ELSEVIER

Catalysis Today 75 (2002) 325–330

CATALYSIS TODAY

www.elsevier.com/locate/cattod

NO_X removal in excess oxygen by plasma-enhanced selective catalytic reduction

H. Miessner[a,*], K.-P. Francke[a], R. Rudolph[a], Th. Hammer[b,1]

[a] *IUT Institut für Umwelttechnologien GmbH, Volmerstraße 9B, D-12489 Berlin-Adlershof, Germany*
[b] *Siemens AG, Corporate Technology, ZT EN3, Paul-Gossen-Str. 100, D-91052 Erlangen, Germany*

Abstract

In the off-gases of internal combustion engines running with oxygen excess, non-thermal plasmas (NTPs) have an oxidative potential, which results in an effective conversion of NO to NO_2. In combination with appropriate catalysts and ammonia (NH_3-SCR) or hydrocarbons (HC-SCR) as a reducing agent, this can be utilized to reduce nitric oxides (NO and NO_2) synergistically to molecular nitrogen.

The combination of SCR and cold plasma enhanced the overall reaction rate and allowed an effective removal of NO_X at low temperatures. Using NH_3 as a reducing agent, NO_X was converted to N_2 on zeolites or NH_3-SCR catalysts like V_2O_5–WO_3/TiO_2 at temperatures as low as 100–200 °C. Significant synergetic effects of plasma and catalyst treatment were observed both for NH_3 stored by ion exchange on the zeolite and for continuous NH_3 supply.

Certain modifications of Al_2O_3 and ZrO_2 have been found to be effective as catalysts in the plasma-assisted HC-SCR in oxygen excess. With an energy supply of about 30 eV/NO-molecule, 500 ppm NO was reduced by more than half at a temperature of 300 °C and a space velocity of 20 000 h^{-1} at the catalyst. The synergistic combinations of NTP and both NH_3- and HC-SCR have been verified under real diesel engine exhaust conditions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: NO_X reduction; Lean-burn conditions; Automotive catalysts; Non-thermal plasma; $SINO_X$; Zeolites; NH_3-SCR; Al_2O_3 catalysts; ZrO_2 catalysts; Hydrocarbon-SCR

1. Introduction

Driven by world-wide emission regulations, there is a need for the removal of nitrogen oxides in engine exhaust gases with oxygen excess (lean-burn and diesel engines) in a wide range of engine operation conditions. Selective catalytic reduction (SCR) has been studied using both NH_3 or HCs as additional reducing agents. However, for the HC-SCR method, until now, lean NO_X catalysts having a satisfying working temperature range, reduction rate and stability could not be developed [1–3]. The NH_3-SCR method works in a wide temperature range starting from 170 °C, but for its utilization an infrastructure for the distribution of urea used as a reducing agent has to be provided. Because of increasing diesel engine efficiencies resulting in decreasing exhaust gas temperatures and because of further reduction of NO_X emission limits, SCR at temperatures below 150 °C will be required. Thus, with respect to future emission regulations, the state of the art of SCR methods is not satisfactory.

There are, on the other hand, investigations for about 10 years now to reduce the NO_X emissions by a non-thermal plasma (NTP) in the gas phase.

---

[*] Corresponding author. Tel.: +49-30-6392-5511/5515; fax: +49-30-6392-4831.

E-mail addresses: h.miessner@iut-berlin.com (H. Miessner), thomas.hammer@erls.siemens.de (Th. Hammer).

[1] Tel.: +49-9131-7-34870; fax: +49-9131-7-24709.

PII: S0920-5861(02)00085-8

High-energetic electrons generated usually in a corona discharge or a dielectric barrier discharge react with the molecules in the gas phase producing reactive species (radicals, excited molecules) that undergo further reactions. The plasma energy is deposited into the electrons, rather than to ions or molecules leaving the gas mixture essentially at the temperature of the environment (cold plasma). The energetic effort is, therefore, modestly and corresponds to an adiabatic heating by less than 100 K for the systems in the present study. It has been shown, however, that an effective reduction of NO_X to molecular nitrogen by NTP is possible only in an atmosphere free of oxygen, even in the presence of reducing agents as NH_3 or hydrocarbons [4–6].

