MnO$_2$-assisted dielectric barrier discharge-driven plasma oxidation for the abatement of n-butane

Dissertation

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“Do or do not. There is no try.”

(Yoda)
The following research was carried out in the period from September 2017 to February 2021 in the Laboratory of Industrial Chemistry, Ruhr University Bochum.

First supervisor: Prof. Dr. Martin Muhler
Second supervisor: Prof. Dr.-Ing. Peter Awakowicz
Third referee: Prof. Dr. Anjana Devi
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Kurzzusammenfassung


In dieser Arbeit wurde die Kombination einer dielektrisch behinderten Barriereentladungs-Elektrodenkonfiguration mit einem $\alpha$-MnO$_2$-Katalysator entwickelt und untersucht. Die Aufbringung des synthetisierten Katalysators auf die doppelflächige Elektrodenkonfiguration wurde hinsichtlich des Beschichtungsprozesses sowie der -geometrie optimiert. Hier erwies sich die Beschichtung mit einer Maske, welche die Aufbringung des Katalysators in der Plasmazone verhindert, als am effektivsten.

Die gebildeten Produkte wurden unter Verwendung eines Massenspektrometers untersucht. Es wurden H$_2$O, CO$_2$, NO$_x$ und O$_3$, jedoch keine organischen Nebenprodukte identifiziert. Die verschiedenen Beschichtungen wurden hinsichtlich ihres Umsatzgrades, ihrer Selektivität für CO$_2$ und CO und der Kohlenstoffbilanz verglichen und bewertet.

Der Umsatzgrad an n-Butan betrug bei Raumtemperatur ohne Katalysator bis zu 25%. Dies konnte bei erhöhten Temperaturen von 160 °C und gleichem Leistungseintrag des Plasmas auf 37% erhöht werden. Die Selektivitäten für CO$_2$ und CO verschoben sich bei 160 °C von 39% auf 44% bzw. von 30% auf 46%.


Das Aufbringen des Katalysators auf die Elektrodenkonfiguration führte zu einer Verschiebung der Selektivitäten in die bevorzugte Richtung. Außerdem kann die entwickelte Methode zur schnelleren Untersuchung anderer Katalysatorsysteme verwendet werden.
Abstract

Non-thermal plasmas provide unique properties for the conversion of volatile organic compounds. They are able to generate highly reactive species with a non-equilibrium of the electrons and atoms by which conversion at ambient temperatures is enabled. This provides potentially higher energy efficiency compared with common techniques such as thermal oxidation, thermocatalytic oxidation, or adsorption. In contrast to thermocatalytic processes, non-thermal plasmas are more robust against the presence of typical catalyst poisons such as CO or S containing compounds. Especially dielectric barrier discharges are a promising and frequently investigated reactor configurations, because they can be operated at atmospheric pressure, have a good scalability, require very short ramp-up times, and have a simple geometry.

In this thesis the combination of a twin-surface dielectric barrier discharge with a known α-MnO$_2$ catalyst was developed and investigated. The application of the synthesized catalyst on the electrode configuration was optimized in terms of coating procedure as well as coating geometry. Separating the plasma discharge zone from the catalyst coating by a mask yielded the best performance.

The formed products were investigated using mass spectrometry. Thereby, the formation of H$_2$O, CO$_2$, NO$_x$, and O$_3$ but no major organic by-products were identified. The performance of the different coating geometries was evaluated by their degree of conversion, selectivities to CO$_2$ and CO, and the achieved carbon balance.

Degrees of conversion at room temperature without catalyst of up to 25% were found. This was increased at elevated temperatures of 160 °C up to 37% for the same power input. The selectivities to CO$_2$ and CO were shifted from 39% to 44% and from 30% to 46% for 160 °C, respectively.

In thermocatalytic oxidation the α-MnO$_2$ catalyst achieved a degree of conversion of 50% at temperatures of 253 °C for the conversion of n-butane and 153 °C for the conversion of CO in simultaneous oxidation experiments. The higher activity for the conversion of CO was beneficial for the application in the plasma process to remove undesired CO. The application of the catalyst on the electrode configuration showed only a minor influence on n-butane conversion. Though, at 160 °C the selectivity to CO$_2$ increased to 89%, and that to CO decreased to 13%. Furthermore, no influence of the catalyst on the reactive oxygen species was found.

The application of the catalyst on the electrode configuration led to a shift of the selectivities in a favorable manner. The developed method can be used for faster screening of other catalyst systems.
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett, and Teller</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett, Joyner, and Halenda</td>
</tr>
<tr>
<td>CAD</td>
<td>Computer-aided design</td>
</tr>
<tr>
<td>CFD</td>
<td>Computational fluid dynamics</td>
</tr>
<tr>
<td>CP</td>
<td>Current probe</td>
</tr>
<tr>
<td>CRM</td>
<td>Collisional radiative model</td>
</tr>
<tr>
<td>CSD</td>
<td>Cycled storage-discharge</td>
</tr>
<tr>
<td>DBD</td>
<td>Dielectric barrier discharge</td>
</tr>
<tr>
<td>SDBD</td>
<td>Surface dielectric barrier discharge</td>
</tr>
<tr>
<td>VDBD</td>
<td>Volume dielectric barrier discharge</td>
</tr>
<tr>
<td>DDBD</td>
<td>Double dielectric barrier discharge</td>
</tr>
<tr>
<td>FKM</td>
<td>Fluorocarbon</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas chromatograph-mass spectrometer</td>
</tr>
<tr>
<td>hcp</td>
<td>Hexagonal close-packed</td>
</tr>
<tr>
<td>HVP</td>
<td>High-voltage probe</td>
</tr>
<tr>
<td>ICDD</td>
<td>International Centre for Diffraction Data</td>
</tr>
<tr>
<td>IPC</td>
<td>In-plasma catalysis</td>
</tr>
<tr>
<td>LED</td>
<td>Light-emitting diode</td>
</tr>
<tr>
<td>LSM</td>
<td>Laser scanning microscope</td>
</tr>
<tr>
<td>MCA</td>
<td>Multi-channel analyzer</td>
</tr>
<tr>
<td>MFC</td>
<td>Mass flow controller</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometer</td>
</tr>
<tr>
<td>NDIR</td>
<td>Non-dispersive infrared</td>
</tr>
<tr>
<td>NTP</td>
<td>Non-thermal plasma</td>
</tr>
<tr>
<td>OES</td>
<td>Optical emission spectroscopy</td>
</tr>
<tr>
<td>PEEK</td>
<td>Polyether ether ketone</td>
</tr>
<tr>
<td>PMT</td>
<td>Photomultiplier tube</td>
</tr>
<tr>
<td>PPC</td>
<td>Post-plasma catalysis</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>QMS</td>
<td>Quadrupole mass spectrometer</td>
</tr>
<tr>
<td>ROS</td>
<td>Reactive oxygen species</td>
</tr>
</tbody>
</table>
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>SCR</td>
<td>Selective catalytic reduction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TPO</td>
<td>Temperature-programmed oxidation</td>
</tr>
<tr>
<td>TPR</td>
<td>Temperature-programmed reduction</td>
</tr>
<tr>
<td>TWC</td>
<td>Three-way catalyst</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic compound</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
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</table>
## Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$, $B$, and $C$</td>
<td>Antoine equation parameters</td>
<td>[-]</td>
</tr>
<tr>
<td>atm</td>
<td>Atmospheric pressure (1.013 mbar)</td>
<td>[mbar]</td>
</tr>
<tr>
<td>$c$</td>
<td>BET constant</td>
<td>[-]</td>
</tr>
<tr>
<td>$d$</td>
<td>Gap distance</td>
<td>[m]</td>
</tr>
<tr>
<td>$E_0$</td>
<td>External electric field</td>
<td>[V m$^{-1}$]</td>
</tr>
<tr>
<td>$E_{\text{local}}$</td>
<td>Local electric field</td>
<td>[V m$^{-1}$]</td>
</tr>
<tr>
<td>$E_A$</td>
<td>Apparent activation energy</td>
<td>[kJ mol$^{-1}$]</td>
</tr>
<tr>
<td>EE</td>
<td>Energy efficiency</td>
<td>[mg$_n$-butane J$^{-1}$]</td>
</tr>
<tr>
<td>$f_{\text{pul}}$</td>
<td>Pulse repetition frequency</td>
<td>[Hz]</td>
</tr>
<tr>
<td>$I$</td>
<td>Current</td>
<td>[A]</td>
</tr>
<tr>
<td>$k$</td>
<td>Rate constant</td>
<td>[-]</td>
</tr>
<tr>
<td>$M$</td>
<td>Molar mass</td>
<td>[g mol$^{-1}$]</td>
</tr>
<tr>
<td>$m_S$</td>
<td>Sample mass</td>
<td>[g]</td>
</tr>
<tr>
<td>$N_a$</td>
<td>Avogadro constant ($6.022 14 \times 10^{23}$)</td>
<td>[mol$^{-1}$]</td>
</tr>
<tr>
<td>$n_e$</td>
<td>Electron density</td>
<td>[cm$^{-3}$]</td>
</tr>
<tr>
<td>$n$</td>
<td>Molar amount</td>
<td>[mol]</td>
</tr>
<tr>
<td>$n_{\text{Ref}}$</td>
<td>Refractive index</td>
<td>[-]</td>
</tr>
<tr>
<td>$p_0$</td>
<td>Saturation vapor pressure</td>
<td>[Pa]</td>
</tr>
<tr>
<td>$P$</td>
<td>Power</td>
<td>[W]</td>
</tr>
<tr>
<td>$p$</td>
<td>Pressure</td>
<td>[Pa or bar]</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant</td>
<td>[J mol$^{-1}$ K$^{-1}$]</td>
</tr>
<tr>
<td>$E/N$</td>
<td>Reduced electric field</td>
<td>[Td]</td>
</tr>
<tr>
<td>$S_{\text{BET}}$</td>
<td>Specific surface area</td>
<td>[m$^2$ g$^{-1}$]</td>
</tr>
<tr>
<td>SED</td>
<td>Specific energy density</td>
<td>[J L$^{-1}$]</td>
</tr>
<tr>
<td>$S$</td>
<td>Selectivity</td>
<td>[-]</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>[K or °C]</td>
</tr>
<tr>
<td>$T_e$</td>
<td>Electron temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Neutral gas temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>$T_i$</td>
<td>Ion temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>$U$</td>
<td>Voltage</td>
<td>[V]</td>
</tr>
<tr>
<td>$U_B$</td>
<td>Breakdown voltage</td>
<td>[V]</td>
</tr>
<tr>
<td>$\dot{V}$</td>
<td>Volume flow rate</td>
<td>[m$^3$ s$^{-1}$]</td>
</tr>
<tr>
<td><strong>Symbol</strong></td>
<td><strong>Description</strong></td>
<td><strong>Unit</strong></td>
</tr>
<tr>
<td>------------</td>
<td>----------------</td>
<td>-------------</td>
</tr>
<tr>
<td>V</td>
<td>Volume</td>
<td>[m$^3$]</td>
</tr>
<tr>
<td>$V_{ads}$</td>
<td>Volume of adsorbate</td>
<td>[m$^3$]</td>
</tr>
<tr>
<td>$V_m$</td>
<td>Molar volume (24.47 L mol$^{-1}$)</td>
<td>[L mol$^{-1}$]</td>
</tr>
<tr>
<td>$V_{mono}$</td>
<td>Volume of a monolayer of adsorbate</td>
<td>[m$^3$]</td>
</tr>
<tr>
<td>$n_{mono}$</td>
<td>Amount of particles forming a monolayer</td>
<td>[–]</td>
</tr>
<tr>
<td>X</td>
<td>Conversion</td>
<td>[–]</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>Relative permittivity</td>
<td>[–]</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
<td>[nm]</td>
</tr>
<tr>
<td>$\rho_{Gas}$</td>
<td>Gas density</td>
<td>[kg m$^{-3}$]</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Occupied area by probe molecule</td>
<td>[m$^2$]</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Residence time</td>
<td>[s]</td>
</tr>
<tr>
<td>$\gamma_{ppm}$</td>
<td>Mole fraction</td>
<td>[ppm]</td>
</tr>
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1 Introduction

One of the major challenges in environmental catalysis is the efficient abatement of volatile organic compounds (VOCs) in ambient air of large cities as well as in exhaust gases from industrial plants, car paint shops, or canteen kitchens etc.\cite{1–7} The purification of contaminated air is regulated and tightened by federal offices and the European Union.\cite{8,9} In 2007, the total emission of non-methane VOCs in the European Union amounted to 6.7 Mt.\cite{10} As shown in Figure 1.1 the main sources of these VOCs are industry, agriculture, road transportation, and energy production. The recent developments of renewable energies and electromobility are an attempt to reduce the VOC emissions. Nevertheless, end-of-pipe technologies are needed for emissions from industry and other non-avoidable exhaust gas sources. Conventional meth-

![Figure 1.1. Emission sources of non-methane VOCs. Adapted from the European Environment Agency\cite{10} under the terms of the Creative Commons Attribution 4.0 license.](image-url)

ods for the abatement of VOCs are thermal oxidation, thermocatalytic oxidation, and adsorption.\cite{7,11–14} These techniques have several disadvantages. Thermal oxidation has high energy requirements (900 °C to 1000 °C) and is only economically favorable for high VOC concentrations. Thermocatalytic oxidation requires a high amount of energy and is prone to catalyst poisoning by compounds such as $\text{SO}_x$, $\text{NO}_x$, or $\text{CO}$.\cite{7,11,12} Both thermal and thermocatalytic oxidation require a ramp-up time to reach operating temperatures. And last, for most of the adsorption techniques the disposal of the adsorbents is challenging and expensive.\cite{11}

Therefore, the removal of VOCs by non-thermal plasmas (NTP) has gained a considerable amount of interest over the last decades.\cite{6,12} NTPs offer the opportunity of higher energy efficiency, scalability, and flexibility for the abatement of VOCs and can be operated at atmospheric pressure and ambient temperature.\cite{7,15,16} Furthermore, plasma reactors can easily be mounted
in parallel and series for upscaling, and there is a ramp-up time of just a few seconds to achieve steady state. Among the different NTP concepts, dielectric barrier discharges (DBD) are frequently chosen for the removal of VOCs.\textsuperscript{[7,17–19]}

The combination of an NTP with heterogeneous catalysts may lead to synergistic effects for the abatement of VOCs at low temperatures.\textsuperscript{[20,21] A promising class of materials for this application are manganese oxides, as they are active in different redox reactions.\textsuperscript{[6,7,18,22–24] MnO\textsubscript{2} has already been applied for the oxidation of VOCs by plasma-assisted catalysis.\textsuperscript{[20] The catalytic activity combined with the potential conversion and production of reactive oxygen species (ROS) such as ozone (O\textsubscript{3}) render it a promising candidate for further studies.\textsuperscript{[7,20,21,25]}}

This work aims at determining the influence of $\alpha$-MnO\textsubscript{2} on VOC conversion, selectivity, and carbon balance using a twin-surface dielectric barrier discharge (SDBD). n-Butane was chosen as a model VOC, since alkanes are easy to handle and rather stable, rendering its full conversion to CO\textsubscript{2} and H\textsubscript{2}O difficult.\textsuperscript{[7,21,26–28]}}
2 State of the Art

2.1 Plasma

Plasma is commonly known as the fourth state of matter.[29] Plasma is a (partially) ionized gas, which means that one or more electrons are not bound to an atom or molecule generating a positively charged ion. The free electrical charge leads to increased electrical conductivity. In spite of the charge separation in a plasma, it is quasi-neutral, because the electron density is balanced by the positive ions.[29] The generated species such as electrons, ions, atoms, radicals, and metastable species can be highly reactive, and all these species can interact with surfaces exposed by catalysts. Generation of these desirable species in conventional chemical technologies in such high concentrations would be challenging.[29]

2.1.1 Non-thermal Atmospheric Pressure Plasma

Plasmas can be categorized into two groups: thermal and non-thermal.[29,30] Thermal plasmas, like arc discharges, are in or close to thermodynamic equilibrium, which means all species within the plasma have the same temperature.[29] In contrast, NTPs like DBDs or corona discharges are transient plasmas, which are not in thermodynamic equilibrium.[31,32] In NTPs the electron temperature ($T_e$) is several orders of magnitude higher than the temperatures of the heavy particles (ions ($T_i$) and neutral gas ($T_g$)). Typical electron temperatures can be in the range of $1 \text{ eV}$ to $10 \text{ eV}$ ($1 \text{ eV} \approx 11600 \text{ K}$).[29] These electrons can induce vibrational or rotational excitation and chemical reactions like bond dissociation, radical formation, ionization and many others.

