

Plasma-enhanced HC-SCR of NO_x in the presence of excess oxygen

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Abstract

The oxidative potential of a non-thermal plasma (NTP) in engine off-gases with excess oxygen results in an effective conversion of NO to NO_2 that can be converted synergistically to molecular nitrogen with appropriate catalysts by selective catalytic reduction of NO_2 with hydrocarbons (HC-SCR). The hydrocarbon added has two essential functions: first, it assists the gas-phase oxidation of NO to NO_2 by the electric discharge in excess oxygen and, secondly, it reacts with NO_2 in the hydrocarbon SCR. Besides CO_2 and CO, significant amounts of formaldehyde and acetaldehyde are formed in the plasma-initiated gas-phase reaction. These and other by-products are involved together with the remaining propene in the subsequent catalytic reaction.

The combination of SCR and cold plasma enhances the overall reaction and allows an effective removal of NO_x at relatively low temperatures. Certain modifications of Al_2O_3 and ZrO_2 have been found to be effective as catalysts in this reaction. With an energy effort of ca. 30 eV per NO-molecule, a temperature of 300 °C and a space velocity of 20,000 h^{-1} at the catalyst, it is possible to reduce 500 ppm NO in excess oxygen by more than half.

The synergistic combination of NTP and HC-SCR has been verified under real conditions with exhaust gas from a diesel engine. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The removal of nitrogen oxides in engine exhaust gases with excess oxygen (lean-burn and diesel engines) is solved so far only insufficiently, despite of extensive world-wide efforts. Both NH_3 (via urea hydrolysis) and hydrocarbons are studied as additional reducing agents (selective catalytic reduction (SCR)) [1–4]. For heavy-duty diesel trucks, a solution on the basis of NH_3 - (urea) SCR seems to

be feasible [4–6]. For availability reasons, however, the use of hydrocarbons as reducing agent (HC-SCR) would be of special interest. According to the present state of development, 60–80% of NO_x can be removed on Al_2O_3 -based catalysts at temperatures ≥ 400 °C [7–11]. The effective temperature window of these catalysts is relatively narrow and should be broadened to lower temperatures for practical applications. Specially designed catalysts on the basis of promoted zeolites [3,12], supported platinum metals [1] or bifunctional catalyst mixtures [13] are active also at lower temperatures (200–400 °C). For a technical application they need further development, especially with respect to their

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stability and selectivity of NO_x reduction to N₂ [1–4].

There are, on the other hand, investigations for ca. 10 years to reduce the NO_x content by a non-thermal plasma (NTP) in the gas-phase. High-energetic electrons produced usually in a corona discharge or in a dielectric barrier discharge react with molecules in the gas-phase producing reactive species (radicals, excited molecules), which undergo further reactions. The energy deposited into the plasma is transmitted to 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 NH₃ or hydrocarbons [14–16].

In recent time, encouraging results have been obtained combining the gas-phase plasma reactions and the reaction of reducing agents on appropriate catalysts. The idea behind is the observation from gas-phase studies that a NTP in an oxygen-containing gas results in an effective oxidation of NO to NO₂ [14–16], which seems to be an essential intermediate step in the SCR reaction both with NH₃ and with hydrocarbons as reducing additives, at least using oxide type catalysts [17–19]. Thus, the plasma-enhanced NH₃-SCR allows an effective removal of NO_x in excess oxygen already at 100–200 °C [20–24]. Also for HC-SCR recent papers report on an efficient combination of a NTP with appropriate catalysts [16,25–33]. As an example, Tonkyn et al. [30] obtained a chemical

reduction of about 50% NO_x over a broad temperature range (175–400 °C) using a NTP assisted propene SCR on NaY zeolite as catalyst. Similarly, Chun et al. [31] found a plasma-catalytical removal of about 50% NO_x at 300 °C using Ag/Al₂O₃ as catalyst. Aardahl et al. [32] report on plasma-enhanced catalytic reduction of NO_x in simulated lean exhaust. Using a non-specified proprietary catalyst the authors obtained a NO_x reduction of 84% at 500 °C in sulphur-free exhaust and 74% reduction in the presence of 20 ppm SO₂. Using a proprietary zeolite catalyst Fisher et al. [33] reached a plasma-catalytic conversion of about 50% NO_x to nitrogen at 200 °C.

In the present work, the role of the catalyst in combination with a NTP has been studied in detail. It will be shown that NTP enhances in combination with appropriate catalysts synergistically the HC-SCR resulting in significantly lower reaction temperatures for NO_x removal.