Recently encouraging results have been obtained combining the gas-phase plasma reactions in the presence of reducing agents with appropriate catalysts [6–15]. The idea behind is the observation from gas-phase studies that an NTP in an oxygen-containing gas results in an effective oxidation of NO to NO_2 [4–6], which seems to be an essential intermediate step in the SCR reaction both with NH_3 and with hydrocarbons as reducing additives.

In this work, the role of the catalyst in combination with an NTP has been studied in detail. It will be shown that an NTP enhances synergistically the SCR resulting in significantly lower reaction temperatures for NO_X removal.

2. Experimental

For laboratory experiments, the NTP was obtained in a coaxial reactor by dielectric barrier discharges, using a glass or a ceramic tube as a dielectric barrier between the inner high voltage electrode and a grounded electrode on the outer wall. The gas discharges were excited by application of a high-voltage pulse generator (ca. 20 kV, repetition rate up to 500 pps). The NTP was characterized by the plasma energy deposited into the gas flow and measured in $\mathrm{W\,h/m^3}$ ($1\,\mathrm{W\,h/m^3} = 3.6\,\mathrm{J/l}$). The catalyst was arranged in a heatable zone in the reactor downstream to the discharge region or in a separate downstream reactor. The analysis was performed using a NO/NO_X detector (chemoluminescence), an FTIR spectrometer with a long-path (20, 25 m) gas cell and a CO/CO_2 monitor (NDIR).

For NH_3-SCR at real conditions, a test bench at Siemens AG with a small diesel engine (Hatz 1D30, 1 cylinder, 377 $\mathrm{cm^3}$, 4.7 kW, 27–30 $\mathrm{N\,m^3/h}$ exhaust gas) was used, equipped with an FTIR spectrometer with a 1 m White cell, a flue gas analyzer (Testo 360-1) and a flame ionization detector (Siemens) as analytical devices. A coaxial dielectric barrier discharge (DBD) reactor with an inner electrode set up of a number of sharp-edged discs connected to a high-voltage pulse generator and a metal-coated alumina tube as grounded outer electrode was used as NTP converter. Downstream this NTP reactor was followed by an injection port for the reducing agent and by a fixed bed reactor containing ca. 1.5 l of the catalyst under investigation.

HC-SCR experiments with real diesel exhaust were performed on the chassis dynamometer at an exhaust emission test bench (Abgasprüfstelle Berlin-Adlershof GmbH) treating a fraction of the full exhaust flow of a Diesel car without catalyst (Multicar M25-10, 1997 $\mathrm{cm^3}$). The analytical devices of the test bench (Horiba) contained two independent channels for comparison. The plasma-catalytic equipment used was the same as in laboratory experiments.

3. Results and discussion

The plasma-enhanced SCR of NO_X by NH_3 has been found to be effective on typical SCR catalysts as V_2O_5–WO_3/TiO_2 between 100 and 250 °C, i.e. at significantly lower temperatures as the non-enhanced SCR (>200 °C) [7–9]. An effective removal of NO is also possible with ammonia stored as NH_4^+ in certain zeolites as, e.g. mordenite or Y-zeolite, especially, if the NO is at least partly oxidized to NO_2 [16]. The oxidative power of an NTP in oxygen-containing gases results in an efficient intermediate oxidation of NO to NO_2 and thus in an significant enhancement of NO_X removal even at temperatures below 100 °C [10,11]. Fig. 1 shows the removal of NO_X in dependence on the energy deposited into the NTP in the presence of NH_4-mordenite as catalyst in comparison with the reaction without catalyst. Without the catalyst, NO is partly oxidized to NO_2, but the total NO_X remains nearly unchanged. With NH_4-mordenite as catalyst, on the other hand, more than 50% of NO_X is converted to N_2 already at 15 $\mathrm{W\,h/m^3}$.

