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Summary

Air quality issues have become a huge concern of environmental legislation as a consequence of growing awareness in our global world. Exhausts, form outdoor sources (various chemical industries, painting and printing industries, cars) as well as from indoor sources, pollute the air with a variety of harmful substances like volatile organic compounds (VOCs) which pose a threat to human health and environment. The complex chemical and physical transformations that these VOCs can undergo in the atmosphere result in effects such as the formation of photochemical smog, secondary aerosols and ozone in the urban areas. They also play a part in the greenhouse effect, the destruction of the stratospheric ozone layer and acid depositions. Moreover, VOCs have been proved to be health hazards due to their potential toxicity, carcinogenicity and mutagenicity. Long exposure to VOCs can lead to a number of human diseases, including cancer and cardiovascular and several other potential diseases. These substances are therefore also classified as priority, toxic pollutants. European legislation has therefore imposed stricter objectives for VOC emissions, including for industrial emissions: VOC emissions must have decreased by 21 and 43% in 2020 for Belgium and France respectively compared with emissions in 2005. Moreover, the 2030 climate plan also provides a reduction of greenhouse gas emissions (of which VOCs form part) by 40% by 2030. The current policy to reduce VOC emissions is to give priority to the total or partial elimination of VOC emissions by removing the VOC source itself. However, if this is not possible for technical reasons, it is necessary to find solutions for the treatment of these emissions by applying new VOC decomposition processes that are adapted to low VOC concentrations and that can achieve complete degradation in an energy-efficient manner without the formation of by-products.

To respond to this industrial problem, this doctoral thesis is focused on the development of a new, innovative treatment method adapted to industrial needs and based on the coupling of existing degradation methods. Conventional techniques used for end-of-pipe treatment of these VOCs are thermal oxidation, catalytic incineration, adsorption, condensation, biofiltration and membrane separation each process having its advantages and limitations. As a cost and energy efficient alternative, the use of non-thermal plasma (NTP) has been recognized to be relevant for the removal of VOCs from dilute atmospheric pressure gas streams. These so-called cold plasmas
have proven to be more efficient than conventional techniques for the treatment of lightly contaminated waste gases, due to the lower energy consumption and its flexibility. The main advantage of NTP is that the supplied energy is used for the acceleration of electrons, instead of heating up the total gas volume. The energetic electrons collide with background molecules leading to the formation of reactive radical species, which in turn react with VOCs. The major drawback of the NTP removal technique is the formation of undesired by-products (e.g. ozone, NOx, aerosols, phosgene and other VOCs), that even increase the overall toxicity of the treated gas stream. In an effort to solve these issues, the combination of NTP and other techniques has been an active area of research since 2000. This thesis is focused in particular on linking plasma technology with heterogeneous catalysis (plasma catalysis), for the abatement of trichloroethylene (TCE), a typical chlorinated VOC.

There are two ways to introduce the catalysts into the plasma: in plasma catalysis (IPC) or post plasma catalysis (PPC). Plasma assisted catalysis can obviously improve energy efficiency and suppress unwanted reaction by-products in VOC decomposition. Furthermore, the development of a suitable catalyst will help to optimize the selectivity into environmentally more friendly end products. By placing the catalyst downstream of the discharge zone (PPC), the catalyst is able to decompose ozone formed in NTP into active oxygen species able to greatly improve the oxidation of both the target VOC and hazardous by-products. In this work, the abatement of TCE in a post plasma catalytic (PPC) system is studied.

This PhD thesis first gives an overview of the air pollutants and their sources. The effect of a poor air quality on human health is summarized and illustrated by a more detailed section on trichloroethylene. Since regulatory initiatives are emerging, the available air cleaning technologies are also summarized. A general overview of the main fundamentals on non-thermal plasma and catalytic oxidation is given separately as introduction for the reader to this promising plasma catalytic system. The main outlines of the fundamentals which governed the plasma catalyst interaction are also discussed. This review is divided in two sections. In the first part, the concept of continuous treatment and sequential treatment is discussed and then compared. In the second part an overview of the literature dealing with only sequential treatment is given. And finally, the influence of critical process parameters on this new technique is summarized.
In order to improve the performance efficiency of a plasma catalytic reactor, one has to understand the effect of the various parameters and choose an appropriate catalytic material depending on the type of the pollutants. Thus, one of the main purpose of this work is to identify the influence of various parameters on the CVOCs removal efficiency and screening for various suitable catalytic materials.

In a first experimental chapter, TCE abatement was investigated in dry air with NTP using a 10-pin-to-plate negative DC corona discharge and CeO$_2$ catalyst placed in downstream. As expected, NTP showed poor CO$_x$ selectivity despite having a high abatement efficiency due to the formation of oxygenated intermediates such as phosgene, DCAC and TCAA, when operated alone. On the other hand, no activity for TCE oxidation over the CeO$_2$ catalyst was observed when solely operating in the examined temperature. In comparison to the total catalytic oxidation and NTP process, PPC was found to be the best process to convert TCE into CO$_2$ with all tested catalyst temperature. A clear synergy was observed in terms of TCE abatement and mineralization. The role of ozone in the plasma catalytic process was investigated and the synergistic reaction of O$_3$ and catalysts was found to be the key point in the process. Additionally, it was found that with the assistance of NTP, CeO$_2$ (at lower catalyst temperature) is only activated enough to selectively react with hazardous polychlorinated by-products (which need less energy to oxidise than TCE) to form the desired product (CO$_2$). Furthermore, a successful long term test (40 h) proved that the combination of plasma with a CeO$_2$ catalyst possesses excellent stability in terms of TCE abatement. These results evident that this plasma catalysis route shows great potential as air pollution control technology for low concentrated VOC air streams.

The final part of this work describes the preparation, characterization and application of cryptomelane type manganese oxides placed downstream from a NTP reactor in the oxidation of TCE. Concerning catalyst preparation, it was observed that it is possible to tailor the shape, crystalline phase and chemical composition of manganese oxide materials by controlling the synthesis conditions, such as through the mode of doping metal (Fe) incorporation. The addition of iron to cryptomelane was performed by 2 different ways: (i) by a co-precipitation (Fe-K-OMS-2: goal is to incorporate Fe in K-OMS-2 structure instead of K or Mn) (ii) by impregnation (Fe/K-OMS-2: goal is to deposit Fe$_x$O$_y$ particles at the surface of K-OMS-2). A reference cryptomelane (K-OMS-2) was also synthesized by a refluxing method at ambient. It was found that regardless of the synthesis route, all three catalysts in PPC
configuration outperformed the NTP alone in total TCE oxidation. The catalysts can be ranked by increasing TCE conversion is as follows: K-OMS-2 < Fe/K-OMS-2 < Fe-K-OMS-2. The superior performance of the Fe-K-OMS-2 materials was attributed to improved textural properties such as high specific surface areas, amorphous state and structural disorder (presence of oxygen vacancies). These characteristics allow facilitating the production of active species from plasma generated ozone and the surface oxygen mobility to promote the degradation of TCE or reaction intermediates into CO₂.
Luchtkwaliteit is een enorme zorg voor de milieuwetgever geworden als een gevolg van een globaal groeiend bewustzijn. Uitlaten, zowel van bronnen buitenhuis (diverse chemische industrieën, schilder- en drukindustrieën, auto’s) als van bronnen binnenhuis, vervuilen de lucht met een verscheidenheid aan schadelijke stoffen zoals vluchtige organische stoffen (VOS) die een bedreiging vormen voor de menselijke gezondheid en het milieu. De complexe chemische en fysische transformaties die deze VOS in de atmosfeer kunnen ondergaan, resulteren in schadelijke effecten zoals de vorming van fotochemische smog, secundaire aerosolen en ozon in de stedelijke gebieden. Ze spelen ook een rol in het broeikaseffect, de vernietiging van de stratosferische ozonlaag en zure deposities. Bovendien is aangetoond dat VOS gevaarlijk zijn voor de gezondheid vanwege hun potentiële toxiciteit, carcinogeniteit en mutageniteit. Lange blootstelling aan VOS kan leiden tot een aantal ziekten bij de mens, waaronder kanker, cardiovasculaire aandoeningen en verschillende andere mogelijke ziekten.


Als respons op dit industriële probleem, is dit proefschrift gericht op de ontwikkeling van een nieuwe, innovatieve behandelmethode die aangepast is aan de industriële behoeften en gebaseerd is op het samenbrengen van bestaande afbraakmethoden. Conventionele technieken die gebruikt worden voor de end-of-pipe behandeling van deze VOS zijn thermische oxidatie, katalytische verbranding, adsorptie, condensatie, biofiltratie en
membraanscheiding waarbij elk proces zijn voordelen en beperkingen heeft. Als een kosten- en energie-efficiënt alternatief wordt het gebruik van niet-thermisch plasma (NTP) erkend voor de verwijdering van VOS uit gasstromen in verdunne atmosferische druk. Deze zogenaamde koude plasma’s zijn efficiënter dan conventionele technieken voor de behandeling van licht verontreinigde afvalgassen, vanwege het lagere energieverbruik en hun flexibiliteit. Het belangrijkste voordeel van NTP is dat de geleverde energie wordt gebruikt voor de versnelling van elektronen, in plaats van het opwarmen van het totale gasvolume. De energetische elektronen botsen met achtergrondmoleculen wat leidt tot de vorming van reactieve radicaaldeeltjes, die op hun beurt reageren met VOS. Het belangrijkste nadeel van de NTP-techniek is de vorming van ongewenste bijproducten (bijvoorbeeld ozon, NOx, aerosols, fosgen en andere VOS), die de totale toxiciteit van de behandelde gasstroom kunnen verhogen. In een poging om deze problemen te lossen, is de combinatie van NTP met andere technieken een actief onderzoeksgebied sinds 2000. Dit proefschrift richt zich in het bijzonder op het samenvoegen van plasmatechnologie met heterogene katalyse (plasmakatalyse) voor de bestrijding van trichloorethyleen (TCE), een typische gechloreerde VOS.

Er zijn twee manieren om de katalysatoren in het plasma te introduceren: in-plasmakatalyse (IPC) of post-plasmakatalyse (PPC). Plasma-geassisteerde katalyse kan de energie-efficiëntie verbeteren en ongewenste reactiebijproducten bij VOS-ontbinding onderdrukken. Bovendien zal de ontwikkeling van een geschikte katalysator bijdragen tot het optimaliseren van de selectiviteit naar milieuvriendelijker eindproducten. Door de katalysator stroomafwaarts van de ontladingszone (PPC) te plaatsen, kan de katalysator ozon, gevormd door gebruik van NTP, afbreken in actieve zuurstofdeeltjes die in staat zijn om de oxidatie van zowel de beoogde VOS als gevaarlijke bijproducten aanzienlijk te verbeteren. In dit werk wordt de reductie van TCE in een post-plasmakatalyse (PPC) systeem bestudeerd.

Deze doctoraatsthesis geeft eerst een overzicht van de luchtverontreinigende stoffen en hun bronnen. Het effect van een slechte luchtkwaliteit op de gezondheid van de mens wordt samengevat en geïllustreerd door een meer gedetailleerd hoofdstuk over trichloorethyleen. Aangezien regelgevingsinitiatieven opduiken, worden ook de beschikbare luchtzuiveringstechnologieën samengevat. Een algemeen overzicht van de belangrijkste zaken over niet-thermisch plasma en katalytische oxidatie wordt afzonderlijk gegeven als inleiding voor de lezer voor deze veelbelovende
plasmakatalyse aanpak. De hoofdlijnen van de fundamenten die de interactie tussen plasma en katalysator regelen, worden ook besproken. Dit overzicht is verdeeld in twee delen. In het eerste deel wordt het concept van continue behandeling en sequentiële behandeling besproken en vervolgens vergeleken. In het tweede deel wordt een overzicht gegeven van de literatuur over alleen sequentiële behandeling. Ten slotte wordt de invloed van de belangrijkste procesparameters op deze nieuwe techniek samengevat.

Om de prestatie-efficiëntie van een plasmakatalyse reactor te verbeteren, moet men het effect van de verschillende parameters begrijpen en een geschikt katalytisch materiaal kiezen, afhankelijk van het type verontreinigende stoffen. Een van de hoofddoelen van dit werk is dus om de invloed van verschillende parameters op de efficiëntie van de verwijdering van VOS te identificeren en om te zoeken naar verschillende geschikte katalytische materialen.

In een eerste experimenteel hoofdstuk werd de TCE-reductie in droge lucht aan de hand van een NTP met een 10-pin-plaat negatieve DC corona-ontlading en een stroomafwaartse CeO₂-katalysator onderzocht. Zoals verwacht vertoonde het gebruik van enkel NTP een lage COₓ-selectiviteit ondanks een hoge reductie-efficiëntie vanwege de vorming van geoxygeerde intermediairen zoals fosgèen, DCAC en TCAA. Aan de andere kant werd er geen TCE-oxidatie over de CeO₂-katalysator waargenomen wanneer enkel deze katalysator gebruikt werd bij een bepaalde temperatuur. In vergelijking met de totale katalytische oxidatie en het NTP-proces bleek PPC het beste proces om TCE om te zetten in CO₂ voor alle geteste katalysatortemperaturen. Er werd een duidelijke synergie waargenomen in termen van TCE-reductie en -mineralisatie. De rol van ozon in het plasma-katalytische proces werd onderzocht en de synergetische reactie van O₃ en katalysatoren bleek het belangrijkste punt in het proces te zijn. Bovendien werd vastgesteld dat met behulp van NTP CeO₂ (bij lagere katalysatortemperatuur) slechts voldoende wordt geactiveerd om selectief te reageren met gevaarlijke polychloor-bijproducten (die minder energie nodig hebben om te oxideren dan TCE) om het gewenste product (CO₂) te vormen. Bovendien bewees een succesvolle langdurige test (40 uur) dat de combinatie van plasma met een CeO₂-katalysator een uitstekende stabiliteit heeft in termen van TCE-reductie. Deze resultaten tonen duidelijk aan dat deze plasmakatalyse-route een groot potentieel heeft als technologie voor de bestrijding van luchtvervuiling in laag geconcentreerde VOS-luchtstromen.
Het laatste deel van dit manuscript beschrijft de bereiding, karakterisering en toepassing van mangaanoxide van het cryptomelaantype die stroomafwaarts van een NTP-reactor in de oxidatie van TCE zijn geplaatst. Voor de katalysatorbereiding werd waargenomen dat het mogelijk is om de vorm, de kristallijnse fase en de chemische samenstelling van mangaanoxide materialen aan te passen door de synthesecondities te regelen, zoals door de manier waarop metalen (Fe) worden gedoteerd. De toevoeging van ijzer aan cryptomelaan werd op 2 verschillende manieren uitgevoerd: (i) door een co-precipitatie (Fe-K-OMS-2: doel is Fe in K-OMS-2-structuur op te nemen in plaats van K of Mn), (ii) door impregnatie (Fe / K-OMS-2: doel is om FexOy-deeltjes af te zetten op het oppervlak van K-OMS-2). Een referentie cryptomelaan (K-OMS-2) werd ook gesynthetiseerd door een reflux-werkwijze bij omgevingstemperatuur. Ongeacht de syntheseweg, presteerden alle drie de katalysatoren in PPC-configuratie beter dan het NTP alleen in totale TCE-oxidatie. De katalysatoren kunnen voor het verhogen van de TCE-omzetting als volgt gerangschikt worden: K-OMS-2 <Fe / K-OMS-2 <Fe-K-OMS-2. De superieure prestaties van de Fe-K-OMS-2 materialen werden toegeschreven aan verbeterde textureigenschappen zoals hoge specifieke oppervlakten, de amorfe toestand en structurele imperfecties (aanwezigheid van zuurstofvacatures). Deze kenmerken maken het mogelijk om de productie van actieve deeltjes uit plasma-gegeneerde ozon en de zuurstofmobilitéit aan het oppervlak te vergemakkelijken, om zo de afbraak van TCE of intermediaren naar CO₂ te bevorderen.
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A
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A.1 International journal publications

*Abatement of VOCs with Alternate Adsorption and Plasma-Assisted Regeneration: A Review*  
Catalysts, 5(2), 718-746, 2015  
IF: 2017, 3.465

*Synthesis and catalytic performances of K-OMS-2, Fe/K-OMS-2 and Fe-KOMS-2 in post plasma-catalysis for dilute TCE abatement*  
Catalysis today, 307, 20-28, 2018  
IF 2017: 4.667

*Post plasma-catalysis for trichloroethylene decomposition over CeO2 catalyst: synergistic effect and stability test*  
Applied Catalysis B: Environmental (submitted in November 2018)  
IF 2017: 11.698

C.1 Articles in proceedings of scientific conferences

*Abatement of trichloroethylene by combined use of non-thermal plasma and CeO2*  

C.4 Active conference participations

1. **20th International Conference on Advanced Oxidation Technologies for Treatment of Water, Air and Soil (AOT’s–21)**, San Diego, CA, USA. (2015)  
“Oral presentation”
2. 22\textsuperscript{nd} International Symposium on Plasma Chemistry (ISPC-22), Antwerp, Belgium. (2015) “Oral presentation”

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INTRODUCTION
1.1 Air Pollution

Air pollution is a major problem that has been recognized a hundred years ago along with the increase of population density and activities. Air pollution is caused by the emission of certain pollutants that, either alone or through chemical reactions, have negative environmental and health impacts. A World Health Organization (WHO) study in March 2014 indicated that, worldwide, 7 million people died prematurely in 2012 due to the effects of indoor and outdoor air pollution [1, 2]. Thus, pollution has become one of the main environmental health risks in the world.

Air pollutants could be discharged to the atmosphere through natural sources such as plants and volcanic eruptions or by several human made activities. The evolutions of modern lifestyles in developed countries led to the massive development of automobile, industry and synthetic materials, in parallel with a considerable increase of the time spent indoor emphasizing people’s exposure to air pollutants. A summary of the main primary pollutants monitored in air related to their sources and potential health and environmental effects is reported in Table 1.1.

Table 1.1 Primary air pollutants: sources, potential health effects and environmental effects

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Natural sources</th>
<th>Anthropogenic Sources</th>
<th>Human health effects</th>
<th>Environmental effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon monoxide (CO)</td>
<td>Volcanic eruptions, forest fires, photochemical reactions in the troposphere</td>
<td>Motor vehicle exhaust, electrical generating facilities, and other incomplete combustion processes.</td>
<td>Blocks the ability of haemoglobin to transport oxygen to the cells of the body. At moderate concentrations, angina, impaired vision, and reduced brain function may likely result.</td>
<td>Greenhouse effect.</td>
</tr>
<tr>
<td>Nitrogen oxides (NOₓ)</td>
<td>Lightning storms and biological decay processes</td>
<td>Primarily from fossil fuel combustion in electrical utilities, high-temperature operations, and operation of motor vehicle exhaust.</td>
<td>Eye, skin, and respiratory tract irritation. Pulmonary edema, bronchitis, bronchiolitis, and emphysema in moderate to high levels.</td>
<td>NOₓ contributes to acid deposition but also to eutrophication of soil and water.</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------------------------------------</td>
<td>--------------------------------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Sulfur oxides (SOₓ)</td>
<td>Biological decay processes, volcanic eruptions.</td>
<td>Burning of fuel (e.g. coal and oil) containing sulfur and during metal melting and other industrial processes.</td>
<td>Respiratory illness, alterations in the lungs’ defenses, and aggravation of existing heart or lung disease in susceptible populations.</td>
<td>SOₓ contribute to acid deposition, the impacts of which can be significant, causing damage to forests and ecosystems in rivers and lakes.</td>
</tr>
<tr>
<td>Particulate matter (PM)</td>
<td>Pollen, bacterial, and fungal spores, dust, soot ash.</td>
<td>Electricity generation, industrial processes, fossil fuel combustion, waste disposal.</td>
<td>Decreased lung function, irritation of the airways, aggregated asthma, and heart problems. Small particles with less than 10 μm in diameter lead to the greatest risk.</td>
<td>Greenhouse effect, PM in the atmosphere can also alter rainfall patterns, and affect the surface albedo properties of snow.</td>
</tr>
<tr>
<td>Volatile organic compounds (VOCs)</td>
<td>Trees and other plants emit hydrocarbons (terpenes).</td>
<td>Solvent use, vehicular exhaust, industrial processes.</td>
<td>Eye, nose, and throat irritations, headaches, loss of coordination, damage to</td>
<td>Enhance greenhouse effect and ground level O₃.</td>
</tr>
</tbody>
</table>
1.2 Volatile Organic Compounds (VOCs): Ubiquitous and Harmful Molecules

The scent of a rose, a wood fire, the smell of leather, the exhaust of a car, the paint that covers the walls of a house, the furniture, the essential oils, etc. volatile organic compounds are everywhere, both inside our homes and outside. VOCs are chemical compounds that exist naturally, but that are also present in mass in manufactured products and have the distinction of vaporizing very easily at room temperature.

According to the ‘Solvents emission directive’ an organic compound is defined as any compound containing at least the element carbon and one or more hydrogen, halogens, oxygen, sulphur, phosphorus, silicon or nitrogen, with the exception of carbon oxides and inorganic carbonates and bicarbonates [3]. In EU legislation (Derwent 1995), several definitions for VOC can be found. The one used in the VOC directive (Directive 1999/13/EC) and now in the industrial emission (IE) directive (Directive 2010/75/EU) states that VOC means “any organic compound having, at 20 °C, a vapor pressure of 0.01 kPa or more, or having a corresponding volatility under the particular conditions of use” [3, 4].

The problem is that, as discreet as they are, these VOCs are not trivial: they present a series of risks for both health and the environment as stated in table 1.1. A first and widespread approach consists in classifying the various VOCs according to their chemical families. VOCs belong to different chemical families: aromatic hydrocarbons, alkenes, alcohols, aliphatic hydrocarbons, aldehydes, ketones, esters, glycols, glycolethers, chlorinated hydrocarbons, cycloalkanes and terpenes. From one VOC to another, the danger varies according to the molecule concerned and its concentration. Some are carcinogenic, others can cause respiratory diseases such as asthma or even enter the bloodstream, and they settle on the soil, contaminate the water and
are absorbed by plants and animals. The danger is further amplified by the "cocktail effect" resulting from the uncontrolled combination of these molecules with each other. Besides, the age at which a person is exposed to these substances also plays a role. The body of adults develops some resistance, but exposure presents a danger for foetuses whose cells do not yet have this ability. As said “In addition, after chemical reactions, chlorinated volatile organic compounds (CVOCs) cause a number of indirect pollution problems such as ozone and smog formation in the troposphere (Figure 1.1) and depletion of the ozone layer in the stratosphere (Figure 1.2). The most persistent compounds can lead to biological accumulation, causing toxic CVOC levels in foodstuffs [5, 6]. The global warming potential (GWP) of 100 years for CVOCs ranges from 10 to 1800 (the GWP for CO₂ is 1) [7]. Because of their harmful properties, the release of CVOCs into the environment is controlled by increasingly stringent regulations setting high demands for CVOC abatement systems” [cited from 12].

Figure 1.1: Schematic picture of photochemical ozone formation from reactions of NOₓ (sum of NO and NO₂) and VOCs (e.g., NMHCs, CH₄, CO) in the troposphere [8].
1.3 Trichloroethylene

Physio-Chemical Properties: In this PhD study, the experimental work was focused on the abatement of trichloroethylene (TCE) as a VOC of the halocarbons family. TCE is a partially chlorinated C2-hydrocarbon with the formula C2HCl3. In standard conditions, TCE is a clear colorless liquid with chloroform like odour. Further chemical and physical properties of TCE are listed in Table 1.2.
Table 1.2: Physical and chemical properties of TCE [10].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight [kg/mol]</td>
<td>0.1314</td>
</tr>
<tr>
<td>Melting point [°C]</td>
<td>-87.1</td>
</tr>
<tr>
<td>Boiling point [°C]</td>
<td>86.7</td>
</tr>
<tr>
<td>Density at 20°C [kg/m³]</td>
<td>1.46x10³</td>
</tr>
<tr>
<td>Vapor pressure at 20 °C [Pa]</td>
<td>7.6x10³</td>
</tr>
<tr>
<td>Viscosity at 20 °C [Pa-s]</td>
<td>0.58x10⁻³</td>
</tr>
<tr>
<td>Auto ignition point [°C]</td>
<td>410</td>
</tr>
<tr>
<td>Upper explosive limit in air [vol. %]</td>
<td>41</td>
</tr>
<tr>
<td>Lower explosive limit in air [vol. %]</td>
<td>11</td>
</tr>
<tr>
<td>Solubility in water [Kg/L]</td>
<td>1.28x10⁻³</td>
</tr>
</tbody>
</table>

**Production:** TCE was first prepared in 1864 by Emil Fischer in experiments on the reduction of hexachloroethane with hydrogen [11]. Commercial production of trichloroethylene began in Germany in 1920 and in the USA in 1925 [11]. For the 2016 Chemical Data Reporting (CDR) period, the reported non-confidential data indicate that there are 13 manufacturers (including importers) of TCE in the United States. The total volume (in lbs.) of TCE manufactured (including imported) in the United States in 2012 was 220,536,812; in 2013: 198,987,532; in 2014: 191,996,578; and in 2015: 171,929,400. Concerns about the environmental, health and safety implications of chlorinated solvents have resulted in stringent regulations and controls that lead to a continuing decline in production. According to Registration, Evaluation, Authorization and restriction of Chemical substances (REACH) registration information which is available on European
Chemicals Agency's (ECHA's), TCE is manufactured and/or imported in the European Economic Area in 10,000 to 100,000 tonnes/year [13, 14].

**Application/Use:** TCE is mainly used for the vapor degreasing and cold cleaning of manufactured metal parts (80–95% of consumption). There are approximately 140,000 firms engaged in the 'treatment and coating of metals' in the EU [13]. Other uses include the manufacture of organic chemicals; as an extraction solvent for greases, oils, fats, waxes and tars; and as a refrigerant for low temperature heat transfer. Consumer products that contain TCE include typewriter correction fluids, paint removers/strippers, adhesives, stain removers, and rug-cleaning fluids. The textile industry uses TCE to scour cotton, wool and other fabrics.

**Occurrence and Exposure:** Although TCE can be formed by one red microalga and in temperate, subtropical, and tropical algae, non-anthropogenic releases of TCE are negligible [15]. TCE is widely distributed in the environment due to industrial emissions during its manufacture, use, and disposal.

TCE can be released in all media but mostly in air due to its volatility. The partitioning tendency of TCE in the environment has been calculated as follows: air, 97.7%; water, 0.3%; soil, 0.004%; and sediment, 0.004% [16]. The release of TCE to ambient and indoor air can occur during degreasing operations and consumption of related products. Contamination of groundwater and water supplies is possible during production and disposal processes, and through leaching from landfills or underground storage tanks due to its moderate solubility in water, widespread use and persistency in the environment.

Most TCE emissions (70%) into the air are from vapor degreasing operations [11, 13]. Releases of TCE to air will also occur at sewage treatment and disposal facilities, water treatment facilities, and landfills. TCE has also been detected in stack emissions from municipal and hazardous waste incinerators. People who live near facilities that use TCE or near hazardous waste sites containing TCE may have a higher exposure to this substance. In 2006 it was estimated that approximately 74,000 workers in the EU were potentially exposed to TCE with most exposed workers being involved in the manufacture of fabricated metal products including machinery and transport equipment or the manufacture of furniture [13]. In these industries, about 28% of workers are exposed to more than 10 ppm and about 2% are exposed to more than 50
ppm [17]. Airborne concentrations of TCE (primarily in degreasing operations) vary internationally from very low to around 140 ppm [18].

Health Effect: Human exposure to TCE may occur through inhalation, ingestion and dermal contact and can cause a variety of symptoms (Table 1.3). The Scientific Committee on Occupational Exposure Limits (SCOEL) reports TCE being well absorbed via all major routes of exposure in humans, with quantitative data available showing an uptake between 28 and 80% by inhalation, with an absolute uptake increasing with increasing physical exercise [19]. TCE has been classified as a group 2A carcinogen by the International Agency for Research on Cancer (IARC) and as a Category 1B carcinogen in the EU under Classification, Labelling and Packaging (CLP) regulation [13, 20, 21]. Exposure to TCE is associated with increased risks of kidney, liver and biliary cancers and non-Hodgkin’s Lymphoma (NHL). Exposures to high concentrations may also cause headaches, lung irritation, dizziness, or nerve, kidney and liver damage in the long-term.

Table 1.3: Potential health effects of TCE.

<table>
<thead>
<tr>
<th>Contact type</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inhalation</td>
<td></td>
</tr>
<tr>
<td>Short term</td>
<td>Irritation, changes in blood pressure, nausea, vomiting, stomach pain, difficulty breathing, irregular heartbeat, headache, drowsiness, dizziness, disorientation, mood swings, tremors, loss of coordination, visual disturbances, bluish skin color, lung congestion, kidney damage, liver damage, unconsciousness, coma</td>
</tr>
<tr>
<td>Long term</td>
<td>Same effects as reported in the short term exposure, loss of appetite, weight loss, blood disorders, brain damage, cancer</td>
</tr>
<tr>
<td>Skin contact</td>
<td></td>
</tr>
<tr>
<td>Short term</td>
<td>Irritation, allergic reactions</td>
</tr>
<tr>
<td>Long term</td>
<td>Irritation, allergic reactions, nausea, loss of appetite, weight loss, difficulty breathing, headache, drowsiness, dizziness, joint pain, loss of coordination, visual disturbances, paralysis</td>
</tr>
<tr>
<td>Eye contact</td>
<td></td>
</tr>
<tr>
<td>Short term</td>
<td>Irritation (possibly severe), blurred vision</td>
</tr>
<tr>
<td>Long term</td>
<td>Irritation (possibly severe), eye damage</td>
</tr>
<tr>
<td>Ingestion</td>
<td></td>
</tr>
<tr>
<td>Short term</td>
<td>Same effects as reported in the short term inhalation</td>
</tr>
<tr>
<td>Long term</td>
<td>Same effects as reported in the long term inhalation</td>
</tr>
</tbody>
</table>
In the EU the predicted number of cancer deaths in 2010 attributable to TCE exposure were 34, 13 and 12 deaths for cancer of liver, kidney and NHL, respectively. The Institute of Occupational Medicine (IOM) study reported estimations on the numbers of deaths and health costs between 2010 and 2069 in case no action is taken regarding carcinogen pollutants. Among them, exposure to TCE which potentially concerns 74,076 workers in Europe is expected to cause 4,800 cases of cancers and 3300 deaths, with estimated health costs between €1,582 m – 5,657 m [17].

Legislation: Concern began to arise in the end of the 1970s about the potential environmental and health effects of TCE [22]. In the USA, several regulations at the county, state and national levels were passed to limit emissions of TCE. In Europe, directives were instituted to restrict marketing and sales to end-users (76/769/EC). During the 1980s, several European countries, and the European Union, began passing regulations to protect workers from exposure to TCE. Exposure levels have generally been decreasing in the past years and this positive trend could continue in the future.

Existing (2012) national occupational exposure limits in the air in the EU member states and in countries outside EU are presented in Figure 1.3 [18]. International time-weighted averages (TWAs: 8 h) for TCE vary considerably from around 10 ppm in Australia and many European countries to 100 ppm in the United Kingdom and the USA. As can be seen from Figure 1.3, the 15 minutes short-term exposure limit (STEL) varies from around 3 ppm to 200 ppm.
Figure 1.3: Current occupational exposure limits for TCE worldwide.

