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Plasmacatalytic processes for environmental problems

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Abstract

The application of non-thermal electrical discharges instead of thermal energy has been shown to be a suitable alternative for the treatment of exhaust gases, especially for low concentrations (<100 ppmv) of contaminants. In the present paper, we describe the synergetic application of plasma and catalytic treatment for the oxidative removal of volatile organic compounds (VOCs) and the low-temperature conversion of NO_x to N_2 in excess oxygen.

The catalytic oxidation of butyl acetate and dichloroethene (DCE) as typical VOC has been studied at 50–200°C in combination with pulse corona or dielectric barrier discharges (DBDs). The best results with a significant synergetic effect were obtained with mixed transition metal oxide catalysts, which are able to decompose the ozone at low (<120°C) temperature. With respect to treatment by the plasma alone, the combination shifts the process towards total oxidation. The amount of reaction by-products such as formyl chloride (in case of chlorocarbons), CO, nitric oxides and ozone is lowered. The synergetic effect has been verified at technical conditions in the plasmacatalytic removal of VOC from stripper air in a groundwater cleaning plant.

The NH_3-SCR of NO_x in excess oxygen using a NH_4-loaded zeolite at 100°C can be significantly accelerated if combined with a plasma discharge. The mechanism of the reaction has been verified by labeling NO with ^{15}NO and by a double-labeled experiment using ^{15}NO and $^{15}NH_4$-zeolite. Experiments with a diesel engine have shown that the plasmacatalytic conversion of NO_x to N_2 is also effective at real technical conditions.

Keywords: Plasmacatalytic process; Volatile organic compounds; Non-thermal electrical discharge; $DENO_x$; NH_3-SCR

1. Introduction

The international regulations for exhaust gases from cars and from industry restrict the contamination to values difficult to handle with conventional removal technologies like thermal and catalytic oxidation or adsorption. As an example, Table 1 shows the occupational exposure limits for some common volatile organic compounds (VOCs). Most of them are in the range of 100 ppmv and below and the German regulations for industrial off-gases, also shown in Table 1, are even stronger. At these low contamination levels a catalytic oxidation requires a substantial supply of thermal energy to be effective. As an alternative, the application of non-thermal electrical discharges instead of thermal energy for removal of toxic components has been discussed and demonstrated [1,2]. In a non-thermal plasma, electrons with high energy can activate the gas molecules by collision processes. If the off-gas contains oxygen and water vapor, oxygen- and hydroxy-radicals, which are two of the main species formed in the discharge, can react with the other molecules and contribute in this way to any oxidation process. In the present paper, we describe the synergetic application of a plasmacatalytic treatment in two environmentally important fields: oxidative removal of VOC and removal of NO_x in excess oxygen [3].

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Table 1
Threshold limit values (TLV), German occupational exposure limits (MAK) and German regulations for off-gases (TA-Luft) for selected VOCs, all in ppmv

Substance	TLV[a]	MAK[a]	TA-Luft
Acetone	750	500	60
Benzene	10	5	2
Butyl acetate	150	100	30
1,2-Dichloroethene	200	200	35
Ethylbenzene	100	100	20
Formaldehyde	0.3	0.5	15
Styrene	50	20	20
Tetrachloroethene	50	50	15
Tetrachloromethane	5	10	3
Toluene	50	50	25
Vinylchloride	5	3	2
Xylene	100	100	25

[a] International chemical safety cards (EU).

2. Experimental

The non-thermal plasma was obtained in several ways. In a pulse corona system (schematically shown in Fig. 1a), consisting of a metallic tube (1 m long, 100 mm diameter) as ground electrode and a stainless steel rod as high voltage electrode, pulses of 50–70 kV (damped 4.5 MHz oscillation with 100 ns rise time and 1–1.5 μs duration) were applied to initiate the discharges in the gas phase between the electrodes. Downstream to the plasma a catalyst can be placed. This reactor has been used for flow rates up to 600 l/h. For the field experiments at flow rates up to 60 m^3/h, a larger corona system with an active length of 7 m was applied [4].

For the removal of NO_x a reactor (Fig. 1b) was used that enables a dielectric barrier discharge (DBD) near to the catalyst bed. A glass tube as dielectric is surrounded by a copper grid as ground electrode and contains an inner electrode, which consists of a rod with equidistant steel disks leaving a gap of 0.5 mm to the glass tube. Between these disks the catalyst can be positioned.

The on-line gas analysis was performed by an FT-IR spectrometer (Perkin Elmer) equipped with a long-path (20 m) gas cell, a photoionization detector (PID) and a GC–PID (IUT) for organic components, a chemiluminescence NO_x analyzer (ECO-Physics) for NO and NO_2, and an NDIR CO–CO_2 analyzer (Fisher Rosemount).