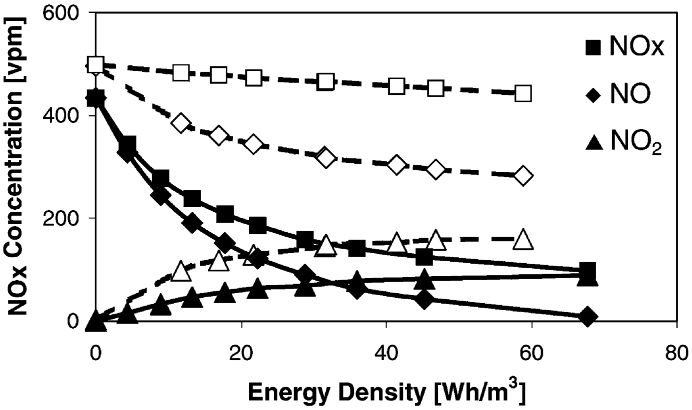

Fig. 1. Effect of the NTP on the NO_X concentration in N_2/O_2 (5%) without catalyst (open symbols) and with NH_4-mordenite as catalyst (filled symbols). Temperature at the catalyst: 100 °C; GHSV = 6000 h^{-1}.

The consumption of the NH_4^+ requires a reloading of the zeolite from time to time with gaseous NH_3 or by ion exchange. Moreover, the experiments were performed at a gas hourly space velocity (GHSV) of 6000 h^{-1}, i.e. at conditions far from real requirements. As an alternative, we studied therefore the plasma-catalytic NH_3-SCR on zeolites at more realistic conditions and with continuous NH_3 addition. Fig. 2 shows the effect of an NTP (15 Wh/m³) on the NH_3-SCR of 500 vpm NO in N_2/O_2 (13%) over an HY-zeolite at 100 °C and GHSV = 20 000 h^{-1}. Without plasma there is hardly any removal of NO_X, whereas the combination with the NTP results again in an NO_X removal by more than 50%.

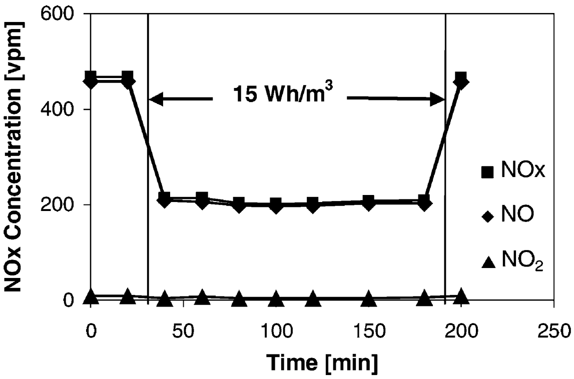

Fig. 2. Effect of NTP (15 Wh/m³) on the NH_3-SCR of 500 vpm NO in N_2/O_2 (13%) over an HY-zeolite at 100 °C and GHSV = 20 000 h^{-1}.

To verify the results obtained in synthetic gas mixtures in the laboratory under realistic conditions, we performed a series of experiments with real diesel exhaust gases. Fig. 3 shows as an example the dependence of NO_X removal on the energy density deposited into the plasma obtained at 160 °C using a H-mordenite as catalyst. From comparison with Fig. 1, it is evident that the enhancement of the NO_X reduction by the plasma at real conditions is even more pronounced than in laboratory experiments. Obviously, the higher oxygen concentration (13% vs.

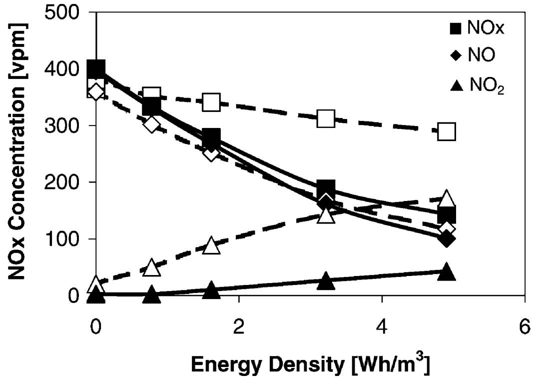

Fig. 3. Influence of the energy density deposited into the NTP on the NH_3-SCR of NO_X in diesel exhaust gas without catalyst (open symbols) and with H-mordenite as catalyst (filled symbols). Gas flow: 31 N m³/h; temperature at the catalyst: 160 °C; GHSV = 20 000 h^{-1}. Addition of NH_3 after NTP treatment: 300–500 vpm.