Paschen Curves

The ignition behavior of plasmas is influenced by the mean free path of the gas and its ionization potential. The mean free path of particles is highly influenced by the pressure ranging from tens of nanometers at $1000 \text{ mbar}$ to kilometers at $1 \times 10^{-6} \text{ mbar}$.[33,34] As a consequence, the plasma ignition behavior depends strongly on pressure. Paschen[35] investigated the breakdown voltage ($U_B$) to ignite and sustain a plasma for different conditions. A simple geometry was used by Paschen consisting of two planar metal electrodes separated by the tested gas. The resulting empirical equation (Equation 2.1) describes the breakdown voltage in a constant electric field depending on pressure, gap distance, and gas composition with the breakdown voltage $U_B$, the
pressure $p$, the gap distance $d$, and the ion-induced secondary electron emission coefficient of the electrode material $\gamma$.\textsuperscript{36,37}

$$U_B = \frac{B \cdot p \cdot d}{\ln(A \cdot p \cdot d) - \ln\left(\ln\left(1 + \frac{1}{\gamma}\right)\right)}$$  \hspace{1cm} (2.1)

The factors $A$ and $B$ are gas-specific empirical factors. The resulting Paschen curves for N$_2$, Ar, CO$_2$, and Air are shown in Figure 2.1.\textsuperscript{36,38} The curves show a minimum for the breakdown voltage for all gases at different pressure · distance ($p \cdot d$). With a fixed $p$ (atm) just the gap distance influences the breakdown voltage of one particular gas. In fact, the shown curves are only valid for the set-up used by Paschen, but they provide an adequate insight in the discharge behavior of different gases.

Figure 2.1. Breakdown Paschen curves for N$_2$, Ar, CO$_2$, and Air. The curves are plotted with Paschen coefficients $A$ and $B$ from ref.\textsuperscript{36,38} The used values of the coefficients are summarized in Table B.2.

**Townsend Mechanism**

In 1900, Townsend described the prevailing breakdown mechanism named after him.\textsuperscript{39} A primary electron (spawned by e.g. cosmic radiation) is accelerated in an electric field ($E_0$) generated by an applied voltage. The accelerated electron collides with gas particles. If the energy of the incident electron is sufficient bound electrons are removed from the gas particles by impact ionization resulting in positively charged ions. The ejected electrons are once again acceler-
ated and then collide with further particles. This leads to an electron avalanche and ionized gas particles. The exponential increase in accelerated electrons is illustrated in Figure 2.2. The electrons are accelerated towards the anode and the ionized particles towards the cathode, which then leads to emission of secondary electrons.

Figure 2.2. Townsend breakdown with electron avalanche formation between two electrodes with electric field \( E_0 \). Adapted from ref.\cite{29} with permission of The Licensor through PLSclear.

**Streamer Mechanism**

The quasi-homogeneous Townsend mechanism is limited to relative low pressures and small gaps.\cite{29} The streamer or spark breakdown mechanism can take place at higher pressures and larger gaps. A spark forms a local narrow breakdown channel. The spark formation cannot be explained by just a single electron avalanche, but by interaction of several avalanches. The interaction of spark breakdowns is based on the streamer concept.\cite{29} It describes the formation of thin ionized channels which propagate rapidly between the electrodes. The propagation path is influenced by the positive charge left by primary avalanches.

The charge separation in an avalanche with electrons in the head and positive ions in the tail leads to a local electric field \( E_{\text{local}} \) superimposing the external field. The superimposition leads to an enhanced primary avalanche and secondary avalanches are formed preferentially in this region. Furthermore, ionization is enhanced because of the enhanced electric field in front of the primary avalanche.\cite{40} The avalanche-to-streamer transition takes place when \( E_0 \approx E_{\text{local}} \). If the gap is short, the avalanche has to reach the anode for this transition. Then, a positive streamer is formed. If the gap and the overvoltage are large, the transition can occur far away from the anode forming a negative streamer which grows towards both the anode and the cathode.\cite{29}

A scheme of the formation of positive and negative streamers is shown in Figure 2.3. The emitted photons at the head of a streamer initiate secondary avalanches by photoionization. The electrons of the secondary avalanches are pulled in the trail of the primary streamer forming a
quasi-neutral plasma channel. The very high electric field on the tip of the positive streamer providing high electron drifts results in streamer growth velocities of about $1 \times 10^6$ m s$^{-1}$.[40]

![Figure 2.3](image)

Figure 2.3. Scheme of the propagation of a positive streamer (a) and a negative streamer (b). Adapted from ref.[29] with permission of The Licensor through PLSclear.

2.1.2 Dielectric Barrier Discharge

The DBD also known as silent discharge was first utilized by Werner von Siemens in 1857.[41–44] The first DBDs were made of two thin coaxial glass tubes and used for the production of ozone (O$_3$). DBDs are self-sustained discharges consisting of two electrodes and at least one name-giving dielectric.[29] This dielectric can be made of glass, ceramics, or other dielectric materials. Generally, for DBDs the discharge takes place between electrodes and the dielectric in gaps of 0.1 mm to several centimeters. The dielectric prevents the formation of arcs and the accompanying local overheating. One electrode is driven by alternating current (AC) voltages of several kV and frequencies of 0.25 kHz to 500 kHz, and the second electrode is usually grounded.[29]

A dielectric is an electrically weakly or non-conductive substance, in which the existing charge carriers cannot move freely.[45] A measure for the dielectric properties is the relative permittivity ($\varepsilon_r$). When the generated electric field is high enough, the occurring discharges follow the streamer mechanism at atmospheric pressure (Section 2.1.1). The formation of new streamers at the same spots is prevented by the build-up of charge at the dielectric during the same half period of the (sinusoidal shaped) AC voltage. This leads to a stochastic distribution over the complete discharge space of short-living (ns range) streamers for each half period.

Owing to the non-equilibrium nature of DBDs, the gas temperature stays near ambient. Therefore, the reactions are induced by the electrons, which contain a major part of the input power,
Figure 2.4. Different DBD geometries. (a) Symmetric volume dielectric barrier discharges (VDBD) with two dielectrics. (b) VDBD with floating dielectric. (c) Asymmetric VDBD. (d) Single-sided SDBD. (e) Twin-SDBD. (f) Coplanar SDBD. (g) Packed-bed or ferroelectric VDBD.[29] (h) Several VDBD with floating dielectric placed in parallel with alternating driven and grounded electrodes. (i) Coaxial cylindrical VDBDs. Adapted from Brandenburg et al.[42] under the terms of the Creative Commons Attribution 3.0 license.

Through ionization, dissociation, and excitation processes,[29] the ionized species have lifetimes of microseconds instead of nanoseconds for the electrons.[29]

The versatility of DBD geometries is beneficial for industrial applications.[42,44,46] DBDs can be put in parallel and series for up-scaling. There are several different geometries described in literature, of which some are shown in Figure 2.4. In the following sections VDBD and SDBD are described as the two main groups.

**Volume Dielectric Barrier Discharge**

VDBDs have at least one gap between the electrodes and the dielectric or in case of two dielectrics a gap between these. The discharge takes place in these gaps. VDBDs are often used in biomedical applications with the human body as counter electrode using short discharge pulses. The plasma can promote wound healing by utilizing the generated NO.[47,48] VDBDs made of an outer glass tube wrapped in a grounded electrode with a driven electrode in the center also surrounded by glass are the traditional geometries of O$_3$ generators introduced by Werner von Siemens.[41]
Special configurations of the VDBD are packed-bed and ferroelectric discharges.\textsuperscript{[11,29]} The gap of VDBDs is filled with dielectric or catalyst pellets in case of a packed bed. Depending on shape, porosity, and dielectric permittivity of the pellets, the electric field is refracted and therefore becoming stronger by a factor of 10 to 250.\textsuperscript{[29]} In case of a very high dielectric permittivity ($\varepsilon_r > 1000$) of the pellets, the discharge is called ferroelectric discharge. There, the discharge takes place in the gaps of the pellets leading to very strong local electric fields. Due to the undefined ignition spaces for catalyst applications of packed-bed VDBDs, the characterization of the plasma is challenging. An additional negative aspect for application is that the packed bed increases the flow resistance.

**Surface Dielectric Barrier Discharge**

When the gap is closed and the electrodes are separated only by the dielectric, an SDBD occurs.\textsuperscript{[29]} The dielectric modifies the shape of the electric field locally enhancing it, which decreases the breakdown voltage, in this way promoting the ignition on the surface of the dielectric.\textsuperscript{[29]}

SDBDs can be used for more complex and defined ignition geometries by building different electrode configurations. The configurations are optimized in order to enhance flow resistance, ignition space, reproducibility, and catalyst applications. A twin-SDBD electrode configuration introduced by Offerhaus et al.\textsuperscript{[49]} (Figure 2.5) shows homogeneous ignition behavior and sufficient space for catalyst application. Furthermore, the electrode configuration has a low flow resistance and can easily be rebuilt.

![Figure 2.5. Twin-SDBD electrode configuration introduced by Offerhaus et al.\textsuperscript{[49]}](image)

### 2.1.3 Reactive Oxygen Species

The formation of ROS is the main driving force for the plasma-assisted catalytic conversion of VOCs.\textsuperscript{[50–52]} DBDs were first used and optimized for the production of O$_3$. Calculations of the processes and reactions in O$_2$ and air were performed showing electrons to be the most important species for the O$_3$ production.\textsuperscript{[51,53]} The electrons trigger the dissociation and excitation
of O₂ and N₂ molecules. In a three-body reaction with O, O₂, and any available neutral gas particle (M) O₃ is formed (Equation 2.2).

\[ O + O₂ + M \rightarrow O₃ + M \]  

(2.2)

The present N₂ also leads to several reactions of the dissociated species leading to the formation of NO. Although the formation of NO is undesired, it also leads to the formation of O as by-product as shown in Equations 2.3 – 2.10.

\[ e^- + N₂ \rightarrow e^- + N₂(A^3Σ^+_u) \]  

(2.3)

\[ e^- + N₂ \rightarrow e^- + N₂(B^3Π^+_u) \]  

(2.4)

\[ N₂^*(A,B) + O₂ \rightarrow N₂ + 2O \]  

(2.5)

\[ N₂^*(A,B) + O₂ \rightarrow N₂O + O \]  

(2.6)

\[ e^- + N₂ \rightarrow e^- + 2N \]  

(2.7)

\[ N + O₂ \rightarrow NO + O \]  

(2.8)

\[ N + NO \rightarrow N₂ + O \]  

(2.9)

\[ O₃ + NO \rightarrow NO₂ + O₂ \]  

(2.10)

In addition to the long-living species O₃ and NO, also the short-living species like OH or O are produced in the plasma as shown exemplary in Equations 2.11 – 2.13.

\[ OH + OH \rightarrow H₂O + O \]  

(2.11)

\[ O + H₂O \rightarrow OH + OH \]  

(2.12)

\[ OH + N \rightarrow NO + H \]  

(2.13)

For a high ROS density the optimal parameters have to be found. Too strong discharges could limit the production (e.g. due to increased recombination), but also the gas temperature and the metal wall surface interactions could affect the ROS densities. 

### 2.2 Conversion of Volatile Organic Compounds

#### 2.2.1 Plasma-alone Conversion of Volatile Organic Compounds

The high electron temperature along with ambient-temperature heavy particles produced by non-thermal plasmas provide conditions for reactions to take place, which are thermodynamically limited at low temperature. One of the most prominent applications is the purification
of exhaust gases containing VOCs.\textsuperscript{[15,19]} VDBDs, SDBDs, packed-bed, and ferroelectric discharge reactors have been used for the abatement of VOCs without catalyst.\textsuperscript{[15,21,59–61]} Different correlations were found according to the ionization energies and the degree of conversion for different reactor geometries, which indicates different decomposition mechanisms.\textsuperscript{[62,63]} Various different VOCs have been chosen as test molecules from different classes such as aromatics, ketones, aldehydes, alcohols, esters, and alkanes.\textsuperscript{[15,19]} Comprehensive studies of the conversion behavior of several different VOCs in the same DBD reactor can deliver insights in the optimal treatment for the different impurities. Zhao et al.\textsuperscript{[62]} found a more difficult decomposition of organic molecules with higher ionization potential. Furthermore, they showed that with higher hydrogen weight fraction the removal efficiency was higher except for alkanes. Moreover, double and triple bonds are beneficial for high degrees of conversion.\textsuperscript{[64]} The conversion of VOCs in plasma can lead to a wide range of organic by-products, which were also analyzed by Zhao et al.\textsuperscript{[62]} as a function of the original VOC.

Hill et al.\textsuperscript{[64]} investigated the conversion of propane and propene using a packed-bed reactor. Propene was found to be oxidized with an energy input an order of magnitude below that needed for the conversion of propane, which can be ascribed to the double bond of propene. It was found that the degree of conversion is independent of the VOC mole fraction. The degree of conversion reached steady state at a specific energy density (SED) of 625 \( \text{JL}^{-1} \), and further increasing the SED to 950 \( \text{JL}^{-1} \) did not lead to an increase in conversion.