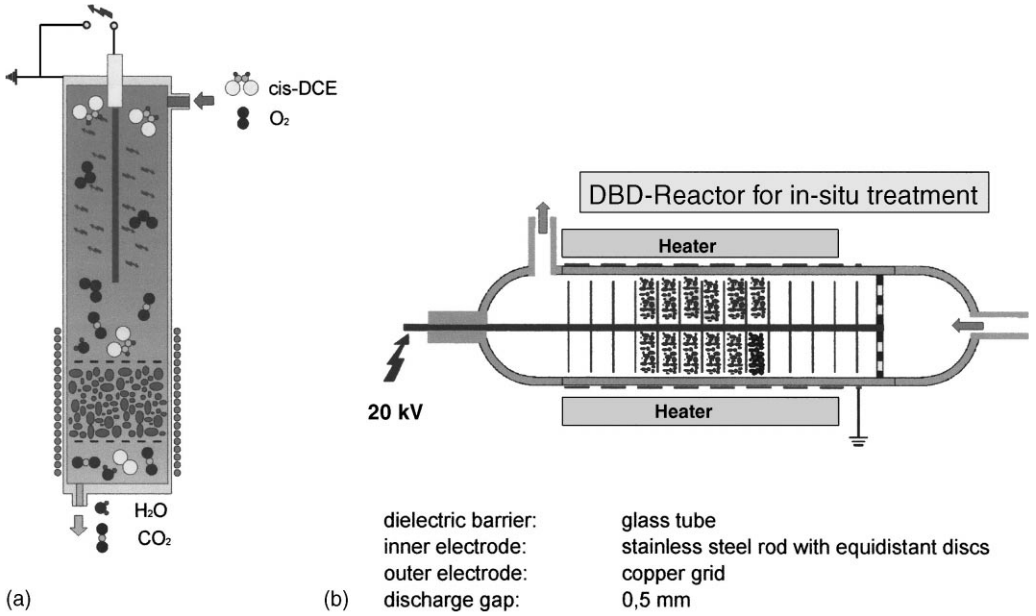


Fig. 1. Pulsed corona reactor (1a, left) and DBD reactor (1b, right) for plasmacatalytic treatment of exhaust gases.

3. Results and discussion

3.1. Oxidative removal of VOC

To study the mutual influence of plasma and catalysts, both pulse corona and DBDs have been used together with a series of catalysts including (1) supported noble metal catalysts, (2) mixed transition metal oxide catalysts and (3) adsorbents such as zeolites and activated carbon. The oxidation of butyl acetate and dichloroethene (DCE) as typical VOC has been studied at 50–200°C. As an example, Fig. 2 shows the removal of 53 ppmv butyl acetate at 120°C. Without catalyst, about 20% of butyl acetate is converted by the plasma alone. On the other hand, also the catalysts alone have a removal effect up to 40% at the given conditions. The combined application shows a remarkable synergetic effect for the mixed transition metal oxides if compared with the removal calculated by the multiplication of the individual effects. The synergy can also be expressed numerically by

$$w = \frac{R^0_{\mathrm{cat}} R^0_{\mathrm{plasma}}}{R_{\mathrm{plasma+cat}}}$$

with R^0 being the remaining butyl acetate after individual effects and $R_{\mathrm{plasma+cat}}$ the remaining butyl acetate after combined application.

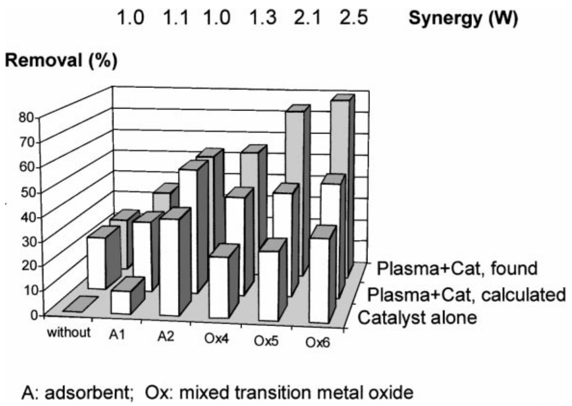


Fig. 2. Plasma treatment of 53 ppmv butyl acetate in combination with different catalysts. A1: Zeosorb 5A, A2: activated carbon; Ox4: Cu/Cr-oxide, Ox5: Cu/Mn-oxide, Ox6: Fe/Mn-oxide; conditions: 53 ppmv butyl acetate in air, GHSV=35–40 000 h^{-1}, 120°C, energy density: 15 Wh/m^3.

