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Improved oxidation of air pollutants in a non-thermal plasma

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Abstract

The performance of non-thermal plasma (NTP) for the removal of organic air pollutants (especially in low concentrations) is improved by the introduction of ferroelectric and catalytically active materials into the discharge zone of an NTP reactor. Experiments with model systems (various contaminants and packed-bed materials) have shown that such a modification of a homogeneous gas-phase plasma can overcome the most serious restrictions of the NTP technique at its present state of the art: the incomplete total oxidation (i.e. the low selectivity to CO_2) and the energetic inefficiency.

Placing a ferroelectric packed-bed material in the discharge zone was shown to result in a lowering of the energy input required. The main effects of plasma catalysis enabled by the introduction of a catalytically active material were an enhanced conversion of pollutants and a higher CO_2 selectivity. These improvements are based on the presence of short-lived oxidising species in the inner volume of porous catalysts. Additionally, the formation of a reservoir of adsorbed oxidants in the NTP zone could be shown. The combination of both modifications (ferroelectric packed-bed materials and plasma catalysis) is a promising method to support the NTP-initiated oxidation of air pollutants.

Keywords: Non-thermal plasma; Ferroelectric material; Plasma catalysis; Air pollutants; Oxidation

1. Introduction

The removal of volatile organic contaminants from effluent streams is a widespread problem of great environmental importance. Established thermal and thermo-catalytic methods for gas-cleaning work very efficiently when the concentration of organic compounds is high enough to allow an autothermal regime. However, at low concentrations alternative methods for effluent treatment are required.

The "cold" oxidation of highly diluted organic substances in an electrical discharge, a so-called non-thermal plasma (NTP), is a relatively new approach towards a more satisfactory solution of such problems. The removal of pollutants from exhaust air has been reported for a variety of substances: aliphatic and aromatic hydrocarbons [1,2], halogenated organic compounds [3,4] and inorganic gases such as SO_2, H_2S and NO_X [5–7]. Various energy sources (based on radio frequency radiation, microwaves, electron guns and pulsed voltages) have been used to produce several discharge types (corona [8], surface-bound [9], packed-bed [1] and electron-beam-initiated discharges [10]). An overview of results with NTP methods is given in Ref. [11].

The non-equilibrium conditions of an NTP are manifested in the fact that the electrons are selectively accelerated by a strong external electric field (resulting in electron temperatures above 10^4 K) while the neutral gas molecules remain nearly cold. This provides an opportunity to markedly enhance the energetic efficiency of oxidation reactions. A quantitative

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comparison with other (particularly thermal) methods can be made on the basis of the adiabatic temperature increase ΔT_{adiab} defined as

$$\Delta T_{\text{adiab}} = \frac{P}{\dot{V}\rho_{\text{air}}c_{p,\,\text{air}}} \tag{1}$$

with the electrical power input P, the gas flow $\dot{V}$, the density and the specific heat capacity of air ρ_{air} and $c_{p,\,\text{air}}$, respectively. An energetic advantage of the NTP technology would be achieved for ΔT_{adiab} values significantly below the typical ΔT values of thermal and thermo-catalytic processes. At the present state of the art, this demand cannot be fulfilled by NTP reactors.

Another general problem of the homogeneous gas-phase NTP techniques is their low selectivity with respect to total oxidation. The selectivity to CO_2 can be expressed by the parameter S_{CO_2} defined by

$$S_{CO_2} = \frac{[CO_2]}{[CO_X] + [C_{\text{org}}]} \tag{2}$$

For a large number of volatile organic compounds (VOCs), S_{CO_2} values between 0.3 and 0.65 are given in the literature [1,12].

In this work, the effect of placing solid materials into the discharge zone has been investigated with the aim of improving the NTP performance.