1.4 Air Pollution Treatment Technologies

Due to their harmful properties, the release of air pollutants into the atmosphere is controlled by stringent regulations setting high demands for the control methods [12]. Controlling air pollution emissions is mainly achieved by process modifications, exhaust treatments or a combination of both. The primary control methods, i.e., modifying the process equipment, changing raw materials and/or the process, are the most effective and preferable methods. If the primary methods are not feasible, then secondary abatement methods (so called add-on-control or end-of-pipe techniques) should be used. The secondary methods are classified into two sub groups, recovery and destruction. High-value pollutants favor recovery methods (adsorption, absorption, condensation and membrane separation) [12, 23], whereas mixtures of pollutants or low-value pollutants favor destruction-based methods (thermal and catalytic incineration, biological oxidative filtering and non-thermal oxidation treatment). A major advantage in the destruction-based abatement is that there is no requirement for the subsequent disposal of the
recovered pollutants [12]. Table 1.4 lists the conventional and currently employed methods for VOCs abatement, their characteristics, working principles and their advantages and disadvantages [10, 23, 24].
Table 1.4: Comparison of various VOC removal techniques

<table>
<thead>
<tr>
<th>Methods (Conventional and upcoming)</th>
<th>Technology involved</th>
<th>Operation Temperature (°C)</th>
<th>Removal Efficiency (%)</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>Activated carbons, zeolites</td>
<td>&lt;55</td>
<td>90-98</td>
<td>Low capital investment, Proven and efficient, Product recovery can offset annual operating cost</td>
<td>Adsorbent is too specific and can saturate fast; Susceptible to moisture, and some compounds (ketones, aldehydes, and esters) can clog the pores; Risk of pollutant reemission</td>
</tr>
<tr>
<td>Absorption</td>
<td>Washing gas with contaminated water</td>
<td>Normal</td>
<td>95-98</td>
<td>Good for inorganic gases, Product recovery can offset annual operating cost</td>
<td>Not suitable for low concentrations, rigorous maintenance, possible pre-treatment of VOCs, generates wastewater</td>
</tr>
<tr>
<td>Condensation</td>
<td>Liquification by cooling or compression</td>
<td>Ambient</td>
<td>50-90</td>
<td>Possible recovery of VOC can offset annual operating cost, compact system</td>
<td>Further treatment is required, applicable in high concentrations only</td>
</tr>
<tr>
<td>Membrane separation</td>
<td>Separation through semi permeable membranes</td>
<td>Ambient</td>
<td>90-99</td>
<td>Recommended for highly loaded streams, Product recovery can offset annual operating cost</td>
<td>Membrane fouling and high pressure is needed, membranes are rare and costly</td>
</tr>
<tr>
<td>---------------------</td>
<td>--------------------------------------------</td>
<td>---------</td>
<td>------</td>
<td>--------------------------------------------------------------------------------</td>
<td>-----------------------------------------------------------------------</td>
</tr>
<tr>
<td>Filtration</td>
<td>Air passed through fibrous material coated with viscous materials</td>
<td>10-41</td>
<td></td>
<td>Efficient for particle removal, compact and commonly used</td>
<td>Unable to remove gases, fouling, particle reemission can occur due to microbial growth</td>
</tr>
<tr>
<td>Microbial abatement</td>
<td>Air passed through a packed bed colonized by attached microbes as biotrickling filters or microbial cultures in bioscrubbers</td>
<td>10-40, 50-105</td>
<td>60-99</td>
<td>Cost effective. More efficient, eco-friendly</td>
<td>Need for control of biological parameters, mostly effective only for low-weight and highly soluble hydrocarbons</td>
</tr>
<tr>
<td>Incineration</td>
<td>Thermal oxidation</td>
<td>700-1000</td>
<td>95-99</td>
<td>Efficient</td>
<td>Not cost effective, incomplete mineralization and release of secondary pollutants</td>
</tr>
<tr>
<td>Catalytic oxidation</td>
<td>Thermal catalysts (Pt, Al, ceramics)</td>
<td>300-500</td>
<td>90-99</td>
<td>Efficient, conserves energy</td>
<td>Catalyst deactivation and its disposal, Efficiency is sensitive to operating condition; formation of by-product</td>
</tr>
<tr>
<td>Method</td>
<td>Description</td>
<td>Initial Conditions</td>
<td>Removal</td>
<td>Additional Effects</td>
<td></td>
</tr>
<tr>
<td>------------------------</td>
<td>------------------------------------------------------------------------------</td>
<td>--------------------</td>
<td>---------</td>
<td>-----------------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Ozonation</td>
<td>Ozone is used to oxidize the pollutants. In this method, ozone is generated by UV or NTP discharge.</td>
<td>-</td>
<td>Removes fumes and gaseous pollutants</td>
<td>Only removes some gaseous pollutants and Generates degradation products.</td>
<td></td>
</tr>
<tr>
<td>Photolysis</td>
<td>UV radiations to oxidize air pollutants and kill pathogens</td>
<td>Normal</td>
<td>Removes fumes and gaseous pollutants</td>
<td>Release of toxic photoproducts, UV exposure may be hazardous and energy consuming</td>
<td></td>
</tr>
<tr>
<td>Photocatalysis</td>
<td>High energy UV radiation used along with a photocatalysts</td>
<td>-</td>
<td>Energy intensive popular method suitable for broad range of organic pollutants</td>
<td>Exposure to UV radiation may be harmful, catalyst deactivation, and potential toxicity by-product formation</td>
<td></td>
</tr>
<tr>
<td>Non thermal plasma (NTP)</td>
<td>Production of ions, electrons, excited atoms, molecules and many highly reactive oxidizing radicals</td>
<td>Ambient</td>
<td>90</td>
<td>suitable for VOCs with low concentration and high volume of air; high processing efficiency and low energy consumption</td>
<td>poor mineralization and release of secondary pollutants, generation of ozone</td>
</tr>
</tbody>
</table>
As mentioned by Pitkäaho, the main selection criteria for the VOC abatement technologies are costs, VOC concentration, vent-gas flow rate, and the required control level, \textit{i.e.}, regulatory factors [12]. Figure 1.4 shows the cost-effective and technically feasible gas flow rate and concentration ranges for the major VOCs control technologies [25]. Since every type of treatment technology has advantages and drawbacks, none is really satisfactory. This means that the choice of an air treatment technique has to be adapted to the environment and the pollution to be treated. Side-product formation is recurrently designated as the dark side of destructive methods and this aspect tends to be overcome by coupling different methods to achieve better mineralization rates as well as conversion rates. Non-thermal plasma coupling with materials and more precisely plasma catalyst coupling has already been investigated, and evidenced good performances. In this PhD study, the experimental work is focused on the abatement of TCE with this innovative hybrid technology.

In the next section, general overview of the main fundamentals on non-thermal plasma and catalytic oxidation is given separately as introduction to this promising plasma catalytic system. The main outlines of the fundamentals which governed the plasma catalyst interaction are discussed in chapter 3.

Figure 1.4: Application limit of flow rate vs VOC concentrations of different VOC control technologies [25].
1.5 Introduction to Plasma

**Plasma:** In physics and chemistry, plasma is a state of matter similar to gas in which certain portions of the species are ionized. It is a combination of charged particles, positive ions and negative electrons. This so-called state of ionized gas was first described by William Crookes in 1879 as ‘a world where matter may exist in a fourth state’. The term plasma was first introduced fifty years later by Langmuir in 1928 because the multi-component and ionized gas he observed reminded him of blood plasma. Langmuir wrote: “Except near the electrodes, where there are sheaths containing very few electrons, the ionized gas contains ions and electrons in about equal numbers so that the resultant space charge is very small. We shall use the name plasma to describe this region containing balanced charges of ions and electrons” [26].

Plasma forms 99% of the universe in many forms such as solar corona, nebula and solar wind. Our sun is a huge plasma ball. Plasma also appears naturally on the earth as aurora and lightning. Plasmas naturally occur but can also be effectively man-made in laboratory and industry, which provides opportunities for numerous applications, including thermonuclear applications, electronics, lasers, fluorescent lamps, ozone production and many others.

In general, when gas atoms are subjected to energy (thermal, electrical or light) they become ions by releasing some of their electrons. Collisions between electrons and molecules and bond breaks in molecules create radicals. Energy will also create excited species that will generate photons. This is how plasma is created with a unique mixture of electrons, ions, radicals, photons and neutral atoms and molecules [27].

**Classification:** Depending on the relative temperature of the species, we can distinguish three main types of plasmas: high temperature plasmas, thermal plasmas and non-thermal plasmas. The critical parameter between these different types of plasmas is electron, ion and gas characteristic temperatures, summarized in Table 1.5.
Table 1.5: Classification of plasmas and related physical characteristics [28].

<table>
<thead>
<tr>
<th>Plasma Type</th>
<th>Temperatures</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>High temperature plasma</td>
<td>$T_e \approx T_i \approx T_g$</td>
<td></td>
</tr>
<tr>
<td>(equilibrium plasma)</td>
<td>$= 10^6 \ldots 10^8 K$</td>
<td>Laser fusion plasma</td>
</tr>
<tr>
<td>Thermal plasma</td>
<td>$T_e \approx T_i \approx T_g$</td>
<td></td>
</tr>
<tr>
<td>(quasi-equilibrium plasma)</td>
<td>$\leq 2 \times 10^4 K$</td>
<td>Arc plasma, plasma torches RF inductively coupled discharges</td>
</tr>
<tr>
<td>Non-thermal plasma</td>
<td>$T_e \gg T_i \approx T_g$</td>
<td></td>
</tr>
<tr>
<td>(non-equilibrium plasma)</td>
<td>$= 300 \ldots 10^3 K$</td>
<td>Glow, corona, dielectric barrier discharges, plasma needle, etc</td>
</tr>
</tbody>
</table>

The different types of plasmas are also distinguished by the ratio of the density of charged species to that of the neutral gas, corresponding to the plasma ionization degree. As the ionization degree is close to 1, it is referred to as completely ionized plasma, a typical property of high temperature or thermal plasmas. A non-thermal plasma is generally weakly ionized (ionization degree $\approx 10^{-7}-10^{-4}$) with an ionization rate less than $10^{-2}$. At atmospheric pressure, it is necessary to limit the ionization degree to maintain non-equilibrium conditions by imposing: (i) low discharge current, (ii) short discharge pulses, (iii) micro-discharges or (iv) dielectric barrier discharge. As the ionization degree is low, the so called weakly ionized plasma allows the gas to remain at, or close to, room temperature and atmospheric pressure, making non-thermal plasmas more compliant with industrial constraints. The main advantage of non-thermal plasmas is their high chemical efficiency which is attributable to their ability of providing a significant concentration of excited and chemically active species that is unavailable in conventional chemistry [29].

**Non-Thermal Plasmas**: In electric discharges, energy from the electric field is first accumulated by the electrons. Due to their small mass, electrons are selectively accelerated under the influence of the electric field. Upon collisions with the neutral gas, they transfer a small portion of their energy to heavier particles. For this reason, the electron temperature in plasma is initially higher than that of heavy particles. The resulting plasma is a non-thermal or cold plasma. However, if the pressure is so high that the charged particles do not move very far before the next collision, the energy of the electrons may
tend towards that of the heavy particles. In this case, the resulting plasma is a thermal or hot plasma which will not be further discussed since it is beyond the scope of this study.

In NTP, ionizations and chemical reactions are directly determined by the electrons temperature and are not so sensitive to thermal processes and the gas temperature. The generation of a NTP consists of many elementary processes which can be divided into primary and secondary processes. These processes and their timescales are summarized in Figure 1.5.

![Figure 1.5: Timescale events of the elementary processes in a non-thermal plasma [30].](image)

The primary process includes charge transfer, ionization, excitation, and dissociation with typical timescales between $10^{-15}$ and $10^{-8}$ seconds. The main primary processes are electron collisions with bulk gas molecules ($N_2$, $O_2$, $H_2O$) resulting in the production of ionized and excited molecules. The primary processes are shown below.

\[
e^- + N_2 \rightarrow e^- + N + N \quad (1.1)
\]
\[
2e^- + N_2 \rightarrow e^- + N^+ + N \quad (1.2)
\]
\[
e^- + O_2 \rightarrow e^- + O(^3P) + O(^3P) \quad (1.3)
\]
\[
e^- + O_2 \rightarrow e^- + O(^3P) + O(^1D) \quad (1.4)
\]
\[
e^- + O_2 \rightarrow 2e^- + O^+ + O \quad (1.5)
\]
\[
e^- + H_2O \rightarrow e^- + H + OH \quad (1.6)
\]
\[
e^- + H_2O \rightarrow 2e^- + H^+ + OH \quad (1.7)
\]
The secondary process is the subsequent chemical reaction between the products of primary processes (electrons, radicals, ions, and excited molecules). Additional radicals and reactive molecules (O₃, HO₂, and H₂O₂) are also formed by radical and recombination reactions. The timescale of the secondary processes is around $10^{-3}$ seconds.

Non-thermal plasma techniques are economically attractive alternatives for conventional air cleaning techniques due to the low energy consumption and high flexibility. In the non-thermal plasma, the majority of the discharge energy goes into the production of energetic electrons, rather than heating up the heavy particles (ions, radicals). Radicals produced during primary and secondary processes are able to react with the pollutant molecules present in the air. The aim is to convert these pollutants into less harmful products such as H₂O and CO₂.

The classification of discharges that can occur in NTP is extensive and depends on a variety of parameters including the type of power supply, the electrode configuration, the voltage level, the gas pressure, etc. Some conventional NTP reactors that are employed in laboratory experiments are pulsed corona discharge, direct current (DC) corona discharge, dielectric barrier discharge (DBD) surface discharge, radio frequency plasma, DC glow discharge, microwave discharge and ferroelectric pellet packed-bed plasma reactors; more detailed overviews on these points can be found in the literature [30-35].

**DC-excited NTP:** The plasma source that is used in this work is a DC-excited atmospheric pressure glow discharge in a multi-pin-to-plate configuration. This type of plasma source was first proposed by Akishev et al. who used transverse flow stabilization to obtain a uniform glow discharge in a (negative) corona (point-to-plane) electrode geometry [36]. The physics of the corona-to-glow transition was studied in detail in previous papers [37, 38].

Figure 1.6 shows a typical voltage-current characteristic plot with the three discharge regimes: corona, glow and spark. As the applied voltage increases, the corona discharge is initiated at an onset voltage, $V_0$. In 1914, Townsend proposed an empirical formula that dictates the relationship between the discharge current $I$ and the inter electrode voltage $V$ for a coaxial geometry [39]:

$$I = CV(V - V_0)$$

(1.8)
where $C$ is a constant depending on the electrode geometry. This means that in the corona regime the reduced current $I/V$ increases linearly with increasing voltage as shown in Figure 1.6. In the intermediate glow regime this relationship is no longer linear but exponential. Finally, the discharge transfers to the spark regime.

The visual aspect of the discharge is quite different in the three regimes. In the corona regime of the discharge, i.e. at low currents, the plasma does not fill the entire discharge gap and light is only emitted at the sharp edges of the point electrode. Increasing the current $I$ results in a gradual filling of the gap with luminous plasma. This visual observation is indicative for the transition of the discharge from corona to glow. The transverse gas flow is also instrumental in increasing the glow-to-spark current threshold [36]. Additional theoretical background regarding these discharges can be found in [31].

This type of discharge was successfully applied for the abatement of VOCs in waste air by using a multi-pin-to-plate configuration [40]. This reactor concept has several desirable features because it can easily be scaled-up, it is cost saving due to the low investment for a DC high voltage source and it allows treating high flow rates at atmospheric pressure and room temperature. In this work, the feasibility of combining this multi-pin-to-plate negative DC glow discharge with heterogeneous catalysts for VOC abatement is investigated in order to enhance the performance of the plasma alone systems.
1.6 Introduction to Catalytic Oxidation

**Heterogeneous Catalysis:** A heterogeneous catalytic process was first observed by Humphry Davy in 1817 by accidentally discovering that a gently heated platinum gauze, foil or wire could bring the slow combustion of mixtures of vapors (such as ether and alcohol) as well as of coal gas and methane below their ignition temperatures [43, 44]. This discovery was acknowledged by the Swedish chemist, Berzelius, in his treatise on catalysis where that word was first used.

Catalysis is defined as the process in which the rate of a reaction is increased without changing the overall standard Gibbs energy change. This rate increase is brought about by the use of a catalyst, which itself is not consumed and regenerated after each reaction cycle. A good catalyst increases the reaction rate by several orders of magnitude and improves the selectivity by virtue of providing alternative reaction pathways with lowered energy barriers (Figure 1.7).
Figure 1.7: Reaction coordinate diagram showing the working principle of a catalyst [45].

**Mechanism:** In the case of a heterogeneous catalysis, the gas phase reaction is replaced by a surface reaction. The heterogeneous reaction path consists of at least three steps: 1) (dissociative) adsorption of the reactants, 2) reaction of adsorbed species on the surface, 3) desorption of products. The mechanisms proposed for the catalytic surface reaction generally fall into three main categories: (i) Langmuir-Hinshelwood (L-H) model, (ii) Eley-Rideal (E-R) model, and (iii) Mars-Van Krevelen (MVK) model.

As shown in Figure 1.8-A, the L–H model reveals that two gaseous reactants are firstly adsorbed on the surface of the catalysts (reactions 1 and 2) before a reaction takes place. The adsorbed species undergo a bimolecular reaction on
the catalysts surface. The whole process can be described in the following scheme:

\[ A + S \leftrightarrow AS \]  (1.9)
\[ B + S \leftrightarrow BS \]  (1.10)
\[ BS + AS \leftrightarrow \text{Products} \]  (1.11)

Where A and B are reactants, S is the adsorption site on the catalyst’s surface.

Generally, the reaction rate between adsorbent 1 and 2 (Figure 1.8-A) is given by \( r = k\theta_A\theta_B \), because the reaction rate at the surface is the rate determining step, where \( \theta_i \) is the surface coverage of species I and k is the rate constant of the reaction. In this type of mechanism, high reactivity can be expected when a good dispersion of the reactants is achieved.

Figure 1.8-B shows the E-R model. The E-R model assumes that only one reactant is adsorbed on the surface of the catalyst (reaction 1, Figure 1.8-B). The second reactant reacts with the first adsorbed reactant directly from the gas phase (reaction 2, Figure 1.8-B). This is followed by the desorption of the new reaction product. The scheme can be described in the following way:

\[ A + S \leftrightarrow AS \]  (1.12)
\[ B + AS \leftrightarrow \text{Products} \]  (1.13)

Where A and B are gaseous reactants, S is the adsorption site.

The second step is considered as the rate determining step. The reaction rate is therefore given by \( r = k\theta_AP_B \) where \( \theta_A \) is the coverage of molecule A on the surface and \( P_B \) is the pressure of the reactant B. A higher reaction rate can be expected if there is a higher coverage of the adsorbed molecule A as well as a higher pressure of gas B.

MVK model considers that the reaction occurs between the adsorbed reactants and the lattice oxygen of the catalyst rather than the oxygen in the gas phase. This model assumes that the oxidation of the reactants takes place in two steps as shown in Figure 1.8-C. In the first step, the adsorbed reactants react with oxygen in the catalyst, resulting in the reduction of the catalyst (reaction 1b, Figure 1.8-C). In the second step, the reduced catalyst is re-oxidized by the gas phase oxygen present in the feed (reaction 1a, Figure 1.8-C). As the catalyst is first reduced and then re-oxidized, this mechanism is also known as the redox mechanism.
\[2[\text{CatO}] + A \rightarrow 2[\text{Cat}] + \text{products}\]  
(1.14) 
\[2[\text{Cat}] + O_{2(g)} \rightarrow 2[\text{CatO}]\]  
(1.15)

[CatO] is the oxidized catalyst surface, [Cat] is its reduced state and A is the gaseous reactant. In the steady state, the rate of catalyst reduction is equal to the rate of catalyst oxidation. Therefore, \(k_{\text{red}}*P_A*(1-\theta) = k_{\text{ox}}*P_{O_2}*\theta\) with

- \(P_A\) and \(P_{O_2}\) are partial pressures of A and \(O_2\), respectively.
- \(k_{\text{red}}\) and \(k_{\text{ox}}\) are the rate constants of the reduction and oxidation catalysts, respectively.
- 1-\(\theta\) and \(\theta\) are the concentrations of the oxidized and reduced sides, respectively.

In the case of VOCs catalytic oxidation, the first step corresponding to the reduction of the catalyst surface is the rate determining step [47].

Properties: The number of surface atoms of the catalytic material, and the total catalyst surface area in the reactor must be optimized for an efficient catalytic process. Therefore, the catalytic material is usually deposited as very small particles on the surface of a highly porous, inert (pre-shaped) support material such as \(\gamma\)-alumina, silica, zeolites and titania. The surface area of the pores can be several 100 m\(^2\)/g support material.

An important class of catalysts are from the group VIII transition metals. The catalytic activity of these metals is understood from the relation between the adsorption properties of atoms/molecules and the occupation of the d-valence band. Moving from left to right in the periodic system, the bond strength of the adsorbate with the metal surface decreases due to the increasing occupation of the d-valence band. The bond strength of the adsorbates with the catalyst and the temperature determine the surface coverage, which has a large impact on the catalytic reaction rate. There is an abundant amount of literature on this subject [48-50].

Another commonly used class of catalyst are metal oxides. Metal oxide catalysts structures are characterized by their redox and acid–base properties which are determined by their ability to accept electron density and thus to be reduced, leading to the generation of Brønsted acid sites or stabilizing the cationic transition state [48]. In general, Brønsted acidity depends on the strength of the metal-oxygen bond and acidity increases with the charge on the metal ion.
Further, the ensemble size and surface structure of catalyst particles are at least as important. The ensemble size can change the selectivity, and the surface structure determines the occupation of the out-of-plane d-orbitals of the surface atoms. Geometric effects are also important with certain adsorbed species being ‘good fits’ to a particular catalytic surface because of the molecular structure of the adsorbate and possible modification of the surface due to local vacancies or impurities [49].

**Catalytic Oxidation of VOCs**: Catalytic oxidation of VOC is a promising technology that offers high destructive efficiency at lower operating temperatures, lower capital cost and smaller units [23]. The key parameter of this technology is the type of catalyst used which depends on several variables, namely the type of effluent to be treated (composition, type of VOC and flow-rate), the presence of poisons or inhibitors in the gas stream, and any inlet temperature constraints.

As mentioned by Pitkääho in 2013: “The catalysts applied in CVOC oxidation should be highly active at relatively low temperatures, maintain high resistance towards deactivation by chlorine and its compounds and have high selectivity towards CO₂ and HCl. The reactivity of CVOCs in the catalytic oxidation, as well as the distribution of the reaction products, depends strongly on the catalyst used and the chemical structure of the oxidised compounds. Among the large number of CVOCs which are discharged into the environment, those compounds containing more chlorine atoms than hydrogen atoms cannot be totally converted by air to the most desirable chlorine containing product: HCl. Therefore, even more toxic products such as chlorine gas (Cl₂) and phosgene (COCl₂) can be formed. Depending on the catalyst, both noble metal and metal-oxide catalysts can be active in the Deacon reaction, leading to the formation of molecular chlorine and undesired chlorinated compounds. To improve selectivity towards HCl, either a hydrogen-rich additive or water vapor should be added to the feed stream” [cited from 12].
CHAPTER 2:

STRATEGY AND
CONTENT OF THE
THESIS
A large and important group of air pollutants consists of Volatile Organic Compounds (VOCs) which particularly harm human health and our environment. Along with carcinogenic and mutagenic effects on human health [51], VOCs are also precursors to ground level ozone which is principally responsible for photochemical smog. The research of innovative technologies for VOC abatement is stimulated to accommodate the new stringent standards in terms of VOC emission. One emerging strategy is the coupling of 2 existing complementary technologies, namely here NTP and Catalytic Total Oxidation (CTO), to get a more efficient process for VOC removal in air.

Indeed, NTP technology has attracted growing interest of scientists over the last three decades due to its distinctive characteristic of providing a highly chemical reactive environment (e−, O*, HO2*, OH*, N2*, O3, etc.) to decompose VOCs at ambient conditions, which repudiates the use of expensive vacuum systems [52, 53]. Although other commercial pollution control techniques (thermal incineration, catalytic oxidation, adsorption, biofiltration) [54] are very efficient for the removal of VOCs, these are energetically expensive and difficult to operate in case of moderate flow rates with low VOC concentration in contrast to NTP [55-58]. In a NTP, electrons with high kinetic energies (1–10 eV) are selectively produced consuming almost all the electric energy supplied to the system instead of heating the entire gas unlike thermal and catalytic oxidation. Collisions of these energetic electrons with neutral background molecules close to room temperature, generate active species such as free radicals, metastables, ions and secondary electrons through different chemical processes such as dissociation, excitation and ionization. These active species are able to decompose pollutant molecules to less harmful products (CO2, H2O, HX and X2 with X being a halogen). Additionally, the abatement of low concentrated VOCs (up to 1000 ppm), feasible in indoor air treatment application, is challenging for conventional methods because when the VOC concentrations decrease, the cost per unit pollutant treatment becomes higher in comparison to NTP. Furthermore, NTP systems have several desirable features resulting from their operating conditions, such as a quick start-up, compact system, rapid response to changes in the composition of the waste gas and non-selectivity for the treatment of waste gases with different pollutants such as PMs, bacteria and VOCs [59-61].

Nonetheless, this technology shows some drawbacks such as the formation of hazardous ozone and an uncontrolled selectivity which requires coupling with other technologies such as catalytic oxidation processes for commercialization.
Indeed, a heterogeneous catalyst is able to decrease a reaction’s energy barriers thus increasing its kinetics and allows a higher selectivity towards the formation of harmless molecules. Through this innovative hybrid technology, namely, plasma catalysis, the feasibility of NTP technology has been improved by enhancing the energy efficiency, carbon mass balance and mineralization degree. The mechanisms that enable a better performance are mainly related to the position of the catalyst either being exposed to the active plasma volume (In Plasma catalysis-IPC) [64] or in close vicinity mainly downstream of the discharge zone (Post Plasma catalysis-PPC) [65]. Interestingly, in both cases, the reactions in the gas phase and on the catalyst surface often add up to induce a synergetic effect on the overall removal efficiency [66, 67]. However, these results should be treated with substantial care, since this seems to be mostly due to a large contribution from the plasma energy and therefore the actual synergy is rather low. This is why the design of a new plasma catalytic reactor seems to be a key point for the implementation of the new research line. Moreover, understanding the physical interaction between NTP and a catalyst is important for further optimization of a given system. Nevertheless, fundamental information on the interaction of NTP with a catalyst and of the occurring surface reactions are still in the early stages even though numerous experimental studies on plasma catalysis have been reported; thus, further study is required.

Therefore, this PhD thesis deals with the search for an innovative hybrid remediation technique by coupling plasma with catalysis. For that, we will study the destruction of a chlorinated VOC called TCE which is very dangerous to human health. TCE has been selected as the target VOC due to its high toxicity. Several bad environmental and health effects of this non-flammable and sweet smelling liquid have been previously reported. In addition to its neurotoxicity, as previously mentioned, according to the IARC, TCE is also carcinogenic to humans, hence it is important to reduce its emission into the atmosphere [20, 21]. Generally, TCE is a chlorinated industrial solvent that is widely used as a degreasing agent in semi-conductor and metal industries. Recently, Vandenbroucke et al. have reviewed different plasma catalytic processes for TCE abatement [68].

Although IPC has been claimed to be superior to PPC, several studies have however shown enhanced performance of different catalysts in PPC rather than IPC [69-71]. In IPC, both plasma and catalyst simultaneously affect each other, resulting in complex interactions. However, in a two-stage process such as PPC, the underlying mechanism is more straightforward while the operating
parameters can be separately optimized enhancing the feasibility of adopting this two-stage configuration in commercialized processes. Moreover, PPC has a simpler configuration compared to IPC, which facilitates the replacement of the used catalyst in practical applications. For these reasons, in this PhD study, PPC technology has been selected to investigate the feasibility of dilute VOC abatement.

The concept of the PPC process is illustrated in Figure 2.1. A VOC (in this thesis TCE) enriched gas stream will firstly pass through the plasma reactor followed by the catalytic reactor. Using this configuration, in the first stage, plasma changes the gas composition by producing oxygenated intermediates which are more easily decomposed through the VOCs reactions with the highly reactive plasma generated species (O, OH, radicals and O3). Moreover, plasma reduces the burden of the downstream catalyst by lowering the TCE concentration via preprocessing. In the next step, the oxygenated by-products along with the unreacted TCE of the plasma reactor will be guided through the catalytic reactor where the total VOC oxidation occurs. Generally, one of the most important by-products in a non-thermal air plasma discharge is hazardous ozone. Therefore, in order to obtain a successful PPC system, catalysts with a high ozone decomposition ability as well as a high VOC total oxidation capacity have to be selected. In this PPC process, long-living ozone molecules produced by plasma are able to reach the catalyst surface where they are decomposed into active oxygen species that are able to oxidize the plasma processed hazardous by-products together with the possibly remaining VOCs into CO2. At this point, a great synergy between the two reactors for the VOC removal processes in terms of higher conversions and selectivities with a minimization of the energy used in both parts of the hybrid system are expected. In this way, a more effective use of NTP is possible by exploiting the oxidative capacity of these harmful ozone molecules by introducing an ozone degrading catalyst downstream of the discharge zone.
Up until now, catalysts have been proposed for use in post processes using various types of discharge treatments (DC or pulse corona/surface/dielectric barrier discharge), including noble metals (Pd) or transition metal oxides (Mn, Ti, Zn, V), gold (Au) or cerium (Ce) oxides, mixed or complex oxides (perovskites) and their combination with supports of zeolites, γ-Al₂O₃, molecular sieves, SMF and AC for the efficient oxidation of different chlorinated volatile organic compounds (CVOCs) [65, 72-78]. Although noble metals are found to be more active than metal-oxide-based catalysts or perovskites regarding CVOC oxidation, their use is however limited by high cost and sensitivity to poisoning especially by chlorine/chloride products [79-82]. Thus, non-noble metal oxide catalysts have been considered as low-cost and environmentally friendly alternatives with better stability for chloroorganics oxidation [83-87].

In the post plasma configuration for the abatement of CVOCs, an environmentally friendly catalyst with appropriate ozone decomposition ability, VOC total oxidation capability (CO₂, H₂O, HCl), hydrothermal stability and specially resistance to chlorine needs to be found. Moreover, it should also have a lower reactive temperature and a stable catalytic performance which stands for the long-term goals of the plasma catalysis process. The desired catalytic properties for effective VOC oxidation are related to redox property, crystal defects, diffusion in the crystal lattice, surface area and high oxygen storage capacity (OSC) and mobility.

In the last decade, the redox properties of ceria (CeO₂) have been intensively analysed. The mechanism of VOC oxidation reactions over ceria is generally considered a redox-type mechanism, in which the key steps are the supply of oxygen by the readily reducible oxide and its re-oxidation by oxygen [88, 89]. Moreover, CeO₂ based catalysts (Al₂O₃-CeO₂, Pt/Al₂O₃-CeO₂, CeO₂/HZSM-
5) are found to be promising in CVOCs abatement due to a combination of their acidic and oxidizing properties, their thermal stability and resistance to poisoning by chlorine [90, 91]. Recently, some researchers studied CeO$_2$ based catalysts, for the plasma catalytic oxidation of (chlorinated) VOCs [92-95]. To our knowledge, using pure CeO$_2$ in post plasma catalysis for VOCs abatement is rather limited.

