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The Design of MnO\textsubscript{x} Based Catalyst in Post-Plasma Catalysis Configuration for Toluene Abatement

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Abstract: This review provides an overview of our present state of knowledge using manganese oxide (MnO\textsubscript{x})-based catalysts for toluene abatement in PPC (Post plasma-catalysis) configuration. The context of this study is concisely sum-up. After briefly screening the main depollution methods, the principles of PPC are exposed based on the coupling of two mature technologies such as NTP (Non thermal plasma) and catalysis. In that respect, the presentation of the abundant manganese oxides will be firstly given. Then in a second step the main features of MnO\textsubscript{x} allowing better performances in the reactions expected to occur in the abatement of toluene in PPC process are reviewed including ozone decomposition, toluene ozonation, CO oxidation and toluene total oxidation. Finally, in a last part the current status of the applications of PPC using MnO\textsubscript{x} on toluene abatement are discussed. In a first step, the selected variables of the hybrid process related to the experimental conditions of toluene abatement in air are identified. The selected variables are those expected to play a role in the performances of PPC system towards toluene abatement. Then the descriptors linked to the performances of the hybrid process in terms of efficiency are given and the effects of the variables on the experimental outcomes (descriptors) are discussed. The review would serve as a reference guide for the optimization of the PPC process using MnO\textsubscript{x}-based oxides for toluene abatement.

Keywords: NTP (Non thermal plasma); principles of catalyst selection; MnO\textsubscript{x}; PPC (Post plasma-catalysis); toluene abatement; ozone decomposition ability; toluene ozonation; CO oxidation; toluene total oxidation

1. Introduction

With the increasing consumption of toluene in commercial and industrial applications [1], the toluene emission problem becomes of serious concern for causing environmental problem as well as inducing negative health effects on humans [2,3]. So it is highly desired to find an economical and green technique for toluene emission control. Comparing to traditional techniques such as high-temperature-based combustion and catalytic oxidation, non-thermal plasma (NTP) technology is capable of operating at room temperature and ambient pressure. Meanwhile, easy operation is another main advantages of NTP technique [4]. However, the energy efficiency and CO\textsubscript{2} selectivity still need to be improved for further industrial application. Hence, plasma-catalysis, including in plasma catalysis (IPC) and PPC configurations, can be a promising approach for toluene abatement having the advantages of higher toluene removal efficiency and lower unwanted byproducts at a low operating temperature, at which it is normally not possible to activate the catalysts [5,6].
To begin with, the physico-chemical properties of toluene are presented and its negative effects on environment and human being are given. Then, after briefly screening the most encountered VOCs (Volatile Organic Compounds) depollution methods, the principles of PPC are exposed based on the coupling of two mature technologies such as NTP and catalysis. The design of manganese oxides is discussed in a fourth part. The choice of MnO₂ as potential catalysts in PPC configuration was motivated due to the fact that except metals of the platinum group, characterized by their high price, the metal oxide catalysts containing manganese oxide exhibit the highest activity in decomposition of gaseous ozone and also in catalytic oxidation of pollutants. In that respect, the presentation of the abundant manganese is firstly given. Then, the important features of MnOₓ allowing better performances in the main reactions expected to occur in the abatement of toluene in a PPC process are reviewed including catalytic oxidation of toluene, ozone decomposition, toluene ozonation and CO oxidation. Finally, in a last part the current status of the applications of PPC using MnOₓ-based type catalysts on toluene abatement is discussed. The selected variables of the hybrid process related to the experimental conditions of toluene abatement in air are first identified. The selected variables are those expected to play a role in the performances of the two-stage plasma-catalyst system towards toluene abatement. The descriptors linked to the performances of the hybrid process in terms of process efficiency are also presented. In a second step the effects of the variables on the experimental outcomes (descriptors) are discussed.

2. The Properties, Applications and Hazardous Effects of Toluene

Toluene (C₆H₅CH₃) is widely investigated as a representative VOCs of the BTX (Benzene, Toluene and Xylene) family. Toluene is a colorless liquid with an aromatic odor. It is a mono-substituted benzene derivative, consisting of a CH₃ group attached to a phenyl group. The basic properties of toluene are presented in Table 1.

| Property                         | Value                                |
|----------------------------------|--------------------------------------|
| Chemical formula                 | C₇H₈                                 |
| No. CAS                          | 108-88-3                             |
| Molar mass (g/mol)               | 92.14                                |
| Density (g/mL)                   | 0.87 (20 °C)                         |
| Melting point (°C)               | −95                                  |
| Boiling point (°C)               | 111                                  |
| Solubility in water (g/L)        | 0.52 (20 °C)                         |
| Vapor pressure (kPa)             | 2.8 (20 °C)                          |
| Odor threshold (ppmv, Parts Per Million by volume) | 0.17 |
| Auto ignition temperature (°C)   | 480                                  |
| Conversion factor                | 1 ppmv = 3.76 mg/m³ (in air, 25 °C)  |

Toluene can react as an aromatic hydrocarbon in electrophilic aromatic substitution [7]. The methyl group has a greater electron-releasing property than that of H atom in the same position. Sulfation, chlorination and halogenation have been undergone via this property. Importantly, comparing to the phenyl group, methyl group is more susceptible to oxidation [8].

Toluene has numerous commercial and industrial applications: for example, toluene is used as a precursor in the synthesis of chemicals, such as xylene, benzene, toluene diisocyanate (TDI) for the manufacture of polyurethane foam and trinitrotoluene (the explosive TNT). Toluene is used as an octane booster in gasoline fuels, which are used in internal combustion engines. In addition, toluene is widely used as a solvent because of its favorable properties, such as high solvency, low flammability, non-corrosiveness and high stability. In many commercial products, toluene is present in paint thinners, silicone sealants, nail polish remover, glues, disinfectants and correction fluid. The global demand for toluene valued at over USD 25.1 billion in 2015, is expected to reach above USD 31.8 billion in 2021 [9].
Toluene worldwide production is estimated to be 19.6 million tons in 2020 comparing to 12.4 million in 2010 [10]. However, it is noteworthy to mention that ~86% of the toluene produced is eventually released into the biosphere (primarily in the troposphere) due to high volatility and low solubility in water. There are several man-made sources of emissions to the atmosphere, including the following [11]:

- Inadvertent sources (65%), such as emissions from motor vehicles and aircraft exhaust, losses during gasoline marketing activities, chemical spills, cigarette smoke, and household products.
- Industrial processes in which toluene is used (33%).
- Toluene production (2%).

Toluene is believed to be one of the most prevalent hydrocarbons in the troposphere. Its dispersion is largely dependent upon meteorological conditions and its atmospheric reactivity. The lifetime of toluene ranges from 4 days (at high-altitudes during the summer) to several months (at low-altitudes during the winter). The average half-life of toluene resulting from atmospheric oxidation is estimated to be 12.8 h [3]. So the contribution of toluene to the photochemical smog is considerable.

The presence of toluene in air has a negative impact on human health. Toluene is a main contributor of indoor environmental pollution. Different sources such as paints, adhesives and cigarette are known to contribute to the increase of toluene concentration in indoor air.

The report entitled “toxicological profile for toluene” published in 2000 conducted by U.S. department of health and human services presents the health effects of toluene [2]. As shown in Table 2, there are three main exposure routes for human: inhalation, oral and dermal. Among them, a lot of data deal with toluene incorporation throughout inhalation. The high hazard profile of toluene is highlighted as it covered all the possible health effects listed in Table 2. For example, in Virginia, it was reported that 39 deaths were attributed to inhalant abuse from 1987 to 1996, and Hobara et al. [12] estimated 1 h of exposure to 1800–2000 ppm toluene may be fatal to humans via inhalation. Regarding oral route, only cases of death and acute effect have been reported. Concerning the dermal route, it has been found that exposure of toluene caused the acute effect and genotoxic effect. Due to the adverse effects on human health, WHO (Word Health Organization) has published guideline for the toluene exposure limit. European Union has followed the instruction of WHO [1]: The lowest-observed-adverse-effect level on the central nervous system (CNS) from occupational studies, is approximately 332 mg/m$^3$ (88 ppmv) and the limit of occupational exposure for 8 h of work is 188 mg/m$^3$ (46 ppmv) in European Union (EU).

Table 2. Existing information on health effects of toluene (black dot: existing data); adapted from reference [2].

| Health Effects        | Oral | Dermal |
|-----------------------|------|--------|
| Death                 | ●    |        |
| Acute                 | ●    |        |
| Intermediate          |      | ●      |
| Chronic               |      |        |
| Immunologic/Lymphoretic|      |        |
| Neurologic            |      |        |
| Reproductive          |      |        |
| Developmental         |      |        |
| Genotoxic             | ●    |        |
| Cancer                | ●    |        |
3. The Treatment Techniques for the Removal of Toluene

The dangerousness of toluene involves researching an economic and green technique for its abatement. There have been developing a few traditional types of VOCs abatement techniques, mainly focus on two directions: one deals with non-destructive methods (adsorption, condensation, membrane separation), the other one concerns destructive methods (biochemical method, thermal and catalytic oxidations). The limits based on VOCs concentration and flow rate for these conventional methods have been depicted in Figure 1. Since every type of treatment technology has advantages and disadvantages, none is really satisfactory.

![Figure 1. Classification of various air pollution control technologies based on air flow rate and initial VOC concentration.](image)

Comparing to conventional methods, NTP technology has been claimed to be an alternative method for reducing VOCs due to its wide applicable range of 10–50,000 Nm³·h⁻¹ and (ppb level)-10,000 ppmv [13–16], especially effective for concentrations lower than 100 ppmv [17]. The application of NTP on toluene abatement has attracted considerable interest because of easy on/off operation and inexpensiveness [18,19]. Generally, NTP consists of energetic electrons, ions, active radicals, neutral particles and UV photons as shown in Figure 2. These species are produced when a sufficient strong electric field was applied allowing gas discharge. The electron energy is usually considered to range from 1 to 20 eV while the temperature of the carrier gas keeps close to room temperature. These high energetic electrons can promote toluene abatement via a primary process such as charge transfer, ionization, excitation, dissociation reactions [20]. The secondary process is characterized by the subsequent chemical reactions involving the products of primary process (electrons, radicals, ions, and excited molecules). However, the overall process is not selective into the desired target which is CO₂. To overcome lack of CO₂ selectivity, researchers have focused on emerging techniques resulting from the coupling of two mature VOCs abatement technologies. Among those, plasma-catalysis is one of the most promising. Attractiveness of this hybrid process stems from the possibility to take full advantages of the two technologies: high selectivity from catalysis and the easy operation from NTP. Thus, previous works have emphasized the beneficial role of plasma-catalysis in VOCs removal allowing to decrease the energy cost as well as minimizing the production of hazardous by-products [17,21,22].