Ferroelectric packed-bed materials (e.g. perovskites) modify the energy distribution of accelerated electrons and, therefore, the pattern of the reactive species in the NTP. Due to the high dielectric constant of these substances, the local field is significantly enhanced in the volume between the grains. This effect is strengthened in the neighbourhood of corners and edges. Consequently, the energy gain of the electrons on the mean free pathway in the gas phase is increased and other initiating reactions with the gas molecules become possible. This can lead to the formation of more-efficient oxidants [13].

The introduction of catalysts into the NTP can lead to synergy effects mainly related to the utilisation of short-lived plasma species (plasma catalysis). However, this concept is based upon the presence of these species in the *interior* of porous catalyst materials. In contrast, a catalytic post-treatment of NTP effluents is only possible with long-lived species, namely ozone. Another advantage of plasma catalysis is due to the preferred adsorption of organic pollutants in comparison to nitrogen and oxygen, which are in a huge surplus in the gas phase. Consequently, surface reactions of adsorbed pollutants are favoured. Additional reaction pathways may be opened due to the formation of active surface sites by NTP impact. To our knowledge, there are only a few examples of plasma catalysis effects for the oxidation of VOCs and CO described in literature [14,15].

In this paper, the NTP oxidation of several organic compounds (toluene, phenol, methyl *tert*-butyl ether (MTBE)) and CO is described in order to give some examples for the effects of several packed-bed materials on VOC conversion and oxidation selectivity. Moreover, the removal of immobilised non-volatile compounds in order to determine whether or not short-lived species are available in the interior of the pore system is investigated. A further improvement was expected from the combination of the two effects using a two-layer reactor, containing ferroelectric and catalytically active materials. The aim of this study was the evaluation of the concepts described above. The optimisation of ferroelectric and catalytically active materials will be the subject of further investigations.

2. Experimental

2.1. Gas-flow system and NTP reactor types

The gas flow (dried and CO_2-free air, pure oxygen (Linde; purity 2.6), nitrogen or helium (both Linde; purity 5.0) and mixtures of these constituents) through the NTP reactor was controlled by electronic gas flow controllers (GFC, Bronckhorst Ruurlo, The Netherlands). The concentrations of volatile contaminants were regulated by the temperatures of saturation units. The effluent flow from the reactor was analysed for CO, CO_2, O_3 and VOC concentrations using a Multor 610 (Maihak Hamburg, Germany), an Ozomat MP (Anseros Tübingen, Germany) and a total oxidation furnace (TOF—CuO at 700 °C; VOC concentration deduced from the difference between the CO_2 after TOF and the total CO_X content measured directly), respectively. The conversion was quantified on the basis of the carbon balance which was shown to be complete with an accuracy of >90% in all cases. Non-volatile products (polymeric deposits) which may constitute a significant fraction from aromatic compounds were determined gravimetrically or deduced from the balance gap.

For all experiments, coaxial dielectric barrier discharge reactors were used (tungsten wire with a diameter of 125 μm as inner electrode, water as outer electrode, discharge gap 5 mm, length 110 mm). Various reactor types based on this geometry were applied:

1. an empty gas discharge reactor (GDR),
2. a GDR filled with a ferroelectric packed-bed material (FER),
3. a GDR filled with a catalytically active material for the investigation of plasma-catalytic effects (in-plasma catalysis reactor—IPCR),
4. a two-stage system consisting of a GDR and a packed-bed reactor for catalytic post-treatment (post-plasma catalysis reactor—PPCR), and
5. a GDR filled with two subsequent layers consisting of identical volumes of a ferroelectric and a catalytically active packed-bed material (TLR).

A high-voltage supply with sinusoidal (50 Hz) characteristics (WGT-301, HCK GmbH Essen, Germany) was applied for the IPCR and PPCR experiments. For all other NTP oxidation tests, high-voltage pulses (duration 11 μs, repetition rate 600 Hz) from a pulse generator (Anseros Tübingen, Germany) were used. The real power input was measured using a capacitor (500 nF) and a GE 3830 voltage probe (Elditest Nürnberg, Germany). Further experimental details are described elsewhere [16].