Therefore, in this PhD study, CeO$_2$ catalyst was investigated in order to determine its activity, selectivity and durability for the abatement of TCE in combination with a negative DC glow discharge. DC excited NTP has been chosen in this present work, since it requires low installation cost compared to pulsed corona discharge. Additionally, it is feasible to work at high flow rates while the system can be easily scaled up [96]. During this initial plasma-catalytic study, we investigated TCE abatement by combining the plasma discharge with a commercial CeO$_2$ catalyst. The decomposition of TCE and the formation of by-products are studied for different configurations such as single NTP, single catalyst and post plasma catalysis (placing the catalyst downstream from the NTP reactor). The long-term performances of plasma catalytic systems using CeO$_2$ downstream in the presence of TCE have also been evaluated. This research was conducted in collaboration with a research group specialized in environmental catalysis at the department of organic chemistry of the university of Cordoba.

The performances of NTP in PPC have already been investigated in particular for trichloroethylene (TCE) removal which is a very reactive molecule towards cold plasma in dry/wet air [68, 97, 98]. Among the different catalysts already investigated MnO$_2$ appears to be very interesting, especially, due to its very high activity towards O$_3$ degradation [99]. However, MnO$_2$ shows various crystallographic phases. Cryptomelane, an octahedral molecular sieve (OMS) is one allotropic form of MnO$_2$ having a (2×2) tunnel structure (OMS-2). The structure is made of the superposition of 4 units of 2 edged MnO$_6$ octahedra building blocks connected by corners along the c axis forming a 1D microporous square tunnel of 0.46 nm in size. K$^+$ cations which are located inside the (2×2) tunnels provide charge balance and stabilize the structure (K-OMS-2; general formula K$_x$Mn$_8$O$_{16}$ with an average manganese oxidation of about 3.8). The open structure of the channels, the easy cycling of Mn$^{4+}$/Mn$^{3+}$ and the high mobility of lattice oxygen as well as more recently the morphology of the particles have been put forward as important characteristics to take into account for their activity in CTO of VOCs [100-109]. In fact, MnO$_2$ oxides have already shown interesting TCE abatement properties in
The TCE total oxidation performed in moist air in the presence of CO\textsubscript{2} was previously investigated as a function of energy density (ED) using an atmospheric pressure negative DC luminescent glow discharge combined with a cryptomelane catalyst positioned downstream from the plasma reactor [62, 75]. The ability of the catalyst to decompose plasma generated ozone allows getting active oxygen species enabling the destruction of plasma generated polychlorinated hazards and the enhancement of TCE abatement. The main limitation is the side formation of some C1 chlorinated compounds believed to be in line with a partial chlorination of the catalyst when the temperature of the catalyst is too low [62, 75]. In order to promote the efficiency of the PPC process towards VOC abatement a possible strategy is to improve the physical and catalytic properties of K-OMS-2 material by doping. Indeed doping of single-type, low or high-valent metal transition cations, has been previously shown to produce cryptomelane with novel morphologies [110] and improved catalytic properties [111]. Doping cryptomelane with various cations of different types can improve the textural properties [112, 113], modify Mn average oxidation state (AOS) [100, 114, 115] and thermal stability [100, 112, 114], increase structural defects, e.g., vacancies [112, 116], and also enhance the reactivity of cryptomelane towards the catalytic oxidation of various organic pollutants [113, 117-119]. It follows from these considerations that the physico-chemical properties of the metal doped K-OMS-2 depend on the nature of the doping metal and on the synthesis conditions, such as the mode of incorporation and temperature of calcination of the oxide precursor material. As a result the doping cations can be incorporated into the channels, partially replacing K\textsuperscript{+} ions and/or substitute M\textsuperscript{3+} or Mn\textsuperscript{4+} cations in MnO\textsubscript{6} octahedra and/or be present as dispersed transition metal oxides supported on the cryptomelane phase [112]. Among the possible transition metal dopants, Fe has been chosen as it has been previously reported that Mn-Fe oxides may be promising catalysts for ozone decomposition [120]. Taking advantage of this property, Mn-Fe oxides dispersed on cordierite have been recently used successfully in a PPC process for the decomposition of diethylether [121]. Additionally, Fe doped cryptomelane catalysts have been reported to enhance VOC total oxidation [122]. Reported Fe-doped cryptomelane synthesis methods include hydrothermal treatment of Fe-doped layered birnessite [100], redox precipitation under reflux [123], sol–gel assisted combustion methods [114], addition of iron precursor to cryptomelane and heating [122].

Therefore, in a second collaboration with the Unité de Catalyse et Chimie du Solide (UCCS) from the University of Science and Technology in Lille (Lille
we further investigated the use of manganese–based catalysts in order to optimize the catalytic formulation for total oxidation of TCE. During this study, we developed and characterized efficient and low-cost catalysts and investigated their performances in PPC processes for TCE abatement. Eco-friendly cryptomelane (KMn₈O₁₆, K-OMS-2): the best one in MnO₂ polymorphs regarding O₃ decomposition has been chosen and the chemical/physical properties of this catalyst were modified by incorporation of Fe in the K-OMS-2 structure (co-precipitation) or FeₓOᵧ particles at the surface of K-OMS-2 (impregnation). The purpose of adding Fe to cryptomelane is to improve its textural properties resulting in an enhanced O₃ degradation efficiency and TCE CTO efficiencies.

This PhD thesis is conceived in the following way. In Chapter 3, an aspect of the current status of plasma catalysis research regarding volatile organic compound decomposition is outlined. Numerous review articles can already be found in literature. In order to avoid repetition and to produce again another overview of plasma treatment of VOCs, we opted to discuss the aspects of continuous and sequential treatment of VOCs although the latter is somewhat beyond the scope of this work. However, the results obtained in this work will also be interesting for future applications in sequential plasma treatment of VOCs. Moreover, phenomena as adsorption and regeneration are also important parameters in the study of the stability of catalysts. This chapter is divided in two sections. In the first part, the concept of continuous treatment and sequential treatment is discussed. Then, a comparison between continuous direct plasma treatment of VOCs and sequential plasma regeneration of VOC saturated sorbents is given. Additionally, a comprehensive short discussion on the synergistic effect and mechanism of these systems is provided. In the second section of this chapter, studies dealing with adsorption followed by NTP oxidation are reviewed. Particular attention is paid to the adsorption mechanisms and the regeneration of catalysts with in plasma and post plasma processes. And finally, the influence of critical process parameters on the adsorption and regeneration steps is summarized.

Chapter 4 presents the materials and methods adopted in this thesis. This includes a detailed description of the experimental set-up, the used experimental procedures and reactors (plasma reactor and catalyst reactor) and the catalyst synthesis methods (co-precipitation and impregnation). Moreover, in order to characterize the catalysts, numerous analytical techniques were used for which the experimental conditions are summarized here.
The work performed during this thesis is presented in the upcoming chapters.

In Chapter 5, the study is devoted to investigate the opportunities of a plasma catalytic system with CeO$_2$ downstream (i.e. PPC) for the abatement of TCE, a typical chlorinated VOC, from dry air. A multi-pin-to-plate negative DC corona/glow discharge is used and showed poor CO$_x$ selectivity despite having high abatement efficiency due to the formation of oxygenated intermediates such as phosgene (PG), dichloroacetylchloride (DCAC) and trichloroacetaldehyde (TCAA), when operated alone. Nonetheless, NTP enables catalyst activation at lower temperature. A clear synergy was observed in terms of TCE abatement and mineralization. As a result, suppression of unwanted chlorinated by-products as well as high CO$_x$ selectivity at lower energy cost have been achieved, proving that this plasma catalysis route shows great potential as air pollution control technology for low concentrated VOC air streams. A long term test to evaluate the stability of CeO$_2$ catalyst has also been successfully performed.

In chapter 6, the study focuses on the preparation, characterization and evaluation in TCE oxidation (in presence of moist air) of Fe-doped KOMS-2 oxides placed downstream from a NTP reactor. Fe-doped manganese oxide octahedral molecular sieves of cryptomelane type structure were synthesized by co-precipitation and impregnation by refluxing at ambient pressure. The influence of Fe in the MnO$_2$ structure was assessed by several characterization techniques such as inductively coupled plasma-optic emission spectroscopy (ICP-OES), X-ray diffraction (XRD), Raman spectroscopy, N$_2$ adsorption analysis, hydrogen temperature programmed reduction (H$_2$-TPR), and thermogravimetric analysis (TGA) / differential thermal analysis (DTA). The co-precipitated sample (Fe-K-OMS-2) shows better performances for TCE removal in moist air when used downstream from a NTP (non-thermal plasma) generated in a DC multi-pin-to-plate corona/glow discharge in comparison to the iron free manganese oxide octahedral sieve (K-OMS-2). The enhanced performances towards TCE removal using Fe-K-OMS-2 downstream from the NTP are attributed to a high surface oxygen mobility and to an increase in structural defects resulting from improved textural properties. These characteristics promote O$_3$ decomposition and TCE CTO efficiencies.

An overall conclusion along with the recommendations for the future works are given in Chapter 7.

As a conclusion, one could say that the work presented in this study explored the use of CeO$_2$ and manganese based catalysts for the plasma-catalytic
removal of low concentrated CVOC air stream at lower energy cost. Different important process parameters were investigated such as the effect of plasma energy density and catalyst temperature. In order to reduce the energy cost of the process, low energy density plasma is successfully used in combination with moderate/low catalyst temperature. Furthermore, long term tests have been carried out to evaluate the catalytic stability in plasma assisted TCE oxidation. Several characterization techniques have also been adopted in order to better understand the CVOC degradation mechanism in plasma catalytic processes.
CHAPTER 3:
CONTINUOUS AND
SEQUENTIAL
TREATMENT OF
VOCS REVIEWED
This chapter is an updated version of the review article published in the following peer-reviewed journal:

S. Sultana, A.M. Vandenbroucke, C. Leys, N. De Geyter, R. Morent

*Abatement of VOCs with Alternate Adsorption and Plasma-Assisted Regeneration: A Review*

Catalysts, 5(2), 718-746, 2015
3.1 Introduction

Non-thermal plasma can induce various chemical reactions at both atmospheric pressure and normal ambient temperature; the formation of highly reactive short-lived species and the subsequent chemical reactions are intrinsic aspects of plasma chemistry. The chemical potential of NTP has been studied with regard to various applications, such as removal of various types of hazardous air pollutants (NOx, SOx, odours and VOCs), ozone generation, surface treatments, CO2 conversion into value-added chemicals and fuels, N2 fixation for the synthesis of NH3 or NOx, methane conversion into higher hydrocarbons or oxygenates and biomedical use.

In particular, the application of electrical discharge plasmas in environmental treatment techniques became a prominent topic of research. In fact, plasma methods possess many distinct advantages such as low cost, compact system, quick start-up and wide applicability for VOCs with low or high concentration, along with providing a “rich” and reactive plasma environment in moderate operating condition. Numerous papers have been published regarding NTP assisted VOCs oxidation for nearly 20 years and considerable progress has been made in assembling a knowledge base and developing an understanding of the processes.

Unfortunately, industrial implementation of NTP for VOC abatement is impaired by three main bottlenecks such as poor product selectivity, formation of undesired by-products (O3, NOx, other VOCs, aerosols) that often increase the overall toxicity of the treated gas stream, and low energy efficiency. In order to overcome these limitations many attempts have been made since 2000 and engendered the development of a hybrid system using multiple techniques such as packed bed NTP reactors [124, 125], NTP/electrostatic precipitation [126], NTP/wet scrubbing [127], NTP with bio-filtration [128] or filter [129], NTP/catalysis [62, 63, 74], photocatalysis [130] and adsorption/NTP [131]. Among these VOC removal techniques, the combination of non-thermal plasma with catalysts/sorbents, i.e. plasma catalysis, is remarkably investigated during the last decade because of its improved performance such as increased energy efficiency and suppressed unwanted by-products distribution for VOC decomposition.

As mentioned before, it is the non-equilibrium nature of the cold, low temperature or non-thermal plasma that offers a number of opportunities for the plasma-catalyst hybridisation, potentially allowing a more efficient
Firstly, by virtue of the occurring plasma chemistry in the gas phase, NTP enables to modify the feedstock which allows thermodynamically difficult reactions to proceed at ambient pressure and temperature. Secondly, by virtue of the plasma/surface interactions, NTP enables catalyst modification which enhances the catalytic reaction. Besides, NTP reduces the operating temperature of the catalyst which both increases the energy efficiency of the process and improves the stability of the catalyst by reducing poisoning, coking, and sintering. Catalytic processes, on the other hand, accelerate a chemical reaction by reducing the energy barrier and inducing an alternative and more energy-efficient reaction pathway which is often very selective towards the desired products. In short, by integrating a catalyst with the plasma, plasma catalysis combines the advantages of gas activation by plasma with high product selectivity from catalysis.

In such a hybrid system, the catalyst can be integrated either inside (IPC) [64] or downstream (PPC) [62, 70] of the discharge region. In addition, few reports on ‘chaining’ of catalysts in PPC or IPC configurations have been made which can be referred as a multi-stage system [132-134]. This is an interesting option to treat complex gas mixtures where each of the catalysts might have a different function in accordance with its position and the expected reaction [132]. Several combination types may be possible in order to treat different components of the gas stream, for example: “initial breakdown of precursor $\rightarrow$ deep oxidation of intermediates $\rightarrow$ O$_3$ killer catalyst”.

Furthermore, depending on the operation mode, plasma catalysis process can be further divided into two categories. One is the continuous operation in plasma catalysis system (CIPC) and the other is the sequential operation in plasma catalysis system (SIPC). These systems have the same structure but different operation modes, resulting in different VOC removal mechanisms and energy utilization efficiencies. Most of the published literature studies are dedicated to continuous operating plasma conditions: a constant amount of pollutant flows through the plasma–catalyst reactor and the discharge is permanently switched on. On the other hand, the SIPC system consists of a two-step process involving first the adsorption of the pollutants, the plasma being switched off, and then the regeneration of the sorbent using a NTP. The latter is a newly developed innovative technique that has attracted growing interest of researchers due to the optimized energy consumption and cost-effectiveness. This could also be an effective regeneration technique compared to conventional techniques like thermal treatment which often leads to catalytic deactivation owing to particle agglomerations on the catalyst.
surfaces, and poses high cost. Recently, Thevenet et al. have partly reviewed the sequential treatment in their publication [135].

This chapter gives an overview of the current status of plasma catalysis research regarding VOC decomposition. Recently, many review papers on VOC removal using continuous plasma catalysis process have been published [30, 48, 49, 136-141]; therefore, only a short description is included here for completeness. Specifically, brief remarks will be given regarding the current understanding of the underlying mechanisms governing this field, rather than collecting a large number of results.

In the first section of this chapter, the concept of continuous treatment and sequential treatment is discussed. Next, a comparison between continuous direct plasma treatment of VOCs and sequential plasma regeneration of VOC saturated sorbents is given in terms of (i) energy efficiency, (ii) VOC abatement and (iii) mineralization aspects. In addition, the synergistic effect and mechanism of these systems is concisely provided.

The second section of this chapter presents an intensive literature review dealing with the sequential treatment for the abatement of VOCs and regeneration of saturated adsorbents with NTP. In the first part of this section, the current status and recent achievements of this new technique for the abatement of VOCs are reviewed. The present understanding of the mechanisms involved in adsorption and oxidation pathways during the regeneration process found in literature are summarized. Finally, the influence of critical process parameters on the adsorption and regeneration step is discussed in detail.

3.2 Continuous Treatment vs Sequential Treatment
(Adsorption followed by NTP Oxidation)

The schematic diagram of a continuous flow process is shown in Figure 3.1. The IPC process is a single stage process where the catalyst is exposed to the active discharge region. In a PPC reactor, the polluted gas stream passes through the plasma discharge followed by the catalytic reactor downstream. For the IPC process, the catalyst is directly in contact with the discharge and exposed to all of the species (e.g. electrons, photons, ions, atoms, radicals, and electronically and vibrationally excited species) generated by plasma. Here, the catalyst and the plasma affect each other, resulting in complex interactions which can alter the properties of the catalyst and/or the plasma which
eventually enhance the performance of plasma catalysis. In contrast, in the two-stage arrangement, along with end-products only long-lived species (> 1 ms) produced by the plasma (e.g. reaction intermediates, ozone, NOx and, possibly, vibrationally excited species) can reach the catalyst surface; as a consequence, the reactivity is related to the kinetic constant of the long-lived species with the VOCs to be treated. For both reactor configurations, the reactions in the gas-phase and on the catalyst surface are important factors in determining the performance of plasma catalysis. In their excellent review, Van drum et al. [138] schematically summarize and thoroughly discuss several physical and chemical processes taking place during plasma catalytic processes.

In both cases, plasma is ignited permanently and the catalyst material can be incorporated in the hybrid reactor in different ways. For instance, as a coating on the reactor walls or electrodes, as a packed bed (powder, pellets, coated fibers or porous solid foam) or as a layer of catalyst material (usually powder/pellets).

The conceptual diagram of sequential treatment or cycled storage discharge (CSD) plasma catalytic process for VOC abatement is shown in Figure 3.2. Firstly, in the adsorption or storage stage, the polluted air stream passes through the catalyst/sorbent bed so that VOCs are removed from the gas phase by adsorption on the catalyst/sorbent until saturation occurs. Next, the saturated catalyst bed is exposed to plasma to oxidize adsorbed VOCs in the regeneration or discharge stage. During this step, the polluted gas stream can be diverted to a fresh catalyst/sorbent bed to ensure continuous operation. It is noteworthy to stress that, most of the reported articles adopted a one stage configuration. In this cyclic approach, surface reactions between adsorbed VOCs/intermediates and plasma generated species such as O3, O radicals on the sorbent are of great importance for the oxidative decomposition of VOCs.
Figure 3.1: Schematic diagram of continuous plasma catalysis process.

Figure 3.2: (a) Conceptual diagram of sequential treatment, (b) difference in discharge power between CSD and a continuous plasma catalytic flow process [142].
In comparison to the continuous treatment, the sequential treatment i.e. adsorption followed by NTP oxidation is expected to treat waste streams over a wide range of VOC concentrations (even indoor ppb levels). In many chemical facilities there is a large variation of VOC concentrations during the operation period. The adsorption step makes this cycled system effective, since energy is not continuously deposited in the treated gas stream, independently of VOC concentration variations. Thus, optimized energy consumption is expected to be achieved with this sequential treatment. Indeed, the most striking difference between continuous and sequential treatments of VOC abatement is the energy demand. The most widely used parameter to determine the energy efficiency of the process is the energy cost $E_c$. The energy cost $E_c$ ($\text{kWh/m}^3$) for a sequential treatment is defined as followed:

$$E_c = \frac{P_{\text{discharge}} \times t_2}{F_1 \times t_1}$$  \hspace{1cm} (3.1)

where $F_1$ is the flow rate (m$^3$/h) during the storage stage and $t_1$ and $t_2$ are the storage and discharge period (h), respectively. In this case, a long storage and a short discharge period are key to achieving low energy cost. The difference in the definition of energy cost between sequential treatment and a continuous flow process is attributed to the energy deposition method. In a continuous flow process, energy density ($J/L$) i.e. the energy deposited per unit volume of process gas, is required to calculate the energy cost as energy is consumed by the discharge to treat the polluted gas stream. Contrarily, in sequential treatment, energy is only alternately deposited during the discharge stage (Figure 3.2-b). Therefore, the energy consumption for sequential treatment is substantially reduced compared to continuous plasma catalysis processes. For instance, Sivachandiran et al. reported that the energy cost for the same amount of Isopropanol (IPA-CH$_3$CHOHCH$_3$) removal using a Mn$_x$O$_y$ packed bed NTP reactor, is 14.5 times less with the sequential approach compared to a continuous treatment process [143]. Furthermore, to achieve the same mineralization degree, sequential treatment consumes 10 times less energy. However, from VOC abatement and mineralization point of views, the continuous treatment appears to be superior since (i) 98% of IPA is converted and (ii) the mineralization rate reaches 78%, which is 1.4 times higher than sequential treatment. Hence, efforts should be made to improve their mineralization ability and to improve the carbon mass balance completion through the investigation of other kinds of sorbents. In this regard, current studies dealing with adsorption followed by NTP oxidation are reviewed in the second section of this chapter.
Nonetheless, in both cases (sequential and continuous treatment) a synergetic effect has been reported in many studies [144-146]. This synergetic effect results in a higher removal efficiency and selectivity compared to the sum of plasma and catalyst processes, when they are used separately. It should be stressed that synergy is not a certain phenomenon in plasma catalysis; it is expected to be observed solely for specific experimental conditions in this system. In fact, careful design is needed to achieve the corresponding synergetic effect by tuning the plasma catalyst interactions. For this reason, the understanding of the underlying mechanisms for the synergy effects is very important. In this regard, several review papers try to raise and validate various hypothesis to explain the performance enhancement of plasma catalysis along with the summaries of many studies presented in literature [30, 136, 138]. For instance, Chen et al. give an excellent review mentioning the underlying reasons for the synergetic effects, based on the effect of plasma on the catalyst and vice versa [136]. Some reviews provide similar explanation in more fundamental perspective [48, 74, 138, 139] while some emphasize on the positive contribution of modelling and simulation to the understanding of such a process [140] or on the positive contribution of in-situ adsorbed phase diagnostics to elucidate reaction pathways and the subsequent plasma material interactions [135]. It is worthy to note that most of these reviews are based on published results in continuous plasma catalysis treatments.

Recently, Feng et. al. emphatically reviewed the status of the synergistic effects and mechanisms in plasma catalysis systems with different operation modes (CIPC, SIPC and PPC) for VOC destruction (Figure 3.3) [146]. It is noteworthy to stress that, the synergetic effect was only observed in the one stage configuration in SIPC system.
In order to facilitate the understanding of the interaction mechanisms between both plasma and catalysts, the interaction in all three processes are broken down into two parts: the effects of the introduction of a catalyst on the performance and the effects of the introduction of a plasma on the performance. Compared to the SIPC and PPC systems, the mechanisms of the CIPC are more complex due to the fact that on one hand both the plasma and the catalyst independently affect the surface processes and on the other hand there are complex interdependence effects of plasma on catalyst and catalyst on plasma. For the former case, the plasma does so by transferring energy (lower breakdown voltage, change of the electron energy…) to activate the gas resulting in the delivery of reactive species, ions, electrons, photons and vibrationally excited species to the surface which promotes a heterogeneous system reactivity (plasma catalyst interaction). On the other hand, partial/soft oxidation of VOCs by active species generated from NTP can significantly enhance the pollutant affinity for the adsorbents [147, 148]. During plasma treatment, modification of the VOCs structure can cause an increase in the molecular size of VOCs. It can also modify their chemical nature through the formation of new polar functions on molecules which lead to better retention of VOCs on the adsorbents. Besides, the catalyst will also affect the surface
reactions since the catalyst renders new reaction pathways in plasma catalysis that have lower activation barriers together with promoting higher rates for specific reactions. Both adsorption and reaction properties of catalysts are used to increase the residence time of VOCs and their reaction probability with active plasma species (e.g. oxygen radicals and ozone) leading to a high mineralization degree [149]. If the catalyst has a high adsorption capacity, the residence time and concentration of pollutant will increase. In addition, it is worthy to note that the catalyst can also adsorb the active species thus preventing their recombination and increasing their lifetime. This will result in a higher collision probability between the pollutant and the active species which will simultaneously stimulate the removal efficiency and mineralization degree. For instance, Song et al. have revealed that with NTP treatment, the removal rate of propane with molecular sieve was significantly higher (85%) than the case with glass beads (17%) or γ-Al₂O₃ beads (23%) reactor [150]. This was attributed to the higher surface area and smaller pore size of molecular sieve compared to the latter cases which have weaker adsorption capability for propane.

On top of this, the catalyst properties themselves are modified by the presence of the plasma, and the plasma properties are also modified by the presence of the catalyst, which are interdependent, leading to a complex synergistic mechanism. For instance, the plasma can modify the catalyst morphology (enhanced dispersion leading to increased surface area and active sites thus promoting the adsorption of pollutants and active species) or work function (depend on morphology, occurrence of contamination and surface reaction), change the oxidation states, excite the activity of the photocatalysts (UV and electron-hole pair creation), heat at a local spot, and modify the catalyst reaction pathways (reaction proceeds through direct E-R mechanism at lower temperature which cannot occur in conventional thermal catalysis at the same condition/temperature).

Indeed the surface chemistry (Figure 3.4) in IPC is expected to differ compared to thermal catalysis which is clearly reviewed by Kim et al. [137]. The immediate difference in the surface chemistry is attributed to the altered chemical environment (presence of novel or additional reactive species) on the catalyst surface which leads to an easy adsorption and desorption. On one hand, plasma produces reactive species such as electrophilic radicals or vibrationally excited molecules that can adsorb more easily on the surface compared to parent molecules or ground stage molecules. On the other hand, ion and electron bombardments promote the desorption process.
Moreover, the plasma properties will be affected via inserting a catalyst in the discharge volume, such as local electric field enhancement, modification of the nature of the discharge, enhancement in plasma generation, and eventually generation of new reactive species. Indeed, by introducing a catalyst in the discharge zone the discharge gap shortens causing an intensification of the electric field strength. In addition, the field enhancement results from the high local curvature of the surface (porous catalyst material), also from the possible accumulation of charges and polarization effects in the case of dielectric pellets and it is governed by the contact angle, the curvature and the dielectric constant of the pellets. This high electric field strength increases the electron density and mean energy which increases the concentration of active plasma species hence promoting high VOC removal efficiency. A second effect that is closely related to the electric field enhancement is the formation of microdischarges in the volume of the catalyst pores leading to different production and loss rates of the various plasma species, and thus to a change in the chemistry. It should be noted that plasma can only be introduced into the pores of a catalyst when these pores are bigger than $\gamma_{De}$, the Debye length on the plasma. Furthermore, by introducing the catalyst inside the gap of a streamer type discharge, the discharge volume is strongly reduced, leading to a modification of the discharge mode from bulk streamers to more intense streamers running along the surface (surface flashover). Malik et al. reported that volume streamers could change into surface streamers near catalyst surfaces in the case of plasma driven catalysis IPC [151]. These surface
streamers show enhanced ionization, which promotes the decomposition of VOCs.

The interaction mechanism of plasma and catalysts is simpler compared to CIPC as surface reactions are mainly considered in a SIPC system which also makes the evaluation of the process performances more straightforward. Indeed, the adsorption of VOCs on the catalyst surface would increase its retention time and even its concentration in the discharge zone. This will result in a higher collision probability between the adsorbed pollutant and the active oxidative species which were directly generated in the vicinity of the sorbent surface leading to higher energy efficiency and mineralization degrees. It is noteworthy to stress that, the adsorption of VOCs on the catalyst surface leads to the formation of surface species which have an influence on the surface reactions determining the decomposition pathway. In this process, pre-emission of side-products is prevented and surface chemistry (O₃ decomposition, redox property..) of the sorbent can be used to enhance the oxidation as a synergetic effect. Moreover, plasma generated active species (like O₃, O and OH radicals) induce oxidative desorption of the VOCs, thus regenerating the catalyst surface.

Figure 3.5: Schematic representation of several factors active in plasma catalysis [151].
Compared to CIPC and SIPC, the mechanism of the PPC system is simpler and more straightforward as there is no direct interaction of the plasma with the catalyst surface. The main role played by the plasma is changing the gas composition fed into the catalyst reactor. Through the homogeneous complex reactions between the background gases (O₂, N₂, possible H₂O), plasma enriches the gas stream with chemically reactive species (O, OH, radicals and O₃), and through the direct reaction of these reactive species with VOCs plasma generates easier treated oxygenated intermediates for catalysis. From the chemical reactive species, only long lived species like ozone and possible vibrational excited molecules can be catalytically exploited in the catalyst bed. In some plasma processes (e.g. oxidative conversion or mineralisation of volatile organic species), there can be a release of chemical energy that can raise the temperature of the gas thus facilitating the catalytic action.

On the other hand, the integration of a catalyst downstream of the plasma discharge zone enhances the VOC degradation efficiency and inhibits the formation of by-products, which is mainly achieved by the following two aspects: catalyst ozone decomposition efficiency and catalyst physio-chemical properties. In the former case, the catalyst effectively decomposes the plasma emitted ozone and generates active oxygen species which further oxidize plasma non-processed hazardous species. As for later case, the redox property, high oxygen vacancies and mobility as well as the textural properties (morphology, surface area) of the catalyst play key roles in the total oxidation of VOCs.

Understanding the physical interaction between NTP and a catalyst is important for further improvement of the process efficiency. However, this field is still in the early research stages and fundamental information on the interaction of NTP with a catalyst is still lacking; thus, further study is required. In this regard, new diagnostic techniques and computational strategies could be adopted to precise measurements and modelling of excited, ionized species and radicals in the plasma, reaction time scales and the nature of the species interaction with the surface of the catalyst (e.g. species pore penetration depth) and the electrode. Another challenge lies in bridging the gap between the fundamental science and process development and optimization.

Plasma catalysis has been considered as the next generation non-thermal plasma technique for VOC removal due to the higher energy efficiency and the better selectivity. From the different plasma catalyst reactor combination
types (according to structure and operation mode), the choice of one configuration rather than the other has to be adapted to the environment (indoor air treatment/end-of-pipe treatment in industry) and the pollutants to be treated. The choice of the catalyst material is also particularly important, since different materials can be more or less suitable for the removal of the target compounds and can react differently depending on their positioning. Several review papers have already overviewed the type of catalysts used, the pollutants treated, the discharge conditions and other critical process parameters used in plasma catalysis [25, 68, 74, 145, 152-154]. The most common non-thermal plasma sources used in plasma catalysis process are corona, dielectric barrier and packed bed discharge reactors. At the same time, from myriad catalysts used in plasma catalytic experiments, it is not yet possible to draw a definite conclusion on the most suitable catalyst. Moreover, different discharge type, reactor geometry, target pollutants, working conditions/process parameters (humidity, flow rate and initial VOC concentration) as well as various catalyst precursor/preparation methods are investigated which may affect the catalytic performance thus making the situation more complex. Indeed, the location and nature (physical, structural and chemical) of the catalyst play a key role in determining the nature of plasma material interactions and consequently its effectiveness towards the process. Therefore, based on all the studies available in literature, it is possible to predict the most appropriate catalyst characteristics in order to successfully hybridize with a particular plasma catalyst discharge configuration.

For instance, for IPC reactor configuration, the appropriate catalyst must be chosen with the following characteristics: 1) has high roughness and dielectric constant to enhance the local electric field in the vicinity of the catalyst and reduce the gas breakdown voltage; 2) has porous structure with higher surface area to increase the lifetime of active species and to increase VOC residence time by facilitating the adsorption of pollutants; 3) has potential surface reactivity such as higher number of active sites to rapidly react with contaminants; 4) can efficiently decompose ozone to prevent secondary pollution. The most common catalysts used in the IPC systems are metal oxides (e.g., MnOₓ, CuOₓ, CeOₓ, CoOₓ, NiOₓ, V₂O₅, Fe₂O₃, WO₃, ...), complex oxides (perovskites- BaTiO₃) as well as metals (e.g., Ag, Ni, Pt, Pd, Cu, Au ...) coated or impregnated on various porous materials (e.g. γ-Al₂O₃, TiO₂, SMF, SBA-15, zeolites and OMS-2) which act as support.