According to the location of catalyst, the plasma catalysis system can be divided into two categories, namely, IPC and PPC configurations. In this study, we will focus only on PPC applied to toluene removal.
4. Design of Catalysts for Toluene Abatement in PPC Process

4.1. Introduction

In PPC configuration the catalyst is located downstream from the non-thermal plasma reactor. In that way homogeneous complex reactions occur between plasma and the carrier gas molecules such as O\textsubscript{2}, N\textsubscript{2}, possible H\textsubscript{2}O and the VOC whose number and extent can be tuned by changing the energy put in the plasma. Due to the low selectivity of the NTP, along the VOC oxidation into CO\textsubscript{2}, its transformation is always accompanied by the formation of unwanted hazardous byproducts (e.g., plasma generated VOCs (reaction intermediates), CO, O\textsubscript{3}, and NO\textsubscript{x}). This problem can be resolved a priori through the high selectivity of the catalyst. For instance, the proper catalyst should be able to oxidize the plasma generated organic by-products and the plasma non processed initial VOC as well as CO to CO\textsubscript{2} and decompose O\textsubscript{3} and NO\textsubscript{x} generally in moist air at a temperature close to room temperature or moderate (≤150 °C) at the same time. The basic idea is to take advantage of the O\textsubscript{3} decomposition efficiency of the catalyst to supply active species enabling the total oxidation of plasma non processed hazardous species. When regarding the nature of the catalysts, noble metals and transition metal oxides have been found to be the most active substances for ozone decomposition. However among the developed catalysts, MnO\textsubscript{x} are considered to be the most efficient and cost-effective for ozone decomposition. Additionally, the possibility of increasing moderately the temperature of the catalyst allows to activate some oxygen of the catalyst. Based on that observation, efficient catalysts for total oxidation of VOC cannot be discarded. Again, the same families of catalysts should be taken into account and again MnO\textsubscript{x} can be good candidates for total oxidation of toluene. Lastly MnO\textsubscript{x} are also recognized as efficient catalysts in CO oxidation which is also an important reaction to consider.

This review attempts to summarize our present state of knowledge using MnO\textsubscript{x}-based catalysts for toluene abatement in PPC configuration. In that respect the presentation of the abundant manganese oxides will be firstly given. Then in a second step the main features of MnO\textsubscript{x} allowing better performances in toluene total oxidation, ozone decomposition, toluene ozonation and CO oxidation will be successively briefly reviewed. Finally, in the last part the current status of the applications of PPC using MnO\textsubscript{x} on toluene abatement will be discussed.
4.2. Presentation of the Main Manganese Oxide Structures

Manganese (Mn) is a multivalent element. Each valence state has a characteristic oxide or oxides. MnO₂ occurs naturally as minerals in at least 30 different crystal structures in a range of manganese oxidation states. Manganese oxides are technologically important materials and have widely been used as effective and inexpensive catalysts and as electrode materials for batteries. Interestingly, some MnO₂ crystal structures exhibit tunnel and/or layered structures with varied proportions of Mn in different oxidation states (+2, +3, and +4). The known binary oxides of manganese include MnO, Mn₂O₃, Mn₃O₄ and MnO₂. Like many monoxides, MnO adopts the rock salt structure, where cations and anions are both octahedrally coordinated. The α-Mn₂O₃ phase is named bixbyite. The Mn⁴⁺ ions are octahedrally coordinated, while the O ions have 4 Mn neighbors. The bixbyite structure can be viewed as a close-packed lattice of Mn with O ions filling three quarters of the tetrahedral interstitials in a pattern with Ia₃ symmetry. Hausmannite Mn₃O₄ has a spinel structure having a composition formula Mn²⁺Mn³⁺₃₂O₄, where Mn²⁺ ions occupy the tetrahedral sites and Mn³⁺ the octahedral sites [23].

Among these oxides is the metastable layered Mn₅O₈ having a compositional formula ((Mn²⁺)₂(Mn⁴⁺)₃O₈). Manganese dioxide, MnO₂, for its own part, shows polymorphism. MnO₂ has several crystalline structures, including α-, β-, γ-, δ-, and λ-MnO₂. The different tunnel structures can be described by the size of their tunnels determined by the number of octahedral subunits (n × m), as depicted in Figure 3. α-MnO₂ (hollandite) consists of double chains of edge-sharing MnO₆ octahedra, which are linked at corners to form 1D (2 × 2) and (1 × 1) tunnels in the tetragonal unit cell. The size of the (2 × 2) tunnel is 0.46 nm, which is a large tunnel for insertion/extraction of alkali cations. β-MnO₂ (pyrolusite) is composed of single strands of edges haring MnO₆ octahedra to form a 1D (1 × 1) tunnel. Because of the narrow (1 × 1) tunnel size (0.189 nm), β-MnO₂ cannot accommodate cations. The structure of γ-MnO₂ is random intergrowths of ramsdellite (1 × 2) and pyrolusite (1 × 1) domains. δ-MnO₂ is a 2D layered structure with an interlayer separation of 0.7 nm. It has a significant amount of water and stabilizing cations such as Na⁺ or K⁺ between the sheets of MnO₆ octahedra. λ-MnO₂ is a 3D spinel structure.

![Crystal structures of selected common manganese oxides](image)

**Figure 3.** Illustration of the crystal structures of selected common manganese oxides: (a) MnO₂ including: α-MnIVO₂ (hollandite); rutile β-MnIVO₂ (pyrolusite); R-MnIVO₂ (ramsdellite); γ-MnIVO₂ (intergrowth); δ-MnIVO₂ (birnessite); λ-MnIVO₂ (spinel); Here, The purple and yellow atoms represent spin-up and spin-down Mn, respectively, while the red atoms represent O [24]; (b) Crystal structures of MnO, α-Mn₂O₃ and Mn₃O₄. The green, blue, and red atoms represent Mn⁺⁺, Mn⁺⁰, and O²⁻, respectively [25].

The richness in MnO₂ structures thus provides a rigorous test system to explore the significance of atomic positions on the catalytic efficiency towards toluene oxidation.
4.3. MnO$_x$ in Catalytic Oxidation of Toluene

The high reactivity of MnO$_x$ towards VOCs abatement is generally ascribed to easy variation of manganese oxidation state (Mn$^{2+}$, Mn$^{3+}$, Mn$^{4+}$), oxygen storage capacity in the crystalline lattice and high mobility of lattice oxygen [26]. Kim and Shim [27] investigated the effect of O/Mn stoichiometry using Mn$_{3}$O$_4$, Mn$_2$O$_3$ and MnO$_2$. It was found that the catalytic activity decreased in the order of Mn$_3$O$_4$ > Mn$_2$O$_3$ > MnO$_2$ in line with the decrease of the specific surface areas and oxygen mobility of the MnO$_x$. Mn$_3$O$_4$ [28], Mn$_2$O$_3$ [29,30] and MnO$_2$ [28] were also previously investigated separately by different research teams for toluene oxidation. F. Wang et al. [31] reported on the external morphology effect of MnO$_x$ (rod-, wire-, tube-, and flower-like morphologies) for the oxidation of toluene. It was found that the oxygen ad-species concentration (related to the Mn$^{3+}$ concentration) and low-temperature reducibility decreased in the order of rod-like $\alpha$-MnO$_2$ > tube-like $\alpha$-MnO$_2$ > flower-like Mn$_2$O$_3$ > wire-like $\alpha$-MnO$_2$, in good agreement with the sequence of the catalytic performance of these samples. The best-performing rod-like $\alpha$-MnO$_2$ catalyst could effectively catalyze the total oxidation of toluene at low temperatures ($T_{50} = 210$ °C and $T_{90} = 225$ °C at a GHSV of 20,000 mL·g$^{-1}·h^{-1}$). It was concluded that the excellent catalytic performance of $\alpha$-MnO$_2$ nanorods might be associated with the high oxygen ad-species concentration and low-temperature reducibility. Verykios et al. [32] showed that $\gamma$-MnO$_2$ which was less affected by the presence of water than other MnO$_2$ polymorphs could be suitable for toluene removal. This catalyst was claimed to be more active than noble metal catalysts.

In a same way, various structures of MnO$_2$ i.e., $\alpha$-, $\beta$-, $\delta$-MnO$_2$ were prepared and their catalytic performances in toluene oxidation were assessed to those of a $\gamma$-like MnO$_2$ obtained by the selective removal of La$^{3+}$ from an acid-treated three-dimensional macroporous and mesoporous LaMnO$_3$ [33]. The best performance of this $\gamma$-like MnO$_2$ over the other MnO$_2$ polymorphs was ascribed both to the open three-dimensional macroporous and mesoporous morphology leading to higher BET surface areas than conventional syntheses, enhanced surface adsorbed oxygen (O$_{ads}$) to lattice oxygen (O$_{latt}$) molar ratio (O$_{ads}$/O$_{latt}$) and easier reducibility. Similarly Liao et al. [34] investigated the external morphology effect over Mn$_3$O$_4$ having hollow and solid sphere morphologies for toluene abatement. The better catalytic activity when using hollow spheres of Mn$_3$O$_4$ was claimed to result from beneficial combined effects such as the cavity morphology leading to high surface area, higher O$_{ads}$/O$_{latt}$ molar ratio, believed to be proportional to active oxygen, and higher Mn average oxidation state (AOS). MnO$_x$ supported catalysts were affected by the same factors too. To conclude catalytic activity is generally associated with several factors, such as the BET surface area, presence of oxygen vacancies, reducibility, and external morphology of the catalyst.

The common oxidation catalytic reactions generally involved three types of mechanism [35]: Langmuir-Hinshelwood, Eley-Rideal and Mars-Van Krevelen (MkV) mechanism [33]. It is well known that MnO$_x$ exhibit strong oxygen storage/release ability due to the fact that they easily undergo a rapid reduction–oxidation cycle through the interaction with reducing or oxidant agents accompany by the formation of manganese ions in various oxidation states. The involvement of lattice oxygen of catalysts in total oxidation of toluene and the strong correlation between labile lattice oxygen and catalytic activity suggest that the reaction could proceed via the MkV model [8,36]. In the case of VOCs catalytic oxidation, the first step corresponding to the reduction of the catalyst surface is generally the rate determining step [37].

4.4. MnO$_x$ in Ozone Decomposition

Decomposition of ozone in the gas phase was carried out on various metal oxides by S. Imamura et al. [38]. It was shown that the activity of the metal oxide catalysts increased roughly in the order of the increase in their surface area and in the amount of surface oxygen on them. These observations are very interesting, as these characteristics resemble to those of total oxidation catalysts because low surface area and a small amount of surface oxygen are generally targeted for partial oxidation catalysts. Interestingly, metal oxide conductance increased throughout ozone
introduction for the most reactive oxides such as Ag$_2$O $\approx$ NiO, CuO, Co$_3$O$_4$ which are p-type oxides suggesting that negatively charged oxygen species were formed on their surface. Ag$_2$O was claimed to be the most effective catalyst in decomposing ozone, increasing its activity as the reaction proceeds while some transition-metal oxides are deactivated during the reaction due to accumulation of oxygen species that cover their active sites. The high reactivity of the oxygen species on Ag was invoked to be due to the especially weak bond between oxygen and silver compared with those between oxygen and other metals. Additionally, the high reactivity of such catalyst for CO oxidation was believed to occur thanks to the production of very active oxygen such as oxygen ion O$^-$ without totally discarding oxygen (O) and ozonide ion (O$_3^-$) resulting from the decomposition of O$_2^-$. 