2.2. *Test substances and materials*

In addition to the gases listed above, a calibration gas containing CO (995 ppmv) and CO_2 (985 ppmv) in nitrogen (Linde; purity 6.0) was used in the CO oxidation tests. The test substances toluene, phenol, MTBE and *n*-eicosane (Eic) were provided by Merck (purity p.a.).

Two ferroelectric materials were applied: $BaTiO_3$ and $PbZrO_3$–$PbTiO_3$ (both from Marco GmbH, Hermsdorf, Germany). $LaCoO_3$ was tested as received from KataLeuna (Leuna, Germany).

The following porous and non-porous alumina and silica packed-bed materials were used without further treatment: γ-Al_2O_3 (Merck, purity >99.9%), α-Al_2O_3 (Aldrich, >99%), silica gel (SilGel; Merck, >99.95%) and quartz powder (Merck, p.a.). The physical parameters of the packed-bed materials are summarised in Table 1. The specific surface areas were determined using the BET method with a Micrometics ASAP 2000 analyser.

The immobilisation of *n*-eicosane on silica and alumina has been described elsewhere [16]. As a result, monolayer coverages of 0.24, 112, 0.08 and 72 were estimated for γ-Al_2O_3, α-Al_2O_3, silica gel and quartz, respectively, assuming a planar adsorption geometry of the eicosane molecules. The carbon content of the samples was determined using a C-MAT 5500 carbon analyser (Ströhlein Kaarst, Germany).

Table 1
Physical parameters of the inert, ferroelectric and catalytically active packed-bed materials

Material	Porosity[a]	Bulk density (g/cm^3)	Relative dielectric constant	Most frequent pore diameter (nm)	Average pore diameter (nm)	Particle size (μm)	Specific surface area (m^2/g)
Glass beads	0.39	2.2	5	NA[b]	NA	5000	≈0
$BaTiO_3$	0.46	5.7	≈3000	NA	NA	1000–1600	<0.01
$PbZrO_3$–$PbTiO_3$	0.47	7.8	≈2000	NA	NA	≈5000	<0.01
γ-Al_2O_3	≈0.8	4.0	13	5.3[c]	7.4[c]	63–200 (72%)	133[c]
α-Al_2O_3	≈0.6	4.0	13	NA	NA	44–149 (99%)	0.26[c]
Silica gel	≈0.8	2.6	5	13[c]	10.4[c]	200–500 (99%)	372[c]
Quartz	≈0.6	2.6	5	NA	NA	200–600 (60%)	0.4[c]
$LaCoO_3$	0.79	5.98	NA	23	NA	500–3000	23.5[c]

[a] Porosity (including intra- and interparticle pore volumes) determined by gravimetric measurements.
[b] Not analysed.
[c] Determined by BET analysis (adsorption/desorption of nitrogen).

