

Review

# Combining non-thermal plasma with heterogeneous catalysis in waste gas treatment: A review

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## Abstract

Plasma driven catalysis is a promising technology for waste gas treatment characterized by higher energy efficiencies, high mineralization rates and low by-product formation. The combination of heterogeneous catalysts with non-thermal plasma can be operated in two configurations: positioning the catalyst in the discharge zone (in-plasma catalysis) or downflow the discharge zone (post plasma catalysis).

In a first part of the review, changes of plasma properties resulting from the introduction of catalyst material are discussed. It has been reported that discharge types can even change. Accordingly, it was reported that microdischarges are formed within the catalyst pores. Changing plasma characteristics can eventually result in enhanced production of new active species, increasing the oxidizing power of the plasma discharge.

In a second part, it is discussed that plasma discharges also affect catalyst properties such as a change in chemical composition, enhancement in surface area or change of catalytic structure. These phenomena partially explain why catalyst adsorption kinetics of airborne pollutants are affected when exposed to plasma discharges.

It is also reviewed that the synergy of combining plasma with catalysts can not only be attributed to the production of new reactive species. Also plasma photon emission or thermal hot-spots can initiate catalytic pollutant oxidation reactions.

To conclude, an overview of recently published manuscripts concerning plasma catalysis for volatile organic compounds abatement is given. It is also discussed why heterogeneous plasma catalysis has high potential for the simultaneous abatement of  $\text{NO}_x$  and hydrocarbons.

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**Keywords:** Plasma driven catalysis (PDC); In-plasma catalysis (IPC); Post plasma catalysis (PPC); Volatile organic compounds (VOC); Nitrogen oxides ( $\text{NO}_x$ ); Waste gas treatment

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## 1. Introduction

The emission of volatile organic compounds (VOC) and  $\text{NO}_x$  by various industrial and agricultural processes is an important source of air pollution and, therefore, a problem for human health and the environment in general [1,2]. The United States Environmental Protection Agency (US EPA) has mandated  $\text{NO}_x$  emission reductions of 90–95% from current levels, starting in 2007 and phasing in completely by 2010. Well established technologies for VOC abatement are thermal and catalytic incineration, adsorption, condensation, biofiltration, membrane separation or ultra-violet oxidation [3,4]. For  $\text{NO}_x$  abatement processes, active lean  $\text{NO}_x$  catalysts, urea-selective catalytic reduction or lean  $\text{NO}_x$  trap catalysis has been used [5]. However, the severe emission tolerances are often difficult to handle using these conventional technologies [6]. Therefore, innovative research in the field of air purification becomes more and more important [4]. Extensive research has been done on using non-thermal plasma (NTP) as a technology for environmental protection, in particular as abatement technology for airborne hazardous compounds [7,8]. Non-thermal plasma typically consists of electrons which are accelerated by an electric field, gaining typical temperatures in the range of 10,000–250,000 K (1–25 eV), and which are not in thermal equilibrium with other particles. Electron–molecule collisions with bulk gas molecules ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ) result in the production of excited bulk gas molecules (e.g.  $\text{N}_2^*$ ). Excited molecules lose their excess of energy by emitting photons or heat. The unstable reactive species (ions and radicals) are formed by dissociative electron attachment processes. Hydroxyl radicals result from water dissociation reactions, also producing hydrogen radicals which are, in oxygen-rich environments, scavenged and converted into  $\text{HO}_2^\bullet$  almost instantaneously [9]. VOC removal is generally attributed to radical reactions initiated by the attack of these O or OH radicals [10,11]. However, depending on the reaction conditions, other radical and ionic reactions also result in VOC conversion to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and other degradation products [12,13].