2. Experimental

2.1. Materials

The properties of the catalysts used in the present work are described in Table 1. They were obtained from the suppliers indicated in the table. ZrO₂ was obtained by a treatment of a zirconia/carbon composite in airflow at 450 °C. The zirconia/carbon composite was supplied by the Institute of Applied Chemistry (ACA, Berlin). It was prepared by sol-gel method according to [34]. Upon calcination in air the carbon is burnt off leaving the ZrO₂ matrix unchanged [34]. Catalytic

Table 1
Materials used as catalysts

Designation	Source	Description	BET-specific surface (m ² /g)	Pore volume ^a (ml/g)	Average pore diameter (Å)
Al ₂ O ₃	Süd-Chemie AG	γ-Al ₂ O ₃	210	0.33	60
TiO ₂	Degussa	Mainly anatase	47	0.17	150
ZrO ₂	See text	Tetragonal and cubic	70	0.08	50
Alumosilicate	Süd-Chemie AG	Amorphous	163	0.45	110
Pd/Al ₂ O ₃	Süd-Chemie AG	0.5 wt.% Pd on γ-Al ₂ O ₃	205	0.41	80
Ag/mordenite	SCW	2.5 wt.% Ag exchanged into mordenite (Si:Al = 6) + 20% Al ₂ O ₃ as binder	325	0.25	30

^a For pores smaller 250 Å.

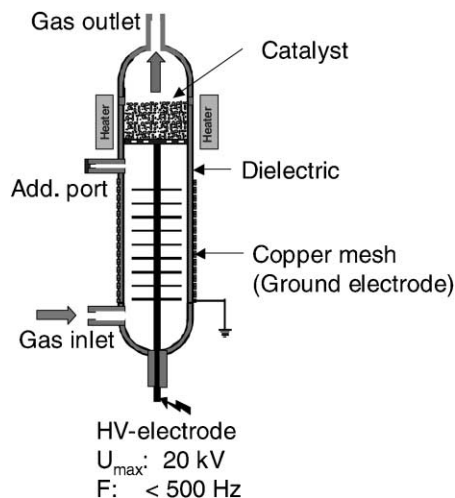


Fig. 1. Schematic view of the plasma-catalytic reactor as used in laboratory experiments. The additional port (Add. port in the figure) allows the introduction of additives or the analysis after the plasma treatment.

tests in the laboratory and characterisation measurements were performed with split material sieved in the range between 0.6 and 2.0 mm. BET surface area (multipoint analysis) and porosity data (BJH) have been measured with nitrogen as adsorbate at -196°C using a BET area analyser NOVA-1200, Quantachrome.

2.2. Laboratory tests

The apparatus used for plasma-assisted catalysis in the laboratory is shown schematically in Fig. 1. NTP is obtained in a coaxial reactor by dielectric barrier discharge, using a glass tube as dielectric between the inner high-voltage electrode and a grounded mesh electrode on the outer glass wall. The gas discharges were produced by a high-voltage pulse generator (ca. 20 kV, repetition rate up to 500 pps). Energy input into the plasma has been derived from the area of the Lissajous figure formed by simultaneous measurements of discharge voltage and transported charge. Voltage was measured with a HV probe (Tektronix P6015A), the charge was determined from the voltage drop over a serial capacitor (30.5 nF). Both quantities were measured and recorded using a digital storage oscilloscope (Tektronix TDS 520).

The catalyst was arranged in a heatable zone in the reactor downstream to the discharge region. The

analytical data were taken at steady state, usually 20 min after setting new parameters (temperature, plasma energy, gas hourly space velocity (GHSV)). NO and NO₂ were analysed using a chemiluminescence-detector (ECO-Physics). CO and CO₂ were determined by a NDIR monitor (Fischer-Rosemount). A FTIR spectrometer (Perkin-Elmer) with a long-path (20.25 m) gas cell was used to analyse the amount of C₃H₆, and of by-products as N₂O, formaldehyde, acetaldehyde, HCN and methyl nitrate (CH₃ONO₂). The quantification was made by comparison with calibration spectra. The analytical data were used to establish the carbon balance. The experiments were performed in nitrogen and, therefore, a nitrogen balance is not available. A careful inspection of the infrared spectra did not indicate other nitrogen-containing species, e.g. as acids.

For the experiments in the laboratory dry synthetic gas mixtures have been used, containing generally 13 vol.% O₂, 500 ppm NO and a variable amount of propene (0–2000 ppm) with N₂ as balance. Gas flows of 1–2 l/min (STP) were used (GHSV = 20,000–40,000 h⁻¹).

2.3. Test bench experiments

The experiments with diesel off-gases were made on the chassis dynamometer at the exhaust emission test bench (Abgasprüfstelle Berlin-Adlershof GmbH) using a diesel car without catalyst (Multicar M25-10, 1997 cm³) and the analytic devices of the test bench (Horiba) with two independent channels for comparison. The typical composition of the exhaust gas at medium load was 10% O₂, 8% CO₂, 5–10% water, 400–500 ppm NO_x, 200–300 ppm CO, and 10–50 ppm hydrocarbons.