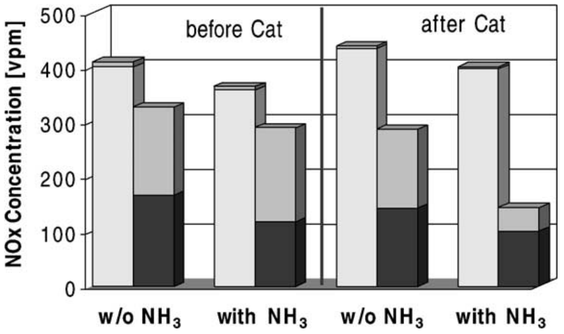

Fig. 4. Effect of the individual contributions to NTP enhanced NH_3-SCR on the NO_X abatement in diesel exhaust gas. For each condition the left column shows the NO-(lower part) and NO_2-concentrations (upper part) w/o plasma treatment, the right column with plasma treatment at a specific energy density of 5 W h/N m^3. Gas flow 31 N m^3/h, Temperature at the catalyst: 160 °C, GHSV = 20 000 h^{-1}.

5% in laboratory) and the presence of remaining hydrocarbons and water in real exhaust gas promote the overall reaction. The 5 W h/m^3, necessary to remove 65% of NO_X, correspond to an equivalent temperature increase of the exhaust gas stream by only 15 °C or 3%, if compared with the engine power.

Fig. 4 demonstrates the effects of the individual factors effective in the plasma-enhanced NH_3-SCR on H-mordenite at 160 °C and an energy density of the NTP of 5 W h/m^3. It is evident that only the combination of all factors, i.e. NTP, the catalyst and the addition of NH_3 yields a significant removal of NO_X. Without plasma there is hardly any conversion independent of the presence of NH_3 and/or the catalyst. The application of NTP converts a significant fraction of NO to NO_2 according to (1) and (2), which is reduced by the NH_3 on the catalyst. Mechanistic studies [8,9,11] revealed that this reduction occurs on the catalyst according to (3):

$$\text{NTP}: \quad e + O_2 \rightarrow e + 2O \tag{1}$$

gas-phase oxidation :

$$O + NO + M \rightarrow NO_2 + M \tag{2}$$

catalytic reduction :

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \tag{3}$$

NTP-induced oxidation can also be utilized for an effective NO_X removal in oxygen containing gas mixtures using hydrocarbons as reductants. We have studied the plasma-catalytic reaction with propene on different catalysts, including supported noble metals, transition metal oxides, metal loaded zeolites and simple metal oxides, as a function of plasma energy input and temperature. Table 1 shows the NO_X concentration in the gas phase after plasma-enhanced HC-SCR of ca. 515 vpm NO at the optimum SCR temperature for some selected catalysts.

The electric discharge alone without any catalyst is not able to reduce NO_X as already stated in Section 1. An analysis of the reaction products indicates that NO is oxidized by the electric discharge in oxygen-containing gas to NO_2 as described for NH_3-SCR and that propene assists this oxidation. The total amount of NO_X remains unchanged.

Pd/Al_2O_3 and Ag/mordenite are active catalysts in the HC-SCR of NO_X. In combination with an electric discharge these catalysts are, however, less suited. An analysis of the reaction products for Pd/Al_2O_3 in dependence on temperature (Fig. 5) demonstrates the

Table 1

NO_X concentration (vpm) and NO_X removal (%) at optimum catalyst temperature (°C) after plasma-enhanced HC-SCR of ca. 515 vpm NO in N_2/O_2 (13%) in the presence of 1000 vpm C_3H_6, GHSV = 20 000 h^{-1}, energy density of NTP: 13–15 W h/m^3

Catalyst	Optimum SCR temperature (°C)	NO_X concentration (vpm)			NO_X removal (%)
		NO	NO_2	NO_X	
Without catalysts		76	439	515	0
$Pd–Al_2O_3$	230	380	55	435	12
TiO_2	350	411	22	433	17
Aluminosilicate	300	150	250	400	22
Ag/mordenite	325	240	102	342	31
γ-Al_2O_3	300	72	111	183	64
ZrO_2	300	135	78	213	58