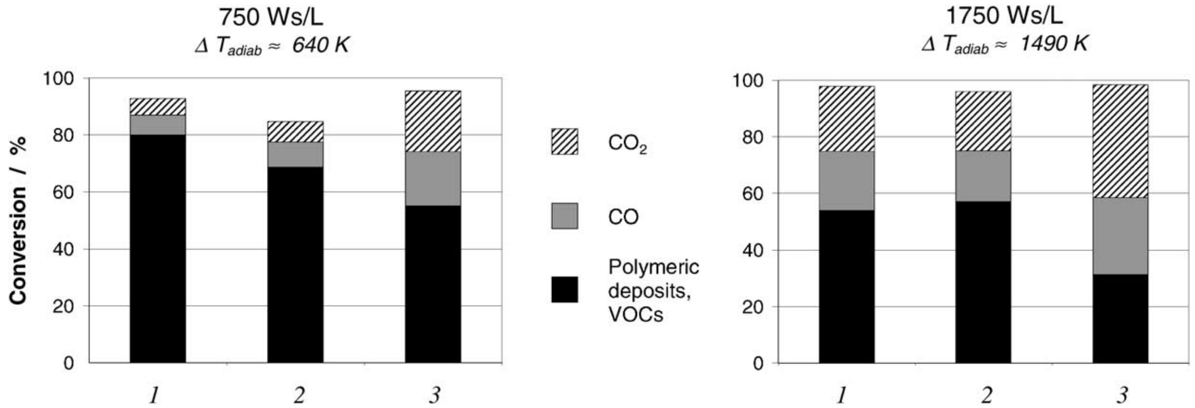

Fig. 1. Product distribution for the NTP oxidation of toluene (450 ppmv in air, 120 v/vh) with different reactor fillings: (1) empty reactor, (2) filled with glass beads and (3) filled with ferroelectric $PbZrO_3$–$PbTiO_3$. For these studies, a larger dielectric barrier discharge reactor (volume 119 ml, barrier material steatite, barrier thickness 7 mm, discharge gap 8 mm) was used.

3. Results and discussion

3.1. Comparison between homogeneous gas-phase and ferroelectric packed-bed reactors

The influence of ferroelectric and inert (glass beads) packed-bed materials on the NTP oxidation of three model compounds (toluene, phenol and MTBE) was studied. In the case of the aromatic compounds (especially phenol), a significant amount of polymeric deposits was found on the reactor walls. The introduction of a ferroelectric material into the discharge zone increased the (real) power input at constant voltage. Therefore, the following discussion is based on the specific power input instead of the applied voltage.

As shown for toluene in Fig. 1, the introduction of glass beads providing a surface comparable to that of the perovskite does not markedly change the performance of the NTP reactor. Therefore, the enhanced surface area can be excluded as the origin of the strong effect observed with a ferroelectric packed-bed.

For all three VOCs, the conversion to CO_X is significantly enhanced by the ferroelectric packed-bed material (Fig. 1, Table 2; except of phenol at low power densities). The most pronounced effect was found for MTBE with CO as the preferential product. Additionally, the formation of polymeric deposits is reduced in the case of toluene and phenol. Therefore, a ferroelectric packed-bed is a useful tool to increase the energetic efficiency but is not sufficient to solve the problem of the low selectivity of oxidation reactions in the NTP.

Table 2
Conversion to CO, CO_2 and polymeric deposit/adsorbate for the NTP oxidation of MTBE and phenol in the GDR and the FER (filled with $BaTiO_3$)[a]

Substance	Energy density (Ws/L)	Conversion to CO_2 (%)		Conversion to CO (%)		Conversion to polymeric deposit/sorbate (%)		Total conversion (%)	
		GDR	FER	GDR	FER	GDR	FER	GDR	FER
Phenol	300	11.1	14	12.9	10	59	50	83	74
	500	12.2	23	13.5	16	59	54	84.7	93
MTBE	500	2.5	24	2.7	17	ND[b]	ND	≥5.2	≥41
	1000	7.2	42.5	14	30	ND	ND	≥21.2	≥72.5

[a] Phenol and MTBE concentrations: 185 and 200 ppmv, respectively; approx. 1000 v/vh.
[b] Not detectable.

The influence of ferroelectric packed-bed materials is not correlated with an increase of the ozone concentration. In contrast, it was shown that the ozone emission exhibits a maximum at relatively low energy densities (below 500 Ws/L). This effect can best be explained by the consumption or diminished formation of the precursor species of ozone, triplet oxygen $O(^3P)$. In this point, our results are in good agreement with the studies of Yamamoto et al. [13].