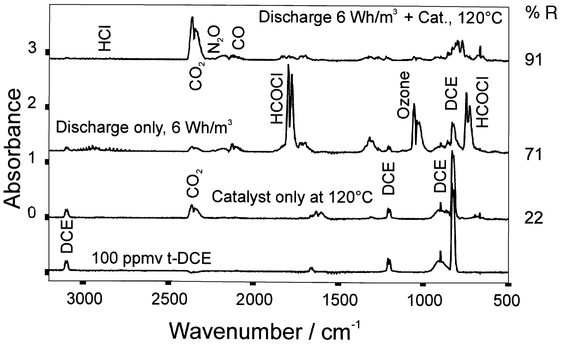


Fig. 3. FT-IR spectra (20 m gas cell) of 100 ppmv trans-DCE in air without treatment (bottom) and after treatment as indicated. Catalyst: Fe/Mn-oxide; GHSV=38 000 h^{-1}. The figures at the right side indicate the % of DCE removed upon treatment.

The corresponding synergetic factors as indicated in Fig. 2 are about 1 (i.e. no synergy) for the adsorbents and significantly higher for the catalysts. The best results were obtained with mixed transition metal oxide catalysts, which are able to decompose the ozone at low (<120°C) temperatures. The observed synergetic effect is, at least partly, due to the catalytic oxidation with the ozone produced in the discharge.

Fig. 3 shows the gas phase IR spectra of 100 ppmv DCE in air after passing a catalyst at 120°C, after application of a non-thermal plasma, and after a combined application. The catalyst alone converts about 20% to CO_2. In the electrical discharge, 70% of DCE is transformed, but not to CO_2. A significant amount of formyl chloride has been formed, and additionally, ozone appears in the gas phase. Only in the combined application of both an electric discharge and an appropriate catalyst, 90% of the DCE is removed and converted to CO_2 as the main oxidation product.

The synergetic effect has been verified at technical conditions in the plasmacatalytic removal of VOC from stripper air in a groundwater cleaning plant (Fig. 4). A pulsed corona reactor was used to obtain the plasma with an energy density of 11.5 Wh/m^3, and a commercial Mn/Fe-oxide catalyst has been used at 90°C and 3000 h^{-1}. The removal of VOC from the stripper air is for all contaminants higher than 85% as shown in Fig. 5. It is worth to note, that for conventional catalytic combustion, the catalyst in that plant is normally heated to 420°C to be effective. The energy of 11.5 Wh/m^3 deposited into the plasma

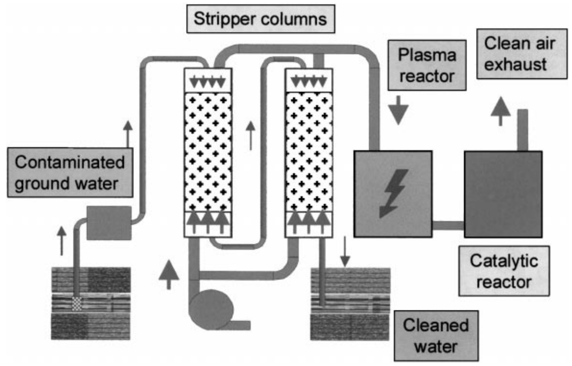


Fig. 4. Principle scheme of groundwater cleaning by air stripping combined with plasmacatalytic treatment.

corresponds, on the other hand, to an equivalent temperature increase of about 35°C.

3.2. NO_x removal with NH_3-loaded zeolites

The selective catalytic reduction (SCR) of NO using the addition of reductants like NH_3, urea, hydrocarbons, alcohols, etc., has been studied intensively as a method to remove NO_x from exhaust gases with excess oxygen [5,6]. Depending on the type of catalyst and the reductant used, SCR is effective in a temperature range between 200 and 600°C.

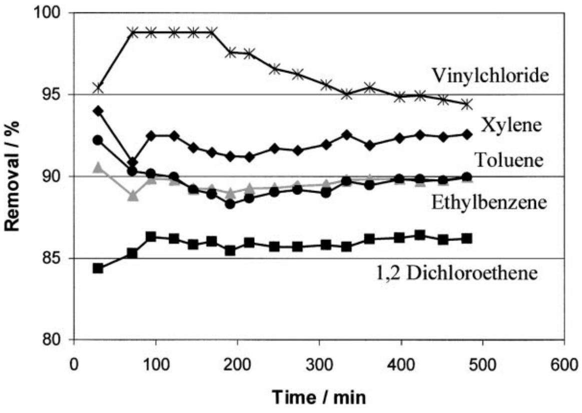


Fig. 5. Removal of VOC from stripper air containing approximately 2% H_2O and a total VOC amount of about 100 ppmv (C_1) with the main components as shown in the figure. Catalyst: Fe/Mn-oxide; temperature: 90°C; flow: 30 m^3/h; GHSV=3000 h^{-1}; energy density: 11.5 Wh/m^3.