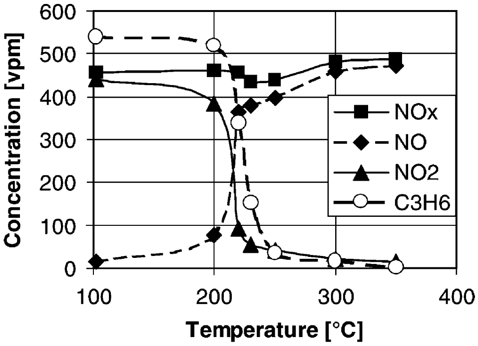

Fig. 5. Removal of 500 ppm NO in N_2/O_2 (13%) in the presence of 1000 ppm C_3H_6; catalyst: Pd/Al_2O_3; GHSV: 20 000 h^{-1}; energy density of the NTP: 25 W h/m^3.

reason for that behavior. It is evident that the hydrocarbon is already burnt at 200–250 °C and cannot be used for the reaction with NO_X at higher temperatures. At the same time, NO_2 formed in the NTP is converted back to NO, thus annulling the effect of the plasma. Redox-active catalysts like Ag/mordenite, Mn-containing catalysts or Cu/ZSM-5 promote in a similar way the reduction of NO_2 to NO, finally resulting in an insufficient removal of NO_X.

Al_2O_3 and ZrO_2, on the other hand, seem to be appropriate catalysts for the reaction. With an energy density of <15 W h/m^3 in the electric discharge, a temperature of 300 °C and a space velocity of 20 000 h^{-1} at the catalyst, 500 ppm NO in oxygen excess is removed by more than half. The analysis of the reaction products in dependence on the temperature at the catalysts (Fig. 6) demonstrates the differences compared to the former example: up to 250 °C only a small amount of propene is oxidized and at 300 °C 70% are still available. As shown in Fig. 6, the back-reduction of NO_2 to NO on Al_2O_3 is limited and the NO_2 concentration exceeds the NO concentration up to 300 °C. As a consequence, both NO_2 and the hydrocarbon are available for the SCR reaction on Al_2O_3, resulting in an effective NO_X removal already at 300 °C. In Fig. 6, the plasma-catalytic NO_X removal in dependence on temperature is compared also to that on the same catalyst, but without plasma assistance. Obviously, the pure catalytic HC-SCR on Al_2O_3 is also effective, but at significantly higher temperatures.

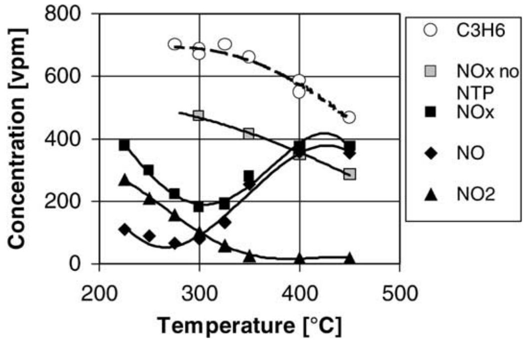

Fig. 6. NTP-assisted HC-SCR of 500 ppm NO in N_2/O_2 (13%) in the presence of 1000 ppm C_3H_6; catalyst: γ-Al_2O_3; GHSV: 20 000 h^{-1}; energy density of the NTP: 13–14 W h/m^3.

The results obtained with synthetic gases in laboratory scale were verified at real conditions with exhaust gases from a diesel engine without catalyst (Multicar M25-10, 1997 cm^3). The typical composition of the untreated exhaust gas at medium load is 400–500 ppm NO_X, 200–300 ppm CO, several ppm of hydrocarbons, 8.3% CO_2 and 8.5% O_2.

Part of the exhaust gas was treated in a plasma-catalytic reactor system that consisted of a plasma reactor followed by a catalytic reactor with two catalysts for removal of NO_X (γ-Al_2O_3, 60 ml) and for the subsequent oxidation (a commercial oxidation catalyst, 60 ml), respectively. Propene was added, if desired, upstream the plasma reactor.

Fig. 7 shows the synergistic effect of catalyst, NTP and HC, if applied together, on NO_X removal.