Part of the exhaust gas (about 10 l/min (STP)) was treated plasma-catalytically. The plasma-catalytic device was modified for higher flow rates (10–20 l/min (STP)) using two separate reactors. The NTP converter consists of an inner high-voltage electrode similar as shown in Fig. 1 and a ceramic tube as dielectric coated with a thin Ni layer as ground electrode. A stainless steel tube is used as catalytic reactor filled with the SCR catalyst (60 ml, 4.5 mm × 3 mm tablets) and an additional oxidation catalyst for the total oxidation of the remaining hydrocarbons and of the by-products. The catalyst zone is surrounded by an electric heater,

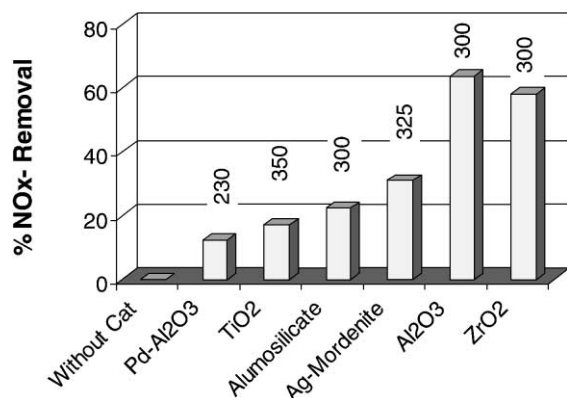


Fig. 2. Removal of 500 ppm NO in N₂/O₂ (13%) in the presence of 1000 ppm C₃H₆; GHSV: 20,000 h⁻¹; energy density deposited into the discharge: 13–14 Wh/m³. The figures in the diagram indicate the temperature (°C) of maximum conversion.

which is controlled using a thermocouple in the catalyst bed.

3. Results and discussion

Fig. 2 shows some typical results of the screening of various catalysts with respect to their efficiency in the plasma-catalytic HC-SCR of NO_x. The data were obtained with dry synthetic gas mixtures at conditions as indicated in the figure caption and varying the catalyst temperatures between 250 and 450 °C. The figure shows the maximum NO_x removal together with the corresponding optimum catalyst temperatures.

Table 2

By-products and carbon balances for the plasma-catalytic removal of 500 ppm NO in N₂/O₂ (13%) in the presence of 1000 ppm C₃H₆ as shown in Fig. 2^a

Catalyst	N ₂ O (ppm)	C ₃ H ₆	Carbon distribution (% initial C)					Carbon balance (%)	
			CO ₂	CO	HCHO	CH ₃ CHO	CH ₃ ONO ₂		HCN
Without catalyst	3	67	1	3	4	11	1	0.1	87
Pd/Al ₂ O ₃	36	14	67	2	2	6	1	0.0	91
TiO ₂	10	40	37	16	1	0	0	0.0	94
Alumosilicate	7	68	5	6	6	13	0	0.4	98
Ag/mordenite	24	48	14	24	3	3	0	1.5	93
Al ₂ O ₃	14	60	19	15	2	1.3	0	0.5	97
ZrO ₂	17	64	16	15	0.7	0.7	0	0.0	96

^a GHSV: 20,000 h⁻¹; energy density deposited into the discharge: 13–14 Wh/m³.

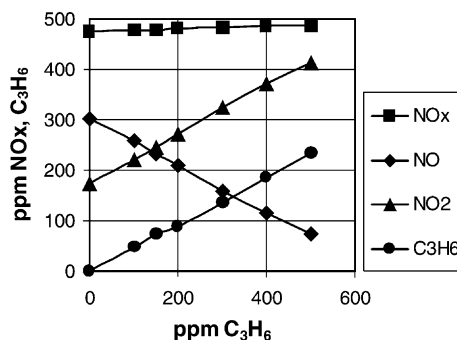


Fig. 3. Influence of the amount of C₃H₆ added on the removal of 500 ppm NO in N₂/O₂ (13%); without catalyst; temperature: 100 °C; energy density of the NTP: 25 Wh/m³.

3.1. Gas-phase reaction initiated by NTP

The electric discharge alone without any catalyst is not able to reduce NO_x as already stated in the introduction. An analysis of the reaction products in dependence on the amount of C₃H₆ added (Fig. 3) indicates that NO is oxidised in the gas-phase containing oxygen by the electric discharge to NO₂ and that propene assists this oxidation. Propene is partly converted at these conditions to CO₂, CO, formaldehyde and acetaldehyde as main products (cf. also Table 2). Similar results have been obtained also by other groups [15,16,35–37]. The same conclusion can be drawn from Fig. 4, where the NO_x-concentrations are shown in dependence on the energy density deposited into the discharge. The amount of C₃H₆ added in these experiments is 1000 ppm. NO is quantitatively converted to NO₂, leaving the total NO_x-concentration

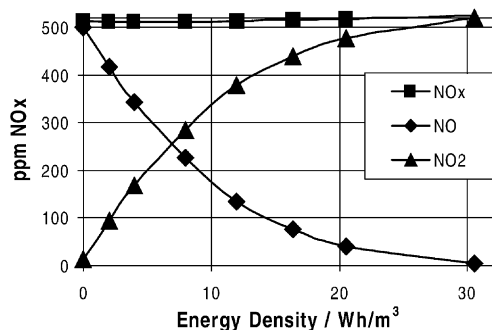


Fig. 4. Influence of the energy density of the NTP on the removal of 500 ppm NO in N_2/O_2 (13%) in the presence of 1000 ppm C_3H_6 ; without catalyst.

unchanged. From the initial slope of the NO decrease an energetic efficiency of 29 eV per NO-molecule can be evaluated. The comparison with the corresponding value of 62 eV per NO-molecule for NO conversion without propene confirms the assistance of the hydrocarbon in the NO oxidation reaction.