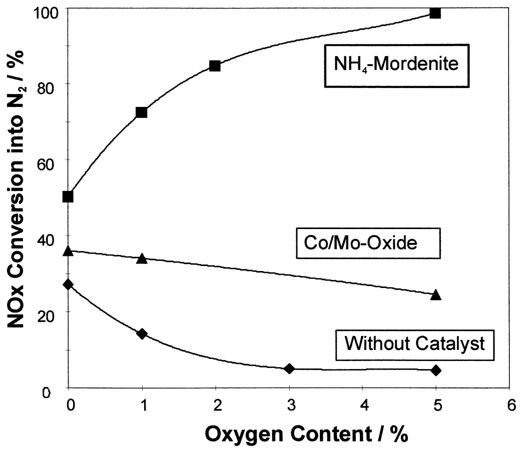


Fig. 6. Plasmacatalytic low-temperature conversion of NO_x on NH_4-zeolites. Temperature: 100°C; GHSV=3000 h^{-1}; energy density: 25 Wh/m^3; gas inlet composition: 500 ppmv NO in N_2, oxygen as indicated.

In a recent publication, Richter et al. [7] have described a catalytic low-temperature conversion of NO_x to N_2 using NH_4^+ ions fixed in zeolites as reductant. NO is converted in these systems to N_2 in excess oxygen even at temperatures as low as 100°C. The intermediate oxidation of NO to NO_2 is supposed to be the key step limiting the reaction rate of the reaction sequence. We supposed that the abatement of NO in excess oxygen can be significantly enhanced further by applying the oxidative power of a non-thermal plasma immediately on the ammonium-loaded zeolite as catalyst.

Fig. 6 shows the plasmacatalytic conversion of NO_x to N_2 in dependence on the oxygen content in the reaction gas. Without catalyst and with a Co/Mo-oxide as catalyst, the NO_x conversion at 100°C and 3000 h^{-1} decreases with increasing oxygen content. It reaches, however, 100% with an NH_4-mordenite at 5% oxygen.

To analyze the influence of the discharge in more detail, the local position of the catalyst was varied in order to have the discharge before, behind and near to the catalyst bed. Fig. 7 shows the effect for these combinations on the NO_x concentration. In the discharge alone, part of the NO is oxidized to NO_2. The catalyst alone removes about 20% of NO by the low-temperature NH_3-SCR at that conditions. If the plasma is applied behind the catalyst, again, a part of the remaining NO is oxidized to NO_2. With the dis-

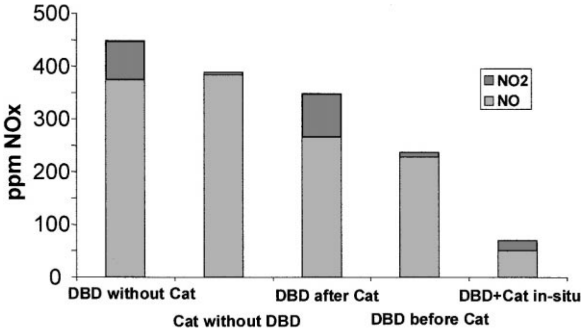


Fig. 7. Removal of 500 ppmv NO in N_2/O_2 (2%). Catalyst: NH_4-mordenite; temperature: 70°C; GHSV=3000 h^{-1}; energy density: 25 Wh/m^3.

charge in front of the catalyst, already a significant part of NO (50%) is removed. Finally, if the plasma is generated near to the catalyst bed, more than 80% of NO is converted to N_2 at these conditions.

This synergy can be explained by the interaction of discharge-induced plasmachemical reactions with the catalysis on the zeolite. A low-temperature electrical discharge in an oxygen-containing gas mixture produces mainly oxygen radicals as active species [8]. Atomic oxygen leads to fast oxidation of NO to NO_2 (1). In case of the discharge alone, this oxidation is limited by the reverse reaction of NO_2 with the oxygen radicals (2) and an equilibrium will be reached depending on the reaction conditions.

$$NO + O \rightarrow NO_2 \tag{1}$$

$$NO_2 + O \rightarrow NO + O_2 \tag{2}$$

In the presence of NH_4-zeolite, however, NO_2 is removed from the gas stream by the fast catalytic reaction (3) [7], thus preventing the undesirable back conversion (2) of NO_2 to NO.