Conversely, in post plasma configuration, the most desirable properties of the appropriate catalyst should be its ozone decomposition ability and VOC total
oxidation capability close to room or moderate temperatures (≤ 150 °C), so that the targets are removed efficiently and economically by PPC. The basic idea is to take advantage of the catalyst O₃ decomposition efficiency to supply active oxygen species enabling the total oxidation of plasma non-processed hazardous species and consequently enhance VOCs removal efficiency and minimize the unwanted by-products of plasma. Moreover depending on the feed gas (humid air) and the target VOCs (chlorinated VOCs), the catalysts should also possess hydrothermal stability and chlorine resistivity. In brief, catalyst’s redox property, crystal defects, diffusion in the crystal lattice, high OSC and mobility and surface area play an important role in the effective VOCs oxidation. Up until now, catalysts have been proposed for use in post processes, including noble metals (pd) or transition metal oxides (Mn, Ti, Zn, V), gold (Au) or cerium (Ce) oxides, mixed or complex oxides (perovskites) and their combination with supports of zeolites, γ-Al₂O₃, molecular sieves, SMF and activated carbon (AC).

It is worthy to mention that some catalysts (for example, MnO₂, and Ba-CuO-Cr₂O₃/alumina) are better in two-stage rather than in single-stage configurations [69, 70, 155]. In many cases, single-stage configuration has been found to be better than two-stage (including ozone injection) for a given catalyst [71, 156-159].

For SIPC, the most relevant catalyst/sorbent to be coupled with plasma should have the following properties: 1) has a large adsorption capacity for pollutants thus increasing surface pollutant concentration leading to an improved energy efficiency; (2) is able to benefit from short life-time as well as long life-time oxidizing species, thus inducing oxidation processes on its surface to regenerate; (3) has tuneable surface reactivity compliant with oxidation reactions and hydrophilicity, and (4) is resistance to poisoning when exposed to pollutants as well as plasma generated species to provide a stable operation of the cyclic process.

Combinations of active transition metals (Ag, Cu, Mn) and Ce loaded on porous supports (such as titania, alumina, silica, activated carbon and zeolite) and metal oxides (MnxOy) are the most commonly used catalysts in the SIPC system.

In general, the sole NTP method is not an effective technique for the removal of VOCs due to high energy consumption and low CO₂ selectivity, producing harmful by-products. The addition of catalysts inside or after the plasma region can increase the efficiency of the NTP method, but a general rule for
selecting the appropriate catalyst for a particular plasma catalysis reaction has not yet been established. Although the history of this research field is relatively short, one simple and straightforward approach to determining the appropriate catalyst for a particular reaction is to use an accumulated database on thermal catalysis. However, due to the reactive plasma environment, the most suitable catalysts will probably be different from thermal catalysts in some cases. Hence, more research is needed to better understand the plasma–catalyst interactions, in order to further improve the applications and move it forward into the market as a commercial product.
3.3 Literature Overview of Sequential Treatment

Since the sequential treatment has gained increased interest over the last decade, an overview will be given of published papers that help to understand the degradation pathway and to optimize the process parameters. Table 3.1 summarizes the results regarding the adsorption and regeneration stage of these publications found in literature.

Zhao et al. have investigated the removal of formaldehyde (HCHO) from air using a CSD plasma catalytic process over AgCu/HZSM-5 (HZSM-5, SiO2/Al2O3=360) catalyst for indoor air purification [142]. Their system combined extremely low energy cost with excellent humidity tolerance while no secondary pollution was detected. In order to achieve 100% conversion of HCHO to CO2, almost the same discharge period (t2=10 min) was required for different storage periods (t1=100, 300, 600 min). This proves that long storage periods can be employed to achieve low energy cost. It is reported that the energy cost to remove 6.3 ppm of HCHO from humid air reaches 1.9x10^{-3} kWh/m³. This cost could be further lowered to 10^{-5}-10^{-4} kWh/m³ by increasing the storage period to purify diluted HCHO (several hundred ppb) in typical indoor air environment.

Almost complete oxidation of benzene (C₆H₆) as well as extremely low energy cost were also achieved by using an Ag/HZSM-5 catalyst-packed dielectric barrier discharge (DBD) in sequential treatment [160]. The energy cost for sequential treatment of air containing 4.7 ppm benzene was 3.7x10^{-3} kWh/m³ while 99.8% CO₂ selectivity was achieved. The catalytic effect of Ag to promote CO oxidation to CO₂ and the strong adsorption of Ag with benzene through π-complexation are found to be responsible for this high selectivity [161].

The effect of different catalysts and reactor configurations on plasma catalytic oxidation of stored benzene was also investigated by the same group [162]. The performance of plasma catalytic oxidation of stored benzene on different metal (Ce, Co, Ag, Mn, Fe, Ni, Cu, Zn) loaded HZSM-5 catalysts was evaluated in terms of carbon balance (Bc) and CO₂ selectivity (SCO₂). Experiments revealed that 0.8 wt% Ag/HZSM-5 catalyst could significantly improve plasma catalytic oxidation of stored benzene to CO₂ (X(C₆H₆) → CO₂ ≈ 100%) in a very short discharge time while the formation of unwanted by-products was almost completely suppressed (Figure 3.6). However, further increase of Ag loading decreases the carbon balance. Regarding the effect of
reactor configuration, both carbon balance and CO$_2$ selectivity reached almost 100% with an IPC reactor (C) within 10 min (Figure 3.6). In contrast, with a PPC reactor (A and B) the stored benzene cannot be completely oxidized even after a long discharge time.

Wang et al. have tested various metal loaded zeolites (Ag/HZSM-5, Mn/HZSM-5, Ce/HZSM-5, Ag-Mn/HZSM-5) to remove low concentration of toluene (C$_6$H$_5$CH$_3$) by intermittent use of adsorption and non-thermal plasma regeneration [163]. In this investigation, a link tooth wheel-cylinder DC plasma reactor is placed upstream of the adsorption/catalyst reactor which is supported by a glass sieve plate. It is suggested that owing to the unique characteristics of the orbitals of Ag or Ag$^+$, normal $\sigma$ bonds to carbon as well as bonds with unsaturated hydrocarbons can be formed in a non-classical manner [164], leading to higher adsorption capacity of Ag loaded zeolites (Ag/HZSM-5, Ag-Mn/HZSM-5). Similar to previous studies, reduced energy consumption (2.2x10$^{-3}$ KWh/m$^3$) is also reported which is related to a high adsorption capacity. Experiments reveal that the catalytic activity for toluene conversion is in the order of Ag-Mn/HZSM-5>Mn/HZSM-5>Ag/HZSM-5>Ce-Mn/HZSM-5>Ce/HZSM-5 which is in accordance with their O$_3$ decomposition ability. Furthermore, it is widely known that oxidation of toluene is significantly affected by lattice oxygen of manganese oxides. Moreover, the ratios of lattice oxygen to surface adsorbed oxygen on the Mn catalysts is enhanced with appropriate Ag loading [165], which explained the high activity and CO$_2$ selectivity (99.9%) of Ag-Mn/HZSM-5 for toluene decomposition.
Figure 3.6: The effect of plasma catalytic reactor configurations on the removal of stored benzene over 0.8 wt% Ag/HZSM-5 catalysts (a) conversion of stored-benzene to CO$_2$, (b) carbon balance and CO$_2$ selectivity (storage stage: 4.7 ppm benzene, 50% RH (25°C), 600 mL/min flow rate of simulated air, $t_1 = 1$ h; discharge stage: 60 mL/min O$_2$, $P = 4.7$ W). Reprinted from Ref. [162], with permission from Elsevier.

Mok et al. have tested a γ-Al$_2$O$_3$ packed DBD reactor for the treatment of toluene in sequential approach [166]. The removal efficiency reached 71.4% while ozone was the only by-product of toluene oxidation besides CO and CO$_2$. The energy yield for the treatment of toluene was reported as 41.2 J/μmol. Experiments revealed that the higher discharge power favored the formation of CO and CO$_2$ at shorter discharge period.
Kim et al. have compared the decomposition of benzene by using flow-type plasma driven catalysis (IPC) and a cycled system [55]. In the flow type IPC reactor, the formation of $N_xO_y$ is unavoidable and is correlated with the increase of the conversion of VOCs. In contrast, oxygen plasma completely oxidized the adsorbed benzene on 2.0 wt% Ag/TiO$_2$ to CO$_2$ in cycled system, which is impossible with the conventional NTP alone process or the flow-type IPC system.

O$_2$ plasma treatment as well as O$_3$ injection were found to be effective for the regeneration of deactivated gold supported TiO$_2$ surface after exposure to 100 ppm toluene or propylene [159]. IPC configuration showed better oxidation performance of adsorbed toluene than PPC configuration. Adsorbed toluene or propylene was preferentially decomposed to CO$_2$ in both regeneration methods. In case of PPC configuration, direct reaction between gas phase O$_3$ and adsorbed toluene instead of desorbed toluene is suggested by the authors as a possible pathway for toluene decomposition.

In order to understand the role of adsorption on the removal of acetaldehyde Klett et al. have used a sequential treatment [167]. A wire to cylinder configuration packed with $\alpha$-Al$_2$O$_3$ pellets was used to adsorb 1000 ppm CH$_3$CHO during the adsorption process. After saturation of the adsorbent it was treated with less than 1 W plasma regenerating only 25% of the saturated adsorbent. In order to analyze the role of surface reactivity on the possible decomposition pathway, adsorption of multicomponent mixtures of CH$_3$CHO, CO, CO$_2$ and O$_3$ was carried out and the interactions existing between different compounds and the catalyst surface have been identified. Authors have also used diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and have detected several intermediates (acetate, formate) during the adsorption step. During the regeneration of saturated alumina with plasma, the DRIFT study revealed both the presence of acetaldehyde and some intermediates on the surface which are incorporated in the decomposition reaction. Adsorbed oxygen species, resulting from O$_3$ decomposition on the surface, lead to CH$_3$CHO decomposition and CO oxidation to CO$_2$. Clearly, more acetaldehyde was decomposed to CO and CO$_2$ due to surface reactions than in the gas phase [167].
Table 3.1. Overview of published papers on sequential treatment

<table>
<thead>
<tr>
<th>Target pollutant</th>
<th>Catalyst/Adsorbent</th>
<th>Specific surface area (m²/g)</th>
<th>Carrier gas and flow rate (mL/min)</th>
<th>Concentration (ppm)</th>
<th>Plasma reactor type</th>
<th>carrier Gas and flow rate (mL/min)</th>
<th>Fs (W)</th>
<th>SIE (J/L)</th>
<th>Time t (min)</th>
<th>Maximum removal efficiency (%)</th>
<th>Mineralization rate m (%)</th>
<th>CO₂ yield c (%)</th>
<th>Ee (kWh/m³)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone (C₃H₆O)</td>
<td>TiO₂</td>
<td>38 ± 3</td>
<td>dry air</td>
<td>180</td>
<td>DBD/IPC</td>
<td>dry air</td>
<td>0.33</td>
<td>W</td>
<td>t₁ = 103 t₂ = 30</td>
<td>27</td>
<td>m = 12</td>
<td>c = 11</td>
<td>1.6x10⁻²⁸</td>
<td>[168]</td>
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<td>DBD/IPC + TPTD</td>
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<tr>
<td>Benzene</td>
<td>Ag/HZSM-5</td>
<td>334</td>
<td>80% N₂ + 20% O₂ (50% RH)</td>
<td>4.7</td>
<td>DBD/IPC</td>
<td>O₂</td>
<td>4.7 W</td>
<td></td>
<td>t₁ = 840 t₂ = 24</td>
<td>100</td>
<td>c = 99.8</td>
<td></td>
<td>3.7x10⁻⁵</td>
<td>[160]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>60</td>
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<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>Ag/HZSM-5</td>
<td>Air</td>
<td>3</td>
<td>link tooth wheel cylinder/PPC</td>
<td>synthetic air (40 ± 5% RH)</td>
<td>62°</td>
<td>c &gt; 90</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.2x10⁻³</td>
<td>[163]</td>
</tr>
<tr>
<td></td>
<td>Mn/HZSM-5</td>
<td></td>
<td>3000</td>
<td></td>
<td>1000</td>
<td>69</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ce/HZSM-5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>56°</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Ce-Mn/HZSM-5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>93</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Ag-Mn/HZSM-5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>70°</td>
<td>c = 99.9</td>
<td></td>
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<tr>
<td>Target pollutant</td>
<td>Catalyst/Adsorbent</td>
<td>Specific surface area (m²/g)</td>
<td>Carrier gas and flow rate (mL/min)</td>
<td>Concentration (ppm)</td>
<td>Plasma reactor type</td>
<td>Carrier gas and flow rate (mL/min)</td>
<td>P_{in} (W)</td>
<td>SIE (J/L)</td>
<td>Time t (min)</td>
<td>Maximum removal efficiency (%)</td>
<td>Mineralization rate m (%)</td>
<td>CO₂ yield c (%)</td>
<td>E₀ (kWh/m³)</td>
<td>Ref.</td>
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</tr>
<tr>
<td>Formaldehyde</td>
<td>Ag(3.6 wt%)-Cu(2.1 wt%)/HZSM-5</td>
<td>229</td>
<td>80% N₂ + 20% O₂ (50% RH) 300</td>
<td>8.8</td>
<td>DBD/IPC</td>
<td>O₂ 60</td>
<td>2.3</td>
<td>t₁ = 690  t₂ = 10</td>
<td>100</td>
<td>≥ 99</td>
<td>1.9x10⁻³</td>
<td>[142]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isopropanol</td>
<td>TiO₂</td>
<td>38 ± 3</td>
<td>Air (50% RH) 1000</td>
<td>163</td>
<td>DBD/IPC</td>
<td>air (50% RH) 1000</td>
<td>t₁ = 60  t₂ = 60</td>
<td>91</td>
<td></td>
<td></td>
<td></td>
<td>[149]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>HZSM-5</td>
<td>328</td>
<td>80% N₂ + 20% O₂ (50% RH)</td>
<td>4.7</td>
<td>DBD/IPC</td>
<td>O₂ 60</td>
<td>4.7</td>
<td>t₁ = 60  t₂ = 9</td>
<td>100</td>
<td>c - 89*</td>
<td>100</td>
<td>[162]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ag(0.8 wt%)/HZSM-5</td>
<td>334</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ag(1.9 wt%)/HZSM-5</td>
<td>329</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[142]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ag(4.2 wt%)/HZSM-5</td>
<td>306</td>
<td></td>
<td></td>
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<tr>
<td>Target pollutant</td>
<td>Catalyst/Adsorbent</td>
<td>Specific surface area (m²/g)</td>
<td>Carrier gas and flow rate (mL/min)</td>
<td>Concentration (ppm)</td>
<td>Plasma reactor type</td>
<td>Carrier gas and flow rate (mL/min)</td>
<td>P_{in} (W)</td>
<td>SIE (J/L)</td>
<td>Time (min)</td>
<td>Maximum removal efficiency (%)</td>
<td>Mineralization rate m (%)</td>
<td>CO₂ yield c (%)</td>
<td>Eₜ (kWh/m³)</td>
<td>Ref.</td>
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</tr>
<tr>
<td><strong>Benzene</strong></td>
<td>Ag(1 wt%)/TiO₂</td>
<td>≤ 68</td>
<td>Air (50% PP) 4000, 5000</td>
<td>200</td>
<td>DBD/IPC</td>
<td>O₂: 5000-8000</td>
<td>169</td>
<td>J/L</td>
<td>100</td>
<td>100°</td>
<td></td>
<td></td>
<td></td>
<td>[169]</td>
</tr>
<tr>
<td></td>
<td>Ag(4 wt%)/TiO₂</td>
<td></td>
<td>Air (60% PP)</td>
<td>200</td>
<td>DBD/IPC</td>
<td></td>
<td>136</td>
<td>J/L</td>
<td>75°</td>
<td>c - 80°</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>0.5%Ag/γ-Al₂O₃</td>
<td>≤ 210</td>
<td>Air (60% PP) 4000, 5000</td>
<td>200</td>
<td>DBD/IPC</td>
<td></td>
<td>160</td>
<td>J/L</td>
<td>90°</td>
<td>c - 75°</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H-Y zeolite</td>
<td>≤ 520</td>
<td>Air (80% PP) 10000</td>
<td>200</td>
<td>DBD/IPC</td>
<td></td>
<td>140</td>
<td>J/L</td>
<td>100</td>
<td>c - 64°</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ag(2 wt%)/H-Y zeolite</td>
<td>≤ 210</td>
<td>Air (60% PP) 4000, 5000</td>
<td>200</td>
<td>DBD/IPC</td>
<td></td>
<td>160</td>
<td>J/L</td>
<td>100</td>
<td>c ≥ 75°</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Formaldehyde</strong></td>
<td>mineral granulate (MP 5)</td>
<td></td>
<td>N₂: 176</td>
<td>99</td>
<td>DBD/IPC</td>
<td></td>
<td>2.2</td>
<td>W</td>
<td>t₁ = 250, t₂ = 4</td>
<td>94</td>
<td>m - 38.7°</td>
<td>c - 26.5°</td>
<td></td>
<td>[170]</td>
</tr>
<tr>
<td><strong>Acetaldehyde</strong></td>
<td>α-Al₂O₃</td>
<td>14</td>
<td>95% N₂ +5% O₂ 100</td>
<td>1000</td>
<td>corona discharge/IPC</td>
<td>95% N₂ +5% O₂ 100</td>
<td>1 W</td>
<td></td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[167]</td>
</tr>
<tr>
<td>Target pollutant</td>
<td>Catalyst/Adsorbent</td>
<td>Specific surface area (m²/g)</td>
<td>Carrier gas and flow rate (mL/min)</td>
<td>Concentration (ppm)</td>
<td>Plasma reactor type</td>
<td>Carrier gas and flow rate (mL/min)</td>
<td>P&lt;sub&gt;in&lt;/sub&gt; (W)</td>
<td>Time t (min)</td>
<td>Maximum removal efficiency (%)</td>
<td>Mineralization rate m (%)</td>
<td>CO₂ yield c (%)</td>
<td>E&lt;sub&gt;c&lt;/sub&gt; (kWh/m³)</td>
<td>Ref.</td>
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<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>γ-Al₂O₃</td>
<td>237</td>
<td>N₂ 2500</td>
<td></td>
<td>DBD/IPC</td>
<td>O₂ 2500</td>
<td>88 W</td>
<td>t₁ = 190  t₂ = 70</td>
<td>71.4</td>
<td>66</td>
<td>m = 56, c = 44</td>
<td>0.210⁶</td>
<td>[166]</td>
<td></td>
</tr>
<tr>
<td>Isopropanol</td>
<td>Mn&lt;sub&gt;3&lt;/sub&gt;O₄</td>
<td>16 ± 2</td>
<td>dry air 1000</td>
<td>165</td>
<td>DBD/IPC</td>
<td>dry air 1000</td>
<td>0.82 ± 0.02 W</td>
<td>t₁ = 6  t₂ = 30</td>
<td>84</td>
<td>96</td>
<td>m = 84, c = 72</td>
<td></td>
<td>[171]</td>
<td></td>
</tr>
<tr>
<td>Isopropanol</td>
<td>TiO₂</td>
<td>45</td>
<td>dry air 750</td>
<td>98</td>
<td>DBD/IPC</td>
<td>dry air</td>
<td>68.2 mW</td>
<td>t₁ = 130  t₂ = 70</td>
<td>24</td>
<td>66</td>
<td>m = 2, c = 1.7⁶</td>
<td></td>
<td>[172]</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>fibrous activated carbon textile</td>
<td>26.32⁶</td>
<td>air 100</td>
<td>200</td>
<td>ac-neon transformer</td>
<td>6 J/cm²</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[131]</td>
</tr>
<tr>
<td>Toluene</td>
<td>zeolites</td>
<td>10 - 120</td>
<td>air 150000</td>
<td></td>
<td>DBD/IPC</td>
<td>air 150000</td>
<td>89 W</td>
<td>90 - 39</td>
<td></td>
<td>2.6 - 13 g/kWh</td>
<td></td>
<td></td>
<td>[173]</td>
<td></td>
</tr>
</tbody>
</table>
TPD-Temperature programmed desorption (296-673 K, 0.4 K/s)
PP- Partial pressure of O₂
RH- Relative humidity

a Approximate value extracted from graphs
b Calculated value from equations
The regeneration of IPA and acetone saturated TiO$_2$ surface under O$_3$ flow produced by NTP (PPC) was investigated by Barakat \textit{et al.} [172]. To elaborate the oxidation mechanism of IPA and acetone, simultaneous analysis of the gas phase and absorbed phase was carried out with Fourier transform infrared spectroscopy (FTIR) and DRIFTS, respectively. The adsorption of IPA on TiO$_2$ surface leads to the formation of three surface species. The formation of monodentate isopropoxy groups and surface hydroxyl species indicates dissociative adsorption of IPA through Eq. (1) [149], where S$_{1b}$, S$_{2d}$ represent two different adsorption sites. Strongly bonded IPA species on surface Lewis acid sites (Ti$^{+\delta}$) and weakly hydrogen bonded IPA species on surface basic sites (Ti$^{-\delta}$) are the result of non-dissociative adsorption of IPA on TiO$_2$ surface. Regarding IPA oxidation, authors reported that O$_3$ is simultaneously adsorbed on TiO$_2$ strong Lewis acid sites and on adsorbed IPA (0.2 O$_3$ molecule per 1 IPA molecule). Experiments revealed that independently of the adsorption modes, dissociated and non-dissociated IPA on TiO$_2$ show the same reactivity with ozone. Only 2% mineralization was achieved (since 7 O$_3$ molecules are required to release 1 CO or CO$_2$ in the gas phase) and 22% of the irreversibly adsorbed IPA was desorbed as intermediate by-product acetone. Agreeing with Arsac \textit{et al.} [174], the authors proposed that, acetone, produced from oxidation of adsorbed IPA on S$_{1b}$ sites, cannot remain adsorbed on similar adsorption sites (due to competitive adsorption phenomena between IPA and acetone). Acetone either rapidly desorb to the gas phase if no surface sites denoted by S$_{2d}$ are available or diffuse toward an available S$_{2d}$ site. Noting that, only a small fraction of TiO$_2$ surface sites S$_{2d}$ are specific to the acetone adsorption (there is no competitive chemisorption with IPA). For IPA, literature data [174-176] strongly suggest that acetone is the single route to produce CO$_2$ and H$_2$O. Experiments revealed that when the TiO$_2$ surface is fully saturated with IPA, small amount of S$_{2d}$ sites are accessible for irreversibly adsorbed acetone and its subsequent oxidation into CO$_2$ [172]. Since, for mineralization, adsorbed IPA needs to go through S$_{2d}$ adsorbed acetone, oxidation of IPA and acetone into CO$_2$ have the same limiting step.

$$\text{CH}_3\text{CHOHCH}_3 + S_{(1)} + S_{(2)} \rightarrow S_{(1)}\text{CH}_2\text{CHOCH}_3^{\text{ads}} + S_{(2)}\text{H}^{\text{ads}} \quad (3.2)$$

The regeneration of acetone adsorbed TiO$_2$ surface has also been conducted with an IPC process by Sivachandiran \textit{et al.} [168]. The NTP regeneration is however limited to 30%. During the adsorption stage, 30% of adsorbed acetone is converted into adsorbed mesityl oxides by surface aldolization. These mesityl oxides are fragmented into carboxylic acid (e.g. formic acid) by
NTP treatment, which was also evidenced by Barakat et al. [172]. It was confirmed that formic acid is poorly sensitive to NTP treatment but directly converted into CO\textsubscript{2} under successive thermal treatment. Hence, enhanced mineralization can be achieved by NTP technique followed by thermal treatment [168].

Recently, three different methods have been used by the same group for regeneration of an IPA saturated Mn\textsubscript{2}O\textsubscript{3} surface [171]. In order to emphasize the proficiency of NTP treatment compared to other regeneration methods, the total carbon mass balances obtained by each method were reported and shown in Figure 3.7. Although 94% regeneration efficiency has been achieved with dry air thermal treatment (DTT), 57% of carbon mass balance is accounted for molecularly desorbed IPA and acetone which is considered as a drawback. Dry air ozonolysis (PPC) achieved the lowest regeneration efficiency (41%) with 23% CO\textsubscript{x} and 12% acetone contribution. In-situ NTP (IPC) treatment is considered as the most efficient method to obtain high mineralization and low VOCs desorption, even though 66% of irreversibly adsorbed IPA has been removed. A possible oxidation/mineralization pathway for adsorbed IPA on Mn\textsubscript{2}O\textsubscript{3} surface by PPC-DTT and IPC treatment was also proposed in equations (2-6) and (7), respectively. Acetaldehyde and isopropyl esters of formic and acetic acids are the main identified intermediate species in both PPC and DTT methods. This indicates the dependency of the adsorbed IPA decomposition pathway on IPA adsorption modes rather than the regeneration methods. In case of IPC treatment, acetone is the main intermediate species. As reported in [172], IPC treatment prior to thermal treatment significantly improves regeneration efficiency and mineralization degree.

Sivachandiran et al. have also studied the influence of air humidity on IPA adsorption on TiO\textsubscript{2} surface and surface plasma regeneration efficiency [149]. During this investigation, only 36% regeneration efficiency has been obtained with dry air NTP treatment. Dry air NTP assisted regeneration of IPA saturated Mn\textsubscript{2}O\textsubscript{3} showed better performance in terms of total carbon mass balance and CO\textsubscript{x} selectivity compared to TiO\textsubscript{2} surface [171]. The superior removal/regeneration efficiency of Mn\textsubscript{2}O\textsubscript{3} metal oxide is ascribed to the higher ability to decompose ozone. These results revealed the importance of surface reactivity of catalyst placed inside the NTP discharge zone.
A new hybrid approach consisting of concentration technique, followed by surface discharge plasma treatment is reported by Yamamoto et al. [177]. The process of alternate adsorption and desorption was carried out in the concentration technique where molecular sieve was used as adsorbent and thermal heat was used to desorb toluene. The purpose of using this concentration technique is to convert low concentrated high flow rate flue
gases into a low flow rate gases with high concentration of VOCs. As a result, the size, energy consumption and operating costs of such cyclic systems are greatly reduced. Experiments revealed that more than 90% toluene decomposition efficiency was achieved by using two surface discharge units at 25 W while the energy efficiency was 34.2 g/kWh. On the other hand, the energy efficiency for continuous plasma treatment was only 1.97 g/kWh. These findings show that the consecutive process of adsorption, desorption and plasma decomposition requires 17 times less energy than the continuous plasma treatment.

The studies mentioned above mainly focus on the adsorbed VOCs oxidation performance by plasma without gas circulation. Few studies have however been conducted on plasma catalytic oxidation performance with a gas circulation. For instance, investigation of plasma catalytic oxidation of adsorbed toluene using gas circulation with MnOx and AgOx catalyst have been reported by Dang et al. [178]. Experiments revealed that when MnOx/ɤ-Al2O3 is used, continuous cycle mode exhibit better COx yield (11% higher) than intermittent cycle mode due to the enhanced utilization of reactive species by gas circulation. It is also observed that CO2 selectivity of MnOx/ɤ-Al2O3 and AgOx/ɤ-Al2O3 catalysts were both close to 100% after a 60 min oxygen plasma treatment.

A pilot-scale test of a toluene oxidation system was developed using an adsorbent (zeolite pellets) and a NTP (surface discharge) with gas circulation by Kuroki et al. [179]. When 1 mL of toluene was oxidized for 90 min, the conversion ratio of toluene to COx was 88% wherein 94% CO2 selectivity was achieved. During 6 mL toluene oxidation for 150 min, these values were decreased to 44% and 89% respectively. However, the authors reported that the conversion rate of toluene to COx and the energy efficiency of the toluene to COx conversion were increased with the amount of adsorbed toluene. By the same research group, a xylene decomposition system was also investigated using different NTP plasma sources (60-Hz neon transformer and inverter-type neon transformer) with gas circulation [180]. Inverter-type neon transformer showed better performance (higher conversion ratio of xylene to COx and higher energy efficiency) than the 60-Hz neon transformer. However, unstable operation and large amounts of NOx production makes the inverter-type neon transformer less suitable. A conversion ratio of adsorbed xylene to COx of 43% was reached at 60 min and 90% CO2 selectivity was achieved with the 60-Hz neon transformer.
Another cyclic operation of adsorption and DBD treatment was demonstrated by Yamagata et al. for the abatement of diluted toluene (10-120 ppm) from air [173, 181]. Experiments were carried out with and without gas circulation. For the latter case, enhanced decomposition efficiency was obtained with insertion of the honeycomb zeolites in the DBD reactor compared to the plasma alone system. It is suggested that an increase of the residence time due to adsorption of toluene on the zeolites honeycomb sheet is responsible for the enhanced performance. Under gas circulation with 150 L/min flow rate, the decomposition ratio was 70 to 93% while the energy efficiency was 19 to 8.4 g/kWh. Successful regeneration of zeolites honeycomb sheet was also reported with this sequential treatment.

3.4 Critical Process Parameters for VOC Adsorption

The most important parameters for the selection of an appropriate adsorbent are capacity, selectivity, regenerability and cost. Adsorption capacity is the most prominent characteristic of an adsorbent which is defined as the amount of adsorbate accumulated on the adsorbent surface, per unit mass or volume of the adsorbent. It is evident that better adsorption capacity assists to reduce the overall energy consumption of the process [142]. In most literature, adsorption capacity is expressed by means of an adsorption isotherm which plots the loading/capacity as a function of concentration at constant temperature. Adsorption isotherms can provide valuable information about the surface chemistry, the fundamentals involved in the adsorption process and estimation of the surface area, pore volume and pore size. Common adsorbents are inorganic materials such as alumina (Al₂O₃), silica gel, zeolites and organic materials such as AC and polymers. In the following sections, the parameters that affect the adsorption process will be discussed in more detail.

3.4.1 Physical Properties of the Sorbent/Catalyst

The adsorption capacity greatly depends on the surface roughness quantified by the specific surface area (m²/g). By increasing the specific surface area, the adsorption capacity will be improved. Activated carbon, alumina and silica gel are considered as excellent adsorbents owing to their highly porous structures and large surface areas. Surface area of a powdered adsorbent depends upon its particle size: the particle size is inversely proportional to the specific surface area. Thus, finely divided metals such as nickel and platinum provide large surface area and are ideal adsorbents. VOC adsorption capacity also depends on material pore volume, pore size, pore size distribution and
diffusion rate, cation exchange capacity, pH and surface functional groups [182-184].