Plasma-driven VOC removal is mainly used for low mole fractions (<1000 ppm). For higher amounts of organic molecules more reactive species are consumed, which leads to lower degrees of conversion.\textsuperscript{[65]} However, the total amount of converted molecules and the energy efficiency increases with higher contents.\textsuperscript{[66,67]}

For the electrodes different materials were used such as steel, tungsten, nickel, or iron in order to optimize the input power and temperature due to ohmic heating.\textsuperscript{[15,19]} In addition, different electrode geometries for VDBDs as well as SDBDs were investigated. The most common dielectric material is quartz, but it is mostly used because of the low price, the availability, and the good shaping ability.\textsuperscript{[15,19]} Nevertheless, alumina and ceramics are frequently chosen as dielectric for VDBDs and SDBDs. For packed-bed and ferroelectric discharges the same materials are used, but in addition beads with higher dielectric permittivity as packing material are used.\textsuperscript{[20,21]} Kundu et al.\textsuperscript{[68]} compared quartz and alumina with the same geometry for the conversion of CH\(_4\). The alumina electrode configuration showed higher input power in the reactor, lower temperature of the electrode, and higher conversion of CH\(_4\) measured at the same applied voltage.

In terms of energy input the applied voltage and the frequency of the AC voltage have to be optimized for best efficiency. Higher voltages and frequencies increase conversion, but the energy
efficiency decreases. Pulsing of the voltage in damped sine waves can increase energy efficiency and homogeneity of the discharge.

2.2.2 Plasma-Catalyst Interactions

Low energy efficiency, undesired by-products, and low selectivity to CO and CO$_2$ (in plasma-related literature referred to as mineralization) are the largest drawbacks of plasma-alone application in the conversion of VOCs. To overcome these drawbacks, a combination of plasma-alone VOC conversion with heterogeneous catalysts, called plasma-catalysis, plasma-assisted catalysis, or plasma-enhanced catalysis is a promising approach. The combination of non-thermal plasma and catalysts can lead to synergistic effects, which can not be achieved based on a single approach. There are three different reactor concepts for the combination of plasma and catalyst: in-plasma catalysis (IPC), post-plasma catalysis (PPC), and cycled storage-discharge (CSD) (Figure 2.6). The straightforward way of combination is IPC. The catalyst is placed right into the discharge zone, where it can interact with long-lived species as well as short-lived species. In contrast, PPC separates plasma discharge zone and catalyst. There, only the long-lived species interact with the catalyst, but e.g. replacement of the catalyst is easier. The plasma is ignited continuously for IPC and PPC, whereas for CSD the VOCs are adsorbed on the catalyst/sorbent, which is then regenerated by plasma processes. All three reactor concepts enable many different physical and chemical interactions. The general principles of catalyst-reactant interaction are the same for plasma catalysis as for heterogeneous catalysis comprising adsorption, surface reaction, desorption, and diffusion. Depending on the occurring mechanism different surface reactions are taking place (Figure 2.7). When both reactants are chemisorbed and reacting, it is the Langmuir-Hinshelwood mechanism, whereas with one chemisorbed reactant and one reactant from the gas phase the Eley-Rideal mechanism takes place. The third possibility is the Mars-van Krevelen mechanism with one adsorbed reactant and lattice oxygen from the catalyst requiring subsequent reoxidation by gas-phase O$_2$.

The largest difference between thermocatalytic processes and plasma-assisted processes are the reactive species occurring in the plasma process. In PPC long-living species reach the catalyst, whereas in IPC also short-living species can reach the catalyst which typical do not occur in thermocatalytic applications. Kim et al. calculated that for instance ground-state oxygen and OH can reach the catalyst in distances of 50 µm, which can enable different reaction pathways in IPC than in thermocatalytic applications. The lifetime of reactants on the surface can be increased by the adsorption of these species.

There are different effects of the catalyst on the plasma and vice versa. Influences of the catalyst
on the plasma behavior are primarily observed for IPC due to the application of solid material in the discharge zone.\cite{83,84} Tu et al.\cite{83} and Gallon et al.\cite{84} placed TiO$_2$ pellets, porous quartz wool, Al$_2$O$_3$, and zeolite 3A in the discharge zone. These materials allow discharge formation only in the voids between the pellets. Furthermore, the packed bed changes the discharge from filamentary to a combination of a discharge on the catalyst surface and spatially limited microdischarges in the voids. Increasing vibrational temperatures of N$_2$ suggest a shift of the electron energy distribution function to higher energies due to the packed bed.\cite{83} The morphology of the packing material such as particle size, particle shape, packing structure, but also the relative permittivity have an impact on the discharge.\cite{40,83,84,86} The energy input in the reactor can be increased by a factor of 6 to 10 by using ferroelectric materials such as BaTiO$_3$ with a very high relative permittivity ($\varepsilon \approx 10000$).\cite{86} Furthermore, it was shown by Hensel et al.\cite{87} experimentally and by Zhang et al.\cite{88} by modeling that porous materials can facilitate the formation of microdischarges in the pores.\cite{40} In addition to the support also metal nanoparticles can increase the surface area of plasma propagation.\cite{89} Without nanoparticles the plasma expansion is limited to the edges of the support.

Influences of the plasma on the catalysts are changes of the surface morphology or electronic properties, adsorption of species blocking sites, or etching.\cite{40,90–92} Gao et al.\cite{90} showed an increase of the catalytic activity of Cu nanotubes after pretreatment with O$_2$ plasma. It was proposed that defects and stabilized surface oxygen species were created which modify the
Figure 2.7. The three proposed mechanisms exemplary shown for MnO$_2$.[85] (a) Langmuir-Hinshelwood mechanism with reactants A and B in the gas phase ①, adsorbing on the surface ②, reacting on the surface ③, and desorbing as product A−B ④. (b) Eley-Rideal mechanism with reactants A and B in the gas phase ①, adsorbing of reactant A on the surface ②, direct reaction of gas phase reactant B with the adsorbed reactant A ③, and desorbing as product A−B ④. (c) Mars-van Krevelen mechanism with CO in the gas phase ①, adsorbing and reacting with lattice oxygen ②, desorbing as CO$_2$ ③, and reoxidation of the lattice oxygen with gas phase oxygen ④.

adsorption of molecules on the surface.[90] Bal et al.[91] show improved relative activity and Guaitella et al.[93] an enhanced filament propagation due to trapped surface charges. Catalyst modification not taken into account by conventional thermocatalytic application may be lead to new catalytic properties.[40]  

2.2.3 Plasma-Assisted Catalytic Conversion of Volatile Organic Compounds

For the plasma-assisted catalytic conversion of VOCs several different catalysts are used such as Ag, Pd, Fe, Ni, Au, but also TiO$_2$, FeO$_x$, and MnO$_x$.[12,19,80,94,95] Among these catalysts MnO$_2$ has distinct advantages.[96] As an abundant transition metal oxide it is relatively inexpensive and easily accessible, and the low toxicity is beneficial. In literature, plasma was combined several times with MnO$_x$ for the conversion of VOCs. Chen et al.[97] impregnated MnO$_x$ (7.5 wt%) and Pt (1 wt%) on γ-Al$_2$O$_3$ for the conversion of hexanal in 79% N$_2$ and 21% O$_2$. A VDBD was heated to 80 °C and the catalyst was placed as packed bed in the discharge zone. Without packed bed there was no conversion, but by placing pure γ-Al$_2$O$_3$ in the discharge zone the degree of conversion increased up to 80%. The degree of conversion increased further by about 10% when using MnO$_x$ and Pt. The high degree of
conversion by using pure $\gamma$-Al$_2$O$_3$ was explained by the high specific surface area. Einaga et al.\[98\] converted benzene in a PPC application comparing MnO, MnO$_2$, Mn$_2$O$_3$, and Mn$_3$O$_4$. The highest degree of conversion was achieved using MnO$_2$ and Mn$_3$O$_4$ followed by Mn$_2$O$_3$ and MnO. The different oxidation states show no influence on the selectivities for CO and CO$_2$. Without catalyst conversion was about 20%, but with MnO$_2$ about 95% was reached. When investigating the degree of conversion and the O$_3$ mole fraction as function of the catalyst loading, it was shown that the degree of conversion does not increase when the O$_3$ mole fraction is at 0. This observation shows that the decomposition of O$_3$ by the catalyst is necessary for conversion. Additionally, the influence of humidity was investigated. The degree of conversion was halved with rel. humidity of 50%, but the selectivity for CO$_2$ increased by about 90%.\[98\] Futamura et al.\[20\] used an IPC reactor concept with commercially available MnO$_2$ pellets as packed bed for the conversion of benzene. For smaller energy inputs there was no effect observed for MnO$_2$, but with higher energies there was an increase in conversion from 35% to 42%. The investigation of the long-term behavior revealed an increase in conversion for the highest energy input with MnO$_2$ from 42% to 54%, while the degree of conversion without catalyst stayed at the same level. Furthermore, MnO$_2$ was shown to be degrading O$_3$. Combining the results Futamura et al.\[20\] proposed a mechanism for the conversion of benzene (Figure 2.8). Atomic oxygen is formed on the MnO$_2$ surface which may desorb as very reactive O($^3$P). Additionally, O$_2$\(^*\) is formed in an Eley-Rideal-type reaction further forming O$_2$\(^*\)MnO$_2$(OH)$_4$ with the catalyst, which is another possible candidate for VOC oxidation.

Guo et al.\[99–101\] used a wire-plate reactor (VDBD, IPC) for the decomposition of toluene. In a first study a MnO$_x$/Al$_2$O$_3$/Ni foam was used as catalyst. Measurements with catalyst were performed with an O$_2$ content between 0% to 20% for different energy inputs. For all energies there was a maximum of the degree of conversion at 5% O$_2$. Further measurements with and without catalyst were performed with 5% O$_2$. The degree of conversion with catalyst was 10% smaller with small SED, but with high SED the degree of conversion was 40% higher. The O$_3$ mole fraction at high SED was double the amount with catalyst compared with the one without.

![Figure 2.8. Proposed mechanism for the conversion of VOCs in plasma-assisted catalysis using MnO$_2$. Reprinted from\[20\] with permission from Elsevier.](image-url)
Furthermore, the CO\textsubscript{2} selectivity with catalyst was 10% to 15% higher in the presence of the catalyst. The second study showed the removal of OH in presence of MnO\textsubscript{x} and a significant increase of the energy efficiency especially at lower SED. In a third study Guo et al.\cite{101} compared the performance of CuO, CoO\textsubscript{x}, FeO\textsubscript{x}, and MnO\textsubscript{x} and additionally the NO\textsubscript{x} by-product formation. The degree of conversion at different SED for CoO\textsubscript{x} (18% to 95%) was always the smallest followed by CuO and MnO\textsubscript{x} (38% to 95%), and the highest degree of conversion was achieved by FeO\textsubscript{x} (44% to 95%). Among these four catalysts MnO\textsubscript{2} showed the highest activity for the decomposition of O\textsubscript{3}. This shows together with the previously mentioned degrees of conversion that a wider variety of reaction mechanisms is possible than the decomposition of O\textsubscript{3} and subsequent utilization of atomic oxygen. MnO\textsubscript{2} also has the highest selectivity to CO\textsubscript{2} (75% to 93%). All catalyst were suppressing the NO and NO\textsubscript{2} formation, but CuO showed the best and MnO\textsubscript{2} the worst performance.

Jarrige et al.\cite{25} investigated the conversion of propane and isopropanol in a corona discharge reactor (VDBD, PPC). The geometry of a corona discharge reactor is similar to a VDBD reactor but using a wider gap and higher voltages (50 kV). Without catalyst a degree of conversion of 70% for propane and of 90% for isopropanol was reached, but the selectivity to CO was always higher than that to CO\textsubscript{2}, and in case of isopropanol the selectivity to acetone was even higher. Also formaldehyde was formed in both reactions. The O\textsubscript{3} content as a function of the SED showed a local maximum between 250 JL\textsuperscript{−1} and 350 JL\textsuperscript{−1}. The degree of conversion increased by applying the catalyst at 100 JL\textsuperscript{−1} from 18% to 62% and at 300 JL\textsuperscript{−1} from 60% to 90%. The formation of formaldehyde was suppressed, but the formation of acetone increased further by introducing the catalyst.

Lu et al.\cite{102} converted benzene using a VDBD and a PPC reactor concept with commercially available MnO\textsubscript{2}. The AC voltage had a continued sinusoidal shape form and average output voltage of 7.8 kV (144 JL\textsuperscript{−1}). There was a degree of conversion without catalyst between 0.5% and 11%. MnO\textsubscript{2} increased conversion by about 5% at the same SED. The CO\textsubscript{2} selectivity increased by about 10% to 20% by using MnO\textsubscript{2}. Additionally, a summary of the energy efficiencies as function of the initial concentration was provided comparing several references converting VOCs.\cite{102}

Lu et al.\cite{103} converted toluene with and without Mn\textsubscript{x}O\textsubscript{y} supported on mesoporous silica (SBA-15) with specific surface areas between 440 m\textsuperscript{2} g\textsuperscript{−1} and 510 m\textsuperscript{2} g\textsuperscript{−1} (VDBD, IPC). By applying pure SBA-15 the degree of conversion increased from 23% to 95%, but with a loading of 1% to 10% Mn the degree of conversion decreased by 1% to 15%. Among the Mn-loaded catalysts the 5% Mn sample showed the highest degree of conversion. For this loading the highest CO\textsubscript{2} selectivity and carbon balance of all measurements with 68% and 82%, respectively were observed. Gas chromatograph-mass spectrometer (GC-MS) analysis found a wider range
of organic by-products for 5% Mn/SBA-15 than for only SBA-15, namely formaldehyde for both, but formic acid, phenylmethyl ester, and benzoic acid only for Mn. Zhu et al.\textsuperscript{[104]} performed a catalyst screening of MO\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} (M = Ce, Co, Cu, Mn, and Ni) for the removal of acetone (VDBD, IPC). The SED range for all measurements was between 650 JL\textsuperscript{−1} and 1050 JL\textsuperscript{−1}. Cu showed the highest increase in conversion (45%) followed by Co and Mn (32% each) and Ni and Ce (20% each) compared with pure γ-Al\textsubscript{2}O\textsubscript{3}. For the CO\textsubscript{2} selectivity the same order was found even though the difference was very small with highest selectivity of 79% (Cu) and the lowest of 72% (γ-Al\textsubscript{2}O\textsubscript{3}). Furthermore, the same trend was seen for the formation of organic by-products.