Analogous relations have been found by Bröer et al. [36], who found an energetic efficiency of 50 eV per removed NO in a gas mixture containing 72% N_2 , 18% O_2 , 10% H_2O and 500 ppm NO and 25 eV/NO in the additional presence of 500 ppm C_2H_4 . The authors explain the enhancement of NO to NO_2 conversion by the involvement of organic peroxide radicals and HO_2 , which are formed in a NTP in the presence of hydrocarbons and which are highly reactive for NO oxidation to NO_2 . Similar conclusions have been drawn by Niessen et al. [15], Penetrante et al. [16] and Shin and Yoon [37] on the basis of kinetic model calculations.

3.2. Plasma-assisted HC-SCR

Pd/Al_2O_3 and Ag/mordenite have been found to be 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 reason for that behaviour. 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. The same reason holds also for the only moderate HC-SCR activity of the Pd/Al_2O_3 catalyst used in our studies without plasma:

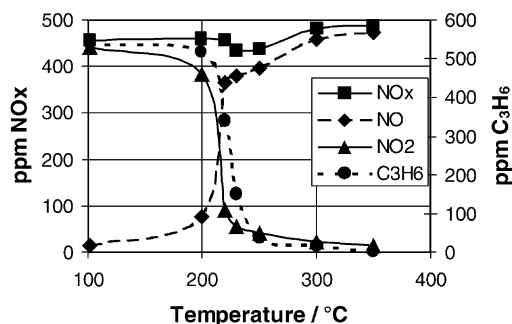


Fig. 5. Removal of 500 ppm NO in N_2/O_2 (13%) in the presence of 1000 ppm C_3H_6 ; catalyst: Pd/Al_2O_3 ; GHSV: $20,000 h^{-1}$; energy density of the NTP: $25 Wh/m^3$.

the total NO_x behaviour shows a similar dependence on the temperature with an optimum conversion of 21% (with plasma 12%) at 230 °C.

At the same time, NO_2 formed in the NTP is converted on Pd/Al_2O_3 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 back reduction of NO_2 to NO, finally resulting in an insufficient removal of NO_x .

Al_2O_3 , on the other hand, seems to be an appropriate catalyst for the reaction. With an energy density of $<15 Wh/m^3$ 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 excess oxygen are removed by more than half. The analysis of the reaction products in dependence on the temperature at the catalysts (Fig. 6)

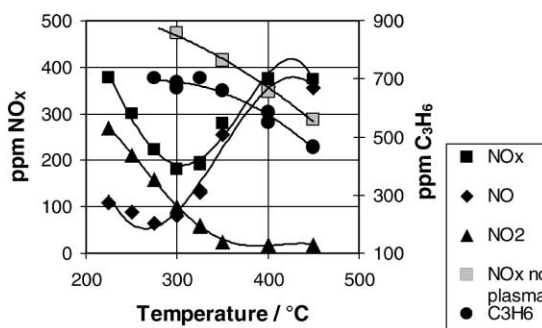


Fig. 6. Removal of 500 ppm NO in N_2/O_2 (13%) in the presence of 1000 ppm C_3H_6 ; catalyst: Al_2O_3 ; GHSV: $20,000 h^{-1}$; energy density of the NTP: $13\text{--}14 Wh/m^3$.

demonstrates the differences compared to the former example: up to 250 °C only a small amount of propene is oxidised and at 300 °C 70% are still available. From the NO_x-concentration after the plasma treatment (cf. Fig. 4) it is evident that already at 10 Wh/m³ most of the NO is converted to NO₂. As shown in Fig. 6, the back reduction of NO₂ to NO on Al₂O₃ is limited and NO₂ predominates NO up to 300 °C. As a consequence, both NO₂ and the hydrocarbon are available for the SCR reaction on Al₂O₃, 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 to HC-SCR on the same catalyst without plasma-assistance. Obviously, the pure catalytic HC-SCR on Al₂O₃ is also effective, but at significantly higher temperatures.

Fig. 7 illustrates the dependence of the plasma-catalytic NO_x removal on Al₂O₃ at 300 °C on the energy density deposited into the plasma. There is a distinct dependence up to 15 Wh/m³ (ca. 50 J/l), whereas an increase of the energy density beyond 15 Wh/m³ does not lead to further removal of NO_x. From the initial slope of the NO_x reduction an energetic efficiency of 29 eV per NO_x can be evaluated, i.e. the same energetic efficiency as found for the non-catalytic conversion of NO to NO₂ by NTP in excess oxygen in the presence of propene (cf. Fig. 4). This analogy is a strong argument for the assumption (cf. Section 1) that the role of the plasma consists in the intermediate oxidation of NO to NO₂ as an essential step for the subsequent catalytic reaction. The