In that way, a comprehensive survey of different oxides (MnO$_2$, Co$_3$O$_4$, NiO, Ag$_2$O, Fe$_2$O$_3$, Cr$_2$O$_3$, CeO$_2$, MgO, V$_2$O$_5$, CuO and MoO$_3$) supported on $\gamma$-Al$_2$O$_3$ for ozone decomposition, but this time in the presence of water (RH (Relative humidity): 40%), was performed by B. Dhandapani et al. [39]. It is found again that p-type oxide semiconductors are the most active substances for ozone decomposition. Among the investigated transition metal oxides MnO$_2$ showed the highest activity explaining its prevalence in patent disclosures. The ozone decomposition pathway over MnO$_2$ supported on $\gamma$-Al$_2$O$_3$ was investigated by T. Oyama et al. The reaction proceeds through two irreversible steps, the adsorption of ozone on the catalyst surface and the desorption of molecular oxygen [40,41]. Ozone is first decomposed/reduced by Mn$^{n+}$ cation into O$^{2-}$ and O$_2$. Then production of active O$_2^{2-}$ and O$_2$ was proposed via reaction of O$^{2-}$ with another O$_2$ molecule in the presence of Mn$^{(n+2)+}$. Next, unstable O$_2^{2-}$ reduced Mn$^{(n+2)+}$ back into Mn$^{n+}$ and desorption of an oxygen molecule occurred [42,43]:

$$O_3 + Mn^{n+} \rightarrow O^{2-} + Mn^{(n+2)+} + O_2$$

(1)

$$O_3 + O^{2-} + Mn^{(n+2)+} \rightarrow O_2^{2-} + Mn^{(n+2)+} + O_2$$

(2)

$$O_2^{2-} + Mn^{(n+2)+} \rightarrow Mn^{n+} + O_2$$

(3)

Oyama et al. found that the difference in the structure of the manganese active center was the origin of support effect on the activity. At low Mn loadings (<6 wt %) the active phase was to be well dispersed on Al$_2$O$_3$ but not well understood. Significant progresses were achieved in 2001 by R. Radhakrishnan et al. by using extended X-ray absorption fine structure (EXAFS) to evaluate the local bonding environment in the MnO$_x$/$\gamma$-Al$_2$O$_3$ catalyst [43]. The catalyst (3 wt %) was prepared throughout incipient wetness impregnation using a manganese acetate precursor. After heating at 170 °C for 6 h, the solid was calcined at 400 °C. Based also on in situ Raman spectroscopy analysis performed before and during ozonation reaction and ab Initio calculations as complementary tools a four mononuclear species was postulated as the manganese active center with a Mn–O distance of 210 pm as shown in Figure 4. During the ozone decomposition reaction, an adsorbed peroxide species was observed on the catalyst surface (Raman line at 880 cm$^{-1}$).

Figure 4. Geometry-optimized four oxygen coordinate Mn structure using the HF/6-311G method [43].

Only a few works have investigated the activity of manganese dioxides with specific crystal phase [44-45]. Ma et al. [46] proposed a scheme of ozone decomposition over transition metal doped cryptomelane–type manganese oxide catalysts ($\alpha$-MnO$_2$) implying the Mn$^{3+/4+}$ mixed valence in the
decomposition/reduction of O₃ into O₂ and O⁻. Consequently, the main differences here stem in the nature of the implied redox couple of manganese and in the nature of the reactive oxygen species: O⁻ instead of O₂²⁻.

\[
\text{O}_3 + (\text{Mn}^{3+}) \rightarrow \text{O}_2 + \text{O}^-_{\text{ads}}(\text{Mn}^{4+}) \quad (4)
\]

\[
\text{O}_3 + \text{O}^-_{\text{ads}}(\text{Mn}^{4+}) \rightarrow 2\text{O}_2 + (\text{Mn}^{3+}) \quad (5)
\]

This scheme highlights the importance of the mixed valence (Mn⁴⁺/³⁺) in α-MnO₂ catalysts. Based on this mechanism the higher content of Mn³⁺ (surface oxygen vacancies) cations present at the surface of the catalyst is expected to promote ozone decomposition.

Interestingly, the effect of MnO₂ structure on ozone decomposition was recently investigated on α-, β- and γ-MnO₂. The activity of these three MnO₂ polymorphs for ozone decomposition followed the order of α- > γ- > β-MnO₂. The superior performances of α-MnO₂ were explained by the combined largest specific surface area and the lowest Mn AOS. Additionally, it was found that the catalytic activity of MnO₂ strongly depended on the density of oxygen vacancies in line with the presence of Mn³⁺. The ozone decomposition mechanism based on the involvement and recycling of oxygen vacancy (V₀) was proposed below and the pertinent points were grasped in Figure 5. Once Mn³⁺ appears in the manganese dioxide, oxygen vacancies were generated to maintain electrostatic balance according to the following process (Equation (6)):

\[
4\text{Mn}^{4+} + \text{O}^2^- \rightarrow 4\text{Mn}^{4+} + 2\text{e}^- / \text{V}_0 + 1/2\text{O}_2 \rightarrow 2\text{Mn}^{4+} + 2\text{Mn}^{3+} + \text{V}_0 + 1/2\text{O}_2 \quad (6)
\]

\[
\text{O}_3 + \text{V}_0 \rightarrow \text{O}_2 + \text{O}^2^- \quad (7)
\]

\[
\text{O}_3 + \text{O}^2^- \rightarrow \text{O}_2 + \text{O}_2^{2-} \quad (8)
\]

\[
\text{O}_2^{2-} \rightarrow \text{O}_2 + \text{V}_0 \quad (9)
\]

- **Figure 5.** Ozone decomposition mechanism based on the involvement and recycling of oxygen vacancy (V₀) [⁴⁴].

When ozone gas flows through MnO₂, the ozone molecule binds to MnO₂ surface by inserting an O atom into an oxygen vacancy site. The oxygen vacancy is 2-electron donor and transfers 2 electrons to an O atom of ozone [⁴⁷,⁴⁸], thus forming an oxygen species (O²⁻) in the oxygen vacancy site and an oxygen molecule, which desorbs into the air (see Equation (7)). Then another ozone molecule reacts with O²⁻ to produce a gas-phase oxygen molecule and a bridging O₂ dimer (peroxide, O₂²⁻), which was observed by in situ Raman spectroscopy (see Equation (8)). Finally, the peroxide species (O₂²⁻) decomposes to release an oxygen molecule (see Equation (9)). The decomposition of peroxide species was believed to be the rate-limiting step.

This study brings important guidelines for the design of future MnO₂-based catalyst for ozone removal.
4.5. MnO\textsubscript{x} in Ozonation Reactions

Catalytic ozonation is an innovative method for oxidation of pollutants in liquid or gas phase. Ozonation reactions mainly referred to catalytic VOCs oxidation by ozone. As this reaction consists of ozone decomposition in the presence of an organic substrate it is not surprising that MnO\textsubscript{x}, which are among the most active transition metal oxides for low temperature decomposition of ozone to generate active oxygen species, are required for oxidation of VOCs by ozone. Application of this method in gas phase has opened a new catalytic approach for low temperature oxidation of VOCs at trace concentration levels. Results of the literature review show that apparent activation energy of VOCs oxidation can be greatly reduced by use of ozone compared to that of oxygen, making total oxidation of VOCs possible at temperatures as low as 100 °C or even lower.

Effect of manganese loading on total oxidation of toluene by ozone using MnO\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} was investigated by E. Rezai et al. [49]. Activities of four loadings of Mn (1%, 5%, 10% and 20%) were studied in the temperature range of 22–100 °C. A direct relationship between Mn loading and average oxidation state of manganese was found. Catalysts at lower loadings, up to 10%, were mostly composed of Mn\textsubscript{2}O\textsubscript{3} while a mixture of MnO\textsubscript{2} and Mn\textsubscript{2}O\textsubscript{3} was present in catalysts with loadings higher than 10%. All catalysts became deactivated at room temperature and their activities were improved by an increase of temperature. It was observed that lower Mn loadings have higher activity in oxidation of toluene. It was proposed that lower oxidation states of manganese are more favorable in decomposition of ozone resulting in higher rate of toluene oxidation. A Langmuir–Hinshelwood mechanism based on activation of toluene molecule via abstraction of hydrogen from the methyl group was postulated to occur over MnO\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} (10 wt %) catalyst [50] explaining the effect of toluene and ozone partial pressures on toluene oxidation rate. Hence the C–H bond cleavage was assumed to be the relevant kinetic step in the oxidation of toluene by ozone.

The mechanism of oxidation of VOCs by ozone is based on ozone decomposition due to Equations (10)–(14) generating atomic oxygen to react with VOCs in the oxidation reaction (Equation (14)) assuming that VOCs are adsorbed on Mn sites (Equation (13)) and the reaction proceeds based on Langmuir-Hinshelwood mechanism between adsorbed species (Equation (14)) [49].

\[
\begin{align*}
O_3 + \text{Mn} & \rightarrow O_2 + \text{O-Mn} \quad \text{(10)} \\
O_3 + \text{O-Mn} & \rightarrow O_2 + \text{O}_2\text{-Mn} \quad \text{(11)} \\
\text{O}_2\text{-Mn} & \rightarrow O_2 + \text{Mn} \quad \text{(12)} \\
\text{VOC} + \text{Mn} & \rightarrow \text{VOC-Mn} \quad \text{(13)} \\
\text{VOC-Mn} + \text{O-Mn} & \rightarrow \text{Products} \quad \text{(14)}
\end{align*}
\]

It is believed that higher dispersion of Mn atoms in catalysts with lower loading levels decreases oxidation state of Mn.

XRD studies showed the presence of β-MnO\textsubscript{2} and Mn\textsubscript{2}O\textsubscript{3} (bixbyite) in the Mn loading of 10%. The percentages of Mn\textsubscript{2}O\textsubscript{3} and MnO\textsubscript{2} in the catalyst estimated from XANES spectra were 91.0% and 9.0%, respectively. The activation energy of the reaction was determined to be 31 kJ/mol obtained by a power law model. The power law model also determined the reaction orders with respect to toluene and ozone as \(-1\) and 2, respectively [50].

Ozonation of toluene catalyzed by MnO\textsubscript{x} supported on siliceous MCM-41 was also investigated by the same team [51]. The performances were found to be similar to those of MnO\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3} at room temperature, the activity decreasing with reaction time as the supported alumina catalyst.

MnO\textsubscript{2}/graphene samples were developed for catalytic ozonation of toluene by M. Hu et al. [52]. The hydrothermal method was used as an effective way to prepare tightly anchored birnessite-type MnO\textsubscript{2} on graphene. The highest toluene degradation rate of \(7.89 \times 10^{-6}\) mol·min\(^{-1}\)·g\(^{-1}\) obtained over the 64.6 wt % MnO\textsubscript{2}/graphene sample was attributed to a synergetic effect of graphene and MnO\textsubscript{2}. 
This synergetic effect was attributed to the tight connection between the active sites on graphene for adsorption of toluene and decomposition of ozone, and the MnO\textsubscript{2} on graphene for decomposition of ozone to form atomic oxygen species. Additionally, MnO\textsubscript{2}/graphene can be regenerated at 325 °C.

MnO\textsubscript{x} dispersed on HZSM-5 (Mn/HZSM-5; Mn: 4 wt %) was shown to be an efficient catalyst for oxidation of 20 ppmv of toluene in the presence of 2000 ppmv of ozone at 30 °C [53]. It was shown by DRIFTS analysis a toluene and ozone conversions of about 78% and 70%, respectively, over Mn/HZSM-5 with a CO\textsubscript{2} (CO + CO\textsubscript{2}) selectivity of 70%. Additionally, the catalytic performances were promoted by Ag which was attributed to induce more oxygen vacancies. The high activity of these catalysts was mainly attributed to the reactive oxygen species generated from ozone decomposition over the oxygen vacancies of these catalysts. Based on the obtained results the possible reaction pathways with or without ozone were given in Figure 6. The toluene can be partially oxidized into benzyl alcohol by the lattice oxygen, but it can be further oxidized into benzaldehyde, benzoic acid and maleic anhydride, ultimately, mineralized to CO\textsubscript{2} by O\textsubscript{3} at room temperature.