Subrahmanyam et al.\textsuperscript{[105]} and Karuppiah et al.\textsuperscript{[106–108]} used a special cylindrical VDBD geometry in which the catalyst served as one electrode. The inner electrode was a sintered metal fiber filter in the shape of a cylinder. The discharge took place outside of the cylinder. The gas was passed through the discharge and then left the reactor through the sintered metal fiber filter, which was impregnated with catalyst. The discharge was generated with voltages between 14 kV and 22 kV resulting in SEDs of 60 JL\textsuperscript{−1} to 650 JL\textsuperscript{−1}. The conversion of toluene, isopropanol, benzene, nitrobenzene, and chlorobenzene was investigated. The first study with toluene shows a decrease in conversion with higher mole fraction of toluene at the same energy input with and without catalyst. The CO\textsubscript{x} selectivity also decreased, indicating production of more organic by-products. The sintered metal fiber filter with Mn impregnation reached 10% higher conversion than without Mn reaching full conversion at 235 JL\textsuperscript{−1} and 265 JL\textsuperscript{−1}, respectively. The treatment of isopropanol showed no difference in conversion with and without catalyst at higher mole fractions (1000 ppm).\textsuperscript{[106]} For smaller mole fractions the degree of conversion was increasing with the catalyst amount (Δ: 20% with 250 ppm and 30% with 100 ppm). The CO\textsubscript{2} selectivity increased with smaller mole fractions of isopropanol. Karuppiah et al.\textsuperscript{[106]} proposed an in situ decomposition of produced O\textsubscript{3} forming reactive oxygen species. The same trend was found for the treatment of nitrobenzene.\textsuperscript{[107]} The Mn-impregnated sintered metal fiber filter showed the lowest mole fraction of O\textsubscript{3} supporting the previous hypothesis. The fourth study with this reactor design investigated the influence of a AgO\textsubscript{x}/MnO\textsubscript{x} mixed metal oxide catalyst and of humidity in the gas stream.\textsuperscript{[108]} The degree of conversion increased by about 10% to 20% when using AgO\textsubscript{x}/MnO\textsubscript{x} to convert toluene, benzene, and chlorobenzene. By adding water vapor (20000 ppm) the degree of conversion increased further reaching full conversion at 260 JL\textsuperscript{−1}. Also the O\textsubscript{3} mole fraction was further decreased in the presence of water vapor. The CO\textsubscript{2} selectivity was increased by AgO\textsubscript{x}/MnO\textsubscript{x} as well as by water vapor.

Liu et al.\textsuperscript{[109]} investigated AgMn/HZSM-5 in a CSD for the oxidation of benzene. For all measurements HZSM-5, Mn/HZSM-5, Ag/HZSM-5, and AgMn/HZSM-5 were compared. AgMn/HZSM-5 showed a storage capacity three times of that of HZSM-5 even though the
specific surface areas were similar. The mole fraction of CO\textsubscript{2} for the conversion of stored benzene was for HZSM-5 and MnHZSM-5 the highest, but the Ag-containing catalyst showed no CO as by-product. Due to the high storage capacity AgMn/HZSM-5 was chosen for further investigation. For the input power and for the humidity the best performing parameters were found at 6 W and 0.4 vol\%, respectively. The temperature-programmed oxidation (TPO) profiles of the catalysts, which were cycled several times, showed an increasing CO\textsubscript{x} production, indicating incomplete regeneration during the plasma discharge time.

Trinh et al.\cite{110} used a VDBD comparing PPC, IPC, and a combination of both for the conversion of diethyl ether over MnFe/cordierite (Mg\textsubscript{2}Al\textsubscript{3}[AlSi\textsubscript{5}O\textsubscript{18}]). For IPC bare cordierite, Fe/cordierite, and Mn/cordierite showed a higher degree of conversion than the blank VDBD and MnFe/cordierite, which had the smallest O\textsubscript{3} output. The reactor temperature of Fe/cordierite and Mn/cordierite was between 28 °C and 63 °C for the SED range (50 JL\textsuperscript{−1} to 600 JL\textsuperscript{−1}). MnFe/cordierite as PPC catalyst showed no benefit, but a combination of Mn/cordierite (IPC) and MnFe/cordierite (PPC) led nearly immediately to full conversion utilizing the produced O\textsubscript{3} and the most active catalyst for O\textsubscript{3} decomposition. It has to be mentioned that the amount of catalyst was doubled for the last measurement due to the combination.

Liang et al.\cite{111} compared five different geometries with Mn/cordierite as catalyst and VDBDs: DBD with catalyst, without catalyst, and reverse-flow geometry with catalyst which can switch the flow direction during the measurement. Additionally, a DBD with a supplementary dielectric (double dielectric barrier discharge (DDBD)) with and without catalyst was tested. The reverse-flow geometry was designed to utilize the waste heat produced by the plasma discharge as efficiently as possible, which was demonstrated by the measured temperature profiles. Comparing the degree of conversion for the DBD and DDBD, there were different trends. The DBD showed an increase in conversion with catalyst (12%), whereas the DDBD showed a decrease with catalyst (5%). Nevertheless, the reverse flow showed the highest degree of conversion of 69%. The highest energy efficiency was achieved by the DDBD without catalyst (5.9 gkW\textsuperscript{−1}h\textsuperscript{−1}). The reverse-flow reactor was optimized in order to find the best reversing cycle time and residence time for conversion, energy efficiency, O\textsubscript{3} production, and selectivity. The CO\textsubscript{2} selectivity was below 20% for all reactors, and several organic by-products were formed.

Blackbeard et al.\cite{21} used a ferroelectric VDBD with MnO\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3} (IPC) for the conversion of propane and propene. The measurements were performed in a range of 180 °C to 330 °C for propane and 90 °C to 270 °C for propene. The applied voltage was fixed in a range of 16.5 kV\textsubscript{pk–pk} to 17.5 kV\textsubscript{pk–pk} with a frequency of 9.6 kHz. The temperature was the only varied parameter. The degree of propane conversion increased from 54% to 70% (200 °C to 300 °C), and propene increased from 46% to 65% (100 °C to 200 °C) for the plasma-alone operation.
The thermocatalytic removal of propane had a threshold temperature of 180 °C, but then the degree of conversion increased to 90% at 280 °C. For propene conversion started at 7% at 140 °C reaching 90% at 260 °C. The plasma-catalytic measurements started at the threshold temperature of the thermocatalytic measurements. For propane and propene the degrees of conversion were slightly below the degree of conversion of the plasma-alone operations. The increase in conversion was similar to the thermocatalytic measurements, but at higher temperatures the degree of conversion came closer to the one of the thermocatalytic measurements. Demidyuk et al. [112] used the same set-up comparing thermocatalytic, heated IPC, and heated PPC measurements and found the highest degree of conversion for the heated IPC. Blackbeard et al. [21] proposed trends in the VOC conversion between thermocatalytic, plasma catalytic, and plasma-alone operations (Figure 2.9) combined with results using other catalysts than Mn. [112,113] The thermocatalytic operations show a strong temperature dependence, and a certain temperature must be reached to achieve conversion. The plasma-alone operations show a minor temperature dependence, but even at small temperatures conversion can be achieved. The plasma-catalytic operation can achieve conversion at even smaller temperatures and the degree of conversion is increasing with temperature.

![Figure 2.9](image)

**Figure 2.9.** Proposed trends between thermocatalytic, plasma-alone, and plasma-catalytic operations for an IPC application. Adapted by permission from ref. [21]

### 2.2.4 Thermocatalytic Conversion of Volatile Organic Compounds

The thermocatalytic conversion of VOCs reduces the operating temperatures to 150 °C - 250 °C depending on the catalyst material and converted VOC. [96] Furthermore, thermocatalytic oxidation can convert low-concentrated gas streams (<1% VOCs). [114] In contrast to thermal oxidation without catalyst temperatures in a range of 800 °C to 1200 °C are required and VOC concentrations below 1% are challenging to convert. [13,14,114] For most of the VOCs a Mars-van
Krevelen mechanism is identified, but also Langmuir-Hinshelwood or Eley-Rideal mechanism can take place depending on the used catalyst similar to the illustration of CO oxidation in Figure 2.7.\textsuperscript{[14,115–118]}

Manganese oxides are widely investigated for the oxidation of VOCs and CO either as single catalysts or as support in mixed metal catalysis.\textsuperscript{[24,96,114,119–123]} They are less toxic compared to other common transition metal oxides and potentially easier to obtain.\textsuperscript{[119]} Manganese oxides with different oxidation states are known like Mn(II)O, Mn\textsubscript{3}(II,III)O\textsubscript{4}, Mn\textsubscript{2}(III)O\textsubscript{3} or Mn(IV)O\textsubscript{2}. The manganese oxidation states are interchangeable from (IV) to (II) by applying thermal treatment in air at different temperatures as illustrated in Equation 2.14.\textsuperscript{[23,119,124]}

\[
\begin{align*}
\text{MnO}_2 & \overset{430^\circ\text{C}/500^\circ\text{C}}{\longrightarrow} \text{Mn}_2\text{O}_3 \overset{>827^\circ\text{C}/900^\circ\text{C}}{\longrightarrow} \text{Mn}_3\text{O}_4 \overset{>1000^\circ\text{C}/1700^\circ\text{C}}{\longrightarrow} \text{MnO}
\end{align*}
\] (2.14)

In addition to the various oxidation states, manganese oxides can form different polymorphic structures like \(\alpha\), \(\beta\), \(\gamma\), \(\delta\), \(\epsilon\), \(\lambda\), and R-MnO\textsubscript{2} which show variable activity in VOC oxidation.\textsuperscript{[125,126]} The most common crystal structures of manganese oxide polymorphs are schematically shown in Figure 2.10.

Due to the large number of different oxides and polymorphic forms, it is challenging to obtain precise information about the influence of various structures on the catalytic activity. All manganese oxide polymorphs are formed by differently connected [MnO\textsubscript{6}] octahedra.\textsuperscript{[125]} The different arrangements can be described as chain, tunnel, or layered structures.\textsuperscript{[127]} The tunnel structure is formed by edge-sharing chains of MnO\textsubscript{6} octahedral units.\textsuperscript{[127,128]} \(\alpha\)-MnO\textsubscript{2} forms a 2\(\times\)2 open tunnel structure. These tunnels can incorporate cations or other small species, whereas \(\beta\)-MnO\textsubscript{2} has a slightly disordered hexagonal close-packed (hcp) oxygen sublattice, in which the Mn\textsuperscript{4+} ions occupy every second octahedral site.\textsuperscript{[128–130]} Due to the dense packing \(\beta\)-MnO\textsubscript{2} cannot incorporate cations.
Total oxidation of short-chain hydrocarbons over manganese oxides is reported at temperatures of approx. 330 °C with an hydrocarbon/oxygen ratio of 1:6.\([120,121,132]\) These experiments were carried out using Mn\(_2\)O\(_3\) and Mn\(_3\)O\(_4\). Cellier et al.\([133]\) was able to achieve full conversion of 125 ppm n-hexane in 20% O\(_2\) with N\(_2\) at 180 °C over γ-MnO\(_2\). Aguero et al.\([134]\) used differently prepared Mn\(_2\)O\(_3/\)Al\(_2\)O\(_3\) catalysts for the conversion of 1 mol% of each ethanol and toluene separately in 20.5% O\(_2\). For ethanol full conversion was reached in a range of 200 °C to 240 °C and for toluene in a range of 310 °C to 340 °C. Einaga et al.\([122]\) oxidized benzene over SiO\(_2\)-supported manganese oxides with addition of O\(_3\). Full conversion was reached at 100 °C. This high degree of conversion is attributed by Einaga et al.\([122]\) to the decomposition of O\(_3\) by manganese oxide catalysts (Equations 2.15 – 2.17) and an autoxidation process involving formed O\(^*\) species (Equation 2.18).

\[
\begin{align*}
O_3 + * & \rightarrow O_2 + O^* \quad (2.15) \\
O^* + O_3 & \rightarrow O_2 + O_2^* \quad (2.16) \\
O_2^* & \rightarrow O_2 + * \quad (2.17) \\
R^* + O_2 & \rightarrow RO_2^* \rightarrow \rightarrow CO_2, CO \quad (2.18)
\end{align*}
\]

For the oxidation of CO manganese oxides show high activity as well.\([24,123]\) Ollegott et al.\([24]\) reach full conversion of CO with O\(_2\) under stoichiometric conditions over α-MnO\(_2\) at 194 °C, but also MnO and Mn\(_2\)O\(_3\) show high activity. Ramesh et al.\([123]\) showed that for Mn\(_2\)O\(_3\) and MnO\(_2\) CO oxidation mainly follows the Langmuir-Hinshelwood or Eley-Rideal mechanisms, whereas the Mars-van Krevelen mechanism predominantly occurs for MnO, but also for Mn\(_2\)O\(_3\) and MnO\(_2\).

Section 2.1.3 describes the formation of NO and NO\(_2\), which can be desirable in plasma processes for the conversion of VOCs, but undesired in the effluent gas due to their toxicity. In large scale or automotive applications the mole fraction of NO\(_x\) is decreased by selective catalytic reduction (SCR).\([135]\) By adding urea (CH\(_4\)N\(_2\)O) in the gas stream, NH\(_3\) is formed, which reduces NO\(_x\) in different pathways over V\(_2\)O\(_5\)–WO\(_3\)–TiO\(_2\) catalysts according Equations 2.19 – 2.21 to N\(_2\) and H\(_2\)O. Also manganese oxide-based catalyst are shown to be active for SCR.\([136]\) Nevertheless, the continuous addition of urea is a major drawback of this approach to remove NO\(_x\).

\[
\begin{align*}
4NH_3 + 4NO + O_2 & \rightarrow 4N_2 + 6H_2O \quad (2.19) \\
2NH_3 + NO + NO_2 & \rightarrow 2N_2 + 3H_2O \quad (2.20) \\
4NH_3 + 3NO_2 & \rightarrow 3.5N_2 + 6H_2O \quad (2.21)
\end{align*}
\]
The application of a three-way catalyst (TWC) is another pathway for the removal of especially NO\textsuperscript{137,138}. TWCs are known from automotive applications. There, NO is reduced and CO and unburnt hydrocarbons are oxidized according Equations 2.22 – 2.25 over Rh/Pt catalysts. However, this pathway relies on stoichiometric conditions, and excess O\textsubscript{2} would oxidize the reductive agents. Therefore, a TWC is also not applicable for the removal of NO\textsubscript{x} from air.

\begin{align*}
2\text{NO} + 2\text{CO} & \rightarrow 2\text{CO}_2 + \text{N}_2 \quad (2.22) \\
2\text{CO} + \text{O}_2 & \rightarrow 2\text{CO}_2 \quad (2.23) \\
\text{NO} + \text{hydrocarbon} & \rightarrow \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O} \quad (2.24) \\
\text{hydrocarbon} + \text{O}_2 & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (2.25)
\end{align*}

A third approach is the reduction of NO with hydrocarbons similar to Equation 2.24. Therefore, reduction takes place in presence of O\textsubscript{2} over Fe- and Cu-zeolites or Ag/Al\textsubscript{2}O\textsubscript{3} catalysts according Equation 2.26.\textsuperscript{137,139} This may enable the removal of produced NO\textsubscript{x} without addition of further reactants such as urea.

\begin{align*}
\text{NO} + \text{hydrocarbon} + \text{O}_2 & \rightarrow \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O} \quad (2.26)
\end{align*}

\subsection{2.2.5 Photocatalytic Conversion of Volatile Organic Compounds}

The photocatalytic conversion of VOCs is also of interest due to low energy costs by using solar radiation.\textsuperscript{140–143} The potentially low temperature conditions may enable indoor air purification applications.\textsuperscript{144–146} The basic principle relies on the separation of electrons and holes by photoexcitation in semiconductors. The electrons are excited to the conduction band by photons with energy larger than the gap between the valence and conduction bands. The excited electrons can react to form radicals, which then react with the VOCs. Most studies are performed with TiO\textsubscript{2}, but also SrTiO\textsubscript{3} is known to be active for the VOC conversion.\textsuperscript{140,142,147–152}
State of the Art
3 Catalyst Characterization, Analytics, and UI-Characterization Methods