The mechanism of adsorption is dependent upon the size of the VOC molecules in comparison with the pore diameter of the adsorbent due to the energetic interactions between the chosen adsorbate and the pores [185]. It has been shown that the adsorption energy depends on the size of pores in adsorbents [186]. The enlargement of pore size reduces the overlapping potential for adsorbate between pore walls leading to lower adsorption energy [187]. Huang et al. have demonstrated that the capacity for VOCs adsorption on ACs is controlled by characteristics adsorption energy which is inversely proportional to the local pore size [188]. VOC molecules tend to adsorb most strongly in areas where the pore diameter of the adsorbent is close to the molecular diameter of the VOCs. For instance, in a silicalite ZSM-5 with narrow pores of 5.5 Å diameter, the methyl ethyl ketone (MEK) molecules with a kinetic diameter of 5.2 Å interact strongly with the channel walls, whereas this interaction is much smaller in large pores of aluminosilicates such as de-aluminated faujasite Y (Fau-Y-7.4 Å) [189]. The effect of the porosity and the surface chemistry of ACs on the adsorption capacity of low concentrated VOCs (benzene and toluene) has been investigated by Lillo-Rodenas et al. [190, 191]. Experiments revealed that in order to maximize the adsorption capacities of diluted VOCs, an AC surface discharge combined with a large volume of narrow micropores (i.e. pore size below 0.7 nm) and reduced surface oxygen groups are desired.

3.4.2 Nature of VOCs

The amount of adsorbate depends on the nature of VOCs. In general, the higher its critical temperature or van der Waal’s force of attraction, the more readily it will adsorb [184]. This is only valid for physisorption since in this case, the adsorbate physically adsorbs on the surface of adsorbents as a result of van der Waals interactions. Generally three different types of interaction exist among molecules which contribute to the van der Waal’s forces. These are instantaneous dipole-induced dipole interactions, dipole-induced dipole interactions between polar and neutral nonpolar molecules and dipole-dipole interactions between polar molecules. Furthermore, the strength of van der Waals’ forces typically depends on three properties such as molecule size, surface area and polarity. For instance, the surface of AC is basically nonpolar and will weakly interact with polar VOC molecules such as acetone [188]. Since chemisorption involves a chemical reaction between the adsorbent and
the adsorbate, new types of electronic bonds (ionic or covalent) are created. Due to specificity, the nature of chemisorption depends on the chemical nature of the VOC and the surface morphology.

VOCs vapor pressure or boiling point is generally used to quantify the intermolecular interactions instead of their polarity. Polar compounds have higher boiling points or lower vapor pressures than non-polar compounds. VOCs which have a high molecular weight and high boiling point can be effectively adsorbed on AC [192]. At higher boiling points, liquefaction and condensation occur more readily leading to increased adsorption capacity [187, 188]. The influence of VOC molecular size and shape on adsorption has also been investigated by Yang et al. [193]. Experiments revealed that the VOC adsorption capacity on metal–organic frameworks MIL-101 \( (\text{Cr}_3\text{F}(\text{H}_2\text{O})_2\text{OE}(\text{O}_2\text{C})\text{–C}_6\text{H}_4\text{–(CO}_2\text{)})_n\text{H}_2\text{O}; n \approx 25 \) decreased with an increase in VOC molecular cross sectional area since large VOC molecules cannot penetrate through the smaller size of MIL-101 cylindrical micropores. Adsorption of VOCs on MIL-101 also showed shape selectivity towards VOCs molecules: the adsorption capacity of p-xylene was higher than that of m-xylene and o-xylene even though they have almost equal molecule cross-sectional areas (Figure 3.8).

![Figure 3.8: Scheme of ethyl benzene, p-xylene, o-xylene and m-xylene entering into MIL-101 pores. Reprinted from Ref. [193], with permission from Elsevier.](image-url)

It has also been observed that the VOC concentration can have a positive influence on the adsorption capacity of a material [131, 192] and that other chemical properties of VOCs such as oxidation state can also influence adsorption.
3.4.3 Relative Humidity (RH)

The effect of humidity is of great interest for practical applications in industry as well as non-industrial buildings since moisture is always present in some content in ambient air. Regarding VOC adsorption, RH might change the chemical state of the sorbent surface or change the adsorption modes and adsorbed amount of VOC on sorbent. It seems that the effect of RH is determined by the VOC-sorbent combination. VOC adsorption can be enhanced, suppressed or remain neutral when air humidity changes, depending on the hydrophobicity of the sorbent and specific VOC properties like e.g. solubility. Kuroki et al. have mentioned that the influence of RH is negligible in a toluene adsorption process since hydrophobic zeolite honeycomb is used [194]. Similarly, Zhao et al. have investigated HCHO breakthrough capacity over AgCu/HZ catalyst in air with varying RH (dry gas and RH=20%, 50%, 80% and 93%) [142]. HCHO breakthrough capacity slightly decreased in humid condition compared to dry gas. However, breakthrough capacity remains almost constant when RH changes from 20 to 93% due to the hydrophobic property of high-silica zeolite. Sivachandiran et al. have precisely investigated the impact of RH on IPA adsorption over TiO₂ [195]. The influence of air RH on reversibly and irreversibly adsorbed IPA on TiO₂ is shown in Figure 3.9. The amount of both reversibly as well as irreversibly adsorbed IPA continuously decreases with increasing RH. The result suggests possible competitive adsorption between water vapor and IPA molecules. Even at the lowest moisture (10% RH) content, the partial pressure of H₂O is quite high compared to IPA. Hence, H₂O adsorption is more favorable in this competitive process. Interestingly, the amount of irreversibly adsorbed IPA increases from 84 to 94% when the water content changes from 35 to 65%. It is expected that water forms a multilayer above 35% RH. Due to high water solubility, part of the irreversibly adsorbed IPA will dissolve rather than directly interacting with TiO₂ surface at the highest RH.
3.4.4 Temperature

Adsorption process spontaneously occurs when the change in free energy, $\Delta G$, of the system decreases. The entropy change, $\Delta S$, in adsorption process is negative since the adsorbed gas is less mobile than its gaseous state [196]. Therefore, the heat of adsorption, $\Delta H$, must always be negative since $\Delta G = \Delta H - T\Delta S$. Thus, adsorption is always exothermic. The heat of adsorption also defines the extent of the interactions between adsorbate molecules and adsorbent lattice atoms. Physisorption is predominant at lower temperature due to weak Van Der Waal’s forces interactions. Since chemical reaction probability increases with temperature, chemisorption is favored at high temperature. In most circumstances, the amount of adsorption decreases however with increasing temperature. For instance, Song et al. demonstrated that the breakthrough time for the adsorption process was significantly reduced at elevated temperature compared to room temperature indicating lower adsorption capacity [150]. Brodu et al. have reported the influence of temperature on MEK adsorption capacity of two aluminosilicates (Fau-Y, ZSM-5) [189]. The quantity of adsorbed MEK on both Fau-Y and ZSM-5 was decreased with increasing temperature. On Fau-Y, the adsorption rate of MEK was 87% at 298K and 51% at 333K, respectively. This clearly indicates a
higher loss of adsorption capacity with rising temperature. However, some researchers have observed an enhanced adsorption capacity of AC in the high temperature range [197]. In this experiment, adsorption of four VOCs including carbon tetrachloride (CCl₄), chloroform (CHCl₃), benzene and methylene chloride (CH₂Cl₂) on AC at different temperatures was carried out. For a given VOC concentration, the adsorbed amount of VOC was decreased with increasing temperature except for benzene. This abnormal behavior of benzene is attributed to the activated entry effect which is responsible for the temperature-dependent nature of equilibrium adsorption [198]. At higher temperature, the diffusion of benzene molecules is facilitated into the narrow micropore channels. This promotes the rate of entry into the micropores leading to an enhanced adsorption capacity.

3.5 Critical Process Parameters for Regeneration

To ensure an economically feasible process with uniform performance of sequential treatment, the regenerability of an adsorbent is considered as the most important parameter. The conventional and most popular regeneration techniques are thermal swing, pressure swing and chemical regeneration (displacement, elution, supercritical extraction) or a combination of those. As this chapter is related to plasma regeneration processes, only the influence of process parameters on the regeneration by plasma will be discussed in the following sections.

3.5.1 Flow Rate

The effect of gas flow rate on the regeneration efficiency has been studied by several groups. When gas flow rate increases the residence time/space time of the gas stream is lowered. This will decrease the plasma exposure time during the regeneration stage leading to a suppression of the decomposition efficiency. Saulich et al. have investigated the influence of the N₂ flow rate in a DBD packed with MP 5 on the decomposition of adsorbed HCHO [170]. From Figure 3.10, it is apparent that with higher N₂ flow rate, the total amount of decomposed HCHO molecules increases and the formation of CO₂ is greatly favored.

However, Kuroki et al. have reported opposite phenomena during the adsorption of toluene with a DBD packed with a hydrophobic zeolite honeycomb [194]. According to the authors, at low gas flow rate, re-adsorption may occur inside the adsorbent during the plasma desorption
process, resulting in a lower decomposition efficiency. Therefore, the optimal gas flow rate should be determined.

Figure 3.10: Influence of flow rate on the decomposition of HCHO adsorbed on MP 5 (adsorption: 176 mL/min flow rate of polluted N₂ with 99 ppm of HCHO, adsorption time t₁ = 250 min, total amount of adsorbed HCHO: 155 µmol; discharge carrier gas N₂, discharge power P = 2.2 W). Reprinted from Ref. [170], with permission from Elsevier.

3.5.2 Temperature

Temperature has an influence on the electrical properties of a NTP discharge. With varying temperature, the gas density varies leading to a change in the reduced electric field strength (E/N). Generally, it is known that the kinetic reaction rate of O radicals with VOCs is an increasing function of temperature due to the endothermic reaction behaviour. However, the effect of temperature on the production of reactive species such as O radicals still needs detailed studies. Nevertheless, the beneficial influence of temperature on the regeneration process is counteracted by a decrease of the adsorption capacity of the sorbent at higher temperatures. These competitive effects on the plasma assisted desorption process have been investigated by Song et al. who have used a γ-Al₂O₃ packed DBD reactor for toluene removal [150]. As expected,
the thermal decomposition of NTP produced ozone increases with elevated temperature. The removal rate of adsorbed toluene on γ-Al₂O₃ beads was also improved at higher temperature compared to room temperature. In addition, γ-Al₂O₃ was able to reduce some other by-products, such as O₃ and HNO₃.

3.5.3 Discharge Power

The oxidative ability of NTP treatment for adsorbent regeneration can be improved by increasing input power. Indeed, there is an optimal discharge power at which high oxidation rate and low energy cost can be achieved. The effect of discharge power on the plasma catalytic oxidation of adsorbed benzene over metal supported zeolite (Ag/HZSM-5) catalyst has been studied by Hong-Yu et al. [160] (Figure 3.11-a). The optimal DBD operating power is found to be 4.7 W at which almost 100% of adsorbed benzene is oxidized to CO₂. The energy cost at this optimal power was as low as 3.7 x 10⁻³ kWh/m³.

Zhao et al. have also investigated the effect of discharge power on the plasma catalytic oxidation of stored HCHO on AgCu/HZ catalyst [142]. The conversion of HCHO to CO₂ dramatically increases (Figure 3.11-b) reaching almost 100% after 5 min of operation at 2.3 W. Further increase of the discharge power did not significantly improve the HCHO conversion. The influence of discharge power on toluene decomposition has also been studied by Mok et al. [166] where complete toluene decomposition towards CO and CO₂ was reported instead of quantifying the COₓ selectivity. With increasing discharge power, the concentration of CO and CO₂ further increased indicating faster oxidation of adsorbed toluene.

![Figure 3.11: (a) Adsorbed-benzene conversion to CO₂ over Ag/HZSM-5 catalysts (b) stored-HCHO conversion to CO₂ over AgCu/HZ catalysts as a function of discharge time at various discharge powers. Reprinted from Ref. [142, 160], with permission from Elsevier.](image-url)
Sivachandrian et al. have precisely investigated the effect of discharge power on the regeneration of adsorbed acetone on TiO₂ surface [168]. They applied a double DBD with TiO₂ coated glass beads. Although the oxidation rate of acetone is improved with increasing input power, the removal efficiency remains constant around 25%. To achieve both sufficient surface regeneration and high mineralization, 0.33 W is considered as an optimal input power. The authors confirmed that even though the regeneration efficiency is limited during NTP treatment, operation at moderate discharge power modifies the nature of organic adsorbed species which facilitates mineralization during successive thermal treatments (Figure 3.12). Modification of adsorbed acetone i.e. mesityl oxides into formic acid is only possible above 0.13 W. Hence, acetone desorption is decreased while CO and CO₂ formation are promoted by increasing input power during successive thermal treatment. Any further increase of input power above 0.33 W is useless regarding conversion of mesityl oxide into formic acid.

Figure 3.12: Contributions of CO, CO₂ and acetone into the carbon balance, calculated after successive plasma treatment and thermal treatment. Data are displayed for various plasma input powers. Reprinted from Ref. [168], with permission from Elsevier.
3.5.4 Relative Humidity

During real-time operation, humidity is permanently present in air which will impact both the adsorption mechanism and regeneration process unless hydrophobic sorbents are used. Fan et al. have studied the removal of low concentrated benzene stored on 0.8% Ag/HZSM-5 catalyst under various humidity conditions (dry air and RH=20, 50 and 80%) [162]. Figure 3.11 shows that the oxidation rate slightly decreases up to 50% RH compared to dry air. However, CO2 selectivity and carbon balance reached almost 100% in all cases. The plausible explanation of this weak effect of humidity on oxidation rate is the hydrophobic property of high-silica zeolite. Therefore, this result should be limited only to hydrophobic surfaces, moreover, no RH was introduced during the plasma assisted regeneration process. The presence of humidity can influence the electrical and physical properties of the discharge as well as the plasma chemistry. For instance, the RH can affect the input power and change the nature and amounts of reactive plasma species which will have an influence on the VOC oxidation pathway.

Figure 3.13: Effect of relative humidity (RH) on plasma catalytic oxidation of stored benzene over 0.8 wt%Ag/HZ catalysts to CO2 (storage stage: 4.7 ppm benzene, 0–80% RH (25°C), 600 mL/min flow rate of simulated air, t1 = 1 h; discharge stage: 60 mL/min O2, P = 4.7 W. Reprinted from Ref. [162], with permission from Elsevier.
To assess the impact of RH on both the adsorption modes and the surface plasma regeneration efficiency, Sivachandiran et al. have investigated the removal of IPA with a packed bed reactor coated with TiO₂ under various RH conditions [149]. Increased RH favored IPA mineralization and diminished acetone formation. With increasing RH from 0 to 65%, the carbon balance was enhanced from 36 to 91% clearly proving that moisture has a positive influence on the plasma surface regeneration efficiency. The authors suggest that the dissociative electron impact with H₂O produces OH radicals which are chemisorbed on TiO₂ leading to re-hydroxylation of the pre-treated TiO₂ surface. Eventually, adsorbed IPA will be replaced by hydroxyl groups and desorb. Generally, the oxidation power of OH radicals is much stronger than other oxidants such as oxygen atoms and peroxy radicals. Increased RH favors the production of OH radicals and the subsequent oxidation of VOCs leading to a high mineralization rate. In comparison to dry-air experiments, almost 80% acetone production was reduced in the presence of only 10% air RH. Low surface coverage of TiO₂ by H₂O molecules allows the adsorption of the deprotonated CH₃-CHOo-CH₃ species onto the TiO₂ surface [35]. Indeed, in the case of humid air, the most common oxidation pathway for VOC removal with NTP is the H-atom abstraction by OH radicals. [199]. In fact, large amounts of OH radicals are produced by the discharge in the surface vicinity which improves the dehydrogenation of IPA hydroxyl groups leading to the formation of acetone [149]. However, above 25% RH, the formation of a water multilayer onto the TiO₂ surface impeded the dissociative adsorption of IPA onto the TiO₂ surface thus obstructing acetone formation.

3.5.5 O₂ Content/O₂ Partial Pressure

Similar to air RH, the discharge properties and VOC abatement process are sensitive to oxygen content. The presence of oxygen in the discharge generally increases the amount of O radicals leading to a high removal efficiency. However, owing to its electronegative character, oxygen limits the electron density and also reduces the formation of other reactive species e.g. N₂ and N₂⁺, which are beneficial for VOC abatement [200-202]. Saulich et al. have used a mineral adsorbent packed DBD reactor to see the effect of O₂ on the plasma decomposition process of adsorbed HCHO [170]. The addition of 10% O₂ to N₂ increased both the formaldehyde decomposition efficiency and the mineralization rate compared to pure N₂. Kim et al. have demonstrated the effect of oxygen content on benzene decomposition using a plasma catalyst reactor (5% Cu/MOR) [203]. Figure 3.14 clearly shows that when the plasma is turned on after the adsorption mode, benzene concentration decreases and
CO and CO$_2$ formation simultaneously increases with increasing O$_2$ percentage. Several catalysts (TiO$_2$, γ-Al$_2$O$_3$, zeolites) loaded with nanoparticles of active metals (Ag, Cu, Zr) or noble metals (Pt, Pd) have also been investigated under various oxygen partial pressures for toluene and benzene abatement [169]. The increase of O$_2$ content enhanced both the decomposition efficiency (~30-100%) and the CO$_2$ selectivity regardless of the catalyst type [169]. Operating the regeneration mode at high O$_2$ content leads to complete oxidation of VOCs without CO, aerosol and N$_2$O$_y$ formation and complete decomposition of VOCs to CO$_2$ is achieved with the CSD system under O$_2$ plasma in most literature so far.

![Figure 3.14: Effect of oxygen content on the VOC decomposition using a plasma catalyst reactor (5 wt% Cu/MOR). Applied voltage and frequency were kept constant at 16 kV and 300 Hz, respectively. Temperature was 100°C. Space velocity was 33000 /h. Reprinted from Ref. [203], with permission from Elsevier.](image)

### 3.5.6 Number of Cycles

Potential irreversible ageing of adsorbent may occur during the regeneration process, which governs the life of an adsorbent. After multiple regeneration cycles, the adsorbent may not fully recover its initial properties, for instance, specific surface area and adsorption capacity [204]. Adsorption capacity may decrease due to surface modification by particle agglomerations or polymerization on the catalyst surface which results in active sites blockage
during the regeneration step. Keeping this in mind, researchers should also inspect the effect of this sequential treatment after the repeatability test. For instance, Kuroki et al. have performed a repeatability test of adsorption and plasma desorption and reported that toluene was almost completely adsorbed over honeycomb zeolites in each adsorption process [205]. Having a 75% regeneration efficiency, both desorption and regeneration efficiencies do not deteriorate for 10 repetitions of the adsorption/desorption processes (Figure 3.15). Similarly, seven repetitive adsorption-discharge cycles were performed for HCHO abatement from mineral adsorbent by Saulich et al. [170]. Adsorption capacity and regeneration efficiency were found to be more or less the same in each cycle [170]. The stability of AgCu/HZ catalyst during five consecutive storage-discharge cycles has also been examined by D. Zhao et al. [142]. HCHO storage capacity was almost constant and CO₂ selectivity and carbon mass balance were maintained at ~100%.

![Figure 3.15: Desorption and regeneration efficiencies denoted by \( \eta_d \) and \( \eta_r \), respectively, as a function of repetitive operation. Reprinted from Ref. [84], with permission from Elsevier.](image)

### 3.6 Conclusions

From the review above, it can be concluded that the sequential treatment has attracted growing interest among researchers and has proven to be an effective method for VOC abatement as well as for regeneration of saturated adsorbents. However, choosing an appropriate catalyst to achieve the best performance is still a challenge since it has to combine a high adsorption capacity with a high catalytic activity for the oxidation of adsorbed VOCs. For
instance, hard-to-adsorb VOC molecules are not appropriate for the adsorption process [181]. The key factor for the abatement of this kind of compounds is either to choose appropriate catalyst materials with a large adsorption capacity or to remove them through continuous treatment.

Although the review of experimental results of cyclic VOC adsorption and plasma assisted regeneration shows substantial progress, many questions still remain unanswered regarding the impact of process parameters and VOCs degradation mechanisms. In this regard, direct in-situ surface monitoring of the catalyst/adsorbent will be crucial to elucidate these important issues. Furthermore, modeling and simulation studies would also contribute to understand the various underlying plasma catalytic effects.

The research on sequential plasma catalysis coupling for VOC abatement has mostly been performed on laboratory scale. Up to now, only a few studies on pilot scale with gas circulation have been reported [179]. To achieve an economically feasible VOC removal process without gas circulation, cyclic operation of VOC adsorption and catalyst regeneration has been proposed by researchers. In this regard, future work should focus on the feasibility and optimization of the duration of the sequential intervals. Finally, to realize industrial implementation of this energy effective method for VOC abatement scalability studies will also need to be carried out in the near future.
CHAPTER 4:
MATERIALS AND
METHODS
4.1 Experimental Set-up

A general scheme of the experimental set-up is shown in Figure 4.1. This set-up can be divided into three main parts: (i) TCE-waste stream generator, (ii) TCE abatement reactor: plasma reactor coupled with a catalyst reactor and (iii) exhaust gas analytical devices: Fourier transform infrared spectrometer (FT-IR), mass spectrometer (MS) and ozone monitor (OM). In the following sections each of these parts will be discussed in more detail.

During the course of this study, modifications and optimizations were implemented to improve the operation and ease of use of the set-up. In this chapter, the preparation of the catalysts is also described. In order to characterize the catalysts, numerous analytical techniques were used for which the experimental conditions are summarized here. Furthermore, the calibration of the FT-IR spectrometer is discussed. Different experimental procedures were adopted during this PhD study and are described. Finally, the experimental parameters used to evaluate the VOC removal process are introduced.

![Figure 4.1: Schematic diagram of the used experimental set-up.](image)

4.1.1 TCE-Waste Stream Generator

The function of this section is to generate a TCE-polluted air/waste stream as feed for the reactor system. It is essential that this system is able to supply a feed stream with stable conditions such as air flow rate, air humidity and initial TCE concentration. To generate a typical feed stream, the inlet gas was supplied by a bottle of pressurized dry air (Alphagaz 1, Air Liquide) and was separated into three flows by means of three mass flow controllers (MFC) (Bronkhorst®, El-Flow®). The upper MFC (0–10 L/min) was used to adjust
the total gas flow rate of the inlet. The experiments were performed at a constant volume flow rate of 0.5 L/min (30 L/h). TCE vapor was generated and its concentration was controlled by varying the flow of dry air through a bubbling bottle containing liquid TCE (99.99% purity, Acros) by using the middle MFC (0-0.2 L/min). The bubbling bottle was located in a thermostatic water bath maintained at –8°C by adding an antifreeze (ethylene glycol) to the water. This low temperature is needed to decrease the volatility of TCE which facilitates the generation of TCE/air mixtures with stable initial concentrations. In order to add humidity to the TCE/air mixture, an additional bubbling bottle containing demineralized water (eurowater) was used. By controlling the flow rate through the water bottle, which was regulated by the third MFC (0 – 0.5 L/min), the air humidity could be fixed at the desired value. TESTO 445 device was used to monitor the induced changes in RH % and the temperature of the gas inlet (Figure 4.2). The temperature/humidity probe (TESTO 445) was located in a closed vessel in which the feed gas can circulate. The vessel was placed between the waste stream generator and the reactor inlet (Figure 4.1). During the experiments, the relative humidity will be varied between 0 – 15% and the temperature variation (20 °C ± 2) in the lab can be neglected. A Digital Pressure Indicator 705 (Figure 4.2) was used to measure the gas pressure of the air flowing through the set-up.

4.1.2 TCE Abatement Reactor

After generating a stable TCE-waste stream with/out air humidity, it was introduced to the TCE abatement reactor which is the coupling of the plasma and catalyst reactors. For these experiments, the plasma reactor was placed
upstream of the catalyst reactor commonly known as post plasma catalysis (PPC) configuration.

4.1.2.1 Plasma Reactor

Configuration: A home-made multi-pin-to-plate configuration is used as plasma reactor (Figure 4.3-a), and is based on the concept of a negative DC corona/glow discharge [206]. The cylindrical casing of the reactor is made of Teflon (polytetrafluoroethylene) and inserted in a glass tube which is closed by airtight fittings in order to prevent any leakages. The feed gas flows through a rectangular channel with a cross section of 40 mm x 9 mm and a length of 400 mm. The plasma source consists of ten aligned sharp hollow crown-shaped cathode pins, connected in parallel and positioned at 28 mm intervals. The anode plate is profiled with spherical surface segments centered on the tip of each crenellated cathode pin. The spherical surface segment has a radius of 17.5 mm and a depth of 5 mm. The distance between the 10 cathode pins and the single anode plate is 10 mm. For a total gas flow of 0.5 L/min, the gas residence time in the plasma reactor is 10.84 s. In order to observe the discharge, small windows were installed at the front side of the reactor (Figure 4.3-b).

Figure 4.3: (a) Photo of the multi-pin-to-plate plasma reactor, (b) a negative DC excited glow discharge at atmospheric pressure observed through the small window.

Electrical Characterization Processing: The electric circuit of the plasma reactor is illustrated in Figure 4.4. The discharge is powered with a 40 KV/30 mA DC power supply (Technix, SR40-R-1200). The NTP was generated at atmospheric pressure and at room temperature. The threshold current for the glow–to–spark transition was increased from the promoting effect of the divergence of electrical field lines provided by the spherical anode curvature
The shift of the glow-to-spark threshold current to higher values was also attributed to a better spreading of the current resulting from evenly spaced cathode spots caused by the crenellated edge of cathode pin [37]. Each cathode pin is connected with an individual 1.5 MΩ ballast resistor \( (R_b) \) in order to ensure uniform and stable glow discharge (Figure 4.4). The fraction of the total electrical power that was dissipated in these resistors amounts to 10% at most. The applied power in the reactor was measured via determination of the plasma/discharge voltage \( (U_{pl}) \) and the discharge current \( (I) \). A high-voltage probe (Fluke 80 K-40, division ratio 1/1000) was used to measure the total voltage \( (U_{tot}) \) applied to the plasma reactor which is distributed over the ballasting resistors \( (U_b) \) and the plasma \( (U_{pl}) \). The discharge current \( (I) \) was determined by recording the voltage signal \( (U_m) \) across a 100 Ω resistor \( (R_m) \) placed in series between the counter electrode and the ground. Two digital multimeters (Ohmeron MT 488B) with an accuracy of 0.8 and 0.5 %, were used to monitor both \( U_m \) and \( U_{tot} \), respectively. During experiments, the energy density (i.e. the ratio of the plasma input power to gas flow rate) of the plasma was adjusted by varying the plasma voltage \( (U_{pl}) \).

Figure 4.4: Electric circuit diagram of the multi-pin-to-plate reactor

with

- \( U_{tot} \) Total voltage [kV]
- \( R_m \) Resistor (100 Ω) needed to determine I
- \( I \) Discharge current [mA]
$U_h$ Voltage over ballasting resistor $R_b$ [kV]

$U_{pl}$ Plasma voltage [kV]

$R_b$ Ballasting resistor (1.5 MΩ) of a cathode pin

As can be seen from Figure 4.4, the plasma voltage $U_{pl}$ was calculated as follows:

$$U_{pl} = U_{tot} - U_m - U_b \tag{4.1}$$

$$U_{pl} = U_{tot} - I \cdot R_m - \frac{I \cdot R_b}{N} \tag{4.2}$$

Where $N$ is the number of cathode pins.

4.1.2.2 Catalytic Reactor

Configuration: As shown in Figure 4.5, the catalytic reactor system consists of a cylindrical glass tube, a vertical tubular oven and a temperature controller. The glass reactor (Figure 4.5-a) is made of Pyrex glass with an inner diameter of 20 mm and an effective length of 100 mm. The catalyst powder is disposed on a sintered and porous plate inside the tube. The catalytic bed is placed in an oven, which allows to vary the catalyst temperature. This oven was a homemade model delivered by UCCS from Lille University. The temperature of the catalyst is controlled by a temperature probe present in the glass wool of the oven (Figure 4.5-b), and is connected to a temperature controller (Figure 4.5-c). Measurements were performed after a thermal balance is reached.

Figure 4.5: Overview of the catalytic reactor components with (a) glass tube, (b) oven and (c) temperature controller
**Pressure Drop over Catalyst Bed:** A gas flowing through a catalyst bed results in a pressure drop, which can be described by Ergun’s equation

$$\frac{\Delta P}{L} = 150 \cdot \frac{\mu_g \cdot v_g}{D_p^2} \left(1 - \frac{\varepsilon}{\varepsilon^2}\right) + 1.75 \cdot \frac{\rho_g \cdot v_g^2}{D_p} \left(1 - \frac{\varepsilon}{\varepsilon^2}\right)$$  \hspace{1cm} (4.3)

with

- $\Delta P$: Pressure drop over catalyst bed [Pa]
- $L$: Length of the catalyst bed [m]
- $\mu_g$: Gas viscosity [Pa·s]
- $v_g$: Gas velocity [m·s$^{-1}$]
- $D_p$: Particle diameter [m]
- $\varepsilon$: Bed porosity [-]
- $\rho_g$: Gas density [kg/m$^3$]

As the vapor–liquid equilibrium in the bubbling bottles is very pressure sensitive, when TCE/air mixture was passed through the catalyst bed, the pressure drop in the catalyst bed resulted in a decreased TCE concentration in comparison with the gas flow through the by-pass. To avoid this effect, the same pressure drop over the catalyst bed is manually set over the by-pass, by manipulating valves 1 and 2 in the by-pass (Figure 4.1). In this way, the same TCE inlet concentration in the by-pass as over the catalyst bed is obtained, and can be measured. Temperature has an effect on the gas density and velocity, but only slightly influenced the pressure drop. An extra valve was installed (Figure 4.1, valve 3) to prevent backflow through the catalyst bed when the 3–way valve was switched from catalyst to bypass.

**4.1.3 Exhaust Gas Analytical Devices**

In order to evaluate the performance of the abatement process of TCE, the influent and effluent of the reactor system were analyzed by FT-IR spectroscopy and in some cases by MS. During the course of this work the original ozone monitor (Teledyne API, Model 450) was replaced by a new descendant one (Teledyne API, Model 465M).
4.1.3.1 FT-IR Spectrometer

IR spectroscopy detects gaseous compounds based on their absorbance of infrared light (electromagnetic radiation). The gas molecules will selectively absorb specific wavelength radiation when the electromagnetic field of the molecule vibrates at the same frequency as the incoming IR radiation. During this adsorption process, the molecule acquires a clearly defined amount of energy \( E = h \nu \) from the radiation, consequently, the vibrational energy levels of the molecules will transfer from a ground state to an excited state. This vibrational energy gap is used to determine the frequency of adsorbed IR radiation by the molecule. The position and intensity of the absorption bands are extremely specific in the case of a pure substance, just like a fingerprint. The number of possible absorption peaks is directly related to the number of vibrational freedoms of the molecule. The absorption wavenumber depends on the relative mass and the geometry of the atoms. The intensity of absorption peaks is related to the extent of the change in dipole moment and the possibility of the transition of energy levels. Therefore, by analyzing the infrared spectrum, one can readily obtain abundant structural information of a molecule. To identify the chemical structure of an unknown substance, the position of its characteristic absorption peaks needs to be compared with a standard reference spectra included in the National Institute of Standards and Technology (NIST) databank. Moreover, the intensity of the signal on the IR spectrum is proportional to the concentration of that specie, making IR spectroscopy appropriate for both qualitative and quantitative analyses. The term Fourier-transform infrared spectroscopy originates from the fact that a Fourier transform (a mathematical algorithm) is required to convert the raw data into the actual spectrum.

Nonetheless, infrared light can only be absorbed by a molecule if the dipole moment of the specific group of atoms changes during the vibration. The greater the change in dipole moment, the stronger the corresponding IR absorption band will be. Vibrations not accompanied by changes in the dipole moment cannot be excited by IR light and are termed IR inactive or transparent. As a consequence, diatomic molecules such as \( \text{N}_2 \) or \( \text{O}_2 \) do not absorb IR light. This is a great advantage since these molecules are the main components of air and thus do not interfere with the IR spectra of molecules of interest such as the target VOC and its by–products.