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

To prove the proposed reaction mechanism (3) between NO_x and NH_3, we labeled both NO and NH_4^+ in the zeolite with ^{15}N and followed the reaction by means of GC–MS. Fig. 8 shows the results of NO_x removal in dependence on the energy deposited into the plasma. The formation of $^{15}N_2$ proves the stoichiometric reaction between NO_x and NH_3. The ammonia bonded to the zeolite is consumed during the reaction with NO_x, leaving the zeolite in the H-form.

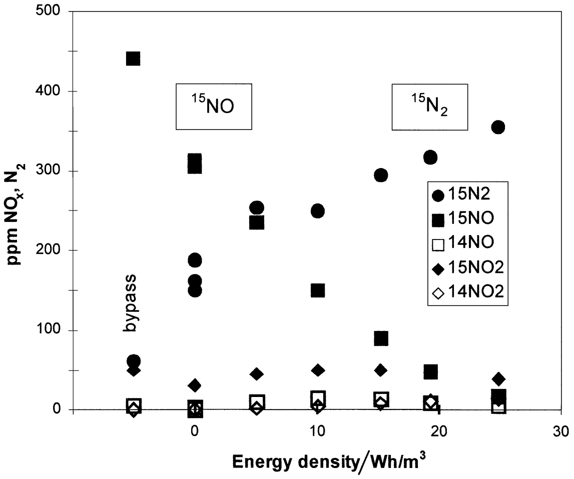


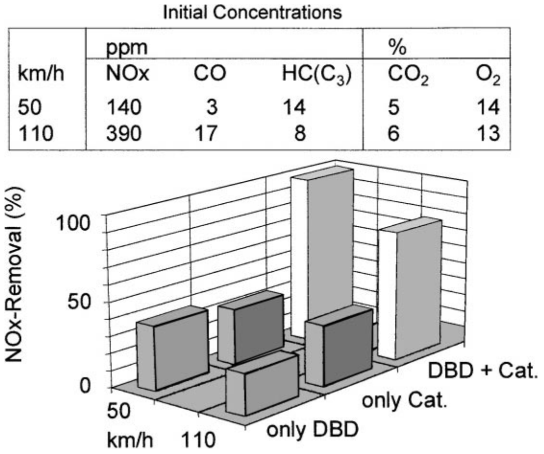
Fig. 8. Reaction of 500 ppmv ^{15}NO with $^{15}NH_4$-mordenite. Temperature: 100°C; GHSV=3000 h^{-1}.

To maintain the catalytic activity, the zeolite has to be reloaded from time to time with gaseous NH_3 or by ion exchange. Initial experiments have demonstrated that this can be done without loss of activity.

To see whether the results obtained in the laboratory can also be found at real conditions, we performed an experiment with a modern diesel car at a test stand. At two different conditions, a part of the exhaust gas was treated plasmacatalytically using NH_4-mordenite as catalyst. The results, shown in Fig. 9, prove the synergetic removal of NO_x also at more realistic conditions.

4. Summary

- Plasma-assisted catalytic processes can provide a suitable alternative for the treatment of exhaust gases, especially for low concentration (<100 ppmv) of contaminants.
- For the total oxidation of VOC, treatment with a low-temperature plasma (pulse corona or DBD) combined with mixed transition metal oxide as catalyst allows an abatement of VOC already at temperatures around 100°C.
- The effect of a combined treatment is higher than the sum of individual steps. This synergy is partly due to the catalytic oxidation with ozone produced in the discharge.



Initial Concentrations

	ppm			%	
km/h	NOx	CO	HC(C_3)	CO_2	O_2
50	140	3	14	5	14
110	390	17	8	6	13

Fig. 9. Plasmacatalytic removal of NO_x from the exhaust gases of a diesel engine. Catalyst: NH_4-mordenite; temperature: 100°C; flow: approx. 60 l/h; GHSV=approx. 3000 h^{-1}; energy density: 25 Wh/m^3. The initial concentrations of NO_x and other components in the gas phase at the two velocities prior to the plasmacatalytic treatment are indicated in the inserted table.

- The catalyst moves the process towards total oxidation. The by-products formed during the plasma treatment are oxidized to CO_2.
- The oxidative potential of electrical discharges in oxygen-containing gases also leads to a synergetic effect in the NH_3-SCR of NO_x. The combination of discharge and a NH_4-loaded zeolite allows the removal of NO_x in excess oxygen already at 100°C.

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