3.1 N₂ Physisorption

N₂ physisorption is one of the most commonly used techniques for the determination of the specific surface area and the pore size distribution of solid materials.\textsuperscript{[153]} In heterogeneous catalysis the reaction occurs on the outer and the inner surfaces of the catalyst grains. Therefore, a high specific surface area of the catalyst is mostly desirable.\textsuperscript{[154]}

N₂ interacts with the surface of the catalyst or with the catalyst support by weak van-der-Waals forces. Therefore, it is often used as probe gas.\textsuperscript{[155]} Brunauer, Emmett, and Teller (BET) developed a method to calculate the specific surface area of solids taking multilayer adsorption into account. The BET calculation is based on Langmuir isotherms with the following assumptions: all adsorption sites are energetically equal, all adsorption layers beyond the first layer have the same heat of adsorption, heat of adsorption is independent of coverage, and the number of adsorption layers tends to infinity. The linearized BET equation\textsuperscript{[155]} (Equation 3.1) leads to the molar amount of a monolayer ($n_{\text{mono}}$).

\[
\frac{p}{V_{\text{ads}} \cdot (p_0 - p)} = \frac{1}{V_{\text{mono}} \cdot c} + \frac{c - 1}{V_{\text{mono}} \cdot c} \cdot \frac{p}{p_0}
\]  

Here, $p$ is the measured equilibrium pressure, $p_0$ is the saturation vapor pressure, $V_{\text{ads}}$ is the volume of adsorbate, $V_{\text{mono}}$ is the volume of an adsorbed monolayer, and $c$ is the BET constant. The BET equation is valid for $(p/p_0)$ in the range of 0.05 to 0.35. By plotting of $(p/V_{\text{ads}} \cdot (p_0 - p))$ vs. $(p/p_0)$, a straight line is resulting. The slope ($(c - 1)/V_{\text{mono}} \cdot c$) and the intercept $(1/V_{\text{mono}} \cdot c)$ of the line result in $V_{\text{mono}}$, which leads to the amount of molecules forming a monolayer $n_{\text{mono}}$. With $n_{\text{mono}}$, the well-known area occupied by a nitrogen molecule ($\sigma = 0.162 \text{ nm}^2$) and the sample mass, the specific surface area ($S_{\text{BET}}$) can be calculated using Equation 3.2.

\[
S_{\text{BET}} = \frac{\sigma \cdot n_{\text{mono}} \cdot N_A}{m_S}
\]  

Here, $N_A$ is the Avogadro constant and $m_S$ is the sample mass. When the measurement is performed over the whole $p/p_0$ range from 0 to 1, the resulting isotherms are separated in five main classes as shown in Figure 3.1.\textsuperscript{[156]} Type I isotherms represent typical monolayer adsorption on microporous ($d < 2 \text{ nm}$) solids. Type II and III indicate adsorption on nonporous solids and type IV and V adsorption on mesoporous solids ($2 \text{ nm} < d < 50 \text{ nm}$). Furthermore, type II and
IV are typical of strong interaction \((c > 20)\) between adsorbate and substrate and type III and V for weak interaction \((1 < c < 5)\).\textsuperscript{[157]} Barrett, Joyner, and Halenda (BJH) developed a method to determine the pore size distribution assuming cylindrical pores filled with adsorbed nitrogen. Depending on the pore size, the pores are filled at different pressures. Therefore, the isotherms deliver information about the pore size at higher relative pressure.\textsuperscript{[158]} Hysteresis of adsorption and desorption isotherms provide information about the pore shape (e.g. cylindrical pores, slit pores, conical pores, non-parallel pores, and "ink bottles").\textsuperscript{[157]}

**Procedure:** The \(N_2\) physisorption measurements were performed in a Belsorp mini measurement system (BEL Japan Inc.) at a constant temperature of 77 K. The sample pretreatment was performed at 250 °C for 2 h in vacuum. Sieve fraction as well as powder catalysts were measured.

### 3.2 X-Ray Diffraction

X-ray diffraction (XRD) is one of the most frequently used techniques to determine the structural properties of crystalline solids such as heterogeneous catalysts. It is used to identify the bulk phase of the solids and delivers information about the degree of crystallinity and the crystallite size.\textsuperscript{[153,159]} For the generation of X-rays an electron-emitting cathode is needed. The emitted electrons are accelerated to the anode with very high voltages (up to 42 kV). When slowed down by the anode, a background radiation is emitted, which is also known as "Bremsstrahlung". Furthermore, a more specific line spectrum overlays the non-characteristic broad spectrum of Bremsstrahlung. The line spectrum is specific for the metal used as the anode material. When the energy of the approaching electron is high enough to penetrate the electron shell, it can excite an electron from an inner shell causing an ejection of this electron. Once an electron from a higher shell drops back to refill the created electron hole, an X-ray
photon is emitted with an energy corresponding to the two involved electron shells. Depending
on the shell of the primary ejected electron in the anode material and the shell position of the
electron, which refills the created electron hole, different kinds of radiation are distinguished.
For XRD, the K_α and K_β radiations are of the largest interest. K_α radiation is emitted, when
an electron is ejected from the K-shell and the created hole is filled by an electron from the
L-shell. K_β radiation is emitted, when the electron refilling the electron hole originated from
the M-shell.[153,159] One of the main principles of XRD is the elastic scattering – or diffraction – of X-ray beams at the crystal lattice of the sample. The wavelength of the used X-ray beams
has to be similar to the distance between the atoms of the investigated crystal. Each atom of
the lattice acts as a scattering point. The approaching X-rays are scattered elastically forming a
secondary wave. All secondary waves are summed up in a reflected wave. Since there is only a
weak absorbance of X-rays through the sample, many parallel lattice planes are able to reflect
the incoming radiation at once. When the path length difference is an integral multiple of the
wavelength, it comes to constructive interference. This interference is described by Bragg’s law
(Equation 3.3), which is illustrated in Figure 3.2. The most common way to evaluate experimental patterns obtained by XRD is to compare these to patterns of reference materials. Hereby,
the intensity and position of reflections provide information about the sample. Since real sam-

ples often contain more than one phase, superposition of reflections can conceal weaker peaks.

\[ n\lambda = 2d_{hkl} \sin(\theta) \]  
(Equation 3.3)

Missing long-range order, which means less equally ordered lattice planes beneath the surface,
lead to a lower number of reflected beams, resulting in weaker constructive interaction between
the outgoing beams and correspondingly broader reflections with lower intensity. XRD can fur-
ther be used to determine the mean crystallite size of the sample, since the reflections become
broader with decreasing size of the crystallites.

\[ l = \frac{K\lambda}{\beta \cos(\theta)} \]  
(Equation 3.4)

Here, \(\lambda\) is the wavelength, \(\beta\) is the peak width, \(\theta\) is the angle and \(K\) is the shape factor. There
are several geometries and set-ups, which are used for XRD experiments. The main geometry
is called Bragg-Bretano, which delivers good angular resolution as well as intensity and peak
shape.

**Procedure:** The XRD pattern were recorded using a Discover D8 (Bruker, USA) diffrac-
tometer with a theta-theta geometry. The powder was investigated with Cu Kα radiation
(\(\lambda = 0.15406\text{ nm}, 40\text{ kV}, 40\text{ mA}\) in a range of 5° to 80° 2\(\theta\) with an increment of 0.02°. The
pattern was examined using Diffrac Eva Software with access to the International Centre for Diffraction Data (ICDD) database.

Figure 3.2. Geometry of Bragg’s equation. Reprinted by permission from Springer Nature.[159]

### 3.3 Transmission Electron Microscopy

Microscopic techniques are used to determine the morphology of catalysts.[153] Due to the Abbe diffraction limit the resolution of a light microscope is limited by the wavelength of visible light. Therefore, electron microscopy uses a focused electron beam with energies between 100 keV and 400 keV to produce enlarged images of catalysts or other materials. These images are used to determine the morphology, surface orientation, particle size, and composition. Electron waves have characteristic wavelengths of less than 10 nm and come close to resolving atomic details. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are both widely used. In SEM the primary electron beam is focused by lenses and scanned across the samples, whereas in TEM the transmitted electrons are utilized. Depending on the operation mode different signals are detected as shown in Figure 3.3. Inelastic scattering and collisions produce secondary electrons of lower energy. Due to the lower energy they are emitted from near-surface regions. The intensity of backscattered or secondary electrons is detected dependent on the position of the primary electron beam, and the measured intensity is influenced by the topography and orientation of the particles. Using this information the image of the sample is generated in SEM. The transmitted electrons generate a two-dimensional projection of the sample on the detector (e.g. CCD camera) in TEM. The electron beam is focused by electromagnetic lenses. In order to prevent scattering of the electrons with gas molecules, these measurements have to be performed under ultra-high vacuum conditions.

**Procedure:** The TEM images of the samples were acquired with a Jeol JEM 2800 set-up operated at 200 kV. The samples were suspended in ethanol and added dropwise to a carbon-coated...
Au grid. To avoid contamination of the set-up caused by magnetic samples, the grid was additionally coated with carbon glue prior to introduction into the measurement chamber.

![Interaction of the primary electron beam with sample and the emitted and scattered electrons. Reproduced with permission of The Licensor through PLSclear.](image)

3.4 Non-dispersive Infrared Spectroscopy

Infrared radiation can excite specific vibrations or rotations in molecules at specific wavelengths. With a non-dispersive infrared (NDIR) detector the mole fraction of particular molecules in a gas stream can be measured.\textsuperscript{[160,161]} The NDIR detector consists of a light source (mostly a Nernst lamp or a globar), a flow-through sample chamber, a wavelength filter, and an IR detector.\textsuperscript{[160]} The sample gas stream flows continuously through the sample chamber and is irradiated by IR light. A separate channel is used per investigated analyte. Each channel has a special IR filter depending of the analyte for specific IR bands of the corresponding molecule. The intensity of radiation measured by the IR detector depends on the amount of analyte in the gas stream corresponding to the Lambert-Beer law (Equation 3.5).

\[
-\log(A) = -\log\left(\frac{I}{I_0}\right) = \varepsilon_\lambda \cdot c \cdot d \quad (3.5)
\]

3.5 Quadrupole Mass Spectrometry

With a mass spectrometer (MS), the mass-to-charge \((m/z)\) ratio of ions and their relative occurrence in a gas sample can be measured. Different possibilities to measure the mass-to-charge ratio are available, e.g. time-of-flight, ion trap, quadrupole mass spectrometer (QMS) and orbitrap mass spectrometer. In the used set-up, a QMS is installed. The molecules must be
transferred into the gas phase and then ionized. The most common technique is the electron ionization. First, the sample is heated to high temperatures to create a molecular vapor, or the analyte is already in the gas phase. Then, the molecules are ionized by a beam of high-energy electrons, as shown in Equation 3.6.

\[ M + e^- \rightarrow M^+ + 2e^- \]  (3.6)

The created ions are accelerated towards the quadrupole, where they are separated according to their mass-to-charge ratio. The quadrupole consists of four poles with different charges (Figure 3.4), which are varied with a certain frequency. Thus, only one mass-to-charge ratio can reach the detector, mostly a photomultiplier tube (PMT). By variation of the frequency of the charge alteration, different ions can be measured consecutively. Only one mass-to-charge ratio can pass the poles at the same time and can cause a signal at the detector.

![Figure 3.4. Four quadrupole rods with different charged poles, which can be passed by ions with a specific mass-to-charge ratio.](image)

### 3.6 Laser Scanning Microscope

For the characterization of planar surfaces a laser scanning microscope (LSM) can be used.\[162–164\] A LSM combines a light microscope with confocal optics producing high resolution images and height profiles of the investigated surface. This non-destructive technique leaves the surface undamaged.\[164\] The schematic structure of a confocal microscope and a photograph of the used model (VK 9710, Keyence) are shown in Figure 3.5.\[164\] The LSM has several lenses for different magnifications and is balanced on an air-cushioned plate. The light emitted by the light source passes a aperture and a semi-transparent mirror, and then it is focused by a lens on the focal plane. The reflected light passes again the lens and is reflected by the semi-transparent mirror towards a further aperture and the detector. The lateral resolution is achieved by scanning of the surface, and the three-dimensional figures are generated by altering the position of the sample or the focal plane (Figure 3.5c).\[166\]
### 3.7 UI-Characterization

The electrical measurements or UI-characterizations of discharges are performed using oscilloscopes. They are mostly used for the visualization of voltages as a function of time.\textsuperscript{[167]} These graphs can be examined with regard to amplitude, frequency, rise time, distortion, and other characteristics. The applied voltage of atmospheric pressure plasma applications is typically in a range of several kilovolt (kV) and is measured using a high-voltage probe (HVP). The high voltage would be destructive for the oscilloscope, therefore a HVP utilizes a precision voltage divider circuit within the probe body in order to reduce the voltage to a level the oscilloscope can resolve. For voltages up to 100 kV typically resistor or capacitive voltage dividers with an input resistance of several hundred megaohm (M\(\Omega\)) are used. A current probe (CP) is used to measure the current of a plasma discharge. Classical CP use Ohm’s Law\textsuperscript{[168]} to calculate the current with the voltage drop across a resistor. This measurement principle has the disadvantage of requiring a direct modification of the probed circuit. Another probe geometry is the Rogowski coil.\textsuperscript{[169]} It can measure high-speed current pulses (AC). The coil consists of a single helical coil toroid. The wire is redirected in the core of the helix from the end to the beginning ensuring that both terminals are at the same point of the toroid. The high-voltage cable leads through the center of the toroid resulting in an uninterrupted measurement of the current. The current passing the high-voltage cable induces a voltage in the Rogowski coil. This induced voltage can be recalculated with the specific coil constant to the current.
### 3.8 Schlieren Imaging

Schlieren imaging is used to visualize the flow characteristics of fluids. An optical set-up can translate phase differences of a light beam into light intensity differences. These are caused by variations of the refractive index $n_{\text{Ref}}$ of the fluid medium based on the local density of the medium leading to different propagation directions of the light. The refractive index of a medium is defined by the ratio of the speed of light in the medium $c_i$ and the speed of light in vacuum $c_0$ (Equation 3.7).

$$n_{\text{Ref}} = \frac{c_0}{c_i} \quad (3.7)$$

The refractive index of gases correlates linearly with the gas density $\rho_{\text{Gas}}$ according the Gladstone-Dale relation (Equation 3.8).\(^{[171]}\)

$$n_{\text{Ref}} - 1 = k \cdot \rho_{\text{Gas}} \quad (3.8)$$

Here, $k$ is the Gladstone-Dale coefficient, which varies between 0.1 cm$^3$ g$^{-1}$ and 1.5 cm$^3$ g$^{-1}$ depending on the gas and the conditions. Schlieren set-ups can be used to visualize gradients in the refractive index of gases caused by changes in the first derivative of the density. These changes are typically induced by temperature differences or high gas velocities.\(^{[171]}\) A schematic illustration of the used set-up for this work is shown in Figure 3.6. A point-like light source is created by focusing a light source with a condenser lens onto an aperture. Behind this aperture another lens collimates the light. Parallel light beams then pass through the reactor. A third lens focuses the light onto a knife edge followed by a lens projecting the schlieren image on the image plane.