The general lay-out of a FT-IR spectrometer using a Michelson interferometer to collect a spectrum, is shown schematically in Figure 4.6. Infrared light
emitted from a source is directed into the beam splitter which splits the beam into two parts. One part is transmitted to a movable mirror, while the other part is reflected to a fixed mirror. The moving mirror moves back and forth at a constant velocity. The two beams are reflected from the mirrors and recombine at the beam splitter. This recombination leads to constructive and destructive interference pattern, since the beam from the moving mirror has traveled a different distance than the beam from the fixed mirror. This interference pattern is called an interferogram and goes from the beam splitter to the sample. The sample absorbs all the different wavelengths characteristic of its spectrum, and this subtracts specific wavelengths from the interferogram. The detector now reports variation in energy versus time for all wavelengths simultaneously. A laser beam is superimposed to provide a reference for the instrument operation. This detector signal is sent to a computer which performs a Fourier transform in order to convert the signal from an intensity-vs.-time spectrum into an intensity-vs.-frequency spectrum [207, 208].

![Diagram of FT-IR spectrometer](image)

**Figure 4.6:** General lay-out of an FT–IR spectrometer using a Michelson interferometer [209].

In this thesis, the real time detection and quantification of the exhaust gas phase species from reactor is performed using Bruker Vertex 70 FT-IR spectroscopy (Figure 4.7-a) equipped with a 20 cm optical-path cell (Figure 4.7-b) and a mercury cadmium telluride (MCT) detector. The MCT detector was cooled with liquid nitrogen every 8 h to ensure stable operation ability. OPUS (Bruker) software is used to collect and analyze the obtained spectra and these spectra were recorded within the range of 600 to 3000 cm⁻¹ at 4 cm⁻¹.
resolution in order to maximize the signal to noise (S/N) ratio. Typically, 10
scans were collected for one spectrum, and the results were presented as
absorbance spectra. The above mentioned experimental conditions were used
to measure both the background and sample spectrum. The latter
measurements were recorded after steady–state condition was reached,
typically after approximately 5 minutes. The optical bench of the FT-IR was
purged with air delivered from a CO₂–dryer while the sample compartment
was purged with dry synthetic air in order to avoid any interference of these
compounds.

Figure 4.7: (a) Bruker Vertex 70 FT–IR spectrometer, (b) gas cells used
during this PhD study.

4.1.3.2 Mass Spectrometer

Mass spectrometry is a powerful analytical technique used to identify and
quantify (un)known compounds within a sample. The process involves the
conversion of the sample into gaseous ions, with or without fragmentation,
which are then characterized by their mass to charge ratios (m/z) and relative
abundances. The different components of a mass spectrometer are illustrated
in Figure 4.8: a sample inlet, an ionization source, a mass analyzer and an ion
detector.

Figure 4.8: Components of a mass spectrometer
The first step in the mass spectrometric analysis of compounds is the generation of gas phase ions of the compound. Ions are generated by inducing either the loss or gain of a charge from a neutral species by cationization, deprotonation, electron ejection, electron capture, or by transferring a charged molecule from a condensed phase to the gas phase.

An extraction system removes the produced ions from the sample, which are then trajected through a mass analyzer. The difference in mass of the fragments allows the mass analyzer to sort the ions by their mass-to-charge ratios. Not all analyzers operate in the same way. Some analyzers separate ions in space (quadrupole, quadrupole ion trap, magnetic sector), while others separate ions by time (time-of-flight, time-of-flight reflectron, quad-time-of-flight). The MS used during this PhD study is a quadrupole mass spectrometer having many advantages such as the simple manner of scanning the entire mass range, high sensitivity, high measuring and repetition rate.

Once the ions are separated by the mass analyzer, they are sent to the ion detector. The most common used detector is the electron multiplier, which transfers the kinetic energy from the incident ions to a surface that in turn generates secondary electrons. The produced electrical signals are then transmitted to a computer that is able to construct the mass spectrum. A typical mass spectrum of TCE is presented in Figure 4.9.

All mass spectrometers operate at vacuum conditions to allow ions to reach the detector without colliding with other gaseous atoms and molecules. These collisions have to be avoided due to their negative impact on the resolution
and sensitivity. High pressures may also cause high voltages to discharge which can damage the instrumentation, electronics, and the computer system running the mass spectrometer [211, 212].

The MS used during the experiments in the course of this PhD thesis is a Quadrupole Triple Filter MS (Hiden Analytical, HPR 20 QIC) and is shown in Figure 4.10. The quadrupole probe of MS is comprising with a Faraday cup and a secondary electron multiplier (SEMP) detector. MASsoft 7 Professional (QGA Professional) software is applied for collecting and displaying data. The qualitative identification of the by-products were achieved using Scan Bargraph mode over the corresponding fragment ions (m/z) with fast response times of less than 150 ms. Depending on the acquisition range (concentration/partial pressure of the trace elements), detectors were chosen to identify the peaks of mass spectra. For instance, in these experiments, Faraday (1*10^-5 to 1*10^-8 Torr) and SEMP (1*10^-8 to 1*10^-13 Torr) detector identified mass spectra in the range of 0-44 m/z and 45-150 m/z, respectively. During the measurements detector voltage of 850 V with electron ionization energy of 70 eV was adopted.

Figure 4.10: Illustration of the quadrupole mass spectrometer (Hiden Analytical, HPR 20 QIC)
4.1.3.3 Ozone Monitor

The detection of ozone molecules is based on absorption of 254 nm UV light due to an internal electronic resonance of the O₃ molecule. The monitor uses a mercury lamp and emits light through a hollow quartz tube that is alternately filled with sample gas, then filled with gas scrubbed to remove ozone. The ratio of the intensity of light passing through the scrubbed gas to that of the sample is determined and forms the basis for the calculation of the ozone concentration via the Beer-Lambert law. The specifications of the ozone monitor are listed in Table 4.1.

Table 4.1: Features of the ozone monitors

<table>
<thead>
<tr>
<th>Model</th>
<th>Measurement range (ppm)</th>
<th>Detectable limit (ppm)</th>
<th>Sample flow rate (L/min)</th>
<th>Accuracy (%)</th>
<th>Resolution (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>0-1000</td>
<td>0.003</td>
<td>1-2.5</td>
<td>± 0.1</td>
<td>0.01</td>
</tr>
<tr>
<td>465M</td>
<td>0-1000</td>
<td>0.001</td>
<td>0.8</td>
<td>± 1</td>
<td>1</td>
</tr>
</tbody>
</table>

4.2 Catalyst Preparation and Characterization

4.2.1 Catalyst Materials

4.2.1.1 Cerium Oxide (CeO₂)

Cerium oxide was purchased from Sigma-Aldrich (22390). Before its use, it was calcined for 4 h at 600 °C under a stream of dry synthetic air with a flow of 200 mL/min. For all tests, 0.5 g of CeO₂ powder is mixed with 2.5 g carborundum (CSi-0.105 mm) (EMB 45053-Prolabo) and then introduced in the catalytic bed.

4.2.1.2 Cryptomelane (KMn₈O₁₆)

Cryptomelane was synthesized by the reflux method (Figure 4.11), involving the oxidation of Mn⁷⁺ by MnO₄⁻, as inspired by the work of Santos et al. [102].
The chemicals used for this synthesis are the following: KMnO₄ (Fluka, 99%), Mn(CH₃CO₂)₂-4H₂O (Prolabo, 99%), KCH₃CO₂ (Sigma-Aldrich, 99%) and CH₃COOH (Sigma-Aldrich, 99%).

The main reactions occurring during the synthesis are the following:

\[
2 \text{MnO}_4^- + 3 \text{Mn}^{2+} + 2\text{H}_2\text{O} = 5\text{MnO}_2 + 4\text{H}^+ \quad (4.4)
\]

\[
2(\text{K}^+; \text{MnO}_4^-) + 3(\text{Mn}^{2+};2\text{CH}_3\text{COO}^-) + 2\text{H}_2\text{O} = 5(\text{K}_0.125\text{MnO}_2) + 6\text{CH}_3\text{COO}^- + 4\text{H}^+ \quad (4.5)
\]

The initial concentrations of the different chemicals used during the synthesis are listed in Table 4.2.

Table 4.2: The required amount of chemicals for the synthesis

<table>
<thead>
<tr>
<th></th>
<th>KMnO₄</th>
<th>Mn(CH₃CO₂)₂-4H₂O</th>
<th>K₀.₁₂₅MnO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>n (mol)</td>
<td>0.04</td>
<td>0.06</td>
<td>0.1</td>
</tr>
<tr>
<td>M (g/mol)</td>
<td>158.04</td>
<td>245.09</td>
<td>91.8</td>
</tr>
<tr>
<td>m_{eq} (g)</td>
<td>6.321</td>
<td>14.705</td>
<td>9.18</td>
</tr>
<tr>
<td>Purity (%)</td>
<td>99.0</td>
<td>99.0</td>
<td></td>
</tr>
<tr>
<td>m_{cu} (g)</td>
<td>6.385</td>
<td>14.854</td>
<td></td>
</tr>
</tbody>
</table>

14.854 g of manganese acetate (Mn(CH₃CO₂)₂-4H₂O) is dissolved in 50 ml of distilled water, resulting in a light pink solution. The concentration of the solution was 0.6 mol/L. The pH of this solution was maintained at 4.5 by adding a buffer solution of KCH₃CO₂/CH₃COOH. Buffer solution: 23.18 g of potassium acetate are dissolved in 25 ml of acetic acid while stirring with distilled water (500 mL volumetric flask is used to determine the solution volume).

Next, 6.385 g of potassium permanganate (KMnO₄) is dissolved in 150 ml distilled water, resulting in a purple solution. The concentration of the solution was 0.4 mol/L. In a following step, this KMnO₄ solution was added dropwise to the former solution while stirring as depicted in Figure 4.11. A black brown precipitate rapidly formed and the mixture was stirred vigorously, using a magnetic stirrer (Fisher Scientific FB15001) and refluxed at 100 °C for 24 h.
In order to maintain a constant acidity (pH ≈ 4.5) of the reaction media during the synthesis process, a suitable amount of buffer solution was added.

The resultant black slurry was transferred to centrifuge tubes and the catalyst was separated through centrifugation (10 min, 10000 rpm). The brown colored supernatant containing impurities was discarded. The precipitated catalyst was collected at the bottom of the centrifugation vial and dispersed in distilled water and recollected by centrifugation (10000 rpm for 10 min) several times until a pH of approximately 6 (the pH of the distilled water) was reached, as depicted in Figure 4.11.

After washing, the obtained precipitate was dried overnight at 100 °C. In a last step, the catalyst was placed into a furnace for calcination. During calcination, air was sent into the reactor at a flow rate of 0.3 mL/min. The calcination temperature was increased from room temperature to 450 °C at a constant heating ramp of 1°C/min using a temperature controller (Eraly BP19-F-78590). Once the calcination temperature was reached, it was kept constant for 4 h. After calcination, a black solid catalyst was obtained which was then grinded manually to obtain the powdered catalyst.
4.2.1.3 Fe Doped Cryptomelane by Co-Precipitation

Fe doped cryptomelanes were synthesized by co-precipitation via refluxing (Figure 4.12) at low temperature under ambient pressure as inspired by the work of Yin et al. [123]. The strategy is to incorporate the Fe cations in the cryptomelane structure by following their synthesis procedure.

For the co-precipitation synthesis of $M_xK_yMn_3O_{2}$ ($M=Fe$), the following chemicals were used: KMnO$_4$ (Fluka, 99%), (CH$_3$COOH; Alfa Aesar, 99%), Mn(NO$_3$)$_2$$\cdot$4H$_2$O (Sigma-Aldrich, 97%) and Fe(NO$_3$)$_3$$\cdot$9H$_2$O (Fisher Scientific, 98%).

The molar ratio of Fe/Mn in the catalyst is 0.05.
The start concentrations of the different chemicals used during the co-precipitation synthesis are listed in Table 4.3.

Table 4.3: The required amount of chemicals for the co-precipitation synthesis

<table>
<thead>
<tr>
<th></th>
<th>KMnO₄</th>
<th>Fe(NO₃)₃·9H₂O</th>
<th>Mn(NO₃)₂·4H₂O</th>
<th>K₆.1₂Mn₂O₃Fe₆O₁₀</th>
<th>n (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m (g/mol)</td>
<td>0.044</td>
<td>0.0046</td>
<td>0.045</td>
<td></td>
<td>0.045</td>
</tr>
<tr>
<td>mₑq (g)</td>
<td>158.04</td>
<td>404</td>
<td>251</td>
<td>91.83</td>
<td>6.91</td>
</tr>
<tr>
<td>Purity (%)</td>
<td>99.0</td>
<td>98.0</td>
<td>97.0</td>
<td></td>
<td>97.0</td>
</tr>
<tr>
<td>mₑq (g)</td>
<td>6.98</td>
<td>1.9</td>
<td>11.76</td>
<td></td>
<td>11.76</td>
</tr>
</tbody>
</table>

6.98 g of KMnO₄ was dissolved in 80 ml of distilled water, resulting in a purple solution, and was heated to 60 °C. The concentration of the KMnO₄ solution was 0.4375 mol/L. Next, 100 mL mixture of 0.5 mol/L Fe(NO₃)₃·9H₂O + Mn(NO₃)₂·4H₂O (the molar ratio of Fe/Mn is 0.1) and 2 mol/L acetic acid (CH₃COOH) solution was prepared and heated at 60 °C. In order to prepare the later solution, 1.9 g of Fe(NO₃)₃·9H₂O and 11.76 g of Mn(NO₃)₂·4H₂O are mixed with 12 mL of acetic acid and dissolved in 88 mL of distilled water.

In a subsequent step, the former KMnO₄ solution was added to the later aqueous acidified solution of Mn and Fe nitrate precursors to get a precipitate, as depicted in Figure 4.12. The mixtures were then heated up to 100 °C and the suspension was stirred vigorously at reflux for 20 min, using a magnetic stirrer (Figure 4.12). An additional amount (≈8 mL) of 2 mol/L acetic acid was added to retrieve the volatilized acetic acid during reaction.

The resultant reddish-black slurry was transferred to centrifuge tubes and the catalyst was separated through centrifugation (10 min, 10000 rpm). The brown colored supernatant containing impurities was discarded. The precipitated catalyst was collected at the bottom of the centrifugation vial and dispersed in distilled water and recollected by centrifugation (10000 rpm for 10 min) several times until a pH of approximately 6 (the pH of the distilled water) was reached, as depicted in Figure 4.12.
After washing, the precipitate was kept to dry at 100 °C for 12 h. In a final step, the catalyst was placed into a furnace for calcination. During calcination, air was sent into the reactor at a flow rate of 0.3 mL/min. The calcination temperature was increased from room temperature to 450 °C at a constant heating ramp of 1°C/min using a temperature controller. Once the calcination temperature was reached, it was kept constant for 4 h. After calcination, a reddish-black solid catalyst was obtained which was then ground manually to obtain the powdered catalyst.

Figure 4.12: The schematic diagrams of Fe doped cryptomelane in co-precipitate preparation method

4.2.1.4 Fe Doped Cryptomelane by Impregnation

The synthesis of the catalyst MzKxMnO2 (M=Fe3O4) was done via a wet impregnation method inspired by literature [213]. By following their synthesis strategy, the deposition of Fe(OH)x (x=2,3) over cryptomelane solid could be obtained. In this synthetic strategy, pH is a key factor in controlling the morphology of cryptomelane and the deposition of Fe3O4 particles at the surface of cryptomelane. In a former step, cryptomelane was prepared via
reflux method followed by the same procedure as described in the earlier section 4.2.1.2. Next, the wet impregnation synthesis was followed as shown in Figure 4.13.

Figure 4.13: The schematic diagrams of Fe doped cryptomelane in impregnation preparation method

The chemicals required for this synthesis process were: Fe(NO₃)₃·9H₂O (Fisher Scientific, 98%), (NH₄)₂Fe(SO₄)₂·6H₂O (Sigma-Aldrich, 98%) and KOH (Sigma-Aldrich-85%).

The required starting concentrations for the wet-impregnation-based synthesis are summarized in Table 4.4.

0.41 g of Fe(NO₃)₃·9H₂O and 0.40 g of (NH₄)₂Fe(SO₄)₂·6H₂O (nFe(II) = nFe(III)) were dissolved in 50 mL of water resulting in a brown solution. The pH of the solution was found to be 2.6. A KOH solution of 1 mol/L was added dropwise to the initial solution, as illustrated in Figure…, under constant stirring, to a final pH of 9.6 allowing the successive precipitation of Fe(OH)x (x = 2,3). In this process, Fe(OH)₃ was mostly precipitated at acidic conditions.
of pH 3.7, whereas Fe(OH)$_2$ was precipitated at pH 9.6. At that stage K$_{0.125}$MnO$_2$ ($n_{Fe}/n_{Mn}= 0.10$) was introduced above this pH as powder to the aqueous suspension in order to avoid the demolition of the mixed valences of Mn (III/IV) by the presence of Fe$^{2+}$ in the solution. KOH was continuously added dropwise until a pH of 12. A complete solid-liquid separation was observed at the end of the process.

### Table 4.4: Summary of the required chemicals

<table>
<thead>
<tr>
<th></th>
<th>K$_{0.125}$MnO$_2$</th>
<th>Fe(NO$_3$)$_3$.9H$_2$O</th>
<th>(NH$_4$)$_2$Fe(SO$_4$)$_2$.6H$_2$O</th>
<th>(FeO$<em>2$)$</em>{0.033}$K$_{0.125}$MnO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$ (mol)</td>
<td>0.02</td>
<td>0.001</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>$M$ (g/mol)</td>
<td>91.82</td>
<td>404</td>
<td>392.14</td>
<td>99.5</td>
</tr>
<tr>
<td>$m_{req}$ (g)</td>
<td>0.4081</td>
<td>0.396</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Purity (%)</td>
<td>98</td>
<td>98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$m_{acc}$ (g)</td>
<td>1.93</td>
<td>0.416</td>
<td>0.404</td>
<td></td>
</tr>
</tbody>
</table>

The synthesized black particles were filtered out and washed several times through centrifuge (10 min, 10000 rpm) process with distilled water until a pH equal to 9 was reached. It was noticed that the color of supernatant was reddish-black, and the amount of precipitated solid was decreasing after each washing step. This phenomenon indicate that the solid was not completely separable even at a longer centrifuge time (30 min). For that reason the washing step has been stopped before obtaining a neutral pH.

The obtained solids were kept to dry overnight at 100 °C. In a final step, the catalyst was put into a furnace for calcination. During calcination, air was sent into the reactor at a rate of 0.3 mL/min, while the calcination temperature was increased from room temperature to 450°C at a constant heating ramp of 1°C min$^{-1}$. Once the calcination temperature was reached, the process was continued for 2 h at constant temperature.

### 4.2.2 Catalyst Characterization Techniques

All catalyst samples were characterized with different techniques before and after the plasma reaction process in order to understand the role of the catalyst in the plasma catalytic process.
4.2.2.1 Structural Properties

**X-ray diffraction (XRD):** XRD allows identifying crystal structures of solids in a simple and rapid way. XRD analysis was performed on undoped cryptomelane catalysts, in order to check different crystalline phases thus guaranteeing that each catalyst was composed of the desired chemical composition.

X-ray diffractograms were recorded using a Bruker AXS D8 Advance diffractometer. Data were collected using the Cu Kα line in the 10–70° 2-theta range with a 0.02° 2θ step and a counting time of 3 s per step. Crystallite size was estimated from the FWHM of the peak located at 2θ = 28.9° using the Scherrer equation, after correction of the FWHM to account for the instrumental broadening using the Diffrac. EVA-crystallite size determination.

**Raman Spectroscopy:** The lattice vibrational behavior of both the undoped and Fe based K-OMS-2 materials was studied by Raman spectroscopy in order to probe the effect of iron addition on the spectral features of the K-OMS-2 material (Fe/K-OMS-2), to validate the postulated formation of cryptomelane and check for the presence of segregated crystalline and/or amorphous metal oxides. The Raman spectra of the cryptomelane samples were recorded at room temperature using a Raman microprobe (Labram HR) equipped with a Peltier-cooled detector. The exciting light source was the 488 nm line of an Ar+-ion laser and the spectral resolution was ± 1.5 cm⁻¹.

4.2.2.2 Textural Properties

**Brunauer–Emmett–Teller (BET) and Barrett-Joyner-Halenda (BJH):** The textural properties that are specific to the surface area and the pore size distribution, were studied via N₂ adsorption-desorption measurements at liquid nitrogen temperature (-196 °C). BET theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for the measurement of specific surface areas. BJH analysis is a pore size distribution determination method, which is typically applied to nitrogen desorption data measured on catalysts at 77 K.

For Cryptomelane catalysts, the specific surface areas were determined using a conventional multipoint BET nitrogen adsorption method with a
Micromeritics Tristar II apparatus. Prior to nitrogen adsorption, the samples were outgassed for 4 h at 150 °C under vacuum.

**Scanning Electron Microscopy (SEM):** The morphology of the cryptomelane catalyst materials was observed using Scanning Electron Microscopy images recorded on a Hitachi S-4700 apparatus. Measurements were done at an accelerating voltage of 15 kV and micrographs were recorded at 10000x and 150000x magnifications for K-OMS-2 and Fe-KOMS-2, respectively.

4.2.2.3 **Chemical Properties**

**Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES):** Inductively coupled plasma optical emission spectrometry (ICP-OES) is an analytical technique used for the detection of trace metals. ICP-OES was applied for determining the relative concentrations of Fe, K and Mn present in the cryptomelane catalyst. K, Mn and Fe elemental analyses were performed by ICP-OES at the REALCAT platform (Lille University). The sample preparation was made by dissolving 10 mg of dried and ground solid in 1.5 mL of concentrated aqua-regia solution. Solutions were heated at 50 °C and stirred during 12 h. All sample solutions were stirred and the volume was adjusted up to 50 mL with ultrapure water before being analyzed by ICP-OES.

**H₂-Temperature-Programmed Reduction (H₂-TPR):** TPR is a common technique for the characterization of heterogeneous catalysts and the quantification of their reduction capacity. The basic strategy of this method is to monitor activation and reaction on solid catalysts with different gases under various temperature conditions. K-OMS-2, Fe/K-OMS-2 and Fe-K-OMS-2 oxides were tested by TPR to compare the relative changes in reduction capacity.

TPR were carried out using a Micromeritics 2920 Autochem II Chemisorption Analyzer. 50 mg sample was put into a quartz U-shaped tubular quartz reactor. The samples were pre-treated in flowing Ar at 150 °C for 60 min followed by cooling down to room temperature. The reducing gas was a mixture of 5 vol. % H₂/Ar at a total flow rate of 50 mL/min. The temperature was increased from 25 °C to 800 °C with a heating rate of 10 °C/min.

**Thermogravimetric Analysis (TGA):** Thermogravimetric analysis (TGA) was performed on sample size of about 10 mg in air flow (50 mL/min) with a
heating rate of 10 °C/min up to 800 °C using a TA Instruments TGA-SDT 2960.

4.3 Quantification Methodology

4.3.1 Calibration of FT-IR

The FT–IR spectrometer was calibrated with calibration mixtures delivered by Air Liquide. Table 4.5 shows the composition of the calibration mixture.

Table 4.5: Composition of the FT–IR calibration mixture

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Concentration (ppm)</th>
<th>Integration limits (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
<td>250</td>
<td>2144–2223</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>250</td>
<td>2283–2393</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>C₂HCl₃</td>
<td>500</td>
<td>916–966</td>
</tr>
</tbody>
</table>

The calibration was repeated approximately each 2 months to ensure accurate determination of the concentration of these compounds. Therefore, the mixture was passed through the gas cell with a flow of 0.5 L/min (identical to the flow rate applied during the experiments) until a steady–state condition was reached. Then, 20 spectra were recorded each minute and averaged to obtain the required surface area of the absorption peaks under consideration. A characteristic IR band (945 cm⁻¹) of TCE having a high intensity, which does not interfere with absorption bands of by-products was chosen as calibration peak, and is integrated between 916 – 966 cm⁻¹ (Figure 4.14). As for CO and CO₂, a peak area in IR absorbance was adopted to calculate the concentration with a special attention to CO peaks due to overlapping with ozone and N₂O peak. A linear regression was applied to the average integration area as a function of time, and the slopes K₁, K₂, K₃ were used to calculate TCE, CO₂ and CO concentrations, respectively.

K₁, K₂ and K₃ were defined as following:

\[
K₁ = \frac{C_{TCE}}{S_{TCE}} \quad (4.6)
\]

\[
K₂ = \frac{C_{CO₂}}{S_{CO₂}} \quad (4.7)
\]
\[ K_3 = \frac{c_{\text{CO}}}{S_{\text{CO}}} \]  

(4.8)

Where \( c_{\text{TCE}}, c_{\text{CO}_2}, c_{\text{CO}} \) are the concentrations of TCE, CO\(_2\) and CO (ppm) present in the calibration mixtures and \( S_{\text{TCE}}, S_{\text{CO}_2}, S_{\text{CO}} \) are the average integration surface areas of TCE, CO\(_2\) and CO absorption peaks.

Figure 4.14: FTIR spectrum of calibration gas mixture (TCE, CO\(_2\) and CO).

4.3.2 Ozone Calibration

During the course of this PhD study the ozone monitor (Teledyne API, Model 450) was broken and was replaced by a new descendant one (Teledyne API, Model 465M). Unfortunately, this updated version ozone monitor has some new features which made it difficult to cope with our experimental condition. For instance, the ozone monitor needs a minimum of 0.8 L/min flow rate to operate which is higher than our experiment flow rate (0.5 L/min). Besides, this ozone analyzer has an auto-zero function (every 6 min) to avoid drift of the analyzer. Normally a differential measurement technique has been implemented in this analyser for which it has to switch between zero and measure in every 6 min, to avoid drift. Since most of our experiments need continuous measurement (almost 6 hours), we cannot put on this auto zero option. That’s why we had to calibrate the FTIR once more with ozone generated \emph{in-situ} by the air plasma discharge (ozone is not commercially
available as a calibration gas) and quantify it with the aid of this ozone monitor.

The quantification of ozone in the gas stream is done by choosing a characteristic IR-band of ozone with a high intensity and no interference with the absorption bands of by-products. The FT-IR spectrum is given in Figure 4.15-a. Based on the available ozone spectra from NIST, the characteristic ozone peaks can be identified in the range of 1067.17 to 1043.78 cm⁻¹, which was the area selected for integration.

As previously mentioned, to quantify the amount of generated ozone during the abatement experiments, an ozone monitor was connected to the system (Teledyne API, Model 465M, see Table 4.1 for more details). Dry air was fed into the NTP reactor at a flow rate of 1 L/min. Different energy densities (20 J/L, 30 J/L, 40 J/L, 60 J/L and 90 J/L) were studied, as shown in Figure 4.15-b. The ozone-enriched gas was passed through the FT-IR spectrometer and the measurements were conducted in threefold for each energy density. The effluent gas was passed through the ozone monitor continuously, thus measuring the ozone concentration in-situ. Based on the measurements at different energy densities, the ozone concentration is obtained via linear regression, similar to what has been described for the other calibration processes. Linear regression analysis was applied to the integration area values. The slope of line K4 was used to calculate the O₃ concentrations. K4 was defined as the following:

\[ K_4 = \frac{C_{O_3}}{S_{O_3}} \] (4.9)
4.4 Experimental Procedure

Abatement of TCE is investigated with NTP alone, heterogeneous catalyst alone and a combined NTP-catalyst system (PPC). All experiments were carried out with a total air flow of 0.5 L/min (30 L/h) containing 300-350/500 parts per million by volume (ppmv) TCE with/without moist air (RH=15% ≈ 4090 ppmv). This TCE/air mixture was stabilized before being introduced into the plasma reactor for a sufficient period (2 h) by fixing the flow rate to the TCE bubbling bottle via a MFC. A quartz tube filled with 0.5 g of catalyst
diluted in 2.5/3 g of SiC (EMB 45053-Prolabo; 0.105 mm) in order to improve isothermicity of the bed and to avoid flow dynamic problems was located downstream of the plasma reactor. A calcination step was performed before each experiment with dry air at 350 °C (cryptomelanes) or at 600 °C (CeO₂) for 4 h (0.2 L/min) to activate the catalyst.

The performances of the hybrid process using cerium oxide catalysts toward TCE removal were assessed regarding the following sequence (Figure 4.16): First of all, the reactive flow (TCE: 500 ppm, total flow rate: 0.5 L/min, RH: 0%) was allowed to stabilize (passed through by-pass) before sending it to the catalyst reactor. In the meantime, the catalyst temperature was increased to the desired value (100 °C) in the oven. Next, the catalyst was exposed to the reactive gas flow at 100 °C for 10 min. Then again the reactive flow was passed through by-pass and the plasma was turned on. After plasma stabilization for 5 min the plasma treated effluent was passed through the catalyst (PPC) and FTIR spectra were measured for 5 min at intervals of 30 s. The energy density was allowed to increase by steps of 40 J/L from 40 J/L to 80 J/L; this measurement of 5 min duration was repeated by following the same procedure (Figure 4.16). This sequence was repeated for catalyst temperatures of 100, 150, 200, 250, 300, 350, 400, 450, 500 and 550 °C. The temperature of the catalyst bed was increased to the desired temperature at the rate of 5 °C/min. It is worthy to note that, this PhD study was focused on operating the PPC system at low energy density plasma in combination with low/moderate catalyst temperature to improve the energy efficiency of the TCE abatement process. Therefore, the discussion of PPC performance will be focused on the catalyst temperatures among 100–300 °C despite plasma catalytic test was performed in a wide range of temperatures (100–550 °C).

The performances of the hybrid process using cryptomelanes catalysts towards TCE removal were assessed regarding the following sequence (Figure 4.17): the catalyst was first exposed to the reactive gas flow (TCE: 300-350 ppm, total flow rate: 0.5 L/min, RH: 15%) at 50 °C for 10 min. Then the plasma was turned on and after plasma stabilization for 5 min the energy density was allowed to increase by steps of 30 J/L for 5 min duration from 30 J/L to 120 J/L. This sequence was repeated for catalyst temperatures of 100 and 150 °C. The temperature of the catalyst bed was increased to the desired temperature at the rate of 3 °C/min.
Figure 4.16: Schematic representation of PPC experiment with CeO₂ catalyst

Figure 4.17: PPC experimental protocol with K-OMS-2, Fe/K-OMS-2, and Fe-K-OMS-2 catalysts.
4.5 Evaluation Parameters

Abatement of TCE is investigated with NTP alone, heterogeneous catalyst alone and a combined NTP-catalyst system (PPC). To evaluate the efficiency of the process the following parameters were estimated:

- **Discharge power** $P$ is the power deposited into the plasma:
  \[ P = U_{pl} I \]  
  where $U_{pl}$ is the plasma voltage and $I$ the discharge current.

- **Energy density** $(ED)$ is the energy deposited per unit volume of process gas:
  \[ ED = \frac{E}{V} = \frac{P}{Q} \]  
  where $E$ is the energy deposited in the treated volume $V$ and $Q$ is the gas flow rate. The unit of $ED$ is J/L although other units such as kWh/m³ are also possible.