![Figure 6](image-url)

**Figure 6.** The pathway of toluene oxidation without ozone (a), with ozone (b) at room temperature adapted from [53].

Commercial honeycomb ozone decomposition catalyst (consisting of MnO\textsubscript{2} as the main active phase with SiO\textsubscript{2} and TiO\textsubscript{2}) immobilized on a nonwoven fabric was investigated for O\textsubscript{3} and toluene removal in dry and humid conditions [54]. It was shown that O\textsubscript{3} was rapidly decomposed only around the entrance of the honeycomb ozone decomposition catalyst. However the amount of converted toluene decreased with time because water molecules competed on the catalyst surface decreasing O\textsubscript{3} and toluene adsorption. To overcome this inhibition MnO\textsubscript{2} catalysts were mixed with alumina or zeolite, which were functional adsorbents, to increase the contact between O\textsubscript{3} and the ozone decomposition catalyst (ODC) surface but however only a small percentage of VOCs reacted.

Table 3 exhibits the salient results in ozonation reactions towards toluene abatement. As mentioned above the active phase is mainly MnO\textsubscript{2} well dispersed on a support which is generally γ-Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}/SiO\textsubscript{2}, graphene and HZSM-5. It has to be mentioned that graphene allows to dispersed huge amount of Mn (60 wt %) as compared to γ-Al\textsubscript{2}O\textsubscript{3} where the Mn content does not exceed the value of 20 wt % [49,55]. All given reactions here are conducted at room temperature. Direct comparison of the different catalyst performances is complicated due to the discrepancy of the operating parameters such as the ratio of generated ozone to the inlet toluene ratio which ranged from 0.55 to 8.75. Beneficial effect is noticeable when this ratio is allowed to increase. Additionally, ozone consumption decreases whatever the catalyst under concern indicating partial deactivation of the catalyst. This decrease is always accompanied to a decrease of the toluene removal efficiency in line with poor carbon mass balance.
Table 3. Overview of ozonation results for toluene abatement.

| Catalyst                  | Active Phase | Flow Rate (mL/min) | GHSV (mL·h⁻¹·g⁻¹) | Temperature (°C) | CC₇H₈ (ppm) | CO₃ (ppm) | O₃/CC₇H₈ | η₄Toluene (%) | η₄Ozone (%) | By-Products                                      | Reference |
|---------------------------|--------------|--------------------|--------------------|------------------|-------------|-----------|-----------|--------------|-------------|-------------------------------------------------|-----------|
| 20% MnO₂/Al₂O₃            | MnO₂         | 100 (dry air)      | 60,000             | 20               | 177         | 98        | 0.55      | ~25 (160 min) then deactivation               | From 100 to 80% in 160 min | Benzoic acid, benzaldehyde, and benzyl alcohol. | [55]      |
| 10% MnOₓ/γ-Al₂O₃          | MnO₂ and Mn₂O₃ | 1000 (dry air)    | 300,000            | 20               | 120         | 1050      | 8.75      | From 100 to 40% in 330 min                   | From 100 to 20% in 330 min | Acetic acid, oxalic acid, benzene and maleic anhydride | [49]      |
| 65 wt % MnO₂/graphene     | MnO₂         | 150 (dry air)      | 112,500            | 20               | 200         | 400       | 2         | ~33.6 (400 min) then deactivation             | ~84.3 (400 min), then deactivation | Organic byproducts                                | [52]      |
| MnO₂/TiO₂/SiO₂ honeycomb  | MnO₂         | 1000 (dry air)     | -                  | 20               | 10          | 38        | 3.8       | ~72 (100 min)                                | -                                                      | Carbon balance: ~22% | [54]      |
|                          | MnO₂         | 1000 (RH: 70%)     | -                  | 20               | 10          | 38        | 3.8       | ~35 (100 min)                                | -                                                      | Carbon balance: ~50% | [54]      |
| Mn/HZSM-5                 | MnOₓ         | 100 (dry air)      | 150,000            | 30               | 20          | 200       | 10        | 78           | 70                      | benzaldehyde, benzoic acid and maleic anhydride | [53]      |
Alcohols, aldehydes and organic acids were identified as intermediates in the reaction process. Heat treatment and excessive ozone feeding favored catalyst generation.

As catalytic ozonation proceeds at lower temperature compared with conventional catalytic oxidation processes, catalyst stability under mild conditions remains a problem. Although aromatic compounds can be oxidized by manganese oxide catalysts at room temperature in an ozone feed, the catalysts generally suffer from severe deactivation because of the build-up of less-reactive by-product compounds on the catalysts.

4.6. The Ability of MnO

Catalytic oxidation of CO has long been studied on various MnO catalysts due to their high CO oxidation ability and low cost in contrast to the expensive noble metal catalysts [56]. Like Cr, Mn has also been used in association with other elements, such as Cu, Co, Ni, and La, to form manganites, which are very active for CO oxidation [57].

In the study of CO oxidation by various bulk MnO at low temperature (<250 °C), Ramesh et al. [56] reported that the ranking for CO oxidation in a mixture of unit ratio of O2/CO by decreasing activity followed the sequence: Mn2O3 > MnO2 ≥ MnO. The CO oxidation over MnO2 and Mn2O3 occurred via Langmuir–Hinshelwood mechanism while over MnO a MvK mechanism prevailed. More energy was needed for activating the CO–MnO2 bond in the reaction which accounted for the low activity of MnO. By opposition, the high reactivity for Mn2O3 was attributed not only to the moderate strength of CO–Mn+3 bond but also to the abundant defects/oxygen vacancies on its surface phase.

Interestingly, Wang et al. [58] compared the catalytic behavior of three manganese oxides (MnO2, Mn3O4 and Mn2O3) doped or not by gold. Mn2O3 appeared to be the most active oxide (T50: +135 °C), reducing at the lowest temperature and undergoing exceptional promotion by gold (T50: −62 °C on 2.9% Au/Mn2O3). Imamura et al. [59] in their investigation of Pd/Mn2O3 catalysts found a similar high activity for the bare support. The role of Mn2O3 would be to permit the incorporation of O2. The slow step would be the surface reaction of CO, which is promoted by Pd.

MnO2 was also the subject of numerous investigations for CO oxidation [60–62]. As discussed above, MnO2 has 4 kinds of polymorphs, denoted as α-, β-, δ-, γ-MnO2. α- and δ-MnO2 were found to be the most active phases for CO oxidation, whereas δ- and γ-MnO2 are much less active [60]. The order of activity was well-correlated to the Mn–O bond strength (α < δ < γ < β), the higher Mn–O bond strength, the lower the activity.

Liang et al. [60] also suggested that the oxidation state of manganese constantly oscillates between Mn4+ and Mn3+. The γ- and β-MnO2 polymorphs would be less active because the re-oxidation of Mn3+ into Mn4+ would be more difficult than in α- and δ-MnO2. This was also confirmed by the work of Iablokov et al. [63].

Among the most common Mn-based oxides, Mn2O3 was the most reactive in CO oxidation, and among the different polymorphs of MnO2, α- and δ-MnO2 were found to be the most active phases. It should be noted, however, that Iablokov et al. [63] were able to prepare an efficient MnOx (1.61 < x < 1.67) oxide, more active in CO oxidation than Mn2O3, via calcination of a manganese oxalato precursor in 10% O2 at 525 °C.

5. MnO3 in PPC for Toluene Abatement

PPC is a two-stage plasma-catalysis system, including two reactors in series with the catalytic reactor located downstream of NTP. The operating mode is the following: the gaseous effluent, consisting of the VOC generally diluted in moist air, is processed by the NTP. The chemical effects occurring within the plasma are the result of an energy injection into the gas effluent by way of electron-impact processes under an electric field. Complex homogeneous reactions take place between the plasma generated reactive species enabling the more or less complete decomposition of the initial VOC. The nature and extent of these homogeneous reactions depend mainly on the energy put per liter in the plasma and to the type of discharge all other things otherwise remaining equal. Usually the NTP
can degrade the VOC to some extent but the main drawbacks are high energy consumption and its non-selectivity. Consequently organic intermediates which can be more harmful than the starting VOC, along with hazardous substances such as O$_3$ and NO$_2$, can evolve from the NTP reactor. By opposition to IPC where the catalyst is integrated in the reactor, the plasma produced short-lived reactive species do not achieve to reach the catalytic reactor in PPC configuration.

Hence the NTP process can lead to the formation of a complex gaseous product distribution. At that stage the design of the catalyst plays a key role to improve CO$_2$ selectivity. Indeed the catalyst should be able to transform all the hazardous species into CO$_2$ taking advantage of active oxygen species from ozone decomposition. Hence once more the catalyst should exhibit high performances in ozone decomposition. Comparing to ozonation reactions where the plasma plays only the role of ozone supplier (ozoner), in PPC, plasma processes alter the gas composition that is fed to the catalyst in a complex manner. In a previous study A. Gervasini et al. investigated the role of the plasma as ozoner and in PPC configuration for the abatement of various VOCs [64]. It resulted that plasma driven catalysis was more efficient than gaseous ozonation for waste gas treatment due to an “ionizing effect”. It was put forwards that plasma could decompose or shatter the organics arranging molecules to be more easily destroyed by the catalyst. Anyway some additional works have to be carried out to ascertain such assumptions.

5.1. Current Applications of MnO$_x$ Catalysts in PPC Systems for Toluene Abatement

5.1.1. The Characteristics of MnO$_x$ in PPC

This part reviewed the performances of post-plasma catalysis towards toluene abatement focusing in particular on the characteristics of MnO$_x$ used as catalyst downstream the plasma reactor. Two Tables have been included in this part for ease of reading. Table 4 compiles information on the synthesis and physico-chemical properties of the catalysts while Table 5 includes the salient parameters generally considered to play a role in the performances for toluene removal in PPC. From a close look at Table 4 it is found that the catalytic formulations, when considering homemade catalysts, include bulk MnO$_x$ as single transition metal (TM) oxide [65,66] or as manganese phosphate Mn–O–P [67] or more usually in a combination with another TM (Cu [65,68–71], Co [66,72], Fe [68,73,74]) with the possible use of Ag as additive [75]. The active phase can be dispersed on a support such as γ-Al$_2$O$_3$, AC (activated carbon) [74], Ni foam [76] and ZSM-5 [72].