A fraction of the light, the cut-off, is blocked by the knife edge. When the light is not refracted by interfaces of regions with different refractive indices in the gas it passes the knife edge uniformly affected. However, when the light is refracted a portion of it is either completely blocked by the knife edge or passes it. This leads to darker or brighter regions in the schlieren image.\(^{[170]}\)

---

**Figure 3.6.** Schematic illustration of a lens-type schlieren set-up as used for this work. Adapted from Ref.\(^{[171]}\)
3.9 Optical Emission Spectroscopy

Optical emission spectroscopy (OES) can be used to determine fundamental plasma parameters such as the electron density or the reduced electric field in addition to the gas temperature. It utilizes the emission spectrum of molecular and ionized \( \text{N}_2 \) and is noninvasive. Therefore, it does not influence the plasma process. The utilized collisional radiative model (CRM), which is the theoretical concept, was described in detail by Bibinov et al.\[172\]. The numerical simulations for the SDBD were described by Offerhaus et al.\[173\] and Kogelheide et al.\[174\] in detail.

The CRM is based on the emission of the second positive \( \text{N}_2 \) (\( \text{C}^−\text{B} \)) and the first negative \( \text{N}_2^+ \) (\( \text{B}^−\text{X} \)) systems. The emissions used for the analysis are \( \text{N}_2 \) (\( \text{C}^−\text{B}, 0−0 \)) at 337.1 nm and \( \text{N}_2^+ \) (\( \text{B}^−\text{X}, 0−0 \)) at 391.4 nm, which have to be measured simultaneously because of the transient character of the discharge.

The rotational temperature \( T_{\text{rot}} \) can be determined by measuring the rotational distribution of \( \text{N}_2 \) (\( \text{C}^−\text{B}, 0−0 \)). This experimental distribution is compared to simulated spectra corresponding to different rotational temperatures to find the rotational temperature of the discharge. An equilibrium between rotational temperature \( T_{\text{rot}} \) and the gas temperature \( T_g \) is assumed because of the high number of collisions between the \( \text{N}_2 \) molecules at atmospheric pressure and by electron excitation of the rotational distribution in the corresponding excited electronic state.\[171\]

The combination of the measured spectra, the CRM, and the Boltzmann equation is used to determine the reduced electric field \( E/N \) and the electron density \( n_e \). The electron distribution function was obtained by the program EEDF from Napartovich et al.\[175\] by solving the Boltzmann equation for several reduced electric fields. The ratios between \( \text{N}_2 \) (\( \text{C}^−\text{B}, 0−0 \)) and \( \text{N}_2^+ \) (\( \text{B}^−\text{X}, 0−0 \)) can be used to determine the reduced electric field according to Equation 3.9.

\[
\frac{I_{N^+_2(B,X,0-0)}}{Q_{N^+_2(B)}} \frac{k_{N_2(X)}}{k_{N_2(C)}} = f \left( \frac{E}{N} \right) \tag{3.9}
\]

Here, \( I \) are the absolute intensities, \( Q \) the collisional quenching factors, and \( k \) the rate constants for the electron impact excitation of the respective states. Similar to Equation 3.9, Equation 3.10 can be used to calculate the electron density.

\[
n_e = \frac{I_{N_2(C-B,0-0)}}{Q_{N_2(C)} \cdot n_{N_2(X)} \cdot k_{N_2(X)}} \tag{3.10}
\]

For the application of the CRM and the numerical simulations the relative and absolute intensities of the \( \text{N}_2 \) emission band are necessary. Therefore, the spatially and temporally averaged
emission spectra are recorded with an absolutely calibrated echelle spectrometer. The absolute intensity $I_{\text{abs}}$ can be calculated according to Equation 3.11.

$$I_{\text{abs}} = \frac{\int_{\lambda_1}^{\lambda_2} I(\lambda) \cdot \varepsilon^{-1}(\lambda) d\lambda}{G \cdot V_{\text{plasma}} \cdot t \cdot d_{c_{\text{plasma}}} \cdot T_{\text{window}}}$$

(3.11)

Here, $I(\lambda)$ is the measured intensity, $\varepsilon(\lambda)$ the spectral efficiency of the spectrometer, $G$ the geometrical factor, $V_{\text{plasma}}$ the investigated plasma volume, $t$ the exposure time, $d_{c_{\text{plasma}}}$ the duty cycle of the plasma, and $T_{\text{window}}$ the transmission characteristics of the quartz window.
4 Experimental

4.1 Synthesis of the Manganese Oxide Catalyst

The comproportionation of KMnO$_4$ and Mn(NO$_3$)$_2$ is a very fast and well known reaction for the formation of MnO$_2$ at ambient conditions (Equation 4.1).[176] In this work, the reaction was carried out in a micromixer and the emerging suspension was quenched rapidly in a spray dryer to prevent further particle growth. This method has been previously developed in our group.[6,24]

$$2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2\downarrow + 4\text{H}^+ \quad (4.1)$$

The comproportionation was performed by using a multi-channel peristaltic pump (IPC 4, Ismatec®) to pump the reactants separately into a micromixer. With this micromixer (Mixing Tee, PEEK, VICI®) a small mixing volume can be reached (<0.03 mL). In Figure 4.1a the micromixer is schematically shown with the transition from laminar to turbulent conditions. A residence time below 0.3 s in the micromixer can be achieved. For the immediate quenching after comproportionation, a commercially available spray dryer (B-290, Büchi) was used. The micromixer was mounted on top of the nozzle of the spray dryer to decrease the reaction time between mixing and quenching. Thereby, residence times of less than 7 s between mixing and quenching can be reached. A polytetrafluoroethylene (PTFE) tube was inserted into the nozzle of the spray dryer until its tip was reached. The complete set-up is shown in Figure 4.1b. The entering product flow was atomized at the nozzle (2.8 mm diameter) by a gas flow from an external compressor, which was regulated by a rotameter and set to maximum flow. The atomized product was sprayed in the aspirating gas flow, which was heated to 220 °C. The aspirator was adjusted to a maximum flow of 35 m$^3$h$^{-1}$. The precipitate was finally separated from the air flow in a cyclone.

The solution of KMnO$_4$ had a concentration of 0.011 molL$^{-1}$ with 0.015 molL$^{-1}$ KOH for alkaline conditions. The solution of Mn(NO$_3$)$_2$ had a concentration of 0.016 molL$^{-1}$. Both were mixed in the micromixer. The peristaltic pump was set to a volume flow of 3 mL min$^{-1}$ per solution. Due to plugging problems of the micromixer during the precipitation, intermittent washing with saturated oxalic acid solution was performed. Oxalic acid dissolved the precipitated manganese oxide inside the micromixer and the tubes. The produced manganese oxalate was easily removed by washing, and residual oxalate decomposed after calcination to MnO$_2$.[177] The micromixer was washed every 20 min for 3 s with saturated oxalic acid solution.

The subsequent washing was performed in a glass crucible with fritted glass (porosity 5, 1.0 µm to 1.6 µm). In the glass crucible the precipitate was converted into a slurry with a magnetic stir-
rer, washed twelve times with 50 mL of water per washing step, and dried over night at 105 °C. Calcination was performed in a bench-top furnace in a quartz tube. The atmosphere was set to 20% O₂ and 80% N₂ with a continuous flow of 100 mL.min⁻¹. A heating rate of 5 °C.min⁻¹ was used and the manganese oxide was calcined for 4 h at 460 °C.

4.2 Coating

One of the most convenient ways for the application of catalysts on surfaces is spray coating. The coating materials are dispersed in liquid media adjusted to the individual sedimentation behavior, usually using alcohols, diols, or water. Different coating techniques can be utilized. In this work the air spray method was chosen, which uses compressed air to atomize the coating suspension by taking advantage of the Venturi effect. This leads to an evenly distributed coating material on the target. Additionally, the target was heated to speed up the evaporation of the liquid medium. In Figure 4.2 the scheme and a photograph of the used coater are shown. The suspension was stored in a stirred reservoir to ensure optimal mixing and avoid sedimentation. The suspension was pumped to the nozzle with a syringe pump. There, it was atomized with compressed air. The nozzle was positioned over the target with a robotic arm. By variation of the distance between the spraying spots, the concentration, or the sprayed volume
Experimental

Figure 4.2. (a) Scheme of the used spray coater. The catalyst suspension was transported with a syringe pump from the reservoir to the nozzle. The compressed air atomizes the suspension towards the heated target where the liquid phase evaporated instantly. (b) Spray coater with coated twin-SDBD electrode configuration.

of the suspension, the catalyst loading on the target was adjusted.

The targets were cleaned for 30 min in an aqueous soap solution before spraying, followed by cleaning with desalinated water and acetone. The cleaned targets were placed on the heating plate for coating, which was set to 200 °C. A detailed method optimization is described in the Bachelor thesis by C. Oberste-Beulmann.\textsuperscript{[180,181]} The suspension was made using a mixture of water and isopropanol (1:1), because this shows a good compromise between temporal stability, even catalyst distribution on the target, and rapid evaporation after spraying. The catalyst was dispersed first in water and then treated in an ultrasonic bath three times for 10 min with manually shaking in-between. Then, the same amount of isopropanol was added, and the suspension was treated for another 10 min in the ultrasonic bath. For coating of targets with MnO$_2$, the concentration of the suspension was 4 mg mL$^{-1}$. The suspension was sprayed with a pump volume of 30 µL per stroke and step width of 2 mm in x- and y-direction, resulting in a loading of 3 mg cm$^{-2}$. For lower loadings concentration and step width were adjusted.

Half-coated electrode configurations were made out of fully coated electrode configurations, which were placed in saturated oxalic acid solution to dissolve MnO$_2$ on half of the coated area. The cleaned area was then washed with desalinated water. The mask-coated electrode configurations were coated using masks shown in Figure 4.3a. The masks were placed on the grid lines with the contact areas for the high-voltage feed throughs as orientation. After coating the masks were removed. Figure 4.3b shows the coating procedure using the masks.
4.3 Thermocatalytic Oxidation

4.3.1 Set-Up

The thermocatalytic investigations were performed at ambient pressure and varying temperatures in the flow set-up shown in Figure 4.4. For each gas line an individual mass flow controller (MFC) was used to control and regulate the flow in the set-up (MFC 1 to MFC 5). The numbers refer to the detailed flow scheme shown in Figure A.2. Each gas line can be closed individually by pneumatic valves. All gases with their respective purity and the maximum flow rate possible of the MFCs are summarized in Table 4.1. Two different reactors were used, a U-tube quartz glass reactor (Figure 4.5a) and a plate reactor (Figure 4.5b), which were switched online or bypassed separately. Both reactors were temperature-controlled with heating cartridges and thermocouples up to 450 °C. For CO\textsubscript{2} and VOCs in the gas mixture a QMS (GAM400, IPI) was installed and a multi-channel analyzer (MCA) with a NDIR detector (Advance Optima URAS 14, Hartmann & Braun) was calibrated to measure the CO contents of the effluent gas.
Table 4.1. Overview of the gases with purities and maximum volumetric flow rates used for the thermocatalytic oxidations.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Purity</th>
<th>MFC</th>
<th>Flow rate mL min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>5.0</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>0.1% C₄H₁₀ in N₂</td>
<td>C₄H₁₀ 2.5; N₂ 5.0</td>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td>N₂</td>
<td>5.0</td>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td>O₂</td>
<td>4.8</td>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>4% CO in N₂</td>
<td>CO 4.7; N₂ 5.0</td>
<td>1</td>
<td>50</td>
</tr>
</tbody>
</table>

The analyzers were connected in series. A LabVIEW software was used to control all valves, the MFCs and the reactor temperatures. Moreover, it was used to save the measured data of the MCA and the thermocouples during the measurement. The QMS data were recorded separately. The measurements were run fully automated with preset programs.

4.3.2 Measurement Procedures

Different measurement procedures were applied. A comparison of the catalyst loading (Section 6.1) was carried out with n-butane and CO to simulate the produced CO during plasma operation. The reactor temperature was controlled in a range from 40 °C to 450 °C using a heating rate of 5 K min⁻¹. The gases were mixed to obtain a gas stream of 78.5% N₂, 20.5% O₂, 1% CO, and 300 ppm n-butane with a volumetric flow rate of 80 mL min⁻¹, which led to the same residence time of 2.3 s as in the plasma-driven measurement series. For the measurements with only one reactant the missing gas flow was replaced by pure N₂. The measurement procedure consisted of seven consecutive steps, which are shown in Figure 4.6. First, three iterations with n-butane and CO were carried out to ensure reproducibility of the catalyst, followed by four
measurements with changing gas mixture to investigate the oxidation behavior with only CO or only n-butane as reactant. After each single reactant measurement a measurement with both reactants was carried out to confirm reproducibility. The catalyst-coated plates were made of alumina and had dimensions of 50 mm × 100 mm × 0.635 mm. The variation of the coated area (Section 6.2) was carried out under similar conditions but without any measurements with CO. Therefore, only three measurements were made for each coated plate to reach steady state. The plates were used with a loading of 3 mg cm⁻², but with different coated areas (Figure A.5). For the measurements in the U-tube reactor a packed bed was used. The packed bed consisted of catalyst diluted with silicon carbide (20:80) to reduce temperature gradients and prevent hot spots. The sieve fraction of the catalyst lies between 250 µm and 355 µm to avoid limitations by heat or mass transfer. The catalyst was pressed with 4 t in cylindrical shape with 13 mm diameter for 1 min and then sieved.

4.4 Plasma-Assisted Oxidation

4.4.1 Flow Set-Up

The plasma-assisted oxidations with and without catalyst were carried out in a flow set-up, which was originally built for the project Carbon2Chem®. A simplified flow scheme is shown in Figure 4.7, which contains all the parts relevant for this work. A detailed version is shown in Figure A.3. The set-up had ten gas lines, which are summarized in Table 4.2 with the purity of the gas and the maximum flow rate of the MFCs. For this work only the N₂, O₂,
Table 4.2. Overview of the gases with the purities and the maximum volumetric flow rates used for the plasma-assisted oxidations.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Purity</th>
<th>MFC</th>
<th>Flow rate mL min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>5.0</td>
<td>1</td>
<td>10000</td>
</tr>
<tr>
<td>H₂</td>
<td>5.0</td>
<td>2</td>
<td>10000</td>
</tr>
<tr>
<td>CH₄</td>
<td>4.8</td>
<td>3</td>
<td>5000</td>
</tr>
<tr>
<td>CO</td>
<td>4.7</td>
<td>4</td>
<td>1000</td>
</tr>
<tr>
<td>CO₂</td>
<td>4.8</td>
<td>5</td>
<td>1000</td>
</tr>
<tr>
<td>O₂</td>
<td>4.8</td>
<td>6</td>
<td>50</td>
</tr>
<tr>
<td>n-C₄H₁₀</td>
<td>2.5</td>
<td>8</td>
<td>50</td>
</tr>
<tr>
<td>mixed Gases</td>
<td>–</td>
<td>9</td>
<td>10000</td>
</tr>
<tr>
<td>N₂ (saturator)</td>
<td>5.0</td>
<td>10</td>
<td>1000</td>
</tr>
</tbody>
</table>

n-butane, and the mixed gases lines are relevant. The gas lines can be closed individually and were merged in mixing valves. All measurements were carried out at atmospheric pressure. If not mentioned differently the gas flow was set to 10 L min⁻¹ with 20.5% O₂, 79.5% N₂, and 300 ppm n-butane. The reactor can be set offline with a 4-port-2-position valve and then the gas flows through the reactor above and below the electrode configuration.