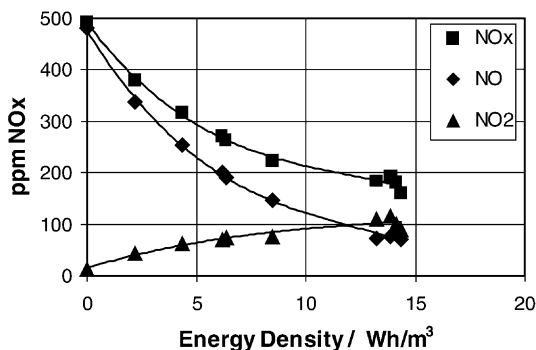


Fig. 7. Removal of 500 ppm NO in N₂/O₂ (13%) in the presence of 1000 ppm C₃H₆; catalyst: Al₂O₃; temperature: 300 °C; GHSV: 20,000 h⁻¹.

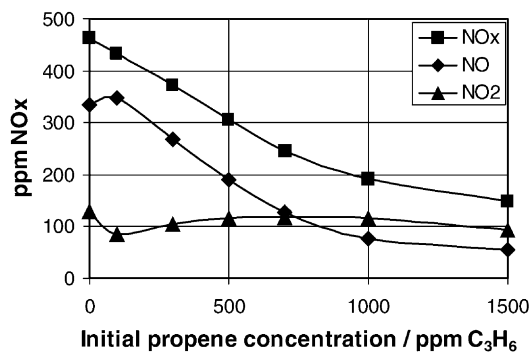
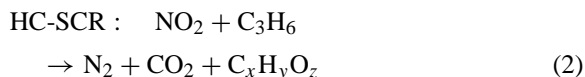
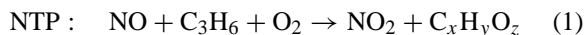


Fig. 8. Removal of 500 ppm NO in N₂/O₂ (13%) in dependence on the initial propene concentration; catalyst: Al₂O₃; temperature: 300 °C; GHSV: 20,000 h⁻¹; energy density of the NTP: 13–14 Wh/m³.

efficient plasma-catalytic NO_x conversion on ZrO₂ (Fig. 2) can be discussed in a similar way.

Fig. 8 shows the dependence of the plasma-catalytic NO_x removal on the concentration of added propene. It is evident that the reduction of NO_x is possible only in the presence of propene: There is hardly any NO_x removal without propene and the strong dependence on C₃H₆ concentration is extended to more than 1000 ppm. The effect of propene is two-fold: first, it assists the gas-phase oxidation of NO to NO₂ by the electric discharge in excess oxygen (Fig. 3) and, secondly, it reacts with NO₂ in the hydrocarbon SCR. The overall reaction can be described schematically as follows:



It should be noted that these formulas are oversimplified. The NTP reaction (1) proceeds, as already mentioned, involving several intermediates as peroxide radicals, but, generally, the effect of the plasma is the hydrocarbon assisted oxidation of NO to NO₂ in the gas-phase.

The SCR reaction (2), on the other hand, includes the reaction of NO₂ with the hydrocarbon and the partially oxidised species forming nitrogen-containing intermediates on the surface and its subsequent reaction with NO₂ to molecular nitrogen.

The plasma-catalytic HC-SCR can be compared with the bifunctional HC-SCR using a mechanical mixture of Mn_2O_3 and a metal (Sn, Ce) loaded ZSM-5 zeolite as described by Misono and co-workers [13,18]. In these bifunctional systems Mn_2O_3 catalyses the oxidation of NO to NO_2 and the subsequent catalytic reaction between NO_2 and C_3H_6 on M/ZSM-5 is significantly improved compared to the reaction between NO and C_3H_6 . Also $\gamma\text{-Al}_2\text{O}_3$ has been found to be more active in the HC-SCR of NO_2 rather than of NO [38,39].

The nature of catalytic active sites and their specific effects is not yet clear. We studied different Al_2O_3 samples, mainly $\gamma\text{-Al}_2\text{O}_3$, with specific surface areas of 100–500 m^2/g and pore volumes between 0.2 and 0.8 ml/g . They show a variable potential for plasma-catalytic NO_x removal, ranging from 20 to 60%, without a simple relation to the specific surface area or the pore volume. Obviously, other properties of the catalysts, e.g. as acid (Brønsted and/or Lewis-acidity) or basic characteristics should be decisive for the catalytic activity.

Similar conclusions were obtained also by Balmer et al. [27], who investigated different catalysts with respect to their effectiveness in plasma-catalytic HC-SCR. In contrast to our results they did not find any activity for ZrO_2 , and their TiO_2 was only active if placed directly in the electric discharge. The authors studied also two $\gamma\text{-Al}_2\text{O}_3$ samples from different sources and with different specific surfaces and found a plasma-catalytic effect only for the sample with the lower specific surface.