Bulk MnO$_x$ were prepared by the conventional precipitation method at pH 9–10 using Mn(II) nitrate as precursor. L. Ye et al. [66] obtained a mixture of Mn$_2$O$_3$ and of the metastable Mn$_5$O$_8$ with a specific surface area close to 28 m$^2$/g after calcination at 400 °C. Quoc An et al. [65] reported the preparation of bulk α-MnO$_2$ (OMS-2) by the redox method performed at 100 °C for 24 h at pH 1.2 using KMnO$_4$ and MnSO$_4$ as Mn precursors in hydrothermal conditions. Magureanu et al. reported the synthesis of manganese phosphate [67]. Three amorphous Mn–O–P catalysts with Mn/P ratios of 1:1.5 (Mn-1), 1:0.04 (Mn-2) and 1:1 (Mn-3) were prepared from the reaction of MnO$_2$ with concentrated H$_3$PO$_4$ in aqueous/aminooalcohol medium via hydrothermal treatment (Mn-1) but under microwave conditions (Mn-2; Mn-3) using structure directing agents. The final catalysts were obtained after calcination at 550 °C. The increase of Mn loading led to an increase in specific surface area (4.5, 20 and 85 m$^2$/g for Mn-1, Mn-2 and Mn-3, respectively) accompanied with a change in the pore size distribution from microporous to mesoporous. The XPS Mn AOS showed values less than 4 due to Mn reduction in the presence of the template.

As MnO$_x$ exhibit many structures the characterization of the catalyst can be very tricky when dispersed on a support. The parameters which are the most relevant to affect the structure and dispersion are the nature of the Mn precursor, the mode of impregnation, the temperature of calcination, the nature of the support and the Mn content. As shown in Table 4, the MnO$_x$/$γ$-Al$_2$O$_3$ have all been prepared via wetness impregnation of Al$_2$O$_3$ with manganese nitrate and calcined at temperature in the range 350–400 °C with Mn amount ranging from 7 to 10 wt % [66,74,77]. It has been found that the
nitrate precursor leads to mainly β-MnO$_2$ for a Mn loading of 10 wt % over γ-Al$_2$O$_3$ at a calcination temperature of 400 °C for 4 h [78]. However decreasing the temperature of calcination is expected to increase the dispersion and change the Mn AOS.

Manganese (Mn: 3 wt %) was also dispersed by wet impregnation using manganese (II) acetate as Mn precursor on an activated carbon (AC) developing very high surface area (1308 m$^2$/g) [74]. The MnO/AC catalyst was obtained after calcination at 300 °C in N$_2$ for 2 h. The low Mn content, the counter-anion nature of the Mn precursor as well as the conditions of calcination ensured a good Mn dispersion combined to a low Mn AOS. Mn$_2$O$_3$ deposited on nickel foam was reported by H. Huang et al. [76]. The Ni foam was a special support having a thin and porous structure enabling the pressure drop in the reactor to be greatly reduced. The formation of Mn$_2$O$_3$ resulted here from a calcination of the Mn nitrate dispersed on Ni foam at a temperature of 600 °C.

Although Ag-Mn/HZSM5 showed good activity in the ozonation of toluene, low cost Ag-free multi-component catalysts were investigated to increase the performances. As previously noticed, a second transition metal (TM such as Cu, Fe and Co) can be integrated in combination with Mn. Among the three TM oxides, Fe$_2$O$_3$ and Co$_3$O$_4$ are p-type metal oxides recognized for having high activity in ozone decomposition by opposition to CuO which is a n-type oxide [39]. However mixing Cu with Mn could lead to hopcalite catalysts recognized as efficient catalysts in O$_3$ removal [79] and CO oxidation at room temperature [80]. The occurrence of the two redox couples Cu$^{2+}$/Cu$^+$ and Mn$^{4+}$/Mn$^{3+}$ in the solid was believed to play a role in these catalytic reaction [81]. Additionally, the Cu–Mn–O system was remarkably active in toluene oxidation [8,82–89]. Beside, enhanced ozone decomposition over Fe–Mn oxides was explained by a lower MnO$_2$ crystallite mean size, a more defective structure and improved textural properties [90].

Quoc An et al. [65] reported the dispersion of copper (5 wt %, 10 wt % and 15 wt %) on α-MnO$_2$ using wetness impregnation method with nitrate Cu precursor followed by a calcination at 500 °C for 4 h. However no physico-chemical characterizations can help to the comprehension of the structure of these catalysts. Ye et al. reported the synthesis of Co–Mn oxides (Co/Mn atomic ratio of 1:6, 1:1 and 6:1) using the co-precipitation at pH 9–10 using Mn and Co nitrate precursors [66]. The calcination step was performed at 400 °C for 2 h. XRD analysis revealed Mn$_3$O$_4$, Co$_3$Mn$_3$O$_4$/Co$_3$O$_4$ and Co$_3$O$_4$ for the three increasing Co/Mn ratios, respectively. Hence the Co/Mn ratio of 1.0 allowed a good mixing of Mn and Co in the presence of segregated oxides. Textural properties were improved for the stoichiometric and Co rich catalyst allowing to double the specific surface area in comparison with the MnO$_x$ reference catalyst. Additionally, the XPS Mn AOS increased when incorporating Co in line with larger number empty d-states and greater reducibility (electron accepting nature) of the active center.

Recently, Y. Huang reported the synthesis of 10 wt % of CoMnO$_x$ and CeMnO$_x$ (M/Mn = 1; M = Co, Ce) active phases supported on ZSM-5 and of a reference MnO$_x$/ZSM-5 catalyst [72]. The textural properties of the porous support ZSM-5 were the following: BET surface area of 306 m$^2$/g and average pore size of 9.1 nm. These catalysts resulted from a coprecipitation at pH 9–10 using nitrate precursors followed by a calcination step at 400 °C for 5 h. The reference MnO$_x$/ZSM-5 revealed a complex mixture of Mn$_3$O$_4$, Mn$_2$O$_3$ and MnO$_2$. The Co-based catalyst exhibited the mixed Co$_3$Mn$_3$O$_4$ phase in accordance with Ye et al. [66]. By opposition only single oxides such as Ce$_2$O$_3$, MnO$_2$, and Mn$_3$O$_4$ were observed on the Ce-containing catalyst.
Table 4. The characteristics of Mn oxides in PPC.

| Exp. | Catalyst | The Shape of Catalyst | The State of Catalyst | The Support | The Nature of Catalyst | Structure(s) (XRD) | The Synthesis Method/Commercial Company | \( \text{S}_{BET} \) (m\(^2\)/g) | \( D_p \) (nm) | Added Characterizations | Reference |
|------|----------|-----------------------|-----------------------|-------------|------------------------|-------------------|----------------------------------------|---------------------------------|----------|------------------------|-----------|
| 1    | Cu–Mn/\( \text{Al}_2\text{O}_3 \) | Powder | Supported | \( \text{Al}_2\text{O}_3 \) | Cu-Mn | - | Heraeus, Hanau, Germany | - | - | - | [70] |
|      | (a) N 150 (MnO\(_2\)–Fe\(_2\)O\(_3\)) | Pellet | Bulk | - | 60 wt % Fe\(_2\)O\(_3\) & 40 wt % MnO\(_2\) | MnO\(_2\) | Sud-Chemie (Munchen, Germany) | 219 | - | - | |
| 2    | MnO\(_2\)/\( \gamma \)-\( \text{Al}_2\text{O}_3 \) | Powder | Supported | \( \gamma \)-\( \text{Al}_2\text{O}_3 \) | 9 wt % MnO\(_2\) | MnO\(_2\) | Incipient wetness impregnation, Precursor: Mn nitrate, calcined at 350 °C for 2 h under 100 mL/min air | 169 | - | - | [74] |
|      | (c) MnO/AC | Powder | Supported | AC \(_2\) | 3 wt % MnO\(_2\) | - | Wet impregnation, Precursor: Mn acetate, calcined at 300 °C for 2 h under N\(_2\) | 1024 | - | - | |
| 3    | (a) Mn-1 (Mn–P–O) | - | - | Mn–P–O | Amorphous phase | Hydrothermal: MnO\(_2\) with H\(_3\)PO\(_4\) (85 wt %) (Mn:P 1:1.5) in 50 mL distilled water + dimethylaminoalcohol, 170 °C for 48 h | 4.5 | - | - | XPS: Mn 2p\(_{3/2}\)/ oxidation state of Mn < 4; P 2p\(_{3/2}\)/ inorganic phosphates | [67] |
|      | (b) Mn-2 (Mn–P–O) | Powder | Bulk | Mn–P–O | Amorphous phase | Hydrothermal treatment under microwaves: starting gel: 1.00 P: 0.04 Mn: 0.48 HDTMABr: 0.48 TMAOH: 174.00 H\(_2\)O, 60 °C (1 h), 80 °C (1 h), and 300 °C (3 h) then calcination at 550 °C | 21 | 1.1 | - | |
|      | (c) Mn-3 (M–P–O) | Powder | Bulk | Mn–P–O | Amorphous phase | Starting gel: 1.00 P: 1.00 Mn: 0.48 HDTMABr: 0.48 TMAOH: 174.00 H\(_2\)O, same operating mode than above | 85 | 3.4, 50 | - | |
| 4    | CuMn/\( \text{TiO}_2 \) | Pellets | Supported | \( \text{TiO}_2 \) | 3% Cu, 6.8% MnO\(_2\) | - | Heraeus, Hanau, Germany | 50 | - | - | [71] |
| 5    | MnO\(_2\)/\( \text{Al}_2\text{O}_3 \) | Pellets | Supported | \( \text{Al}_2\text{O}_3 \) \(_5\) | 7 wt % MnO\(_2\) | - | Wetness impregnation Precursor: Mn nitrate, calcined at 400 °C | - | - | - | [77] |
| 6    | MnO\(_2\)/Ni foam | Foam | Supported | Ni foam | MnO\(_2\) | MnO\(_3\) | Impregnation Precursor: Mn nitrate, calcined at 600 °C | 10.8 | - | - | XRD: before 400 °C, ultra-fine or amorphous features of phase. After 500 °C, MnO\(_3\) | [76] |
|      | (a) Cu–Mn/\( \text{TiO}_2 \) (a) | Pellet (1.5 mm) | Supported | \( \text{TiO}_2 \) | CuO (3 wt %) MnO\(_2\) (6.8 wt %) | - | Heraeus Hanau, Germany | 32 | - | - | |
|      | (b) Cu–Mn/\( \text{TiO}_2 \) (b) | Pellet (1.5 mm) | Supported | \( \text{TiO}_2 \) | CuO (3 wt %) MnO\(_2\) (6.8 wt %) | - | Heraeus Hanau, Germany | 50 | - | - | |
|      | (c) Fe\(_2\)O\(_3\)-MnO\(_2\) (N 150) | Pellet (6 mm) | Bulk | >40 wt % Fe\(_2\)O\(_3\) >25 wt % MnO\(_2\) | - | Süd-Chemie (Munchen, Germany) | 100 | - | - | [68] |
|      | (d) CuO-MnO\(_2\) (N 140) | Pellet (5 mm) | Bulk | >15 wt % CuO >25 wt % MnO\(_2\) | - | Süd-Chemie (Munchen, Germany) | 100 | - | - | |
| Exp. | Catalyst | The Shape of Catalyst | The State of Catalyst | The Support | The Nature of Catalyst | Structure(s) (XRD) | The Synthesis Method/Commercial Company | \( S_{BET} \) \((m^2/g)\) | \( D_p \) \((\text{nm})\) | Added Characterizations | Reference |
|------|----------|-----------------------|-----------------------|-------------|-----------------------|------------------|----------------------------------------|----------------|------------------|----------------------------------------|-----------|
| 8    | Fe\(_2\)O\(_3\)-MnO\(_2\) | Honeycomb | Bulk | - | 60 wt% Fe\(_2\)O\(_3\), 30 wt% MnO\(_2\) | - | Süd-Chemie (Japan) | - | - | - | [73] |
| 9    | (a) MnO\(_2\)/Aluminum honeycomb | Honeycomb | Supported | Aluminum honeycomb | MnO\(_2\) | - | Honeycle ZA (Nichias Corporation) | - | - | - | [69] |
|      | (b) MnO\(_2\)-CuO | Pellet (4-6 mesh) | Bulk | - | MnO\(_2\)-CuO | - | Molecular (Molecular Products Limited) | 20-30 | - | - | |
|      | (a) OMS-2 | Powder | - | 5 wt% MnO\(_2\) | - | Hydrothermal treatment, Redox method, Precursors: KMnO\(_4\) + MnSO\(_4\) | - | - | - | [65,91] |
|      | (b) Cu-OMS-2 | Supported | 10 wt% Cu | - | Wetness impregnation, Precursor: Cu(NO\(_3\))\(_2\) | - | - | - | |
|      | (c) Cu-OMS-2 | Supported | 15 wt% Cu | - | Calcined at 500 \(^\circ\)C for 4 h | - | - | - | |
| 10   | Ag-Mn-O | Powder | Bulk | 10 wt% Ag-MnO\(_x\) Mn\(_3\)O\(_4\) + Ag | Ag-Mn-O: Co-precipitation, pH 10, Precursors: Mn(NO\(_3\))\(_2\) + AgNO\(_3\) | - | - | - | [75] |
|      | (a) MnO\(_x\) | Powder | Bulk | MnO\(_x\) | Mn\(_3\)O\(_4\) + Mn\(_5\)O\(_8\) | Precipitation, pH 9–10, then calcined at 400 \(^\circ\)C for 2 h in air | 27.9 | - | - | XPS: lattice oxygen 53.1% | [66] |
| 12   | (b) Co\(_3\)O\(_4\)-MnO\(_2\) | Powder | Bulk | 1:6 = Ce:Mn | Mn\(_3\)O\(_4\) | Coprecipitation at pH 9–10, Precursor: Mn and Co nitrates calcined at 400 \(^\circ\)C for 2 h under air. | 29.5 | - | - | XPS: lattice oxygen 56.2% | |
|      | (c) CeMnO\(_x\) | Supported | 1:1 = Ce:Mn | Co\(_3\)Mn\(_3\)O\(_4\) + Co\(_3\)O\(_4\) | - | - | - | |
|      | (d) Co\(_3\)O\(_4\)-MnO\(_2\) | Supported | 6:1 = Ce:Mn | Co\(_3\)O\(_4\) | - | - | - | |
| 13   | (a) MnO\(_x\)/ZSM-5 | Powder | Supported | ZSM-5 | 10 wt% MnO\(_x\) Mn\(_3\)O\(_4\), and Mn\(_3\)O\(_4\) | Precipitation, pH 9–10, calcinated at 400 \(^\circ\)C for 2 h in under air. Then wet impregnation with ZSM-5, calcinated at 400 \(^\circ\)C for 5 h | 290.7 | 3.4 | - | XPS: lattice O at 532.9 eV: 55.2% | [72] |
|      | (b) CoMnO\(_x\)/ZSM-5 | Powder | Supported | ZSM-5 | 10 wt% Co\(_3\)Mn\(_3\)O\(_4\) (Co/Mn = 1) | Co\(_3\)Mn\(_3\)O\(_4\) | Coprecipitation. Same experimental procedure than above | 302.8 | 2.9 | - | XPS: lattice O at 532.9 eV: 59.2% | |
|      | (c) CeMnO\(_x\)/ZSM-5 | Powder | Supported | ZSM-5 | 10 wt% CeMnO\(_x\) (Ce/Mn = 1) | CeO\(_2\), Ce\(_2\)O\(_3\), Mn\(_3\)O\(_4\) | - | - | - | XPS: lattice O at 532.9 eV: 58.3% | |