- The TCE abatement is the basic parameter which indicates the relative amount of removed TCE:
  \[ \text{TCE abatement} \% = \frac{[\text{TCE}]_{in} - [\text{TCE}]_{out}}{[\text{TCE}]_{in}} \times 100 \]  
  where $[\text{TCE}]_{in}$ is the initial TCE concentration and $[\text{TCE}]_{out}$ the concentration in the effluent. In this work, other terms are also used such as removal efficiency and conversion.

- The selectivities of CO, CO₂, COₓ are defined as:
  \[ S_{CO}(\%) = \frac{[CO]}{2 \times [\text{TCE}]_{conv}} \times 100 \]  
  \[ S_{CO₂}(\%) = \frac{[CO₂]}{2 \times [\text{TCE}]_{conv}} \times 100 \]  
  \[ S_{COₓ}(\%) = S_{CO} + S_{CO₂} \]
where \([CO]\) and \([CO_2]\) are the concentrations of carbon monoxide and carbon dioxide detected in the effluent gas as a result of TCE oxidation and \([TCE]_{conv}\) is the concentration of TCE converted by the plasma.

- The yields of CO and CO\(_2\) and CO\(_x\) are defined as follows:

\[
Y_{CO}(\%) = \frac{[CO]}{2 \times [TCE]_{in}} \times 100
\]

(4.15)

\[
Y_{CO_2}(\%) = \frac{[CO_2]}{2 \times [TCE]_{in}} \times 100
\]

(4.16)

\[
Y_{CO_x}(\%) = Y_{CO} + Y_{CO_2}
\]

(4.17)
CHAPTER 5:

POST PLASMA CATALYSIS FOR TRICHLOROETHYLENE DECOMPOSITION OVER CeO₂ CATALYST: SYNERGETIC EFFECT AND STABILITY TEST
5.1 Introduction

CeO$_2$ is a multifunctional rare earth oxide, which possesses excellent physical and chemical properties and has been widely used in several advanced applications such as heterogeneous catalysis [214, 215], electrochemistry [216], photochemistry [217] and material science [218]. CeO$_2$ has been chosen as catalyst due to its unique properties such as a higher oxygen storage/transport capacity [219]. Additionally, the ability to easily shift between reduced and oxidized states (i.e. Ce$^{3+}$–Ce$^{4+}$), which results in an increase in oxygen vacancies, leads to an increased catalytic activity [220].

The aim of this chapter is devoted to investigate the possibility of using a plasma catalytic system with a commercial CeO$_2$ catalyst downstream (i.e. PPC-post plasma catalysis) for the abatement of trichloroethylene, a typical chlorinated VOC, from dry air. Also, special attention is given to the effect of catalyst temperature, the role of ozone in the plasma–catalytic TCE abatement and the possible synergy between NTP and catalysis. Finally, a long term test to evaluate the stability of CeO$_2$ catalyst has also been successfully performed.

5.2 Experimental Conditions

The experimental conditions used in this study are summarized in Table 5.1.

Table 5.1: Experimental conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Air source</strong></td>
<td>Air Liquide, Alphagaz 1</td>
</tr>
<tr>
<td><strong>Flow rate</strong></td>
<td>500 mL/min</td>
</tr>
<tr>
<td><strong>Relative humidity (20 °C)</strong></td>
<td>0%</td>
</tr>
<tr>
<td><strong>Initial TCE concentration</strong></td>
<td>~500 ppm</td>
</tr>
<tr>
<td><strong>Energy Density (J/L)</strong></td>
<td></td>
</tr>
<tr>
<td>Plasma alone</td>
<td>40-240</td>
</tr>
<tr>
<td>PPC</td>
<td>40 and 80</td>
</tr>
<tr>
<td>Catalyst</td>
<td>CeO$_2$ (0.5 g of catalyst mixed with 2.5 g SiC)</td>
</tr>
<tr>
<td>Activation conditions</td>
<td>200 mL/min, 600 °C for 4 h</td>
</tr>
<tr>
<td><strong>Catalyst temperature (°C)</strong></td>
<td></td>
</tr>
<tr>
<td>Catalyst alone</td>
<td>100–550</td>
</tr>
<tr>
<td>PPC</td>
<td>100-550 (discussion is focused on the range between 100-300)</td>
</tr>
</tbody>
</table>
5.3 Results and Discussion

To investigate the performance of the combined plasma–catalytic system, both parts are initially considered separately, i.e. destruction of TCE through the use of NTP and via catalytic oxidation.

5.3.1 TCE Abatement with NTP Alone

Figure 5.1 shows the TCE abatement and CO, CO₂ and COₓ selectivity as a function of the energy density for the plasma alone case. As expected, with increasing energy density the abatement of TCE increases. At higher energy density, more energetic electrons are produced which trigger the formation of radicals capable of decomposing TCE. For an energy density of 240 J/L the abatement and COₓ selectivity reach a maximum at 97.7% and 19.1%, respectively. This low selectivity is related to the formation of unwanted and toxic by-products such as PG and DCAC [206].

It is important to get insight on the underlying mechanisms and reactions of the removal process, which can yield measures to improve the removal efficiency and COₓ selectivity. The destruction of TCE with NTP takes place through many possible pathways [221]. Electron attachment of TCE, leading to the formation of C₂HCl₂ and a chlorine anion is one of the possible pathways for TCE decomposition. The contribution of the electron attachment of TCE depends on the electron density in the plasma discharge. Since low
energy density has been used in these corona discharges, the contribution of electron attachment of TCE will be significantly lower compared with other NTP processes such as dielectric barrier discharges (higher electron density). Metastable nitrogen molecules are also considered as dominant dissociation species occurring in a NTP destruction process of VOC polluted air streams. However, no reaction rate coefficients for TCE with metastable nitrogen have been found in literature. Although different opinions exist among researchers about the primary initial steps for TCE decomposition (electron impact dissociative attachment/reactions with radicals/oxydation of negative ions) [35, 58, 222-225], it is however generally accepted that the chlorine radical chain reaction is the main decomposition mechanism of TCE [98, 223, 224, 226]. Cl$^-$ addition is faster and occurs more easily than with other radicals owing to the presence of C=C π bond in TCE, [223]. According to Vandenbroucke et al., the ClO$^-$ radical is also an important intermediate which oxidizes TCE [227]. Table 5.2: Detected by-products with NTP shows the by-products of NTP treatment detected with FT-IR and MS. DCAC, PG, CO and CO$_2$ were observed with both techniques. The decomposition of TCE with NTP led to the formation of PG, DCAC and TCAA as incomplete oxidation products. These results are in agreement with Vandenbroucke et al. [206]. According to Kirkpatrick et al. [228], TCE oxidation with NTP produces a significant amount of DCAC by the following reaction:

$$\text{C}_2\text{HCl}_3 + \text{ClO}^{} \rightarrow \text{CHCl}_2\text{COCl} + \text{Cl}^{}$$

(5.1)

Table 5.2: Detected by-products with NTP.

<table>
<thead>
<tr>
<th>By-product</th>
<th>Structure</th>
<th>FT-IR</th>
<th>MS</th>
<th>Unwanted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichloroacetylchloride(DCAC)</td>
<td>CHCl$_2$COCl</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Trichloroacetaldehyde (TCAA)</td>
<td>CCl$_3$COH</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Phosgene (PG)</td>
<td>COCl$_2$</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td>HCl</td>
<td>√</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl$_2$</td>
<td></td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO$_2$</td>
<td>√</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Ozone</td>
<td>O$_3$</td>
<td>√</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.3.2 TCE Abatement with the CeO₂ Alone

Figure 5.2 shows the TCE abatement, CO, CO₂ and COₓ selectivity as a function of the temperature of CeO₂. The catalyst activity was evaluated for the temperature range of 100–550 °C. Figure 5.2 clearly shows that CeO₂ is not active below 300 °C. Above this temperature, the abatement slightly increases until 450 °C whereafter it sharply increases with increasing temperature. The maximum obtained value of TCE abatement is 90% at 550 °C. COₓ selectivity reaches a plateau (87%) at 450 °C and remains more or less constant with further increase of the temperature. These results prove that high temperature is essential to achieve both high TCE abatement and selectivity.

It is noteworthy to state that the main products found in the catalytic destruction of TCE over CeO₂ are CO₂, CO, H₂O, COCl₂, CCl₄, C₂Cl₄ and HCl recorded by FT-IR and Cl₂ recorded by MS. In general, it is commonly accepted that the catalytic oxidation process of VOCs over metal oxide catalysts occurs according to the Mars Van Krevelen mechanism where both gas phase oxygen and lattice oxygen participate. Dai et al. proposed possible reaction paths of TCE degradation over CeO₂ catalyst [229, 230]. Briefly, the formation of intermediate species C₂HCl resulted from the C-Cl bond cleavage during TCE adsorption on CeO₂ active sites. This reactive intermediate can be easily further dissociated by CeO₂ and can be totally oxidized by adsorption of oxygen species (O⁻), to form final reaction products such as CO₂ and H₂O.

![Figure 5.2: TCE abatement, CO, CO₂ and COₓ selectivity as a function of the catalyst temperature](image-url)
5.3.3 TCE Abatement with Post Plasma Catalytic System

In order to reduce the energy cost of the process, low energy density plasma is used in combination with moderate catalyst temperature. Therefore, the discharge is operated at 40 and 80 J/L and the process was examined for catalyst temperatures between 100–300 °C.

Figure 5.3: TCE abatement, CO, CO₂ and COₓ selectivity as a function of the catalyst temperature for energy density 80 J/L.

Figure 5.3 shows the TCE abatement, CO, CO₂ and COₓ selectivity as a function of catalyst temperature for a fixed energy density of 80 J/L. The abatement increased with around 10% with plasma catalysis (90%) at 100 °C catalyst temperature compared to NTP alone (79.6%). The abatement of TCE in the catalyst alone system operating at the same temperature was negligible. This means that the combination of NTP with CeO₂ induces a synergetic effect on TCE abatement. In order to quantify the observed synergy, a synergy factor $f$ for TCE abatement is used as proposed by Vandenbroucke et al. [62] and defined as follows:

$$f_{TCE} = \frac{(TCE \text{ abatement})_{plasma-catalysis}}{(TCE \text{ abatement})_{plasma} + (TCE \text{ abatement})_{catalyst}}$$  \hspace{1cm} (5.2)

If this value of $f_{TCE}$ exceeds 1, one can conclude that TCE abatement for plasma catalysis is higher than the sum of its individual values for the plasma and catalyst alone which shows a synergetic effect. Table 5.3 shows that the synergy factor for TCE abatement ranges from 1.15 to 1.04.
Although at low catalyst temperature plasma catalysis improves TCE abatement, at higher temperatures, the abatement however slightly decreases (5%). Hence, the effect of the catalyst temperature on the synergy factor $f_{TCE}$ is much smaller (Table 5.3). The small decrease of the synergy factor with increasing temperature can possibly be explained by deactivation of the catalyst due to irreversible adsorption of chlorinated by-products on the catalyst surface. It should be noted that the PPC experiment was continuously carried out by increasing the catalyst temperature in steps of 50 °C from 100 °C to 300 °C. Hence, during the experiment at 300 °C it is plausible that a part of the active sites were poisoned by TCE degradation products, already formed during previous experiments, thereby inhibiting the decomposition of TCE. The study of catalyst stability in PPC configuration is necessary to establish the evolution of such a catalyst which is investigated and will described in section 5.3.5.

The PPC system also remarkably enhanced the CO$_x$ selectivity/yield (≈ 90/75%) compared to the plasma alone system (14/9.2%), as shown in Figure 5.3 and Figure 5.4. It is noticeable that as the catalyst temperature increases only the CO$_x$ selectivity/yield improves while TCE abatement remains more or less constant. This can be ascribed to the efficient oxidation of oxygenated by-products (DCAC, PG) instead of TCE molecules in the subsequent catalytic reactor because DCAC is more easily destroyed due to its weak bonding energy (3-4 eV) compared to the double bonding energy of TCE (9.45 eV) [98, 231-233]. This statement is in agreement with a previous study by Vandenbroucke et al. on plasma catalytic removal of TCE over a MnO$_2$ catalyst downstream [62]. It was reported that the oxygenated intermediates (DCAC, PG) produced by partial oxidation of TCE in plasma are more reactive than TCE, reach the catalyst surface with a degree of excitation and are more easily decomposed resulting in an improved catalytic performance. This suggests that the polychlorinated intermediates produced by plasma were more susceptible to catalytic oxidation than TCE. Furthermore, a clear synergy was observed for the CO and CO$_2$ yields (Table 5.3) which indicates that the plasma catalytic system greatly enhances the selectivity of the process towards total oxidation compared to plasma alone case.
Table 5.3: Synergy factors for plasma catalytic TCE abatement.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$f_{\text{TCE}}$</th>
<th>$f_{\text{CO}}$</th>
<th>$f_{\text{CO}_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40 J/L</td>
<td>80 J/L</td>
<td>40 J/L</td>
</tr>
<tr>
<td>100</td>
<td>1.15</td>
<td>1.11</td>
<td>1.82</td>
</tr>
<tr>
<td>150</td>
<td>1.16</td>
<td>1.14</td>
<td>2.84</td>
</tr>
<tr>
<td>200</td>
<td>1.12</td>
<td>1.11</td>
<td>3.41</td>
</tr>
<tr>
<td>250</td>
<td>1.04</td>
<td>1.09</td>
<td>5.90</td>
</tr>
<tr>
<td>300</td>
<td>1.04</td>
<td>1.07</td>
<td>7.11</td>
</tr>
</tbody>
</table>

The synergy factor $f$ for CO and CO$_2$ yields are calculated as followed:

$$f_{\text{CO}} = \frac{(Y_{\text{CO}})_{\text{plasma–catalysis}}}{(Y_{\text{CO}})_{\text{plasma}} + (Y_{\text{CO}})_{\text{catalyst}}} \quad (5.3)$$

Figure 5.4: (a) TCE abatement, (b) CO and CO$_2$ yield as a function of the catalyst temperature for energy density 40 and 80 J/L.
The synergy factor for CO and CO$_2$ yields ranges from 1.64-7.11 and 1.52-18.05, respectively. The increased CO$_x$ selectivity in the PPC system can be explained by the activated oxidation reactions on the catalyst surface. It is found that p-type oxide semiconductors can effectively decompose ozone which enables the supply of active oxygen species that assist the destruction of the remaining VOC and polychlorinated by-products exiting the plasma reactor [95, 99]. Ozone can be cleaved at the catalyst surface, leading to the formation of active oxygen species via [234]:

\[
O_3 + \ast \rightarrow O_2 + O^* 
\]  
\[
O_3 + O^* \rightarrow O_2 + O_2^* 
\]  

where $\ast$ is an active site and O* is the active oxygen specie on the catalyst surface. The active oxygen species may react with remaining VOC or chlorinated by-products adsorbed on the catalyst surface towards total oxidation products (CO$_x$, H$_2$O) through Langmuir-Hinshelwood (L-H) mechanism [21], as follows:

\[
O^* + VOC_{ads} \rightarrow CO_x + H_2O + \ast 
\]  

Figure 5.5: Ozone outlet concentration of the plasma treated TCE gas in a plasma alone and plasma catalytic (CeO$_2$) systems for different temperatures.

Figure 5.5 shows the ozone concentration in the outlet gas of the plasma alone and the PPC system. The use of a catalyst (at 100 °C) downstream of the
plasma (operated at 80 J/L) resulted in a decrease of the ozone outlet concentration from 138 to 41 ppm, compared to the plasma alone system. The experiments at an energy density of 80 J/L resulted in a higher ozone production than the 40 J/L case due to the presence of more electrons in the plasma when operating at a higher energy density. An increase of the catalyst temperature further decreased the ozone concentration. Wu et al. reported the ozone decomposition ability of a CeO₂ catalyst (40 °C) in PPC process [95]. Naydenov et al. have also suggested the production of atomic oxygen species by ozone decomposition on the oxide surface of CeO₂ (10-70 °C) [235]. From these results it can be suggested that ozone dissociates on the catalyst surface to form gas phase molecular oxygen and peroxide groups which enhance the complete oxidation of TCE [62].

However, the decrease in outlet ozone concentration with increasing catalyst/oven temperature could also be attributed to the thermal dissociation of ozone. Therefore, to elucidate the latter assumption, PPC experiments without CeO₂ catalyst (empty glass reactor and with CSi only) have been performed over the temperature range from 100 °C to 300 °C. These results were compared with the CeO₂ and CSi mixture which is the actual experimental condition. The outlet ozone concentration was more or less similar in each PPC experiment especially above 100 °C (Figure 5.6) indicating that ozone could be consumed in the oxidation reaction or dissociated by high temperature.

![Figure 5.6: Ozone outlet concentration for the PPC experiment with/without CeO₂ catalyst as a function of operating temperature.](image)

Additionally, an increased TCE abatement ranging from 7 to 10 % was observed (not shown) in these PPC processes compared to the NTP alone case. It is known that dissociation of ozone into molecular oxygen and atomic
oxygen occurs at 100 °C [236]. These molecular/atomic oxygens may react with unreacted TCE, hence promoting higher TCE removal efficiency in each PPC experiment. Nonetheless, the CO₂ selectivity is only much higher in the presence of CeO₂ compared to others situations (Figure 5.7) showing the importance of the reactive surface. Indeed the VOC removal by plasma catalysis is not only governed by gas phase reactions but also by surface reactions on the catalyst [237].

Figure 5.7: CO and CO₂ selectivity for the PPC experiment with/without CeO₂ catalyst as a function of operating temperature. Energy density = 80 J/L.
Teramoto et al. also reported another possible mechanism in which gas phase ozone directly reacts with adsorbed VOCs or chlorinated by-products through an Eley-Rideal (E-R) mechanism [238], as follows:

\[
O_3 + VOC_{ads} \rightarrow CO_x + H_2O + *
\]  

(5.8)

However, this phenomenon is only valid if the catalyst acts below 100 °C temperature since \(O_3\) can be decomposed at higher temperatures before interacting with the adsorbed VOCs. Hence, this mechanism can be ruled out in our experimental condition.

It is expected that the increase of the catalyst reactor temperature may increase the thermal decomposition of ozone in the vicinity of the catalyst leading to a decrease in the disposal of \(O_3\) which will be catalytically decomposed on the catalyst. However, at the same time, reactions at the catalyst surface, such as decomposition of ozone and interactions between reactive adsorbed oxygen atoms and TCE and related gaseous polychlorinated by-products, are also accelerated. Higher catalyst temperature promotes the catalyst activity such as high oxygen storage capacity due to its high bulk oxygen mobility and oxygen vacancies. The oxygen storage capacity can be determined by the redox couple of Ce\(^{4+}/\)Ce\(^{3+}\) [239]. Ceria itself has a certain amount of surface active oxygen species which may contribute to surface reactions. Moreover, CeO\(_2\) can also act as local source/sink of oxygen species which favors the generation of surface adsorbed oxygen species enabling the deep oxidation of the target pollutant/by-products. The increased value of CO and CO\(_2\) selectivity clearly suggests the surface reaction of the plasma processed gaseous polychlorinated by-products as well as the remaining TCE with the active oxygen species on CeO\(_2\) catalyst surface. As previously stated, according to Dai et al., adsorbed oxygen species play a key role for TCE decomposition on CeO\(_2\) catalyst [230]. Therefore, one may conclude that adsorbed VOCs (TCE and by-products) may react with adjacent reactive oxygen species (active O species by \(O_3\) decomposition/lattice O) through L-H mechanism where the resulting oxygen vacancies on the catalyst surface can be replenished by gas phase atomic O formed by thermal dissociation of \(O_3\). The increase of CO\(_x\) selectivity with an elevated temperature clearly shows the acceleration of the catalytic activity of CeO\(_2\) with increasing temperature.

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5.3.4 By-Product Distribution of TCE Decomposition

As previously discussed, the use of NTP in combination with a catalyst clearly enhances the CO\textsubscript{X} selectivity which reduces the formation of chlorinated by-products. Therefore, it is interesting to identify the chlorinated by-products and to investigate if new products are formed in the PPC system. Figure 5.8 shows the FT-IR analysis of both inlet and outlet streams when plasma is operated at 80 J/L with or without CeO\textsubscript{2} catalyst maintained at 300 °C. The by-products formed by NTP treatment which have already been mentioned in Table 5.2 are identified by carefully comparing these spectra with NIST IR spectra standard reference database.

![Figure 5.8: FT-IR spectra of (a) inlet TCE, (b) Catalyst alone (300°C), (c) NTP (80 J/L) and (d) PPC (80 J/L- 300°C).](image)

The TCE abatement is calculated by taking the ratio of the integrated surface area of the inlet and outlet band of TCE at 945 cm\textsuperscript{-1} which is not interfered by other by-products IR bands. From Figure 5.8 it is clearly evident that plasma catalysis suppresses the unwanted by-products (DCAC, PG and O\textsubscript{3}) formed in NTP treatment. Furthermore, two new IR bands appear at 794 and 773 cm\textsuperscript{-1} in minor extent which have been previously ascribed to CCl\textsubscript{4} and CHCl\textsubscript{3}, respectively [63]. These new C1 chlorinated products may be produced from the reaction of adsorbed chlorinated species with CHCl\textsubscript{2} and CCl\textsubscript{3} radicals resulting from the catalytic cleavage of the TCAD and DCAC molecules. As for the formation of NO\textsubscript{2}, it was neither detected by the NTP nor by PPC process unlike the work of Nguyen Dinh et al. [65].
The enhanced oxidation in PPC system with increasing catalyst temperature resulted in an increased formation of CO\textsubscript{x} and HCl and a decreased formation of DCAC, as shown in Figure 5.9 (c) and (d). The increased formation of HCl, compared to the plasma alone system can be explained by the production of oxygen radicals on the catalyst surface, enhancing the rate of the following oxidation reaction

\[
C_2HCl_3 + 4O \rightarrow 2CO_2 + HCl + Cl_2
\]  

(5.9)

The increased phosgene production at a higher catalyst temperature as shown in Figure 5.9 (a) is remarkable. A possible explanation is the increased formation of ClO radicals with the catalyst temperature which further reacts with TCE towards phosgene via:

\[
Cl_2 + O \rightarrow Cl + ClO
\]  

(5.10)

\[
C_2HCl_3 + ClO \rightarrow COCl_2 + CHCl_2
\]  

(5.11)

However, above 200 °C the formation of PG was completely suppressed.

Figure 5.9: FT-IR spectra of the gaseous phase at the exit of the catalytic reactor at different temperature between (a) 700-1100, (b) 1730-1880, (c) 2010-2430 and (d) 2700–3000 cm\textsuperscript{-1}.
In addition to FT-IR, mass spectra of the inlet and outlet gas streams are also recorded in order to identify additional by-products which have also been mentioned in Table 5.2: Detected by-products with NTP. It is important to analyze MS results since the presence of some products cannot be identified with only FT-IR due to the interference of other by-products bands. Additionally, diatomic molecules such as Cl₂ and IR-transparent cannot be identified with FT-IR. Figure 5.10 exhibits the mass spectra of inlet and outlet gas streams when plasma is operated at 80 J/L with or without CeO₂ catalyst, where the temperature of the catalyst was maintained at 300 °C. All the peaks in these spectra are identified by comparison to the NIST mass spectral library. The typical characteristic TCE fragment ions, C₂HCl⁺ (m/z: 60, 62), C₂HCl₂⁺ (m/z: 95, 97, 99) and C₂HCl₃⁺ (m/z: 130, 132, 134, 136), are detected in the inlet TCE gas stream (Figure 5.10-a). Figure 5.10-b represents the mass spectrum of the outlet gas stream, treated at an energy density of 80 J/L. The detailed mass spectra analysis is described in a previous study [206]. A brief description is however given here. The figure shows a decrease in the abundance of the TCE fragment ions suggesting partial TCE decomposition. Simultaneously some additional peaks were also detected which confirms the formation of polychlorinated by-products due to incomplete oxidation of TCE in the plasma reactor. For instance, the characteristic fragment ions of m/z 83, 85 (CHCl₂⁺), m/z 63, 65 (CClO⁺), m/z 48, 50 (CHCl⁺) can be ascribed to DCAC. The characteristic fragment ions of m/z 146, 148 (C₂HClO⁺), m/z 117, 119 (CCl₃⁺), m/z 111, 113 (C₂HClO⁺) can be ascribed to TCAD but also to DCAC. The characteristic fragment ions of m/z 82, 84 (CCl₂⁺) can be ascribed to TCAD only. However, the lower intensity indicates low content of TCAD formation. Phosgene is also detected by the characteristic fragment ions at m/z 63 and 65 (CO¹⁵Cl⁺ and CO¹⁷Cl⁺) present in the mass spectrum of the outlet gas. The mass spectrum of the outlet gas revealed the formation of Cl₂ by the peaks at m/z 70 (³⁵Cl²Cl⁺), 72 (³⁵Cl³⁷Cl⁺) and 74 (³⁷Cl³⁷Cl⁺). The formation of HCl and CO₂ are established by the peaks in mass spectrum at m/z of 36 (H²⁺Cl⁺) and 44 (CO₂⁺) which is not shown here. Figure 5.10-c shows the mass spectra in case of plasma catalysis operated at 80 J/L and 300 °C. The suppression of all detected chlorinated by-products except Cl₂ molecules is clearly evident by the decrease in the abundance of corresponding fragment ions in this figure. Nonetheless, trace amounts of CHCl₂ and CCl₄ have been confirmed by the characteristic fragment ions of m/z 83, 85 (CHCl₂⁺) and 117, 119 (CCl₄⁺), respectively.
5.3.5 Stability of the Catalyst

Next to activity and selectivity, stability is also an important feature of the catalyst, especially for practical applications. In this regard, a stability test of the plasma catalytic process has been performed at low energy density (80 J/L) and moderate catalyst temperature (200 °C).

The experiment was carried out over 4 days with a daily startup–shutdown. During the 4 days run, TCE waste gas stream ($C_{TCE} = 500$ ppm, $Q = 0.5$ L/min) was treated with plasma catalysis each day for about 10 hours (total time on stream was around 40 hours). During the shutdown period (at night), plasma was turned off and a 0.2 L/min air flow rate was passed through the catalytic bed. Figure 5.11 displays the TCE abatement, CO, CO$_2$ and CO$_x$ selectivities obtained with the stability test of plasma catalysis. Both plasma and catalyst are found to be stable over the tested time on stream. The experiment demonstrated that plasma catalysis maintained the same initial activity over 40 hours in terms of TCE abatement (90%). However, CO$_x$ selectivity decreased around 13% during the reaction period. This could be attributed to the deactivation of the catalyst surface either by chlorination or by blocking of active sites [229, 230].

Notably, roughly a similar amount of TCE abatement was observed in each PPC test regardless the type of material introduced downstream (discussed in...
section 5.3.3) and a high CO$_x$ selectivity was observed only in the presence of the catalyst (Figure 5.7). Moreover, with time on stream TCE abatement is not altered but the CO$_x$ selectivities decrease. This may suggest that with the assistance of NTP, CeO$_2$ (at lower catalyst temperature) may be enough activated to only selectively react with hazardous polychlorinated by-products (which need less energy to oxidise than TCE) to form the desired product (CO$_2$).

![Figure 5.11: Stability test of catalyst](image)

### 5.4 Conclusions

The abatement of TCE from dry air was investigated by a combined use of a multi-pin-to-plate negative DC corona/glow discharge with a CeO$_2$ catalyst downstream.

NTP enables catalyst activation at lower temperature. The ozone degradation capacity combined with high oxygen storage capacity of the CeO$_2$ catalyst may contribute to the generation of active oxygen species and the enhancement of oxygen mobility enabling the deep oxidation of the unreacted TCE and the polychlorinated by-products exiting from NTP leading to an improved TCE abatement and CO$_x$ selectivities. It was found that the polychlorinated intermediates produced by plasma were more susceptible to catalytic oxidation than TCE.

By examining the effect of catalyst temperature, it was observed that low energy density plasma in combination with moderate catalyst temperature
successfully abated dilute TCE in air streams. Hence, this plasma catalysis route shows great potential as air pollution control technology for low concentrated VOC air streams at a lower energy cost.

Furthermore, a long term test to evaluate the stability of CeO₂ catalyst has also been successfully performed.
CHAPTER 6:
SYNTHESIS AND CATALYTIC PERFORMANCES OF K-OMS-2, Fe/K-OMS-2 AND Fe-K-OMS-2 IN POST PLASMA CATALYSIS FOR DILUTE TCE ABATEMENT
The results of chapter 6 were published in the following international peer-reviewed journal:


*Synthesis and catalytic performances of K-OMS-2, Fe/K-OMS-2 and Fe-K-OMS-2 in post plasma-catalysis for dilute TCE abatement*

Catalysis Today, 307, 20-28, 2018
6.1 Introduction

In this chapter, special attention was paid to the development of tailored catalysts to be coupled with plasma. The use of a commercially available material was a first step (chapter 5) in order to have the basic understanding and optimization of the PPC process. In post plasma configuration, the most desirable properties of the appropriate catalyst should be its ozone decomposition ability and VOC total oxidation capability close to room or moderate temperatures (≤ 150 °C), so that the targets are removed efficiently and economically by PPC. In this regard, it is crucial to have a sufficient and reliable range of (i) specific surfaces, (ii) morphology, (iii) porosity and (iv) crystalline phases for an efficient catalyst which is not available in a commercial catalyst. Therefore, the synthesis of the proper materials with the required characteristics is targeted. Metal oxides which are characterized by labile oxygen atoms are important for such application and thereby investigations were focused on MnO₃ based catalysts. In addition, among the developed catalysts, cryptomelane type manganese oxide catalysts are considered to be the most efficient and cost-effective for ozone decomposition. Again manganese oxides is reported as a good candidates for total oxidation of trichloroethylene. Lastly manganese oxides are also recognized as efficient catalysts in CO oxidation into CO₂ which is also an important reaction in the PPC process. The open structure of the channels, the easy cycling of Mn⁴⁺/Mn³⁺ and the high mobility of lattice oxygen as well as more recently the morphology of the particles have been put forward as important characteristics to take into account for their activity in CTO of VOCs.

During the course of this chapter, Cryptomelane catalyst K-OMS-2 of ideal formula K(Mn₇IVMnIII)O₁₆ is modified with Fe doping, followed by characterization and testing in post plasma catalysis (PPC) in the course of total trichloroethylene (TCE) oxidation in moist air (RH=15%). The addition of iron to cryptomelane was performed in 2 different ways: (a) by co-precipitation (Fe-K-OMS-2) and (b) by a successive Fe(OH)x (x = 2; 3) precipitation on cryptomelane (Fe/K-OMS-2) through refluxing at ambient pressure. Particular attention has been paid to the assessment of the physio-chemical properties of three catalysts. The characterization includes ICP-OES, XRD, Raman spectroscopy, SEM, BET N₂ adsorption analysis, TGA/DTA, and TPR. Concerning the performance of plasma assisted catalysts for dilute TCE abatement, the effect of the energy density and temperature of the catalyst were
investigated and evaluated in terms of total TCE conversion, CO₂ and CO yields and by-products distribution.

### 6.2 Experimental Condition

Table 6.1 summarizes the basic experimental conditions used in this chapter. The detail preparation process, characterization process of catalysts and experiment process can be seen in chapter 4.