Also for pure catalytic HC-SCR on Al_2O_3 derived catalysts, the relation between the properties of Al_2O_3 as support and/or catalyst and its effectiveness is a problem still under discussion. Okazaki et al. [40] and Chen et al. [41] relate the different activities found for different Al_2O_3 sources to the purity of $\gamma\text{-Al}_2\text{O}_3$. According to Jen [9], the pore size distribution seems to be an important factor to the activity. Small pores of ca. 50 Å in diameter and a narrow size distribution should be essential for the HC-SCR.

Shimizu et al. [42,43] discuss on the basis of in situ FTIR experiments the importance of basic sites for the HC-SCR on Al_2O_3 , whereas Gerlach et al. [44,45], studying also by FTIR the HC-SCR of NO_2 on mordenite catalysts, draw the attention to the Brønsted acid sites as responsible for the catalytic

activity. Obviously, further work is necessary to clarify the essential properties of Al_2O_3 for HC-SCR with and without plasma-assistance.

3.3. Formation of by-products

The HC-SCR of NO_x is usually accompanied by the formation of various by-products, either from incomplete oxidation of hydrocarbons (CO, formaldehyde, acetaldehyde) or from the insufficient selectivity of the reaction of N-containing species (HCN, N_2O). Therefore, studying the plasma-assisted HC-SCR special attention has been devoted to the formation of by-products and the carbon balance in dependence on the catalysts used and the experimental conditions applied. Table 2 shows the results for the catalysts at the conditions of maximum NO_x conversion, as shown in Fig. 2, together with the results of the gas-phase NTP reaction before the catalyst. As already mentioned, significant amounts of formaldehyde and acetaldehyde are formed in the plasma reaction, besides smaller amounts of methyl nitrate and HCN. Methyl nitrate is decomposed at $>250^\circ\text{C}$, whereas the quantities of the other by-products depend on the catalyst. Formaldehyde and acetaldehyde are obviously involved in the HC-SCR on most catalysts. Only on aluminosilicate additional aldehydes are formed. Also HCN is formed during HC-SCR on aluminosilicate, Ag/mordenite and Al_2O_3 . Additional N_2O is formed on all catalysts, especially on the metal containing catalysts, which is in agreement with [1–4]. It is interesting to note that the plasma-assisted HC-SCR on ZrO_2 used in our experiments is not only effective, but also relatively free from by-products.

The carbon balance, also shown in Table 2, indicates that especially for the gas-phase NTP reaction and for the reaction on $\text{Pd}/\text{Al}_2\text{O}_3$ a part of carbon is missing. In case of the NTP reaction, probably not all of the products could be identified, whereas in the reaction on $\text{Pd}/\text{Al}_2\text{O}_3$ at 230°C a part of the products might be adsorbed on the catalyst. Summarising, it is evident that the formation of by-products is a serious problem that cannot be neglected and should be solved by appropriate measures. One possibility is the application of an additional oxidation catalyst at the end of the plasma-catalytic system. Corresponding studies have shown that using conventional oxidation catalysts the by-products can be reduced significantly and,

Table 3

Averaged composition of exhaust gas of a diesel engine (Multicar M25-10, 1997 cm³) without and with plasma-catalytic treatment^a

	CO (ppm)	CO ₂ (%)	HC (ppm C ₁)	O ₂ (%)	NO _x (ppm)
Without treatment	249	8.3	13	9.5	434
Only catalyst	0	8.2	0	9.4	428
Plasma-catalytic without C ₃ H ₆	0	7.2	0	10.7	404
Plasma-catalytic with C ₃ H ₆	0	7.9	0	9.7	190

^a Exhaust gas stream: ca. 600 l/h (STP) (GHSV \approx 10,000 h⁻¹); energy density of the electric discharge: 15 Wh/m³; catalyst temperature: 250 °C; propene added: 1.2 l/h (STP).

moreover, the remaining hydrocarbons can be oxidised to CO₂.

3.4. Test with real diesel exhaust gas

The results obtained with synthetic gases in laboratory scale were verified in a test experiment at real conditions with exhaust gases from a diesel engine (Multicar M25-10, 1997 cm³, without catalyst). The composition of the exhaust gas at medium load without and with plasma-catalytic treatment is shown in Table 3.

Fig. 9 shows the influence of the energy density deposited by the electric discharge into the plasma on NO_x removal. Without addition of propene, the plasma-catalytic treatment results only in a marginal decrease of the NO_x-concentration with increasing energy density (cf. also Table 3, plasma-catalytic without C₃H₆). The pure catalytic HC-SCR (energy density 0 Wh/m³) using propene as additional

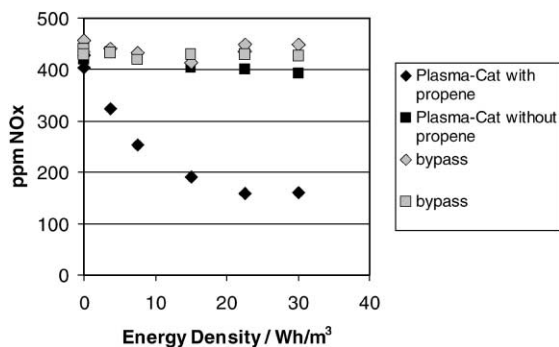


Fig. 9. Plasma-catalytic removal of NO_x in diesel exhaust gas without and with (1.2 l/h (STP)) addition of propene; exhaust gas stream: ca. 600 l/h (STP); catalyst: Al₂O₃ + oxy-catalyst; temperature: 250 °C. The corresponding data for the untreated exhaust gas (bypass) were monitored independently by a second analysis channel (cf. Section 2).

reducing agent does not cause any removal of NO_x with the catalysts used at the given conditions (250 °C, cf. Table 3, only catalyst). With the assistance of the electric discharge, however, it is possible to reach an effective NO_x removal at these conditions.