3.2. Comparison between in-plasma catalysis and post-plasma catalysis reactors

To distinguish plasma-catalytic effects (utilising short-lived as well as long-lived species) from those due to the reactions with long-lived species formed in the NTP, comparative experiments with the IPCR and PPCR were carried out. In the latter case, the conversion of volatile and immobilised hydrocarbons seems to be mainly due to ozone acting either directly or indirectly via decomposition on catalyst surfaces (e.g. γ-Al_2O_3, Co_3O_4, Mn_XO_Y) [16,17]. A contribution of nitrogen oxides could be excluded by comparative studies using either air or an O_2/He mixture. In both cases, similar conversion rates and selectivities were obtained [16].

Clear evidence for specific in-plasma catalytic effects is given by the oxidation of an immobilised non-volatile hydrocarbon, *n*-eicosane, on quartz or silica gel (Fig. 2a). For both systems, no carbon removal was found in the post-plasma-treatment mode (PPCR). Neither ozone nor other long-lived species are able to react with Eic to form volatile organic compounds or carbon oxides. Ozone is not decomposed on either type of silica. In contrast, degrees of carbon removal above 80% occur in the case of plasma catalysis (IPCR). Thus, the presence of other, presumably short-lived species in an NTP must open additional reaction pathways leading to the oxidation of the immobilised hydrocarbon. It is noteworthy that the oxidation also takes place when Eic is adsorbed in the interior of a porous catalyst, in this case silica gel. This finding is a strong indication for the presence of short-lived species in the pore volume.

The situation is slightly different for the oxidation of Eic on alumina (Fig. 2a). For non-porous α-Al_2O_3, the same behaviour as for silica is observed: no reaction in the PPCR and a conversion of about 70% in the IPCR. A significant carbon removal (≈70%) is also found for γ-Al_2O_3 in the plasma catalysis mode (IPCR). However, due to the potential of γ-Al_2O_3 for ozone decomposition (forming reactive O radicals), a DR_C value of about 50% is also found in the post-treatment mode (PPCR). Further experiments showed that the conversion in the IPCR includes additional reaction pathways beside that via O_3 scission. In particular, the reaction in the IPCR continued even when the catalyst had lost its capability to decompose ozone [16]. The results with Eic/γ-Al_2O_3 prove once

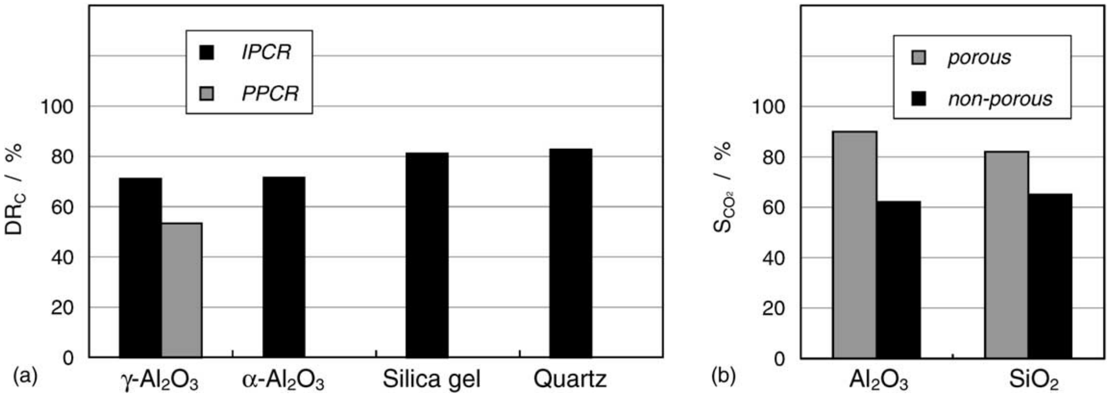

Fig. 2. Comparison of the (a) degrees of carbon removal (DR_C) and (b) CO_2 selectivities for the oxidation of *n*-eicosane immobilised on porous and non-porous alumina and silica in IPCR and PPCR experiments (air flow 100 mL/min, power input approx. 4 W, values after long-term treatment (duration < 12 h, extrapolation for $t \to \infty$), details in [16]).