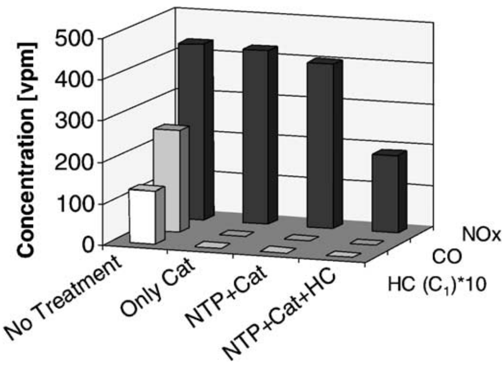

Fig. 7. Successive combination of catalyst, NTP and HC to plasma-enhanced HC-SCR of diesel exhaust gas. Exhaust gas stream: ca. 600 sl/h; energy density of the NTP: 15 W h/m^3; propene addition: 1.2 sl/h. Catalyst: γ-Al_2O_3; +oxy-cat; temperature: 250 °C; GHSV: 10 000 h^{-1}.

Without addition of propene, the plasma-catalytic treatment results only in a marginal decrease of the NO_X concentration. The pure catalytic HC-SCR (not shown in Fig. 7) using propene as additional reducing agent does not cause any removal of NO_X with the catalysts used at the given conditions (250 °C). It is obvious from Fig. 7 that CO and the remaining hydrocarbons are completely oxidized by the oxidation catalyst independent of the electric discharge. NO_X is, on the other hand, removed by more than half only with the assistance of the plasma and the addition of C_3H_6.

Acknowledgements

This work was supported by the German Federal Ministry of Education, Science, Research, and Technology (Contract No. 13N7192/0). The authors thank the Alcoa Industrial Chemicals, the CONDEA Chemie GmbH, the Degussa AG, the S. Goldmann GmbH Bielefeld, the SCW GmbH Berlin-Adlershof and the Südchemie AG for the supply and the ACA Institute of Applied Chemistry, Berlin-Adlershof, for supplying and characterization of catalysts. D.L. Hoang and M. Richter (ACA Berlin) are acknowledged for stimulating discussions and J. Hoard (Ford Motor Co.) for his help in the identification of byproducts.

References

[1] R. Burch, Pure Appl. Chem. 68 (1996) 377.
[2] A. Fritz, V. Pitchon, Appl. Catal. B 13 (1997) 1.
[3] M. Shelef, R.W. Mccabe, Catal. Today 62 (2000) 35.
[4] M.A. Tas, R. van Hardeveld, E.M. van Veldhuizen, Plasma Chem. Plasma Process. 17 (1997) 371.
[5] W. Niessen, O. Wolf, R. Schruft, M. Neiger, J. Phys. D 31 (1998) 542.
[6] B.M. Penetrante, R.M. Brusasco, B.T. Merritt, W.J. Pitz, G.E. Vogtlin, M.C. Kung, H.H. Kung, C.Z. Wan, K.E. Voss, SAE Technical Paper Series No. 982508, 1998.
[7] T. Hammer, S. Broer, SAE Technical Paper Series No. 982428, 1998.
[8] T. Hammer, T. Kishimoto, H. Miessner, R. Rudolph, SAE Technical Paper Series No. 1999-01-3632, 1999.
[9] S. Bröer, T. Hammer, Appl. Catal. B 28 (2000) 101.
[10] H. Miessner, R. Rudolph, K.-P. Francke, Chem. Commun. (1998) 2725.
[11] K.-P. Francke, H. Miessner, R. Rudolph, Catal. Today 59 (2000) 411.
[12] J. Hoard, M.L. Balmer, SAE Technical Paper Series No. 982429, 1998.
[13] M.L. Balmer, R. Tonkyn, A. Kim, S. Yoon, D. Jimenez, T. Orlando, S.E. Barlow, J. Hoard, SAE Technical Paper Series No. 982511, 1998.
[14] M.L. Balmer, R. Tonkyn, S. Yoon, A. Kolwaite, S.E. Barlow, G. Maupin, J. Hoard, SAE Technical Paper Series No. 1999-01-3640, 1999.
[15] H.H. Kim, K. Takashima, S. Katsura, A. Mizuno, J. Phys. D 34 (2001) 604–613.
[16] M. Richter, R. Eckelt, B. Parlitz, R. Fricke, Appl. Catal. B 15 (1998) 129–146.