Similarly as in the laboratory experiments, there is a significant influence of the energy density on NO_x-concentration up to 15 Wh/m³. We assume, therefore, that the effect of the plasma is also at real conditions the intermediate oxidation of NO to NO₂ and that this reaction is almost completed at an energy density of ca. 15 Wh/m³. The energy density of 15 Wh/m³ corresponds to an adiabatic gas heating by approximately 45 K.

Table 3 summarises the concentration data of the exhaust gas at the different experimental arrangements. It is obvious from the data that CO and the remaining hydrocarbons are completely oxidised by the oxidation catalyst independently of the electric discharge. On the other hand, NO_x is removed by more than half only with the assistance of the plasma and the addition of C₃H₆.

These first experiments with real diesel exhaust gas should be extended in future work, especially with respect to the optimisation of influence factors as plasma-reactor design and plasma energy, catalyst parameters (material, space velocity, temperature), long-term stability and sensitiveness against SO₂, etc. The energy density of 15 Wh/m³ as used in the present work, is e.g. far from being optimised. A rough estimation of the plasma energy that should be applied, results in an extra fuel consumption of 4–5% [32,46].

4. Conclusions

- The combination of HC-SCR and cold plasma enhances the overall reaction and allows an effective

removal of NO_x at relatively low temperatures. The oxidative potential of a NTP in off-gases with excess oxygen results in an effective conversion of NO to NO_2 that can be converted synergistically by HC-SCR to molecular nitrogen with appropriate catalysts. The hydrocarbon added has two essential functions: first, it assists the gas-phase oxidation of NO to NO_2 by the electric discharge in excess oxygen and, secondly, it reacts with NO_2 in the hydrocarbon SCR.

- Besides CO_2 and CO, significant amounts of formaldehyde and acetaldehyde are formed in the plasma-initiated gas-phase reaction. These and other by-products are involved together with the remaining propene in the subsequent catalytic reaction.
- Certain modifications of Al_2O_3 and ZrO_2 have been found to be effective as catalysts in this reaction. With an energy supply of about 30 eV per NO-molecule, a temperature of 300 °C and a space velocity of 20,000 h^{-1} at the catalyst, it is possible to reduce 500 ppm NO in excess oxygen by more than half.
- The synergistic combination of NTPs and HC-SCR has been verified under real conditions with exhaust gas from a diesel engine.
- Further work is necessary to clarify the active sites responsible for the reactions and the mechanism of the NO_x conversion and, in that connection, to optimise the catalyst and the parameters of the plasma-catalytic process.

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References

- [1] R. Burch, *Pure Appl. Chem.* 68 (1996) 377.
- [2] A. Fritz, V. Pitchon, *Appl. Catal. B* 13 (1997) 1.
- [3] P. Gilot, M. Guyon, B.R. Stanmore, *Fuel* 76 (1997) 507.
- [4] M. Shelef, R.W. McCabe, *Catal. Today* 62 (2000) 35.
- [5] J.P. Warren, *Platinum Met. Rev.* 45 (2001) 31.
- [6] A. Döring, E. Jacob, in: A. Leipertz (Ed.), *Proceedings of the 5th Congress on Engine Combustion Processes, Current Problems and Modern Techniques, Berichte zur Energie- und Verfahrenstechnik, Schriftenreihe Heft 2000.1*, Erlangen, 2001, p. 513.
- [7] J.Y. Yan, M.C. Kung, W.M.H. Sachtler, H.H. Kung, *J. Catal.* 172 (1997) 178.
- [8] T.E. Hoost, R.J. Kudla, K.M. Collins, M.S. Chattha, *Appl. Catal. B* 13 (1997) 59.
- [9] H.W. Jen, *Catal. Today* 42 (1998) 37.
- [10] M.C. Kung, P.W. Park, D.W. Kim, H.H. Kung, *J. Catal.* 181 (1999) 1.
- [11] M. Haneda, Y. Kintaichi, H. Hamada, *Appl. Catal. B* 20 (1999) 289.
- [12] H.Y. Chen, T. Voskoboinikov, W.M.H. Sachtler, *J. Catal.* 180 (1998) 171.
- [13] M. Misono, Y. Hirao, C. Yokoyama, *Catal. Today* 38 (1997) 157.
- [14] M.A. Tas, R. van Hardeveld, E.M. van Veldhuizen, *Plasma Chem. Plasma Process.* 17 (1997) 371.
- [15] W. Niessen, O. Wolf, R. Schruft, M. Neiger, *J. Phys. D: Appl. Phys.* 31 (1998) 542.
- [16] 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.
- [17] M. Sasaki, H. Hamada, Y. Kintaichi, T. Ito, *Catal. Lett.* 15 (1992) 297.
- [18] C. Yokoyama, M. Misono, *Catal. Lett.* 29 (1994) 1.
- [19] F.C. Meunier, J.P. Breen, V. Zuzaniuk, M. Olsson, J.R.H. Ross, *J. Catal.* 187 (1999) 493.
- [20] T. Hammer, S. Broer, *SAE Technical Paper Series No. 982428*, 1998.
- [21] T. Hammer, T. Kishimoto, H. Miessner, R. Rudolph, *SAE Technical Paper Series No. 1999-01-3632*, 1999.
- [22] S. Bröer, T. Hammer, *Appl. Catal. B* 28 (2000) 101.
- [23] H. Miessner, R. Rudolph, K.-P. Francke, *J. Chem. Soc. Chem. Commun.* (1998) 2725.
- [24] K.-P. Francke, H. Miessner, R. Rudolph, *Catal. Today* 59 (2000) 411.
- [25] J. Hoard, M.L. Balmer, *SAE Technical Paper Series No. 982429*, 1998.
- [26] 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.
- [27] M.L. Balmer, R. Tonkyn, S. Yoon, A. Kolwaite, S.E. Barlow, G. Maupin, J. Hoard, *SAE Technical Paper Series No. 1999-01-3640*.
- [28] M.D. Hemingway, D. Goulette, G. Ripley, T. Thoreson, J. Kupe, D. Herling, S. Baskaran, M. Smith, D. Lessor, J. Virden, *SAE Technical Paper Series No. 1999-01-3639*.