Today, VOC abatement technology is most useful for moderate gas flow rates containing low VOC concentrations. Urashima and Chang [14] compared the economical application range of NTP processes with other chemical methods for the effective treatment (removal or conversion) of VOC. From their results, the applicable range of electrical discharges is about 0.01–1000 ( $\text{N m}^3 \text{ h}^{-1}$ ) and 1–10,000  $\text{ppm}_v$ , similar conclusions were made by Lu et al. [4]. Although NTP applications as end-of-pipe technology for the removal of VOC,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$  and  $\text{NO}_x$  are frequently reported [15], it is seldom used due to site-specific constraints such as energy inefficiencies, poor mineralization, and by-product formation. One of the main problems of NTP technology is by-product formation such as a high CO formation. Magureanu et al. [16] reported that during trichloroethylene removal experiments, NTP gives  $\text{CO}_2$  selectivities lower than 25%, while the major reaction product was CO with selectivities up to 70%. Van Durme et al. [17] detected

several higher hydrocarbons in the effluent gas during NTP toluene removal experiments including formic acid, benzaldehyde, benzyl alcohol, methyl-nitrophenols, ... Recent developments in NTP research focus on generating more oxygen active species to further oxidize CO into  $\text{CO}_2$  molecules, eventually leading to a higher  $\text{CO}_2$  selectivity [18]. The generation and stable operation of atmospheric non-thermal plasmas remains a challenge for modern plasma science and technology [19]. Next, conventional plasma technology often proves not to be competitive in both removal efficiency as in overall cost. The latter is determined by production costs and life span combined with the energy consumption [19].

A more effective use of plasma is possible by exploiting its inherent synergetic potential through combination with heterogeneous catalysts [8,20,21]. In the field of air purification, plasma driven catalytic technology has high potential as can be seen by increased mineralization efficiencies. Wallis et al. [22] measured no  $\text{CO}_2$  during the destruction of 500  $\text{ppm}_v$  dichloromethane when using only plasma. However, when  $\gamma\text{-Al}_2\text{O}_3$  was introduced in the plasma discharge,  $\text{CO}_2$  outlet concentrations were 32  $\text{ppm}_v$  proving an increased mineralization rate. It can be concluded that by-product formation, such as aerosols, ozone and smaller organic compounds, is strongly reduced when using hybrid plasma catalyst technology [12]. Van Durme et al. [17] also reported that the energy efficiency for toluene degradation strongly increases using  $\text{TiO}_2$  as in-plasma catalyst. Indeed, for dry air and an energy density of  $17 \text{ J L}^{-1}$ , adding 15 g  $\text{TiO}_2$  increased the toluene ( $C_{in} = 0.5 \text{ ppm}_v$ ) removal rate from  $27 \pm 4$  to  $82 \pm 2\%$ . Similarly, introducing 15 g  $\text{MnO}_2\text{-CuO/TiO}_2$  downstream the plasma discharge, resulted in 78% toluene removal efficiency for an energy density of  $2.5 \text{ J L}^{-1}$ , while this was only 2% in the absence of a catalyst.

Based on recent papers (2004–2007) the different mechanisms occurring in-plasma/catalyst hybrid configurations are reviewed. In a first part of this review it is shown that some authors report heterogeneous catalysts to affect plasma characteristics, while others claim that NTP initiate and influence catalyst mediated reactions. Secondly, the state-of-the-art of plasma/catalyst combined systems in the field of waste gas treatment is presented.

## 2. Plasma catalytic mechanisms

Heterogeneous catalyst can be combined with NTP in two ways: by introducing the catalyst in the discharge zone (in-plasma catalysis, IPC) or by placing the catalyst after the discharge zone (post plasma catalysis, PPC) (Fig. 1a and b) [2,15]. For both IPC as PPC configuration, heterogeneous catalyst material can be introduced into the reactor in several ways (Fig. 1c): as coating on the reactor wall or electrodes, as a packed-bed (granulates, coated fibers, pellets) or as a layer of catalyst material (powder, pellet, granulates, coated fiber). In both designs many catalyst formulations have been proposed and tested. Reported in-plasma catalysts are  $\text{BaTiO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{MnO}_2$  and their derivatives (Table 1) [23]. Wallis

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