Table 3
Mean lifetimes and accessible ranges of diffusion for short-lived species formed in an NTP at ambient pressure

Short-lived species	Mean lifetime in the gas phase[a]	Accessible range		Mean diameter (μm)	
		Normal diffusion	Knudsen diffusion[b]	Silica gel grains	γ-Al_2O_3 grains
O (^{1}D)	1.4 ns	270 nm	20 nm		
O (^{3}P)	14 μs	27 μm	≈2 μm	175	65
OH	≤100 μs	≤80 μm	≤5 μm		

[a] According to Refs. [11,18].

[b] Accessible ranges without consideration of heterogeneous reactions, e.g. with adsorbed hydrocarbon molecules.

more the presence of short-lived species in the inner volume of a porous catalyst.

A theoretical consideration [16] on the basis of the mean lifetimes of various radicals (O(^{1}D), O(^{3}P), OH) formed in an NTP shows that their formation in the gas phase and a subsequent migration (by Knudsen diffusion) into the pore volume is very unlikely. This is especially valid when reactions of the reactive species with adsorbed hydrocarbons are taken into account. The mean lifetimes in the gas phase (according to [11,18]), the accessible ranges λ_{acc} for gas-phase and Knudsen diffusion and, for comparison, the mean diameters of the catalyst grains are summarised in Table 3.

In principle, there are two possibilities to explain the presence of short-lived species in the pore system of catalysts: (i) the prolonging of their lifetimes by adsorptive interactions with the surface of the catalyst or (ii) the formation of these species inside the pores due to the existence of strong local electric fields. On the basis of the experimental results described above, a clear distinction between these two hypotheses is not possible. However, some experimental indications of a stabilisation of atomic oxygen species on a catalyst surface are presented in the following section.

The porosity of the supports has a marked influence on the selectivity to total oxidation, as can be seen from the S_{CO_2} values for the removal of immobilised Eic in the IPCR (Fig. 2b). The effect of the catalyst in the plasma zone is probably based on the retardation of partially oxidised intermediates and CO [16].

Another example for the potential of plasma catalysis is the oxidation of CO on $LaCoO_3$. Although a catalytic post-treatment with ozone did not affect the conversion, a considerable CO removal was achieved by in-plasma catalytic treatment. For example, the CO concentration was reduced to <10% by an NTP treatment (30 kV) of a CO/N_2-air (1:1) mixture.

The potential of $LaCoO_3$ to oxidise CO can be used to improve the performance of an NTP reactor for the removal of hydrocarbons, e.g. phenol. During a long-term experiment, the phenol concentration in the gas flow was reduced from 220 to <1 ppmv. Thereby, the emission of CO could be completely prevented. Only after deactivation of the catalyst due to the formation of polymeric deposits (after more than 200 h on-stream) some CO was able to break through.

3.3. Stabilisation of NTP-formed oxidants

The stabilisation of atomic oxygen species by adsorptive interactions to catalyst surfaces is well known and intensely studied. The chemisorption of O^- species on n-type semiconducting metal oxides such as SnO_2, TiO_2 and ZnO has been proved by electric conductivity measurements and ESR spectroscopy [19,20]. Its lifetime is significantly prolonged due to the electron transfer from the solid to the adsorbed oxygen radical. Another example for long-lived atomic oxygen species has been described by Delmon and co-workers [21,22] in the framework of selective oxidation reactions. According to his remote control concept, the synergy effects of two-phase catalysts (e.g. Sb_2O_4/MoO_3) are based on the migration of spilt-over oxygen species from one phase to another [22].

To study a possible formation of reactive oxygen species by an NTP and their stabilisation by a support, the catalytic oxidation of CO on $LaCoO_3$ was used as model reaction.

A low degree of conversion of CO to CO_2 (about 7%) was observed for a 1:1 mixture of CO/N_2

(1000 ppmv CO) and air at ambient temperature without NTP. Obviously, the catalyst exhibits a limited activity for the oxidation with molecular oxygen.