1 Pore diameter; 2 Activated carbon; 3 Hexadecyltrimethylammonium bromide; 4 Tetramethylammonium hydroxide; 5 Al\(_2\)O\(_3\): diameter of granules being 3–4 mm and total surface area being 180 m\(^2\)/g, 6 Diameter: 15 mm, length: 75 mm, 800 cells per inch; 7 OMS-2: cryptomelane type manganese octahedral molecular sieve.
Table 5. Overview on toluene removal with MnO<sub>x</sub>-based catalysts in PPC.

| Exp. | Discharge Type (NTP Reactor) | Catalyst (weight/g) | Configuration | Carrier Gas Flow Rate (mL/min) | Toluene (ppm) | RH (%) | Inlet Ozone/Inlet Toluene | GHSV (mL·g<sup>−1</sup>·h<sup>−1</sup>) | MRE<sup>1</sup> (%) | ED<sup>2</sup> (J/L) | EY<sup>3</sup> (g/kWh) | ScO<sub>2</sub>/ScO<sub>3</sub><sup>3</sup> (%) | Y<sub>CO2</sub> (%) | By-Products CB<sup>4</sup> | Reference |
|------|-----------------------------|---------------------|---------------|--------------------------------|---------------|-------|--------------------------|------------------|-----------------|-----------------|----------------|-----------------|----------------|------------------|----------|
| 1    | Positive Corona discharge (pin-plate) | Cu–Mn/Al<sub>2</sub>O<sub>3</sub> (-) | PPC | Air 133,600 | 45 | - | 60 | 1.3 | - | 22.8 | 18.7 | 8 | - | - | - | [70] |
|      | - | NTP | Air 133,600 | 45 | - | - | - | - | 10.8 | 18.7 | 4 | - | - | - | - |          |
| 2    | Glass beads packed bed DBD (cylindrical reactor) | (a) Mn<sup>1</sup> (Mn–P–O) (0.2) | PPC | Air 315 | 240 | - | - | - | 18,900 | 99.7 | 172 | 18.9 | 30.2 (24.8) | 30.1 | CB: 55%, O<sub>3</sub>: 8 ppm | [74] |
|      | (b) Mn<sup>2</sup> (Mn–P–O) (0.2) | - | - | 30 | - | - | - | - | 72 (28) | 64.8–68.4 | CB: ~100% | - | - | - | - |          |
|      | (c) Mn<sup>3</sup> (Mn–P–O) (0.2) | - | - | 30 | - | - | - | - | 68 (32) | 61.2–64.6 | CB: ~100% | - | - | - | - |          |
| 3    | DBD (Cylindrical reactor) | (a) N 150 (MnO<sub>2</sub>–Fe<sub>2</sub>O<sub>3</sub>) (1) | PPC | Air 300 | 200 | - | 6000 | 30 | 90,000 | 90–95 | 1400 | 1.7–1.8 | 73 (27) | 65.7–69.4 | CB: ~100% | [67] |
|      | (b) MnO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (1) | - | - | - | - | - | - | - | - | - | - | - | - | - | - |          |
| 4    | Positive DC corona discharge (Pin-plate) | CuO:MnO<sub>2</sub>/TiO<sub>2</sub> (10) | PPC | Air 10,000 | 0.5 | - | ~18 | 36 | 60,000 | 78 | 2.5 | 2.1 | - | - | NO<sub>2</sub>: ~550 ppm at 15 J/L | [71] |
|      | NTP | Air 10,000 | 0.5 | 27 | - | - | - | 60,000 | 4 | 2.5 | 0.1 | - | - | - | - |          |
| 5    | BaTiO<sub>3</sub> packed bed DBD (Cylindrical reactor) | 7 wt % MnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (7 mL) | PPC | Air 1000 | 500 | - | - | - | 60,000 | 97<sup>3</sup> | 60 | - | - | CO: ~300 ppm | [77] |
|      | NTP | Air 1000 | 500 | - | - | - | 8600 h<sup>−1</sup> | 74<sup>3</sup> | 60 | - | - | - | - | - | - |          |
| 6    | DBD (wire-plate) | MnO<sub>2</sub>/Ni foam (-) | PPC | Air 200 | 100 | - | 150 | 1.5 | - | 82 | 700 | 1.6 | - | - | Ozone: 9 ppm | [76] |
|      | NTP | - | - | - | - | - | - | - | 44 | 700 | 0.8 | - | - | - | - |          |
| 7    | Positive DC corona discharge (pin-plate) | Cu–Mn/TiO<sub>2</sub>O<sub>2</sub> (15) | PPC | Air 10,000 | 0.5 | 50 | - | 70 | 140 | 40 | 14 | 0.19 | - | - | - | - | [68] |
|      | Cu–Mn/TiO<sub>2</sub>O<sub>2</sub> (15) | - | - | - | - | - | - | - | 40,000 | 63 | 20 | 0.21 | - | - | - | - |          |
|      | Fe<sub>2</sub>O<sub>3</sub>–MnO<sub>2</sub> (N 150) (15) | - | - | - | - | - | - | - | 34 | 15.8 | 0.14 | - | - | - | - |          |
|      | CuO/MnO<sub>2</sub> (N 140) (15) | - | - | - | - | - | - | - | 47 | 0.20 | - | - | - | - | - |          |
Table 5. Cont.

| Exp. | Discharge Type (NTP Reactor) | Catalyst (weight/g) | Configuration | Carrier Gas Flow Rate (mL/min) | Toluene (ppm) | RH (%) | Inlet Ozone (ppm) | Inlet Ozone/Inlet Toluene | MRE ¹ (%) | ED ² (J/L) | EY ³ (g/kWh) | SCO2/SCO1 (%) | YCO2 (%) | By-Products CB ⁴ | Reference |
|------|-----------------------------|---------------------|---------------|--------------------------------|--------------|--------|-----------------|--------------------------|-----------|----------|-------------|--------------|---------|----------------|---------|
| 8    | DBD (tubular reactor)       | Fe₂O₃·MnO (-)       | PPC           | Air 2500                       | 85           | -      | 330             | 3.9                      | 67        | 72       | 10.7        | -            | 13      | Fe₃O₄, MnO₂, MnO, benzoaldehyde, methylbenzoquinone, benzyl alcohol, benzoic acid, and benzyl benzoate | [73]     |
|      |                             |                     |               |                                |              |        |                 |                          |           |          |             |              |         |                |         |
|      |                             | NTP                | Air 2500      | 85                             | -            | -      | -               | -                        | 18        | 72       | 2.8         | -            | 7       | Formic acid, Acetic acid and benzene |         |
| 9    | Multistage reactor          | (a) MnO₂/Aluminum honeycomb (-) | PPC | Air +10,000 | 70 | - | 766 | 10.9 | - | 100 | 16.3 | 16.3 | CO: 48 ppm; N₂O: 18 ppm | [69]     |
|      |                             | (b) MnO₂-CuO (-)    | PPC           | Air +10,000                     | 70           | -      | 766             | 10.9                      | 342       | 2.8      |             |              |         |                |         |
|      |                             |                     |               |                                |              |        |                 |                          |           |          |             |              |         |                |         |
|      |                             | (c) MnO₂/Aluminum honeycomb+MnO₂-CuO (-) | PPC | Air +10,000 | 70 | - | - | - | - | - | - | - | CO: 16 ppm; O₃: 1327 ppm; N₂O: 23 ppm |         |
| 10   | DBD (Cylindrical reactor)   | (a) OMS-2 (0.2)     | PPC           | 80%                            | -            | -      | -               | -                        | -         | -        | -            | -            | -       |                |         |
|      |                             | (b) 5 wt % Cu-OMS-2 (0.2) | PPC | 80% N₂:20% O₃:66.67 | - | - | - | 20,000 | 67 | - | - | - | - |                | [65,91] |
|      |                             | (c) 10 wt % Cu-OMS-2 (0.2) | PPC | 80% N₂:20% O₃:66.67 | - | - | - | 20,000 | 68 | - | - | - | - |                |         |
|      |                             | (d) 15 wt % Cu-OMS-2 (0.2) | PPC | 80% N₂:20% O₃:66.67 | - | - | - | 20,000 | 66 | - | - | - | - |                |         |
| 11   | DBD (tubular reactor)       | Ag-Mn-O (0.2)       | PPC           | Air +498                       | 108          | -      | 650             | 6.0                      | 150,000   | 100      | 60           | 24.3         | -       | N₂O and CO: O₃:650 ppm; N₂O: 363 ppm | [75]     |
|      |                             | NTP                | Air +498      | 108                             | -            | -      | -               | -                        | 150,000   | 60       | 60           | 14.6         | -       |                |         |
Table 5. Cont.