- [29] K. Shimizu, T. Hirano, T. Oda, *IEEE Trans. Ind. Appl.* 37 (2001) 464.
- [30] R. Tonkyn, S. Yoon, S.E. Barlow, A. Panov, A. Kolwaite, M.L. Balmer, SAE Technical Paper Series No. 2000-01-2896.
- [31] B.-H. Chun, H.-S. Lee, C.-S. Nam, K.M. Chun, J.H. Ryu, K.-Y. Lee, SAE Technical Paper Series No. 2000-01-2897.
- [32] C.L. Aardahl, C.F. Habeger, M.L. Balmer, K.G. Rappe, D.N. Tran, M. Avila, P. Park, K.A. Koshkarian, A. Chanda, SAE Technical Paper Series No. 2000-01-2961.
- [33] G.B. Fisher, C.L. DiMaggio, A. Yezerets, M.C. Kung, H.H. Kung, S. Baskaran, J.G. Frye, M.R. Smith, D.R. Herling, W.J. LeBarge, J. Kupe, SAE Technical Paper Series No. 2000-01-2965.
- [34] D.L. Hoang, H. Preiss, B. Parlitz, F. Krumeich, H. Lieske, *Appl. Catal. A* 182 (1999) 385.
- [35] J.W. Chung, M.H. Cho, B.H. Son, Y.S. Mok, W. Namkung, *Plasma Chem. Plasma Process.* 20 (2000) 495.
- [36] S. Bröer, T. Hammer, T. Kishimoto, in: *Proceedings of the 12th International Conference on Gas Discharges & their Applications*, Vol. 1, Greifswald, 1997, p. 188.
- [37] H.-H. Shin, W.-S. Yoon, SAE Technical Paper Series No. 2000-01-2969.
- [38] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, M. Tabata, *Appl. Catal.* 70 (1991) L15.
- [39] M.C. Kung, J.-H. Lee, A. Chu-Kung, H.H. Kung, in: *Proceedings of the 11th International Congress on Catalysis—40th Anniversary*, Elsevier, Amsterdam, 1996, p. 701.
- [40] N. Okazaki, Y. Shiina, H. Itoh, A. Tada, M. Iwamoto, *Catal. Lett.* 49 (1997) 169.
- [41] L.Y. Chen, T. Horiuchi, T. Osaki, T. Mori, *Appl. Catal. B* 23 (1999) 259.
- [42] K. Shimizu, H. Kawabata, A. Satsuma, T. Hattori, *Appl. Catal. B* 19 (1998) L87.
- [43] K. Shimizu, H. Kawabata, A. Satsuma, T. Hattori, *J. Phys. Chem. B* 103 (1999) 5240.
- [44] T. Gerlach, U. Illgen, M. Bartoszek, M. Baerns, *Appl. Catal. B* 22 (1999) 269.
- [45] T. Gerlach, F.W. Schutze, M. Baerns, *J. Catal.* 185 (1999) 131.
- [46] T. Hammer, in: A. Leipertz (Ed.), *Proceedings of the 5th Congress on Engine Combustion Processes, Current Problems and Modern Techniques, Berichte zur Energie- und Verfahrenstechnik, Schriftenreihe Heft 2000.1*, Erlangen, 2001, p. 529.