The addition of 800 ppmv ozone (externally produced by a gas-phase NTP reactor) did not result in a significant change of the oxidation rate. Therefore, a direct reaction between CO and O_3 as well as an oxidation via O_3 decomposition on $LaCoO_3$ can be excluded.

Prior to the following experiments, the $LaCoO_3$ catalyst was placed in the NTP reactor and exposed to a stream of pure oxygen (100 mL/min) for 30 min. The gas flow was then switched off and the NTP was applied for a limited period of time (up to 10 min). Subsequently, the gas flow was changed to CO/N_2 (170 mL/min; corresponding to 1030 v/vh and a residence time of 3.5 s) and the oxidation of CO was monitored. The values were related to the CO_2 formation without NTP treatment, thus showing the effect of oxidising species formed by the NTP.

The concentration of CO in the effluent gas as a function of NTP treatment time is shown in Fig. 3a. The time profile of the CO_2 concentration is strongly affected by adsorption, and therefore, not suitable for the evaluation of the NTP effects. The integrated value of the differences between the CO concentrations with and without NTP application over reaction time can be interpreted as being due to the titration of an oxygen reservoir. The corresponding calculation gives the amounts of adsorbed O species presented in Fig. 3b. Because the oxidation activity diminishes after about 20 min, the above interpretation is more likely than a formation of new active sites at the catalyst surface.

3.4. *Combination of ferroelectric and catalytically active packed-bed materials*

The combination of ferroelectric and catalytically active packed-bed materials was studied in order to achieve an optimum performance of the NTP reactor. $BaTiO_3$ was applied as the ferroelectric component, mainly enhancing the degree of conversion. $LaCoO_3$ was applied as the catalytically active component, leading to a shift towards total oxidation (i.e. an increase of S_{CO_2}). The results are discussed for two energy densities (one mean and the maximum value applied for the different configurations; similar results were obtained for the experiments with other energy densities).

In the case of phenol (Fig. 4), a significant fraction of polymeric deposits and adsorbed VOCs (including phenol) remained in the reactor independent of the packed-bed material. However, the lowest conversion to these products was achieved for the two-layer reactor. A comparison with the $LaCoO_3$-filled reactor shows that this component is in particular responsible for the oxidation of CO to CO_2. This effect is quite clear for larger energy densities (e.g. 920 Ws/L). For lower power input (460 Ws/L), the advantage of the two-layer combination is less pronounced.

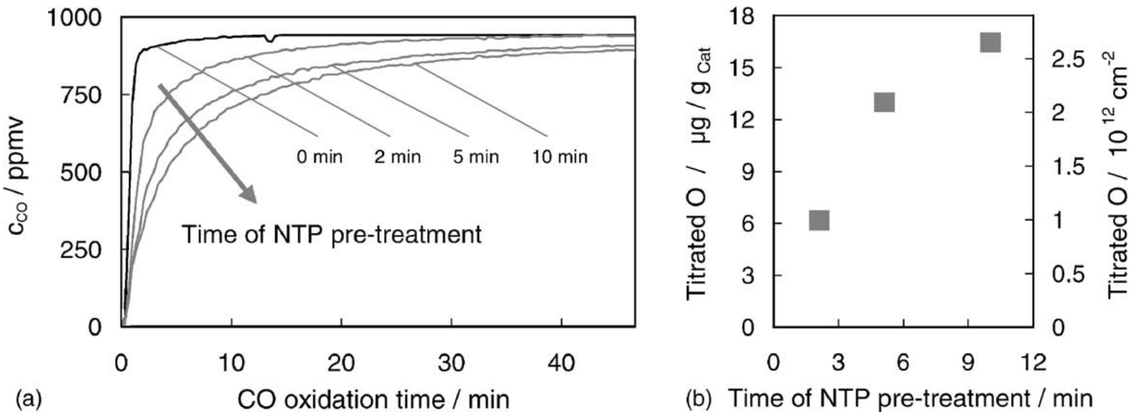

Fig. 3. Oxidation of CO on a $LaCoO_3$ catalyst in a nitrogen atmosphere after an NTP pre-treatment in oxygen: (a) CO concentration as a function of reaction time for different pre-treatment times and (b) quantity of adsorbed oxygen species as a function of NTP pre-treatment time.