The effluent gas was analyzed by a QMS and a MCA. The QMS (GAM400, IPI) was connected to the set-up using a heated capillary probing the effluent gas and was calibrated for the analysis of n-butane, toluene, O₂, and CO₂. The flexibility of the QMS also enables the calibration for other VOCs than toluene and n-butane. Furthermore, the QMS was used to analyze the formation of possible by-products formed in the plasma process. Analog scans were used for the identification of these by-products. The QMS was also used for monitoring ROS formed by the plasma like NO₂, NO, and O₃. For the ROS no calibration was carried out and just the ion currents were monitored. The measurement settings of the QMS are summarized in Table B.1.

The QMS has a high flexibility for the analysis of the effluent gas, but also a high maintenance effort is needed for calibration. Additionally, it was not possible to measure the mole fraction of CO with a QMS when N₂ was in the gas stream as well because of overlapping mass-to-charge ratios. Therefore, an MCA (X-Stream, Emerson) was used for the analysis of n-butane, CO₂, and CO. The MCA uses an NDIR sensor to measure the mole fractions. CO₂ and CO can be measured in a range from 0 ppm to 10000 ppm and n-butane in a range from 0 ppm to 500 ppm.

The QMS and the MCA were calibrated with calibration gas mixtures with known mole fractions of toluene, n-butane, CO, CO₂, and O₂. The MFCs, the mixing valves, the MCA, and the applied voltage were controlled and monitored with a control panel programmed in LabVIEW.
The QMS and dissipated power were monitored separately. The gas stream was enriched with liquid VOCs using a saturator. Figure 4.8a shows the three-stage-saturator tailored for this set-up. In the first stage the main reservoir of the VOC was at room temperature (RT). There, the gas stream was over saturated using fritted glass to create fine bubbles. On top of the first stage a Grahams condenser was placed to return most of the excess VOC by cooling. The second and the third stage were placed in a temperature-controlled bath, which was set to the targeted temperature needed for the correct mole fraction of the VOC. This elaborated procedure with a three-stage-saturator was needed for the saturation because of the high gas flow used in the set-up. The targeted temperature \( T \) for a certain mole fraction at a certain pressure \( p \) was calculated using the Antoine equation (Equation 4.2).\(^{[182]}\)

\[
\log(p) = A - \frac{B}{(T + C)} \tag{4.2}
\]

The Antoine equation parameters \( A, B, \) and \( C \) depend on the substances and were taken from NIST.\(^{[183]}\) Figure 4.8b shows the comparison of calculated and measured mole fractions of toluene for a 10 L min\(^{-1}\) gas flow. There was an increasing difference found. When the QMS was calibrated with known gas mixtures this was no issue, but when the calibration of the QMS is to be carried out for other VOCs in future measurements, the calibration will have to be performed with flow rates below 100 mL min\(^{-1}\).

---

Figure 4.8. (a) Three-stage-saturator for the enrichment of the gas streams with VOCs. (b) Comparison of calculated mole fractions with the Equation 4.2 and measured mole fractions with the QMS for a gas flow of 10 L min\(^{-1}\). The comparison was made at atmospheric pressure and -12.5 °C.
4.4.2 Surface Dielectric Barrier Discharge Reactor

The used electrode configuration was made out of two symmetrical, grid-like electrodes separated by a dielectric plate. The discharge was formed by applying a high-voltage on one electrode and grounding the other.\cite{7} The electrodes of the SDBD were both in contact with the dielectric and therefore produced a plasma igniting along the surface of the dielectric. Both electrodes and the dielectric used in this work were combined into a single plate, which in the following is referred to as electrode configuration or twin-SDBD. The dielectric consisted of an alumina plate (190 mm × 88 mm × 0.635 mm) with two electrodes, which were Ni-coated metal grids (molybdenum silicate and manganese silicate (80:20)) screen-printed on either side of the dielectric. The grid lines had a width of 0.45 mm and a square size of 1 cm². On each side 5 × 15 squares were printed. The twin-SDBD was originally designed and characterized by Offerhaus et al.\cite{49} and Kogelheide et al.\cite{174} with respect to the plasma parameters, power densities, and scalability. Schücke et al.\cite{184} performed studies on the dissipated power as a function of the applied voltage, pulse repetition frequency, and VOC mole fraction and on the formation of by-products from different VOCs.

The original SDBD reactor was designed and is described in greater detail by project partners \cite{171,173}. The reactor was connected to the flow set-up on both ends with KF25 flanges. The circular KF flanges expand to a rectangular cross-section of 17 mm × 105 mm (Figure 4.9c). The reactor was made out of anodized aluminum and can be dismantled into an upper and a lower part. In both parts there were three windows for optical access perpendicular to the electrode configuration. When the reactor was assembled there were two windows on each side of it for optical access in parallel to the electrode configuration. The reactor was sealed with fluorocarbon (FKM). For the windows quartz glass was used in two different versions. In general, for conversion measurements natural quartz was used (FN08, GVB GmbH) and in all applications in which a wide spectral range was necessary, synthetic quartz was used (Viosil SQ, GVB GmbH). The synthetic quartz has a light transmission of 90% in a range from 200 nm to 900 nm. A comparison of the transmission of both used glasses is shown in Appendix A (Figure A.4). The high-voltage connection was made out of KF16 metal ceramic vacuum feed-throughs (A0532, MPF). At these feed-throughs metals springs were installed, which were connected to the electrode configuration. The electrode configuration was centered vertically, horizontally, and laterally in the reactor. A high-voltage pulse generator (G2000, Redline Technologies) was used to apply the voltage. The secondary side inductance of the high-voltage transformer and the capacitance of the electrode configuration form a series resonant circuit, which was excited by high-voltage pulses (0 V to 300 V) provided by the high-voltage pulse generator.\cite{7} If not mentioned differently, the high-voltage pulses were supplied
at a pulse repetition frequency of 4000 Hz and excited the resonance circuit, forming a damped sine wave at an eigenfrequency of 86 kHz in the kilovolt range.

### 4.4.3 Oscilloscope, High-Voltage Probe, and Current Probe

The monitoring of the UI-characteristics was carried out with a digital oscilloscope (DPO5204B, Tektronix). A high-voltage probe (P6015A, Tektronix) and a current probe (Model 6585, Pearson Electronics) were connected to the oscilloscope. By combining the high-voltage probe and the current probe the dissipated power \( P \) in the system can be calculated according to Equation 4.3.

\[
P = U(t) \cdot I(t)
\]  

(4.3)

For the applied method the resolution \( \text{Res} \) of the high-voltage signal \( U \) and the current signal \( I \) in the oscilloscope have to be set depending on the sample rate \( \text{SR} \) and the pulse repetition frequency \( f_{\text{pul}} \) according to Equation 4.4.

\[
\text{Res} = 2 \cdot \frac{\text{SR}}{f_{\text{pul}}}
\]  

(4.4)

In order to average two pulses the factor of 2 was added. With these settings the dissipated power \( P_{\text{diss}} \) was calculated. The high-voltage probe signal can be used as received, but for
the current probe signal a device specific factor of 2 was necessary for data processing. The received power was averaged over time. With this method the dissipated power in the system is obtained, which also includes ohmic and dielectric losses in addition to the plasma power.

### 4.4.4 Applied Figures of Merit

For all measurements the degrees of conversion, the selectivities, and the carbon balance were derived. The conversion (Equation 4.5) is a measure of the converted molar amount ($n$) of n-butane relative to the molar amount in the feed.

$$X = \frac{n_{\text{butane, initial}} - n_{\text{butane}}}{n_{\text{butane, initial}}}$$  \hspace{1cm} (4.5)

The selectivity (Equation 4.6) is the ratio of the amount of a certain reaction product to the amount of converted reactant. CO and CO$_2$ were the only measured products and therefore only their selectivities ($S$) were calculated. The factor of 4 is based on the stoichiometry of the reaction $\text{C}_4\text{H}_{10} + 6.5 \text{O}_2 \rightarrow 4 \text{CO}_2 + 5 \text{H}_2\text{O}$.

$$S_{\text{CO/CO}_2} = \frac{n_{\text{CO/CO}_2}}{4 \cdot (n_{\text{butane, initial}} - n_{\text{butane}})}$$  \hspace{1cm} (4.6)

The carbon balance (Equation 4.7) compares the amount of carbon in the feed with its amount in the effluent. When the carbon balance is smaller than 100%, it is an indication of the formation of organic by-products, which were deposited in the reactor as soot or carbonaceous deposits. Carbon balances over 100% could indicate conversion of carbonaceous species, which had been deposited on the exposed surfaces beforehand. The carbon balance was derived from the mole fractions of n-butane, CO, and CO$_2$.

$$\text{carbon balance} = \frac{n_{\text{CO}} + n_{\text{CO}_2} + 4 \cdot n_{\text{butane}}}{4 \cdot n_{\text{butane, initial}}}$$  \hspace{1cm} (4.7)

For the calculation of the residence time (Equation 4.8) the hydrodynamic residence time ($\tau$) was used, which describes the ratio of the volume above and below the electrode ($V_{\text{electrode}}$) and the volume flow ($\dot{V}$).

$$\tau = \frac{V_{\text{electrode}}}{\dot{V}}$$  \hspace{1cm} (4.8)

The figures of merit are shown as a function of the applied voltage or as a function of the specific energy density (SED). The applied voltage was directly measured using the oscilloscope. For
the calculation of the SED the dissipated power \( (P_{\text{diss}}) \) is divided by the gas flow \( (V) \) of the respective measurement as described by Equation 4.9.

\[
SED = \frac{P_{\text{diss}}}{V} \tag{4.9}
\]

In addition, also the energy efficiency (EE) was calculated according to Equation 4.10, with the molar mass \((M)\), the mole fraction of n-butane \((y_{\text{ppm}})\), the degree of conversion \((X_\%\)\), the SED, and the molar volume \((V_m)\) and several factors for unit conversion resulting in converted mass of n-butane per energy input \([mg_{n\text{-butane}}/J]\).

\[
EE = \frac{M \cdot y_{\text{ppm}} \cdot X_\% \cdot 10^6}{SED \cdot 1000 \cdot V_m \cdot 100} \tag{4.10}
\]

### 4.4.5 Applied Measurement Methods

The flow set-up and the PhD project were subject to constant change because of new insights or expansions. Therefore, different analysis methods were applied in the sections of Chapter 7. In Table 4.3 the applied analysis methods are summarized for the relevant sections. It is also summarized whether the figures of merit are shown as function of applied voltage \((U)\) or SED. The analysis methods of the thermocatalytic measurements described in Section 7.8 are excluded in this list, but described in Section 4.3.

**Table 4.3. Applied analysis methods for Sections 7.1 – 7.11 either as a function of the applied voltage \((U)\) or the SED.**

<table>
<thead>
<tr>
<th>Sections</th>
<th>QMS</th>
<th>MCA</th>
<th>( U ) / ( SED )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Section 7.1</td>
<td>Mass spectra</td>
<td>–</td>
<td>( U )</td>
</tr>
<tr>
<td>Section 7.2</td>
<td>( O_2 )</td>
<td>n-butane</td>
<td>( U )</td>
</tr>
<tr>
<td>Section 7.3</td>
<td>toluene</td>
<td>–</td>
<td>( U )</td>
</tr>
<tr>
<td>Section 7.5</td>
<td>( CO_2 )</td>
<td>n-butane</td>
<td>( U )</td>
</tr>
<tr>
<td>Sections 7.7 – 7.8</td>
<td>–</td>
<td>n-butane, ( CO_2 ), ( CO )</td>
<td>( U )</td>
</tr>
<tr>
<td>Sections 7.9 – 7.11</td>
<td>NO, ( NO_2 ), ( O_3 )</td>
<td>n-butane, ( CO_2 ), ( CO )</td>
<td>( SED )</td>
</tr>
</tbody>
</table>

### 4.4.6 Camera Set-Up

The photographs of all set-ups and of the plasma shown in Section 7.5 were taken with a Nikon D5300 with an AF-D DX VR Zoom-Nikkor 18-55mm f/3.5-5.6G. All photographs were taken in automatic mode.

For the photographs shown in Section 7.12 a Sony ILCE-6300 with a Sigma 30mm f/1.4 DC
DN Contemporary was used. Here, all photographs were taken with an exposure time of 10 s, a sensitivity of ISO100, and an aperture of f/8.0. The post processing of all pictures was executed using RawTherapee 5.8.

### 4.5 Photocatalytic Oxidation

The photocatalytic oxidation of n-butane, which is presented in Section 7.14, was carried out with the photoreactor shown in Figure 4.10. The reactor was made of stainless steel and equipped with catalyst-coated quartz glass plates (100 mm × 150 mm × 2 mm), and used in the plasma flow set-up. To enable the irradiation with light the lid of the reactor was also made of quartz glass. Between the catalyst coating and the quartz lid there was a gap of 1 mm for a gas flow of 1 L min⁻¹. The reactor was heated with the custom-made heating plate which is described in Section 7.6.1. The air-cooled light-emitting diode (LED) panel (λ = 368 nm) was made of 5 × 6 LEDs with an applied power of 2.22 W. The power output was measured with the THORLABS PM100D with a THORLABS S175C sensor. The mixture was as in Section 4.4 made out of 20.5% O₂, 79.5% N₂, and 300 ppm n-butane. The irradiation was performed until a steady state was reached. The plate was coated with 3 mg cm⁻² of SrTiO₃.

![Figure 4.10. Photoreactor with heating plate and air-cooled LED array.](image-url)
Experimental
5 Catalyst and Plasma Characterization

A detailed characterization of the $\alpha$-MnO$_2$ catalyst had been performed in our group before.[6,24] Elemental analysis showed a residual potassium (K) content of 4.6 wt%. This residual K was found to be necessary to form $\alpha$-MnO$_2$, because K has a stabilizing effect on the $\alpha$-MnO$_2$ tunnel structure.[24,128] Furthermore, X-ray photon spectroscopy (XPS) and temperature-programmed reduction (TPR) with H$_2$ and CO were performed for a deeper insight in the catalyst behavior.

For the reproduced catalyst only a few characterization methods were applied reported in Sections 5.1 – 5.3.

