was added to the gas mixture before DBD-treatment, the results changed only slightly: The  $^{15}\text{NO}_x$ -removal decreased to 54 ppm, the  $^{14}\text{NO}_x$ -formation increased to about 61 ppm, the formation of  $^{14}\text{N}^{15}\text{NO}$  increased to 6 ppm, that of  $^{14}\text{N}_2\text{O}$  remained unchanged, and about 50 ppm of the  $\text{NH}_3$  disappeared. The ratios  $[\text{NO}]/[\text{NO}_2]$  increased for nearly 30 %. In contrast to these observations in gas mixtures containing

water strong NO<sub>x</sub>-removal occurred [2]. These results suggest, that plasma-induced reactions of NH<sub>3</sub> do not advance NO-removal but form NO and N<sub>2</sub>O as long as no water is present in the gas mixture.

**Combination of NTP- and Catalytic Treatment** – In experiments performed with the gas mixture and the catalyst containing no NH<sub>3</sub>, no changes were observed compared to plasma treatment only. Prior to these experiments all NH<sub>3</sub> stored on the catalyst surface was removed by reactions with NO.

When NH<sub>3</sub> was added to the gas mixture and the catalyst surface was saturated with NH<sub>3</sub>, selective catalytic reduction of NO<sub>x</sub> occurred with the well-known temperature dependency [2]. In combination with NTP treatment enhanced NO<sub>x</sub>-removal was observed (Figure 9). Within the error limits there were no differences between the catalytic removal of <sup>14</sup>NO<sub>x</sub> and <sup>15</sup>NO<sub>x</sub> relative to the concentrations measured without catalyst. At low temperatures a lower NO<sub>x</sub>-removal was observed when NH<sub>3</sub> was added to the gas mixture before NTP-treatment (traces marked with (b)), for temperatures above 200 °C NO<sub>x</sub>-removal was lower when NH<sub>3</sub> was added after NTP-treatment.

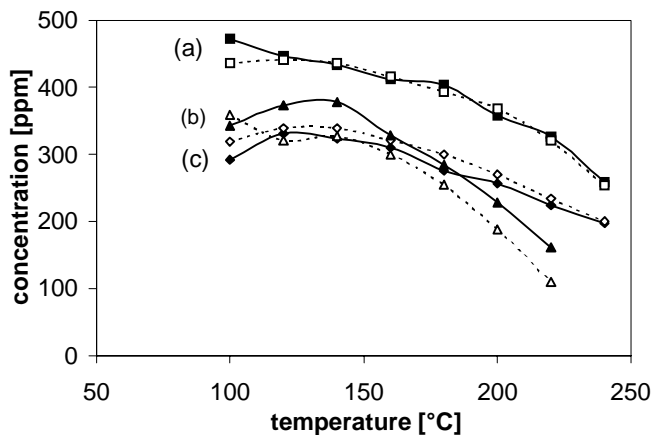


Figure 9. Concentrations of NO<sub>x</sub> (filled symbols) and NH<sub>3</sub> (open symbols) for (a) SCR, (b) PE-SCR with NH<sub>3</sub> added before plasma treatment, (c) PE-SCR with NH<sub>3</sub> added after plasma treatment.

## CONCLUSION

Various analytical methods were used to investigate NO<sub>x</sub>-removal mechanism and formation of by-products in PE-SCR experiments with synthetic gas mixtures and Diesel exhaust. Non-thermal plasmas were generated in a DBD-reactor constructed for the treatment of exhaust gas flows of several hundred liters/min. A monolithic V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-catalyst was used for SCR with NH<sub>3</sub> as a reducing agent. The following conclusions can be given:

- The removal of NO and NO<sub>2</sub> at temperatures between 100 °C and 200 °C is mainly caused by catalytic reduction, not by adsorption or NH<sub>4</sub>NO<sub>3</sub>(s)-formation.
- A part of the NO<sub>x</sub> adsorbed on the catalyst at T < 200 °C may not be completely reduced until T is increased to about 200 °C.
- For plasma treated exhaust gases containing equal concentrations of NO and NO<sub>2</sub> an upper limit of about 12 % can be estimated for the ratio of NH<sub>4</sub>NO<sub>3</sub>(s) formed to NO<sub>x</sub> removed.
- EDX-analysis of PM formed in Diesel exhaust shows, that formation of NH<sub>4</sub>NO<sub>3</sub>(s) plays a minor role compared to formation of sulfates.
- NTP treatment of Diesel exhaust improves the SCR of NO<sub>x</sub> but does not change HC-removal significantly. CO is formed as a byproduct.
- For moderate specific energies plasma induced formation of NO<sub>x</sub> and N<sub>2</sub>O from N<sub>2</sub>, O<sub>2</sub> and NH<sub>3</sub> can be neglected.
- Plasma treatment of NH<sub>3</sub> does not enhance catalytic NO<sub>x</sub>-reduction rates.

In summary the PE-SCR process has the potential for NO<sub>x</sub>-reduction in Diesel exhaust at low temperature.

## ACKNOWLEDGMENTS

The authors would like to thank the Siemens Ceramics and Porcelain Manufacturing Plant for supplying the catalyst. This work is financially supported from the Federal Ministry for Education, Science, Research and Technology (BMBF) under contract nos. 13N7194 and 13N17192.

## REFERENCES

1. Information from Siemens AG, KPW Redwitz and VDI Nachrichten Nr. 4, p. 24, 24. Januar 1997.
2. Thomas, Hammer, Stefan Bröer, "Plasma Enhanced Selective Catalytic Reduction of NO<sub>x</sub> for Diesel Cars", SAE paper no. 982428, 1998.
3. Thomas Hammer, Stefan Bröer, Tetsuo Kishimoto, "Pulsed Excitation of Silent Discharges for Diesel Exhaust Treatment", presented at the 4<sup>th</sup> Int. Conf. on Advanced Oxidation Technologies for Water and Air Remediation (AOTs-4), Orlando, Florida, USA, September 23-26, 1997, full paper submitted to J. Adv. Oxidation Technol.
4. John Hoard, M. Lou Balmer, "Analysis of Plasma-Catalysis for Diesel NO<sub>x</sub> Remediation", SAE paper no. 982429, 1998.
5. Ralph Slone, Madhu Ramavajjala, Vishwesh Palekar and Victor Puchkarev, "Pulsed Corona Plasma Technology for the Removal of NO<sub>x</sub> from Diesel Exhaust", SAE paper no. 982431, 1998.

6. Christopher R. McLarnon, Bernie M. Penetrante, "Effect of Gas Composition on the NO<sub>x</sub> Conversion Chemistry in a Plasma", SAE paper no. 982433, 1999.
7. B.M. Penetrante et al., "Plasma Assisted Catalytic Reduction of NO<sub>x</sub>", SAE paper no. 982508, 1998.

## **DEFINITIONS, ACRONYMS, ABBREVIATIONS**

**SCR:** Selective catalytic reduction

**PE-SCR:** Plasma enhanced selective catalytic reduction

**NTP:** Non thermal plasma

**DBD:** Dielectric barrier discharge

**HC:** (unburned) hydrocarbons