| Exp. | Discharge Type (NTP Reactor) | Catalyst (weight/g) | Configuration | Carrier Gas Flow Rate (mL/min) | Toluene (ppm) | RH (%) | Inlet Ozone (ppm) | Inlet Ozone/Inlet Toluene | GHSV (mL·g⁻¹·h⁻¹) | MRE ¹ (%) | ED ² (J/L) | EY ³ (g/kWh) | S₂CO₂/(S₂CO) (% | Y₂CO₂ (%) | By-Products CH ⁴ | Reference |
|------|-----------------------------|---------------------|---------------|-------------------------------|--------------|--------|------------------|--------------------------|-----------------|-------------|-------------|---------------|---------------|-----------|----------------|---------|
| 12   | DBD (tubular reactor)       | (a) MnOₓ            | PPC           | Air + 500                     | 107          | -      | -                | -                        | 32,233 h⁻¹     | 71          | 21.5        | -            | -            | -         | O₂: 280 ppm N₂O, CO | [66]    |
|      |                             | (b) (1:6) Co₃O₄-MnO₂ |               |                               |              | 580    | 5.4              | 84                      |                 | 32,233 h⁻¹ | 48          | 25.5        | -            | -         | O₂: 180 ppm N₂O, CO |         |
|      |                             | (c) (1:1) Co₃O₄-MnO₂ |               |                               |              | 5.4    | 93               | 28.1                    |                 |             | 83          | 25.0        | -            | -         | O₂: 90 ppm N₂O, CO |         |
|      |                             | (d) (6:1) Co₃O₄-MnO₂ |               |                               |              | 5.4    | 83               |                        |                 |             | 25.0        | -            | -         | O₂: 110 ppm N₂O, CO |         |
| 13   | DBD (tubular reactor)       | (a) MnOₓ/ZSM-5      | PPC           | Air + 1000                    | 107          | -      | -                | -                        | 32,233 h⁻¹     | -24         | 48          | 7.3          | -            | -         | -              | [72]    |
|      |                             | (b) CoMnOₓ/ZSM-5    |               |                               |              | -      | -                | -                        |                 |             | 68          | 3.1          | 50 (8)      | 34         | N₂O, O₃: 370 ppm |         |
|      |                             | (c) CeMnOₓ/ZSM-5    |               |                               |              | -      | -                | -                        |                 |             | 94          | 4.3          | 7.8 (8)     | 73.3       | N₂O, O₃: 200 ppm |         |

¹ MRE: Maximum removal efficiency; ² ED: Energy density; ³ EY: Energy yield; ⁴ Carbon balance; ⁵ PPC and NTP experiments performed at 330 °C; ⁶ Y₂CO₂ (CO + CO₂).
5.1.2. The Performances in Toluene Abatement Using \( \text{MnO}_x \) in PPC

In a first step, the selected variables of the hybrid process related to the experimental conditions of toluene abatement in air were identified. The selected variables were those expected to play a role in the performances of the two-stage plasma-catalyst system towards toluene abatement. The descriptors linked to the performances of the hybrid process in terms of efficiency of the process were also presented. In a second step the effect of these variables on the experimental outcomes (descriptors) was discussed.

Based on data given in the literature the pertinent variables which can play a role have been identified and are related to the NTP reactor (geometry and type of discharge), the (specific) energy density at maximum of toluene conversion, nature of the gaseous effluent, type, shape and weight of the catalyst, GHSV, carbon balance and identified gaseous by-products. Information on the nature of the gaseous effluent includes variables such as kind of the carrier gas, flow rate, inlet toluene concentration and inlet ozone concentration injected into the catalytic reactor. When possible the same type of information is delivered in similar NTP experiments for easier comparison. Information on PPC performances towards toluene abatement includes the following descriptors: toluene removal efficiency associated with the energy put per plasma liter, \( \text{CO}_2/\text{CO} \) selectivity (\( S_{\text{CO}_2}/S_{\text{CO}} \)), \( \text{CO}_2 \) yields (\( Y_{\text{CO}_2} \)) and energy yield (EY).

Table 5 compiles the salient information on the application of post-plasma catalysis using MnOx-based type catalysts for toluene abatement in air in accordance with the above paragraphs.

First of all, the types of discharges were briefly discussed based on the information given in Table 6. Two discharge types were commonly used, such as DBDs (dielectric barrier discharges) with tubular/cylindrical configuration of the NTP reactor [65–67, 72–75] or packed bed DBDs (packing material: glass [69] or BaTiO\(_3\) [77]) and positive DC (direct current) corona discharge with pin-to-plate configuration [68, 70, 71].

The most important characteristic of DBDs is that non-equilibrium plasma conditions can be provided in a much simple way. At about atmospheric pressure electrical breakdown occurs in many independent thin current filaments due to the presence of the dielectric. The reactors are generally of tubular/cylindrical forms. These short-lived micro-discharges have properties of transient high pressure glow discharges with electron energies ideally suited for exciting or dissociating background gas atoms and molecules. The flexibility of the NTP reactor with respect to geometrical configuration, operating medium and operating parameters is well recognized. Efficient available low cost power supplies and additionally easy scaling up for laboratory experiments to large industrials installations taking into account the drawback of high pressure drop make DBDs attractive [92].

The presence of a packing material in the reactor leads to a packed bed DBD reactor. The promising utilization of such reactor is that the dynamics of plasma discharges are predominantly influenced by the properties of the packing material in terms of its dielectric constant. Increasing the dielectric constant enhances the electric field in the vicinity of pellets contact points [93]. Consequently the dielectric constant of a packing material determines the amount of energy that the reactor can store during a single discharge [94].

A corona discharge is an electrical discharge brought on by the ionization of a fluid such as air surrounding a conductor that is electrically charged. Corona discharges take place at or near atmospheric pressure using relatively low power. Corona discharge is a self-sustained discharge which occurs in sharply non-uniform electric field, typically operated in needle-to-plate or wire-to-plate configuration. Corona discharge mainly produces burst pulses corona, then streamer corona, glow corona and spark discharge as the applied voltage increases. Once the streamer corona discharge is formed in a closed chamber, a low temperature dense plasma environment can be generated over a large volume [92]. Hence, corona discharge is another approach that can avoid spark formation in streamer channels. The streamers propagation affects the NTP reactions like ionization, excitation, dissociation for VOCs abatement [20].
The experiments listed in Table 5 are all carried out at room temperature and atmospheric pressure except Exp.5 for which the catalyst has been heated at 330 °C. Dry air is used as carrier gas if nothing is mentioned otherwise. The total flow rate and the toluene concentration range from 67 to 133,600 mL-min⁻¹ and 0.5 ppmv (indoor pollution) to 800 ppmv (range of industrial emission), respectively. The GHSV ranges from about 19,000 to 150,000 mL·g⁻¹·h⁻¹. These extreme values show the wide range of plasma-catalysis application in terms of volume and VOC concentration for treating a waste gas containing toluene. However it has to be mentioned that initial toluene concentration is close to 100 ppmv in most reported studies. The concentrations of ozone at the inlet of the catalytic reactor vary tremendously from 70 to 6000 ppmv depending on the nature of the NTP and to the inlet concentration of toluene. To get read of the influence of the initial toluene concentration the inlet ozone/inlet toluene molar ratio has been given. The values exhibited in Table 5 range herein from 1.3 to 200.

To evaluate the efficiency of the NTP reactors in terms of geometry-discharge, the toluene conversion has been plotted as a function of ED as shown in Figure 7. With that respect the characteristics of the NTP reactors have been recalled in terms of geometry and discharge and initial inlet toluene concentration \([C_{7}H_{8}]_0\) as shown in Table 6. The gap between the 2 electrodes ranges from 2 to 10 mm. The reactor volume \(V_R\) ranges from 8.5 to 250 mL and the corresponding residence time \((t_r)\) ranges from 1.4 to 2.5 s except in Exp.1 for which the residence time is very short \((4.5 \times 10^{-4} \text{ s})\). The toluene removal efficiencies using corona discharge (Exp.1 and Exp.4) are relatively low compared to those of DBD (Exp.5 and Exp.11) for similar energy density. However this observation has to be tempered as the inlet toluene concentrations associated to corona discharge are rather low (45–0.5 ppmv) compared to those for DBD (100–500 ppmv). However among DBD reactors it is found that Exp.3 and Exp.5 lead to similar toluene conversion but with an energy density ratio \(ED(\text{Exp.5})/ED(\text{Exp.3})\) of about 24 noticeably higher than the inlet toluene concentration ratio of 2.5. The \(\text{BaTiO}_3\) packed bed DBD reactor (Exp.5) exhibited herein the highest toluene removal efficiency (74%) at the lowest ED (60 J/L) thanks to the presence of \(\text{BaTiO}_3\) which enhances the average electric field and to the temperature of the catalytic reactor at 330 °C. In this set of experiments, the effect of the residence time \(t_r\) in the NTP reactor is difficult to apprehend as the range of values is too narrow to allow a pertinent discrimination.