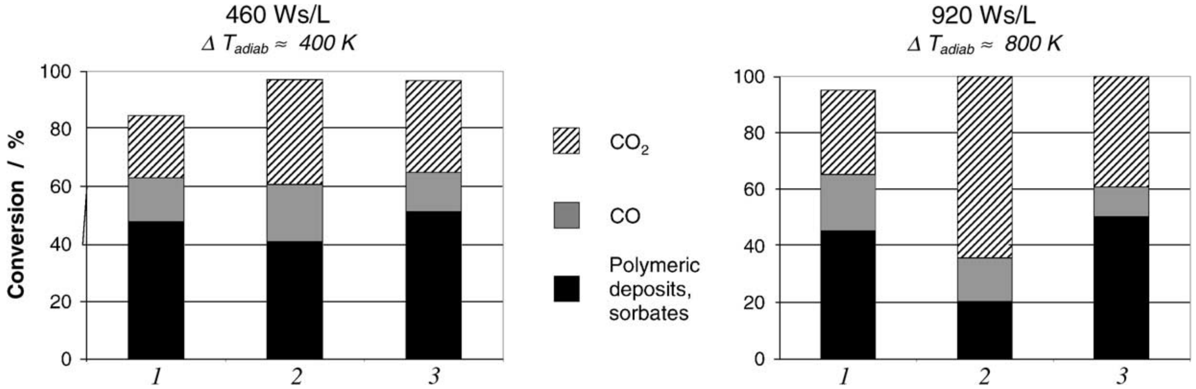

Fig. 4. Product distribution for the NTP oxidation of phenol (185 ppmv in air, approx. 1000 v/vh) with different reactor fillings: (1) ferroelectric $BaTiO_3$, (2) $BaTiO_3 + LaCoO_3$ (two separate layers) and (3) $LaCoO_3$.

The model experiments carried out with two-layer arrangements using other hydrocarbons (e.g. MTBE) showed that the extent of advantageous synergy effects strongly depends on the materials applied, the contaminants to be eliminated and the specific energy input.

4. Conclusion

By studying the NTP oxidation of CO and various organic compounds either in the gas phase or immobilised on carriers, the advantageous effect of packed-bed materials in the discharge zone has been proved. Modifications of a homogeneous gas-phase NTP by ferroelectric and catalytically active solids have a marked influence on the reaction pathways.

Within a ferroelectric layer, the external electrical field is considerably enhanced in the vicinity of the edges and corners of the packed-bed grains. As a result, the energy gain of the accelerated electrons is increased, leading to a modified pattern of reactive species. In many cases, this results in higher conversion degrees, and therefore higher removal rates of organic pollutants.

In contrast to a catalytic post-treatment, where the oxidation is mainly due to direct or indirect reactions of ozone, plasma catalytic processes involving short-lived species can take place when the catalyst is placed in the NTP discharge zone. These reactive species have been shown to be available in the interior of porous catalysts. In the case of $LaCoO_3$, a reservoir of reactive species capable of CO oxidation is formed in the course of an NTP pre-treatment. On the basis of these results, in situ catalysis can be considered as a suitable tool to improve the performance of the NTP oxidation method, especially by enhancing the selectivity to CO_2. Under certain conditions, a combination of plasma catalysis with ferroelectric modification results in synergy effects (higher conversion degrees and better product selectivity).

However, at the present state of development, the large energy input required (corresponding to an adiabatic temperature rise of several hundred K in most cases) is a striking hindrance for the broad application of an NTP-based cleaning of effluent streams.

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