<table>
<thead>
<tr>
<th>Table 6.1: Experimental conditions.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Air source</strong></td>
</tr>
<tr>
<td><strong>Flow rate</strong></td>
</tr>
<tr>
<td><strong>Relative humidity (20 °C)</strong></td>
</tr>
<tr>
<td><strong>Initial TCE concentration</strong></td>
</tr>
<tr>
<td><strong>Plasma alone Energy Density</strong></td>
</tr>
<tr>
<td><strong>PPC Energy Density</strong></td>
</tr>
<tr>
<td><strong>Catalyst</strong></td>
</tr>
<tr>
<td><strong>Activation conditions</strong></td>
</tr>
<tr>
<td><strong>Catalyst temperature</strong></td>
</tr>
</tbody>
</table>

### 6.3 Results and Discussion

#### 6.3.1 Main Characteristics of the Materials

6.3.1.1 **Chemical Analysis**

The physico-chemical characterizations of the fresh materials are given in Table 6.2. A formula of K₀.₁₂MnO₂ was obtained for K-OMS-2 sample based on the ICP-OES analysis. Charge balance calculation gives a Mn AOS of 3.88 which agrees with those of 3.87 [115] and of 3.89 [240] reported elsewhere for cryptomelane synthesized hydrothermally [115] or by reflux method [240], respectively. It is worth mentioning that in cryptomelane-type solid, Mn AOS usually varies between 3.6 and 3.8 in line with the mixed-valence Mn(IV) and Mn(III) structures [241]. Based on elemental analysis, the Fe/K-OMS-2 and
Fe-K-OMS-2 samples exhibit Fe/Mn atomic ratios of 0.10 and 0.077, respectively, which is in perfect agreement with that present in the reaction mixture of 0.10 for the impregnated sample but at a slightly higher value for the co-impregnated sample (Fe/Mn ratio of 0.52 in solution). As expected, Fe/K-OMS-2 oxide displays a comparable K/Mn ratio than that of K-OMS-2 which is in agreement with the dispersion of iron based oxides over K-OMS-2 acting as the support. Conversely, the K/Mn ratio of 0.027 is far less than that expected and shows that the mode of introduction of the dopant plays a key role in the nature of the final oxide.

Table 6.2: Chemical composition of the fresh catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Mn</th>
<th>Fe</th>
<th>K</th>
<th>K/Mn</th>
<th>Fe/Mn</th>
<th>K/(Mn+Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-OMS-2</td>
<td>59.76</td>
<td>-</td>
<td>5.03</td>
<td>0.12</td>
<td>-</td>
<td>0.12</td>
</tr>
<tr>
<td>Fe/K-OMS-2</td>
<td>59.50</td>
<td>6.10</td>
<td>5.88</td>
<td>0.14</td>
<td>0.10</td>
<td>0.13</td>
</tr>
<tr>
<td>Fe-K-OMS-2</td>
<td>58.69</td>
<td>4.53</td>
<td>1.11</td>
<td>0.027</td>
<td>0.077</td>
<td>0.025</td>
</tr>
</tbody>
</table>

6.3.1.2 Structural Properties

The X-Ray diffraction patterns of K-OMS-2 and Fe/K-OMS-2 catalysts (Figure 6.1) showed peaks which can be indexed to the tetragonal K-OMS-2 phase (JCPDS: 44-0141) (space group (I 4/m) with unit cell parameters $a = b = 9.81 \, \text{Å}$ and $c = 2.85 \, \text{Å}$ [242]. Furthermore the mean crystallite size stays rather constant, of about 14-15 nm (Table 6.3), for both solids. Additional peaks located at 36.1° and 63.0° can be attributed to Fe-Mn spinels such as Fe(Fe$_{1.08}$Mn$_{0.92}$)O$_4$ (JCPDS 01-077-9278) or/and FeMn$_2$O$_4$ (JCPDS 04-006-9026), rather than maghemite ($\gamma$-Fe$_2$O$_3$) phase (JCPDS 13-0458), dispersed on cryptomelane without discarding the possibility of segregated amorphous or/and low content Fe and/or Mn (hydroxy)oxide phases. Otherwise the XRD pattern of Fe-K-OMS-2 shows very broad envelopes of overlapping low intensity peaks whose positions match those of K-OMS-2 to be consistent with the presence of a very disordered cryptomelane phase.

The lattice vibrational behaviors of both the undoped and Fe based K-OMS-2 materials were studied by Raman spectroscopy in order to probe the effect of iron addition on the spectral features of the K-OMS-2 material (Fe/K-OMS-2), to validate the postulated formation of cryptomelane and check for the presence of segregated crystalline and/or amorphous metal oxides. OMS-2 type materials crystallize into a body centered tetragonal structure with a space
group $I4/m$. Group theory predicts 15 Raman-active modes $6A_g + 6B_g + 3E_g$ [243]. The Raman spectrum of K-OMS-2 displayed in Figure 6.2 reveals only 9 characteristic peaks at 185, 280, 330, 386, 470, 512, 575, 630 and 745 cm$^{-1}$ for the regular K-OMS-2 which are in good agreement with the data reported by Gao et al. [243]. The 2 most intense peaks at 574 and 634 cm$^{-1}$ which have been previously associated to Mn-O vibrations along and orthogonal to the direction of the MnO$_6$ octahedral double chains ($A_g$ modes), respectively have been recognized to correspond to a well-developed tetragonal structure with 2×2 tunnels [243]. The Raman spectrum of Fe/K-OMS-2 shows these 2 characteristic lines but these are much more enlarged than those of the K-OMS-2 oxide. Conversely, the Raman contributions in the 200-400 cm$^{-1}$ spectral region have almost disappeared and an apparent additional line is now observed at 556 cm$^{-1}$ which can be due to the presence of segregated phases or different local environments of manganese.
Figure 6.1: XRD patterns of the synthesized materials.

Table 6.3: Textural, structural and reducibility properties of the fresh catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Textural properties</th>
<th>Redox properties</th>
<th>Thermal behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S_{BET}$ (m$^2$/g)</td>
<td>$V_p$ (cm$^3$/g)</td>
<td>$d_c$ (nm)</td>
</tr>
<tr>
<td>K-OMS-2</td>
<td>46</td>
<td>0.25</td>
<td>14.0</td>
</tr>
<tr>
<td>Fe/K-OMS-2</td>
<td>73</td>
<td>0.44</td>
<td>15.4</td>
</tr>
<tr>
<td>Fe-K-OMS-2</td>
<td>199</td>
<td>0.44</td>
<td>-</td>
</tr>
</tbody>
</table>

a: Pore volume  
b: Mean crystallite size
6.3.1.3 **Textural Properties**

The textural properties are significantly improved when adding Fe. In particular, the BET specific surface increased 4 times and the pore volume 2 times for Fe-K-OMS-2 in comparison with K-OMS-2 (Table 6.3: Textural, structural and reducibility properties of the fresh catalysts.). The representative SEM image of K-OMS-2 solid which is similar to that of Fe/K-OMS-2 solids is displayed in Figure 6.3 a. The needle-like morphology is clearly observed (average length: 1 \( \mu \)m). Conversely, the SEM image of the Fe-K-OMS-2 solid exhibits particles of pseudo-spherical morphology (average size: 300 nm) as shown in Figure 6.3 b. It turns out in that case that the elongation growth of the particles is partially inhibited. This observation may suggest some Fe incorporation into the Mn framework of cryptomelane as previously reported in the literature [123]. However, the assignment of the exact position of Fe in the structure is a difficult task. Complementary experiments have to be implemented to assess the effect of the Fe addition on the location of Fe in the structure through isomorphic substitution of Mn\(^{n+}\) in the octahedral sites of Mn\(^{n+}\) or partial replacement of K\(^+\) into the tunnels of the structure.
Figure 6.3: Representative SEM images from (a) K-OMS-2 and (b) Fe-K-OMS-2 solid

6.3.1.4 H₂-Temperature Programmed Reduction (H₂-TPR)

Figure 6.4 shows the TPR profiles of the materials. It is worthy to mention that the H₂ consumption profile of K-OMS-2 shows a global envelope rather similar to those reported by T. Chen et al. and W. Y. Hernández et al. [244, 245]. Four peaks at 300, 338, 356 and 374 °C can be seen. The lowest temperature reduction process has been previously attributed to the consumption of structural oxygen close to the surface leading to oxygen vacancies [245]. The three other ones are in line with a consecutive reduction scheme involving the successive steps: MnO₂ -> Mn₃O₄ -> MnO [246]. The peaks observed at 289, 325, 334, 338 and 365 °C in the Fe/K-OMS-2 solid were shifted to lower temperatures in comparison to the K-OMS-2 oxide. The TPR profile appears more complex due to the additional reducibility of the Fe-Mn spinel dispersed on K-OMS-2, among others. By opposition, the Fe-K-OMS-2 solid shows 3 contributions at 210, 277 and 301 °C in the low temperature range which are well separated from the peak at higher temperature (407 °C). It is worth mentioning that the temperature of the onset of reduction decreases as follow: K-OMS-2 > Fe/K-OMS-2 > Fe-K-OMS-2. The improved oxygen lability observed for Fe-K-OMS-2 may be related to many defects such as oxygen vacancies which would promote the degradation of the VOC and reaction intermediates.
Figure 6.4: H$_2$-TPR profiles for the synthesized materials.

Table 6.3 lists the H$_2$ consumption of the different catalysts in the reduction process. The H$_2$ consumptions of K-OMS-2, Fe/K-OMS-2 and Fe-KOMS2 are 9.90, 9.29 and 8.75 mmol/g, respectively. Based on the H$_2$ consumption and the corresponding Mn content given in Table 6.2, the Mn AOS for K-OMS-2 by assuming MnO as final product [246] is calculated and found to be equal to 3.82 which is in good agreement with the value 3.88 obtained by ICP-OES. The Mn AOS of Fe/K-OMS-2 and Fe-KOMS2 are calculated and found to be equal to 3.68 and 3.61, respectively, by assuming all iron in the samples to be Fe$^{3+}$ and by assuming that Fe$_3$O$_4$ is the end product of reduction. As a result, the Mn AOS decreases with the introduction of Fe. When considering Fe/K-OMS-2, the Mn AOS decrease is mostly due to the reduction of segregated Fe-Mn spinel species which is in accordance with XRD results. In a similar way, segregated amorphous or well dispersed related Fe-Mn may also contribute to the Mn AOS decrease for Fe-K-OMS-2 sample.

6.3.1.5 Thermal stability

Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) profiles for the different solids performed in dry air are displayed in Figure 6.5 a-b and the relevant results are shown in Table 6.3. The differential thermogravimetric (DTG) curves of K-OMS-2 and Fe/K-OMS-2 samples have similar behaviors showing three separate steps in the temperature range
of 25 °C–800 °C. The two first steps at temperatures up to 200 °C correspond to the elimination of physisorbed and chemisorbed water in different environments [247]. When the temperature exceeds 200 °C, the weight loss slows down until a temperature of about 500 °C. With the temperature increase up to 780 °C, the third weight losses which increase to 3.6 and 2.4% for K-OMS-2 and Fe/K-OMS-2, respectively, have been ascribed to the desorption of water inside the (2×2) channels as well as the departure of some structural oxygen close to the surface inducing oxygen vacancies without destroying the materials [248]. The removal of these species is in agreement with the presence of an endothermic peak located at 642 and 673 °C for the free and iron containing oxide, respectively. In comparison with the two previous solids, the DTA trace of Fe-KOMS-2 shows two weight loss steps in the ranges 25-200 °C and 400-550 °C which stabilize beyond 550 °C. As previously observed, the first weight loss corresponds to the removal of water while the second weight loss is related to the crystallization of the solid consistently with the DTA behavior.

![Figure 6.5: (a) TGA/DTG and (b) DTA profiles as a function of temperature over the synthesized materials.](image)

6.3.2 Plasma Catalysis

6.3.2.1 Plasma Alone

The performance of the NTP alone toward TCE abatement has been investigated as a function of energy density which is defined as the energy given by the plasma to 1 liter of gaseous gas. The TCE conversion increases with ED due to the formation of more energetic electrons as shown in Figure 6.6. The production of plasma generated ozone increases linearly with time to
reach 150 ppmv at 120 J/L. The COx yield is low, about 15% (not shown), demonstrating the poor mineralization of TCE into CO₂. This is in line with the formation of polychlorinated by-products such as phosgene (PG), dichloroacetylchloride (DCAC) and trichloroacetaldehyde (TCAD) identified from FT-IR spectra as previously reported [206].

Figure 6.6: TCE conversion and O₃ production as a function of temperature with NTP alone.

6.3.2.2 Post Plasma catalysis

Figure 6.7 and Figure 6.8 show the evolution of TCE abatement and CO₂ yield as a function of energy density for the 3 catalysts working in post plasma configuration compared to those of NTP alone. First of all with plasma turned off, at a catalyst temperature (Tc) of 50°C, 62% TCE abatement is observed over Fe-K-OMS-2 oxide in comparison to the 2 other catalysts for which the TCE abatement is close to zero. This is explained by the high surface area of the catalyst enabling the retention of a high amount of TCE which is in agreement with a CO₂ yield close to zero. When the surface of the catalyst will be saturated with the VOC, a decrease in TCE conversion is expected. With plasma turned on, the TCE conversion was less than that of NTP at ED of 30J/L suggesting that the downstream catalyst was working in unsteady-state conditions. At higher ED the TCE conversion profiles as a function of ED over K-OMS-2 and Fe-K-OMS-2 catalysts behave similarly with that of NTP. This
clearly indicates that only NTP is responsible for TCE degradation. Although the TCE conversion is much higher than that of NTP for PPC-Fe/K-OMS-2 process, no CO₂ yield improvement was observed in a comparison with the two other PPC configurations.

Figure 6.7: TCE conversion in PPC experiments as a function of ED and catalyst temperature.

However, no matter the catalyst under concern, the CO₂ yield values at 120 J/L of about 20% (Figure 6.8) are higher than the CO₂ yield value for NTP of about 4.6%. When the temperature of the catalyst is increased to 100 °C the physical TCE adsorption over the catalysts can be neglected. With plasma turned off, a CO₂ yield of 52% at 38% TCE conversion was observed for PPC-Fe-K-OMS-2 configuration. The TCE conversion was seen to continuously
increase with ED up to 88% at ED of 120 J/L while the CO₂ yield globally decreased to reach a final value of 43%. Conversely, both TCE conversion and CO₂ yields increased with energy density when taking into account the two other configurations. Additionally, it is worthy to mention that CO is the main gaseous by-product of the reaction. In terms of increasing CO₂ and COₓ (x=1-2) yields, the hybrid processes can be ranked as follow (Tc: 100 °C; ED: 120 J/L): PPC-K-OMS-2 (33; 52) < PPC-Fe/K-OMS-2 (40; 58) < PPC-Fe-K-OMS-2 (44; 60). When the temperature of the catalyst is varied to 150 °C, the TCE conversion and CO₂ yield as a function of ED were found to once more increase in PPC-K-OMS-2 and PPC-Fe/K-OMS-2 configurations. However the beneficial effect of temperature on TCE conversion when increasing the temperature from 100 °C to 150 °C is not so clear as it is only observed for ED lower and higher than 60 J/L for PPC-K-OMS-2 and PPC-Fe/K-OMS-2 processes, respectively. These results can be consistent with changes in the physical/chemical properties of the catalysts. Future work involving the study of catalyst stability in PPC configuration is necessary to establish such catalyst evolution. By opposition, at a catalyst temperature of 150 °C, a significant improvement in TCE abatement performances (TCE abatement: 78%; CO₂ yield: 52%) is observed over Fe-K-OMS-2 catalyst due to an efficient thermal activation. With plasma turned on, it is found that both TCE conversion and CO₂ yield globally increase as a function of ED showing in that way the beneficial assistance of NTP. As a result, 63% of CO₂ yield can be achieved for a TCE conversion close to 100%.

The efficiency of the PPC process towards TCE total oxidation in comparison with that of NTP was assessed when looking at the FT-IR spectra of both the inlet and outlet streams recorded between 700 and 1100 cm⁻¹ and 1720-1880 cm⁻¹, respectively, (Figure 6.9 a-b) at Tc of 150 °C for an energy density of 90 J/L. With plasma turned on, the TCE decomposition is revealed by the decrease in intensity of the C–H out of plane deformation band of TCE at 945 cm⁻¹ (Figure 6.9 a) while ozone production from dioxygen is detected in the outlet stream by bands at 1014-1046 cm⁻¹ [249, 250]. In the 1720-1880 cm⁻¹ FT-IR window, the characteristic bands at 1790 and 1820 cm⁻¹ can be ascribed to the presence of dichloroacetylchloride (DCAC), that at 1830 cm⁻¹ to phosgene (PG) and that at 1780 cm⁻¹ to trichloroacetaldehyde (TCAD) (Figure 6.9 b).

The detection and possible reaction schemes of formation of such intermediate oxidation products have already been observed and discussed elsewhere [63, 206]. In PPC configuration the intensity of the band of TCE at
945 cm$^{-1}$ decreases once more to almost disappearing in the case of PPC-Fe-K-OMS-2. Whatever the PPC configuration, the bands relative to $O_3$ and polychlorinated compounds disappear while analysis of the different FT-IR spectra shows the emergence of new bands located at 795 and 774 cm$^{-1}$ characteristic of the C-Cl bond vibration relative to $CCl_4$ and HCCl$_3$, respectively [63]. HCCl$_3$ and CCl$_4$ formations can be explained by the reaction of CHCl$_2$ and CCl$_3$ radicals resulting from the easy cleavage of the carbon-carbon bond of DCAC and TCAD with adsorbed Cl. However, the intensity of these characteristic bands is minimized in PPC-Fe-K-OMS-2 configuration showing in that way the importance of the nature of the catalyst.
Figure 6.8: CO$_2$ yields in PPC experiments as a function of ED and catalyst temperature.

Figure 6.9: FTIR spectra between 1800 and 1700 cm$^{-1}$ (a) and 1100 and 700 cm$^{-1}$ (b) of inlet and outlet stream ($T_c = 150$ °C; ED = 90 J/L; PG: Phosgene; DCAC: Dichloroacetylchloride; TCAD: Trichloroacetaldehyde.

These above observations attest to the beneficial role of ozone to give active oxygen species over the catalyst surface enabling the production of active species prone to oxidize the plasma processed gaseous polychlorinated by-products as well as the remaining TCE owing to the formal equations:

\[
\begin{align*}
\text{Cl}_2\text{CO} + (5/3)\text{O}_3 & \rightarrow \text{CO}_2 + \text{Cl}_2 + 2\text{O}_2 & (6.1) \\
\text{C}_2\text{Cl}_3\text{OH} + (10/3)\text{O}_3 & \rightarrow 2\text{CO}_2 + \text{Cl}_2 + \text{HCl} + 3.5\text{O}_2 & (6.2) \\
\text{C}_2\text{Cl}_3\text{H} + 4\text{O}_3 & \rightarrow 2\text{CO}_2 + \text{Cl}_2 + \text{HCl} + 4\text{O}_2 & (6.3)
\end{align*}
\]

To sum-up, the introduction of iron by co-precipitation has a significant beneficial impact on the properties of the catalyst: K-OMS-2 like structure with many defects, particles of pseudo-spherical morphology, high specific surface area and an increase of the reducibility of surface Mn$^{4+}$. A possible interaction between Mn and Fe in the Fe-K-OMS-2 framework as well as an increase of the active site density may contribute to an easy decomposition of O$_3$ to get active oxygen species and to enhance the catalyst surface oxygen mobility enabling to specifically oxidize the different plasma generated
hazardous gaseous species such as phosgene, trichloroacetaldehyde and dichloroacetylene. These characteristics explain the better performances of the NTP coupled with Fe-K-OMS-2 towards TCE abatement in our experimental conditions.

6.4 Conclusion

Plasma assisted Fe-K-OMS-2 catalyst working in post plasma configuration at a temperature of 150 °C presents a high activity for TCE removal in moist air and relevant CO$_2$ yields. The improved performances of this material can be related to an increase of oxygen vacancies and oxygen mobility in comparison to those of the K-OMS-2 catalyst. These characteristics facilitate the production of active species from plasma generated ozone and the surface oxygen mobility to promote the degradation of VOC or intermediates of reaction into CO$_2$. 
CHAPTER 7: GENERAL CONCLUSION AND FUTURE WORK
7.1 General Conclusion

The main objective of this research was to study and deliver an innovative and efficient air purification technology by combining a multi-pin-to-plate negative DC corona/glow discharge system with heterogeneous catalysts placed in the plasma downstream. Combination of non-thermal plasma and heterogeneous catalysts provides various advantages such as a higher energy efficiency and CO$_2$-selectivity, a reduced formation of unwanted by-products and a better carbon balance. TCE has been chosen as target pollutant since it is commonly used as an industrial solvent. A series of TCE abatement experiments were performed in a post plasma catalytic process. Focus was on operating the PPC system at low energy density in combination with a low catalyst temperature to improve the energy efficiency of the TCE abatement process. Screening of different catalytic materials for TCE oxidation were performed and compared with the plasma alone system. The comparison in the performance of the process was made based on the TCE abatement efficiency, the CO$_x$ yield/selectivity and the formation of harmful by-products.

In this thesis, special attention was paid to the development of tailored catalysts to be coupled with plasma. The use of a commercially available material was a first step in order to have the basic understanding and optimization of the PPC process. It is crucial to have a sufficient and reliable range of (i) specific surfaces, (ii) morphology, (iii) porosity and (iv) crystalline phases for an efficient catalyst. Therefore, the synthesis of the proper materials with the required characteristics is targeted. Metal oxides which are characterized by labile oxygen atoms are important for such application and thereby investigations were focused on MnO$_2$ based catalysts. Different preparation methods were studied and physicochemical properties were discussed to investigate the relationship between characteristics and catalytic activities of the samples towards TCE oxidation and mineralization with the assistance of plasma discharge. In addition to screening, synthesis and evaluation of post plasma catalysis efficiencies, attention was directed towards the stability behaviour of the hybrid system.

In a first step (Chapter 5), commercial cerium oxides were chosen in combination with the plasma source in order to enhance the performance of the plasma alone system in terms of removal efficiency, selectivity and energy cost. To investigate the performance of the combined plasma–catalytic system in dry air, both parts are initially considered separately, i.e. destruction of TCE through the use of NTP and via catalytic oxidation. As expected, NTP showed
poor CO\textsubscript{x} selectivity despite having a high abatement efficiency due to the formation of oxygenated intermediates such as phosgene, DCAC and TCAA, when operated alone. On the other hand, no activity for TCE oxidation over the CeO\textsubscript{2} catalyst was observed when solely operating in the examined temperature. By combining both systems, TCE abatement was increased, the formation of by-products was significantly reduced and a high CO\textsubscript{x} selectivity was achieved. This implies that, complete oxidation of TCE was enhanced by the synergistic effect of plasma and catalysis; thus, more intermediates were oxidized to CO\textsubscript{2}. The role of ozone in the plasma catalytic process was investigated and the synergistic reaction of O\textsubscript{3} and catalysts was found to be the key point in the process. Additionally, it was found that with the assistance of NTP, CeO\textsubscript{2} (at lower catalyst temperature) is only activated enough to selectively react with hazardous polychlorinated by-products (which need less energy to oxidise than TCE) to form the desired product (CO\textsubscript{2}). Furthermore, a successful long-term test (40 h) proved that the combination of plasma with a CeO\textsubscript{2} catalyst possesses excellent stability in terms of TCE abatement.

In the final part (Chapter 6) of this thesis, developed (manganese-based) catalysts were studied to promote the generation of even more efficient and environmentally sound catalysts for the plasma assisted TCE abatement. Cryptomelane type manganese oxide catalyst (K-OMS-2: the best one in MnO\textsubscript{2} polymorphs) has been chosen and the chemical/physical properties of this catalyst were modified by incorporation of Fe in the K-OMS-2 structure (co-precipitation) or Fe\textsubscript{2}O\textsubscript{3} particles at the surface of K-OMS-2 (impregnation). It was found that the co-precipitation method has significant impact on the properties of the catalyst: poor crystalline structure with many defects, particles of pseudo-spherical morphology, high specific surface area and better reducibility of Mn\textsuperscript{4+}. Based on the overall results of ICP and SEM, it was found that part of the incorporated Fe is adsorbed in the tunnel instead of K\textsuperscript{+} and part of it is in the substitution position in the Mn\textsuperscript{4+} framework. Furthermore, the impregnation of Fe on cryptomelane results into the dispersion of nano $\gamma$-Fe\textsubscript{2}O\textsubscript{3} particles which is confirmed by XRD. It was found that Fe-doped cryptomelanes prepared by co-precipitation used in a post plasma catalysis process improved the total oxidation of trichloroethylene in moist air and resulted in relevant CO\textsubscript{2} yields. A CO\textsubscript{2} yield of about 63\% can be achieved in PPC with Fe-K-OMS-2 at 150 °C and an energy density of 120 J/L, which is 75\% higher than with the undoped catalyst. The enhanced catalytic performances of the hybrid process were attributed to the improved properties given above. These characteristics allow facilitating the production of active species from plasma generated ozone and the surface oxygen.
mobility to promote the degradation of VOC or reaction intermediates into CO₂.

7.2 Future Work

This work regarding NTP and plasma–catalytic abatement of VOCs shows that there are still scientific challenges that have to be addressed in the future.

7.2.1 Catalytic Formulation

Expecting the abatement of toxic waste gases, plasma catalysis technology has the most potential, but the energy consumption is a great challenge. This thesis proved that the combination of low energetic plasma and moderate catalyst temperature is effective for the total oxidation of VOCs. Further improvement of the energy efficiency could be realized by operating catalysts at room temperature which would exclude catalyst heating. This means however that the catalytic formulations need to be further optimized in terms of activity and selectivity. The work presented in this study explored the use of cerium oxides and cryptomelane type manganese oxides catalysts for the plasma–catalytic removal of TCE. The good results obtained with the iron modified cryptomelane catalyst opened up some new frontiers for further research. Other metal ions like cerium, cobalt, copper and zirconium can also be incorporated into the tunnel/framework of cryptomelane in order to further improve its catalytic properties. Metal ion doped cryptomelane catalysts operating at room temperature have been recently reported to be used successfully in a PPC process for acetaldehyde degradation [251]. Furthermore, meso-macro porosity effect of cryptomelanes can be explored in order to facilitate the diffusion rate of reactants and provide accessibility to more catalytic sites.

7.2.2 Mixtures of Pollutants

In this work, we only studied the influence of one pollutant on the performance of the plasma catalytic system. In general, real industrial effluents are rarely composed of well-defined single compounds; therefore, an additional effort should be invested in the plasma catalytic oxidation of VOC mixtures. Binary and ternary mixtures with different compositions should be tested.

Concerning VOC mixtures remediation by plasma catalysis, despite having issues of complex interacting chemistry [252, 253], promotional reaction effects (enhanced removal efficiency, formation of reactive intermediates and
reduction of undesired by-products) have been reported [254, 255]. For instance, Liang et al. showed such a promotion effect on toluene in a ternary mixture with p-xylene and acetone [256]. This enhancement was interpreted in terms of possible cross reactions between by-products and enhanced reactivity. In opposition, negative interferences on the catalysts have also been reported which are attributed to the competitive adsorption of intermediates or blockage of active sites on the catalyst surface [257]. These interferences may vary depending on the number of co-existing VOC species, their properties and concentrations [253, 258]. Further research on these topics is thus highly recommended.

7.2.3 Multi Stage Plasma Catalysis

A multi stage system instead of a single stage system is an interesting option to investigate specially to treat complex gas mixtures. Since multiple VOCs degradations may lead to a wider diversity of side-products formation compared to single VOC treatment, the chaining of catalysts in IPC or PPC configuration can be key to minimize this and to achieve increased removal efficiency. The most interesting aspect is that each catalyst can have a different function in accordance with its position and the expected reactions. Several combination types may be possible in order to treat different components of the gas stream, for example: “initial breakdown of precursor ⟷ deep oxidation of intermediates ⟷ O₃ killer catalyst”. Additionally, different reactor configurations can be explored where IPC and PPC are combined to further enhance the performance for total VOC oxidation [259].

7.2.4 In-Situ Measurements

In this PhD thesis, in order to understand the mechanism of TCE oxidation on post plasma catalysis, the process of conversion in the gas phase and the surface reactions are observed separately through gas phase characterization and catalyst surface characterization. Based on these analysis, various hypothesis such as adsorption and desorption of organic reactants and intermediates, ozone decomposition on the catalyst surface and their interaction with adsorbed pollutants are pointed out to interpret plasma catalyst positive interactions. More researches and in-situ methods are needed to confirm the proposed oxidation pathways. Moreover, the formation of low concentrated by-products and unstable components are still unclear and undefined. The oxygen transfer in the oxidation process, the determination of active sites and which chemical species play a dominant role in the
decomposition of VOCs together with the catalysts as well as understanding the limiting steps are still of great interest. From this point of view, the development of well-designed instruments specialized in \textit{in-situ} measurements is crucial.

Furthermore, to understand the various underlying plasma catalytic effects, computational strategies could also be adopted to precise measurements and modelling of excited, ionized species and radicals in the plasma, reaction time scales and the nature of the species interaction with the surface of the catalyst (e.g. species pore penetration depth) and the electrode.

### 7.2.5 Regeneration Techniques

One possible way to exploit oxidative efficiency of NTP is to regenerate VOC saturated surfaces. This new approach consists of adsorbing the pollutant on a porous adsorbent/catalyst which is sequentially regenerated by plasma; the main advantage of the proposed technique is that the plasma is switched on for a limited time thus significantly reducing the power consumption in comparison to continuous plasma treatments and thermal regeneration of sorbents. Chapter 3 provided a detailed review of this new technique for the abatement of VOCs as well as for regeneration of adsorbents. Although the review of the experimental results of cyclic VOC adsorption and plasma assisted regeneration shows substantial progress, many questions still remain unanswered regarding the impact of process parameters and VOCs degradation mechanisms. Therefore, further progress on this subject is still necessary to evolve to a competitive air purification technology.
Figure 7.1: Summary of the optimal results obtained in this work

<table>
<thead>
<tr>
<th>Process</th>
<th>$[\text{TCE}]_0$ (ppm)</th>
<th>RH (%)</th>
<th>ED (J/L)</th>
<th>Temp. ($^\circ$C)</th>
<th>TCE abatement (%)</th>
<th>CO Yield (%)</th>
<th>CO$_2$ Yield (%)</th>
<th>CO$_x$ Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NTP</td>
<td>500</td>
<td>Dry air</td>
<td>80</td>
<td>T$_{room}$ 79.6</td>
<td>7.68</td>
<td>2.5</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>NTP + CeO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NTP + K-OMS-2</td>
<td>300-350</td>
<td>15</td>
<td>90</td>
<td>150</td>
<td>68.5</td>
<td>19.7</td>
<td>33.8</td>
<td>53.5</td>
</tr>
<tr>
<td>NTP + Fe/K-OMS-2</td>
<td></td>
<td></td>
<td></td>
<td>150</td>
<td>68.4</td>
<td>19.1</td>
<td>40.0</td>
<td>59.1</td>
</tr>
<tr>
<td>NTP + Fe-K-OMS-2</td>
<td></td>
<td></td>
<td></td>
<td>150</td>
<td>97.6</td>
<td>20.8</td>
<td>62.2</td>
<td>83.0</td>
</tr>
</tbody>
</table>
Philosophical Transactions of the Royal Society of London, 107 (1817) 77-85.


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