![Figure 7. Toluene removal efficiency as a function of ED for NTP reactor. The figures mentioned inside the graph refer to the number of the experiment (see Tables 4 and 5).](image-url)
Table 6. Characteristics of the NTP reactors.

| Exp.  | Characteristics | C<sub>tol</sub> (ppm v) | Gap (mm) | V<sub>R</sub> 1/L (tr 2/s) |
|-------|-----------------|--------------------------|----------|---------------------------|
| 1 [70] | Positive DC Corona discharge (pin-plate) | 45 | 9 | 72 (4.5 x 10⁻⁴) |
| 2 [74] | Glass beads packed bed DBD (cylindrical reactor) | 240 | 6 | 13.2 (2.5) |
| 3 [67] | DBD (cylindrical reactor) | 200 | 2 | 8.5 (1.7) |
| 4 [71] | Positive DC Corona (pin-plate) | 0.5 | 20 | 250 (1.5) |
| 5 [77] | BaTiO<sub>3</sub> packed bed DBD (cylindrical reactor) | 500 | - | - |
| 6 [76] | DBD (wire-plate) | 100 | - | - |
| 7 [68] | Positive DC corona discharge (pin-plate) | 0.5 | - | 250 (1.5) |

1 Reactor volume; 2 Residence time.

In order to investigate the benefit of adding a catalytic reactor downstream the NTP, toluene removal efficiency from PPC experiments has been plotted in Figure 8 as a function of toluene removal efficiency from separated NTP experiments. It is remarkable that all the points lie above the bisector showing the beneficial role of integrating a MnO<sub>x</sub>-based catalyst downstream the NTP reactor. All the points deviate from the bisector; all the more the catalyst plays a beneficial role when integrated in the PPC process all other things being otherwise equal. The most improvement is obtained in Exp.12 with a decreasing beneficial effect, depending on the nature of the catalyst, as follows: Exp.12c > Exp.12b > Exp.12d > Exp.12a. Hence, in this case, a direct comparison of the catalyst performances can be undertaken. It is thus found a beneficial role of integrating Co to Mn in equal amount (Exp.12c). The presence of Co<sub>3</sub>Mn<sub>3</sub>O<sub>4</sub> along with a segregated Co<sub>3</sub>O<sub>4</sub> spinel phase, promotes toluene removal efficiency compared to the reference MnO<sub>x</sub> solid. Similarly the catalysts in Exp.13 can be ranked by decreasing activity: Exp.13b > Exp.13c > Exp.13a or more clearly: 13b (10 wt % CoMnO<sub>x</sub>/ZSM-5, Co/Mn = 1) > 13c (10 wt % CeMnO<sub>x</sub>/ZSM-5, Ce/Mn = 1) > 13a (10 wt % MnO<sub>x</sub>/ZSM-5). Thus, good performances for toluene abatement can be obtained over CoMnO<sub>x</sub>, as bulk or dispersed on the ZMS-5 support. It was claimed that the mixture of Co<sub>3</sub>Mn<sub>3</sub>O<sub>4</sub>, MnO<sub>2</sub> and Mn<sub>3</sub>O<sub>4</sub> phases in enhancing structural defects significantly promotes the toluene abatement reaction. Likewise, the different catalysts investigated in Exp.2 can be ranked as follows: MnO/AC (Exp.2c) > MnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (Exp.2b) > MnO<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub> (Exp.2a). This study underlined the important role of the support as the activity of the catalyst depends mainly on the support. When regarding MnO/AC, the low Mn content, the high surface area of the support, the nature of the counter-anion of the Mn precursor (OAc) as well as the conditions of calcination (in N<sub>2</sub> at 300 °C) ensured a good Mn dispersion combined to a low Mn AOS. These two properties are responsible for toluene oxidation into CO<sub>2</sub> in an effective way. A series of CuO/MnO<sub>2</sub> catalysts with different Cu loadings were synthesized by the incipient wetness impregnation method in Exp.10. Higher activity of 10 wt% CuO/MnO<sub>2</sub> can be attributed to a better dispersion of the active phase. However caution must be exercised in the interpretation of these results due to lacking key information such as the [O<sub>3</sub>]/[Toluene]<sub>0</sub> ratio defined above as well as the CO<sub>2</sub> yield. Additionally, the 100% toluene conversion achieved over Ag–Mn–O (Exp.11) has also to be highlighted but however the high silver content (10 wt %) can be a drawback.
To achieve a better insight in terms of efficiency of the process, which means the total oxidation of toluene into CO₂ and H₂O, the toluene conversion into CO₂ (CO₂ yield) has been drawn as a function of toluene removal efficiency (see Figure 9). This representation highlights more accurately the efficiency of the PPC process as the toluene removal efficiency takes only account for the amount of toluene removed making no distinction between CO₂ and other possible organic by-products. The representation allows to distinguish two sets of PPC processes: set 1 delimited by the blue circle and set 2 consisting in the remaining ones. The set 1 includes the most efficient PPC configurations 13b, 3a, and 13a, namely (DBD; CoMnOₓ/ZSM5), (DBD; Mn–P–O, Mn-1), and (DBD; CeMnOₓ/ZSM5). Set 2 includes the PPC configurations 2c, 9c, 9a, 9b, 2b, 2a and 13a, namely (Glass packed bed DBD; MnO/AC), (multistage DBD; MnO₂-CuO + MnO₂/Aluminum honeycomb), (multistage DBD; MnO₂/Aluminum honeycomb), (multistage DBD; MnO₂-CuO), (Glass packed bed DBD; MnO₂/γ-Al₂O₃), (Glass packed bed DBD; Ni50 (MnO₂-Fe₂O₃)) and (DBD; MnOₓ/ZSM-5). A direct comparison is unfortunately restrictive as it is not possible to get the information in terms in CO₂ yield from numerous papers as in many papers mineralization rate (or CO₂ selectivity) is given.

Improving the global efficiency of the PPC process requires that the NTP works at low ED while minimizing the formation of undesirable by-products. CO₂ yield as a function of reactor energy density given shown in Figure 10 emphasizes the efficiency of the CoMnOₓ/ZSM5 (Exp.13b) and CeMnOₓ/ZSM-5 (Exp.13a) catalysts located downstream of a DBD reactor to convert toluene into CO₂ at low ED. Additionally, as a good performance in terms of CO₂ yield is also achieved with a pulsed DBD reactor in combination with the manganese phosphate catalyst [67] a quite high ED results in an energy yield of 1.84 g/kWh (see below) with a factor of about 2 lower than that of Exp.13 of 4.2 g/kWh. When considering PPC, the ratio \( R = [O_3]_{in}/[Tol]_{0} \) ([O₃]: concentration of ozone injected in the catalytic reactor; [Tol]₀: concentration of toluene injected in the NTP reactor) is a key parameter as the O₃ may be in a sufficient amount enabling total mineralization of toluene. Considering the mode of decomposition of O₃ over MnOₓ the reaction of toluene abatement by O₃ can be formally written as follows:

\[
C_7H_8 + 18O_3 \rightarrow 7CO_2 + 4H_2O + 18O_2
\] (15)
The fundamental assumption is that each O$_3$ is converted to a single O radical and that toluene is oxidized only by active oxygen species on the surface of the catalyst. However, at low toluene conversion, active oxygen species mainly degrade the plasma non processed toluene while at higher conversion they are mainly implied in the degradation of the gaseous carbonaceous by-products produced in the course of the NTP treatment whose relative distribution is dependent on the nature of the NTP all things being equal.

$R$ has been represented as a function of toluene conversion into CO$_2$ in Figure 11. Despite the very limited set of values it is observed a clear linear dependence of $R$ as a function of toluene conversion into CO$_2$. This shows the efficiency of these catalysts to decompose ozone when the value of $R$ is higher than 18.

![Figure 9. CO$_2$ yield as a function of Toluene removal efficiency in PPC.](image9.png)

![Figure 10. CO$_2$ yield as a function of energy density in PPC.](image10.png)
Secondly, adsorbed degradation products may also be oxidized efficiently due to high pressure and room temperature in combination with manganese phosphate catalyst (Mn-I) placed downstream. 

CO and N$_2$O can be detected as by-products. Benzaldehyde, formic acid, methylbenzoquinone, benzyl alcohol, benzoic acid, and benzyl benzoate constitute some examples of organic by-products which can be identified as intermediates on the surface in the reaction process. These by-products derived from the partial oxidation of toluene. The detection of such ad-species in a strong interaction with the catalyst can cause a decrease in activity of the catalyst in the course of the reaction and leads to a decrease of the carbon mass balance. In the experiments given here no O$_3$ is detected at the catalytic reactor confirming the efficiency of the catalysts in O$_3$ decomposition. 

The efficiency of the process has also been evaluated in terms of energy yield expressed in grams of toluene removed by kWh (g/kWh). The histogram given in Figure 12 sums up the results. The ranking of PPC configurations in terms of decreasing energy efficiency for the most efficient configurations is: Exp.12 (22–28) ≈ Exp.11 (24) > Exp.2 (14–19) > Exp.8 (11) > Exp.1 (8) > Exp.13 (3–4) ≈ Exp.9 (1.7–3.1). The energy yields can vary from a factor 20 considering all the configurations.

The stability of the Mn oxide-based catalysts in the reactive gaseous mixture over time was investigated in few PPC processes. Durability test carried out for 43 h showed good stability for Ag-Mn–O (Exp.11) [75] in terms of either CO$_2$ generation, toluene decomposition and ozone degradation. The strong interaction between metallic Ag and Mn$_3$O$_4$ was postulated to promote the oxidation of intermediate compounds at room temperature. Durme et al. [71] also reported that no deactivation of the commercial catalyst Cu-Mn/TiO$_2$ (10 g, 3 wt % Cu, 6.8 wt % MnO$_2$) was observed for 48 h on stream in PPC configuration at room temperature. The reasons were ascribed to two points. Firstly, no significant amounts of active sites were blocked due to low amount of toluene (0.5 ppmv). Secondly, adsorbed degradation products may also be oxidized efficiently due to high ozone decomposition ability of Cu–Mn/TiO$_2$. Therefore, the high ozone decomposition ability of metal-MnO$_2$ (e.g., Ag, Cu) can prevent catalyst deactivation.
6. Conclusions and Outlook

The desire to increase the efficiency of toluene depollution processes by reducing their energy consumption while simultaneously reducing toluene emission to meet the more stringent limits has motivated considerable research in advanced toluene oxidation processes. Among them, PPC is a promising method which takes full advantages of the two technologies: high selectivity from catalysis and the easy operation from NTP allowing the hybrid system to work at ambient temperature. A greater CO\textsubscript{2} selectivity can be achieved due to the production of active oxygen produced from plasma generated O\textsubscript{3} catalytic decomposition to remove the by-products. Recent progress in the research on noble metal-free catalysts has highlighted the importance of manganese oxide-based formulations to be involved in such a process. This is because manganese oxides are low-cost, easily synthesized, environmentally friendly and efficient catalysts in ozone decomposition and toluene ozonation.

The best catalytic formulations include Ag–Mn–O, amorphous manganese phosphate, 10 wt % (CoMnO\textsubscript{3})/ZSM-5 and MnO/AC. Besides, Co, Ce and Ag are the most efficient additives to promote O\textsubscript{3} decomposition in interaction with manganese oxide. Furthermore, Co allows achieving good performances in moist air, which opens encouraging perspectives. It has to be mentioned that some Ag has to be introduced in the formulation to promote the desorption of organic ad-species and to ensure a good time-on-stream-stability. In terms of energy yields, the PPC configuration of the DBT tubular reactor with Co\textsubscript{2}(Mn:C = 1:6) catalyst downstream ensures an efficient use of the energy. Despite the promising improvements resulting from several studies about using related Mn-based oxides active phases, there are still open issues to be addressed regarding the design of the catalyst in order to develop an efficient hybrid process. To improve the efficiency of the catalysts many strategies can be pursued, such as external morphology control, doping, optimization of the active Mn related phase with the nature of the support. Interestingly, the effect of the external morphology of MnO\textsubscript{x} which is easily to tune has to be deeply investigated as it may have a significant impact on the density of vacancies, of defects, as well as on the Mn average oxidation state and textural properties of the materials. The role of additives has not been cleared up sufficiently and the effect of other TM oxides has to be investigated in order to minimize CO, NO\textsubscript{x}, N\textsubscript{2}O and possible O\textsubscript{3} as by-products.

Finally, the stability of the-based Mn oxide catalysts in the reactive gaseous mixture over time has to be investigated more deeply. The carbon balance has to be carried out. Although the beneficial cleaning effect of Ag has been evidenced, the decrease of Ag loading has to be performed while...
maintaining satisfactory catalytic performances. In regard the effect of inhibitors such as water as also to be investigated.

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