5.1 N$_2$ Physisorption Results

The N$_2$ adsorption and desorption isotherms derived for the reproduced catalyst are shown in Figure 5.1a. An H3 hysteresis loop was found indicating plate-like particles and loose agglomerates.[24,187] The specific surface area was 37 m$^2$ g$^{-1}$ with a pore volume of 0.19 cm$^3$ g$^{-1}$. These results are in good agreement with the ones presented by Ollegott et al.,[24] while the pore size distribution (Figure 5.1b) showed a different trend. The maximum of the pore size is shifted from 22 nm to now 43 nm.

![Figure 5.1. (a) Adsorption and desorption isotherms for $\alpha$-MnO$_2$. (b) BJH plot for $\alpha$-MnO$_2$.](image-url)
5.2 X-ray Diffraction Results

The calcination temperature of 460 °C (Section 4.1) was chosen according to Equation 2.14. An in situ XRD measurement was performed in ambient air to confirm the optimal calcination temperature for the formation of $\alpha$-MnO$_2$. The measurement was carried out in the temperature range of 25 °C to 800 °C with steps of 25 °C and a control measurement at 25 °C at the end. Figure 5.2a shows the in situ XRD patterns as top view of a 3D visualization. More intense red indicates more intense reflections. The first reflections of $\alpha$-MnO$_2$ were observed at 375 °C and there were no reflections of other phases until 525 °C. At higher temperatures the formation of $\alpha$-Mn$_2$O$_3$ was observed. There is a slight shift of the reflections attributed to the high temperatures. This measurement confirms the transition temperature of Equation 2.14 and also the calcination temperature of 460 °C as suitable for the manganese oxide catalyst.

The XRD pattern of the reproduced catalyst (Figure 5.2b) shows the formation of phase-pure $\alpha$-MnO$_2$ as reported by Ollegott et al.\[24\]

![Figure 5.2](image)

Figure 5.2. (a) In situ XRD pattern in a temperature range of 25 °C to 800 °C in steps of 25 °C. (b) XRD pattern of the reproduced catalyst.

5.3 Transmission Electron Microscopy Results

TEM images were made in addition to the SEM images presented by Ollegott et al.\[24\] In Figure 5.3 the TEM images with a magnification of $1 \cdot 10^6$, $5 \cdot 10^6$, and $10 \cdot 10^6$ are shown. In contrast to the SEM images of Ollegott et al.\[24\] the TEM images show no agglomerates but single crystallites. The size of these crystallites is in a range of 30 nm to 100 nm, which is in a similar range as the particle size observed by SEM and the derived particle size from XRD.
using the Scherrer equation by Ollegott et al.\textsuperscript{[24]}

Analyzing the lattice plane distances of the sample using Figure 5.3c shows a distance of 0.47 nm. This is in good agreement with lattice plane distances of 0.49 nm found in literature for the $\alpha$-MnO$_2$ tunnel structure.\textsuperscript{[188,189]}

![Figure 5.3. $\alpha$-MnO$_2$ at three different magnification levels in a TEM.](image)

5.4 Surface Evaluation of $\alpha$-MnO$_2$-Coated Alumina Plates

Alumina plates coated with $\alpha$-MnO$_2$ were analyzed using a LSM. Three plates were coated with 0.19 mg cm$^{-2}$, 0.75 mg cm$^{-2}$, and 3 mg cm$^{-2}$ of $\alpha$-MnO$_2$. In Figure 5.4 the catalyst distribution and the surface structure are shown. For each of the coatings a light microscope image is shown. In addition, heat maps of the same area were made with the LSM illustrating the relative height of the coatings. The light microscope images reveal that the coated area is increasing with higher loading. For the loading of 0.19 mg cm$^{-2}$ there are separated island-like catalyst-coated regions. These regions are connected for the loading of 0.75 mg cm$^{-2}$ with a coated area of approx. 50%. At last, for the highest loading nearly full coverage of the alumina plate with few uncoated regions is observed.

From the heat maps of the LSM images the heights of the coatings were derived. The average heights of the coatings are summarized in Table 5.1. The heights are independent of the loading in a range of 10.4 µm to 10.7 µm.
Figure 5.4. Light microscope and LSM images of alumina plates with different loadings of $\alpha$-MnO$_2$.

Table 5.1. Averaged heights of the coating for different loadings of $\alpha$-MnO$_2$.

<table>
<thead>
<tr>
<th>Loading (mg cm$^{-2}$)</th>
<th>Height (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.19</td>
<td>10.6</td>
</tr>
<tr>
<td>0.75</td>
<td>10.7</td>
</tr>
<tr>
<td>3</td>
<td>10.4</td>
</tr>
</tbody>
</table>

5.5 Characterization of the Electrical and Flow Behavior of the Plasma-Assisted Oxidation

The twin-SDBD was introduced and characterized by Offerhaus et al.[49] and Kogelheide et al.[174] with respect to the plasma parameters, power densities, and scalability. Schücke et al.[184] performed studies on the dissipated power as a function of the applied voltage, pulse repetition frequency, and VOC mole fraction and on the formation of by-products from different VOCs. Studies on the flow behavior in the SDBD reactor using Schlieren imaging were carried out by Ollegott et al.[171]. Therefore, only a brief introduction to the electrical characterization and to the flow behavior is shown here. For all measurements the high voltage was applied as a pulsed damped sine wave as shown in Figure 5.5a. The pulse repetition frequency ($f_{\text{pul}}$) was set to 4 kHz as described in Section 4.4.2, but the eigenfrequency of 86 kHz was a result of the inductance of the high-voltage transformers secondary winding and the capacitance of the electrode configuration and is independent of the adjusted pulse repetition frequency. The plasma ignition takes place during the first few half-waves of each pulse. The spikes in the cur-
The flow behavior in the SDBD reactor was investigated using Schlieren imaging.\textsuperscript{[171]} In Figure 5.6 Schlieren images are shown of synthetic air using a flow of 10 L min\textsuperscript{-1} and different applied voltages. These images were obtained with the revised reactor introduced in Section 7.6. For all applied voltages there were schlieren occurring with increasing intensity. The points of origin of the schlieren were at the positions of the grid lines perpendicular to the flow direction. For a couple of measurements described in Sections 7.2 – 7.3 the formation of tar-like deposits was observed. These deposits were covering the electrode configuration. After dismantling of the reactor the deposits were also found on the inner wall of the reactor across from the electrode configuration displaying a negative image of the grid line of the electrode configuration.
(Figure 5.7). In addition, measurements by Schücke et al.\textsuperscript{[184]} delivered insights in the flow behavior in the reactor. For some of the oxidized VOCs full conversion was achieved. The Schlieren images, the pollutant deposition, and the results shown by Schücke et al.\textsuperscript{[184]} indicate a strong influence of the plasma ignition on the flow behavior in the reactor. This mixing perpendicular to the flow direction enables high degrees of conversion despite the large difference in dimension of reactor volume and the volume filled with plasma.

![Figure 5.7. Deposits on the inner wall of the reactor displaying a negative image of the grid lines.](image)
6 Thermocatalytic Conversion of n-Butane

6.1 Simultaneous Oxidation of n-Butane and CO over Different Loadings of MnO₂

Ollegott et al. [24] investigated the utilized α-MnO₂ catalyst with respect to its activity for thermal CO oxidation (2% CO / 2% O₂). The formation of CO as one major product during the oxidation of VOC in plasma-assisted applications is known in literature. [64] Therefore, the thermocatalytic activity of α-MnO₂ for the simultaneous oxidation of n-butane and CO in synthetic air was investigated in this work.

Figure 6.1a shows the oxidation of 300 ppm n-butane and 1% CO in synthetic air over 1 mg cm⁻² (m_total = 50 mg) of α-MnO₂ with heating rates of 5 K min⁻¹ and 1 K min⁻¹. The heating rate variation was carried out to investigate its influence on the oxidation behavior. For the n-butane mole fraction only a minor influence of the heating rate on the activity is observable with a slight shift of the 1 K min⁻¹ measurement to higher temperatures. For both measurements the mole fraction of n-butane decreased in a single step. The oxidation of CO showed for both heating rates the same behavior until 230 °C. Then for both heating rates a second stage is observed. This stage is more pronounced for the 1 K min⁻¹ measurement, which showed lower activity. The second stage may indicate two different active sites on the catalyst for the oxidation of CO. Full CO conversion is reached at 450 °C for both heating rates. The CO₂ plot shows the mole fraction of formed CO₂ for both oxidations. Based on this, a carbon balance of >98% was obtained for both heating rates. The comparison of the heating rates showed that all observations can be made independent of the heating rate albeit less pronounced for 5 K min⁻¹. Therefore, for all measurements a heating rate of 5 K min⁻¹ was chosen, because it allows a faster workflow.

Figure 6.1b shows three measurements over 0.2 mg cm⁻² of α-MnO₂ (m_total = 10 mg). The red graph shows the simultaneous oxidation of n-butane and CO, the yellow graph the oxidation of only n-butane, and the blue graph the oxidation of only CO as described in Figure 4.6. The oxidation of n-butane in the presence of CO shows higher activity than the oxidation without CO. In presence of CO the same degrees of n-butane conversion were reached 17 °C to 36 °C below the temperatures without CO during the heating. A degree of conversion of 50% was achieved at temperatures (T₅₀) of 435 °C for n-butane with CO and 450 °C without CO. Once 450 °C was reached a higher degree of conversion was achieved in the absence of CO, namely
58% without and 55% with CO. The degree of CO conversion in the absence of n-butane was higher and temperature differences for the same degree of conversion in a range of 40 °C to 100 °C were observed. The degree of CO conversion in the absence of n-butane was higher and temperature differences for the same degree of conversion in a range of 40 °C to 100 °C were observed. The differences are intensified by the two stages observed for CO oxidation. The highest degree of CO conversion at 450 °C was achieved for the measurement with only one reactant as shown for n-butane. Degrees of CO conversion of 50% and 63% were achieved in the presence of n-butane and without n-butane, respectively. T_{50} of CO with both reactants was 450 °C and without n-butane 399 °C. During the temperature plateau at 450 °C the CO mole fraction is slightly increasing indicating a decrease of activity during the measurement. However, the reproduced measurements showed that this was no permanent deactivation. The mole fraction of CO\textsubscript{2} reveals a high selectivity to CO\textsubscript{2} and a carbon balance of >95%.

The same measurements are shown in Figure 6.2a over 1 mg cm\textsuperscript{-2} of α-MnO\textsubscript{2} (m_{total} = 50mg). The n-butane plot shows an increased difference between the n-butane mole fractions depending on the presence of CO. The same degrees of n-butane conversion were
Thermocatalytic Conversion of n-Butane

Figure 6.2. (a) Oxidation of n-butane and CO in different compositions over 1 mg cm$^{-2}$ of $\alpha$-MnO$_2$. (b) Oxidation of n-butane and CO in different compositions over 3 mg cm$^{-2}$ of $\alpha$-MnO$_2$.

reached in presence of CO 17°C to 33°C below the temperatures without CO during the heating. T$_{50}$ of n-butane with both reactants was 322°C and without CO 339°C. Both measurements achieved a degree of n-butane conversion of 96% at 450°C. For the oxidation of CO the difference between the mole fractions is also increased up to a difference of 80°C. T$_{50}$ of CO with both reactants was 247°C, and without n-butane it was 208°C. In contrast to Figure 6.1b and the measurement with n-butane and CO, the measurement without n-butane shows only one stage for the CO oxidation. This observation indicates that the more active sites are sufficient to oxidize all CO in the absence of n-butane, but with n-butane some of these sites are occupied leading to the necessity of the less active sites to achieve full conversion. Full conversion of CO without the presence of n-butane was achieved at 318°C and with both reactants at 404°C. With 1 mg cm$^{-2}$ catalyst a carbon balance >97% can be derived from the mole fractions of CO$_2$.

A coating with 3 mg cm$^{-2}$ catalyst ($m_{total} = 150$ mg) was investigated as the highest loading as shown in Figure 6.2b. The gap between both measurements visible in the n-butane plot reveals the same degrees of conversion in presence of CO 20°C to 25°C below the measurement.
without CO. \( T_{50} \) of n-butane with both reactants was 253 °C, and without CO it was 278 °C. Reaching \( T_{95} \) at 339 °C and full conversion at 398 °C for both measurements. The degree of CO conversion was further shifted to lower temperatures with \( T_{50} \) of CO with both reactants of 153 °C and without n-butane 133 °C. Now for both measurements only one stage is observed indicating no disturbance of CO conversion by occupation of the more reactive sites by n-butane. Full conversion of CO without the presence of n-butane was achieved at 174 °C and with both reactants at 196 °C. The mole fraction of CO \(_2\) reveals a high selectivity to CO \(_2\) and a carbon balance of >97% for each of the measurements.

The simultaneous oxidation of n-butane and CO over different loadings of \( \alpha \)-MnO\(_2\) showed a higher activity for the oxidation of n-butane in the presence of CO and a shift to lower temperatures with an increasing amount of catalyst. In contrast, the oxidation of CO is less efficient in the presence of n-butane. Furthermore, the different amounts of catalyst indicate two CO oxidation pathways at different temperatures. At 174 °C full conversion of CO was achieved, but the degree of n-butane conversion was 11%, which is highly beneficial for the oxidation of formed CO during the plasma-assisted oxidation of n-butane at low temperatures.

### 6.2 Variation of the Coated Area and Determination of the Activation Energy

The investigation of the reactions over thin catalyst coatings enables a simple control of the residence time of the reactant over the catalyst by variation of the coated area. Therefore, four plates were coated with a loading of 3 mg cm\(^{-2}\) of \( \alpha \)-MnO\(_2\). One plate was fully, one \( \frac{3}{4} \), one \( \frac{1}{4} \), and one \( \frac{2}{4} \) coated, resulting in catalyst amounts of 150 mg, 112.5 mg, 75 mg, and 37.5 mg, respectively (Figure A.5). These plates were compared to a packed-bed reactor with 37.3 mg and 18.7 mg catalyst. The measurements were carried out in a range of 40 °C to 450 °C and a heating rate of 5 K min\(^{-1}\) with 300 ppm n-butane in synthetic air.

With these measurements the apparent activation energy (\( E_A \)) for the oxidation of n-butane was derived using the Arrhenius equation (Equation 6.1). It describes the temperature dependence of the rate constant (\( k \)) of a chemical reaction.

\[
k = A \cdot e^{-\frac{E_A}{RT}}
\]  

(6.1)
Here, $A$ is the pre-exponential factor, $E_A$ the apparent activation energy, $R$ the universal gas constant, and $T$ the temperature. For the determination of the rate constant $k$ the power-law rate equation is used (Equation 6.2).

$$r_{n\text{-butane}} = k \cdot y_{n\text{-butane}}^l \cdot y_{O_2}^m$$  \hspace{1cm} (6.2)

Here, $r_{n\text{-butane}}$ is the reaction rate, $y$ is the mole fraction of the reactant, $l$ is the formal reaction order of n-butane, and $m$ is the formal reaction order of $O_2$. For the experimental determination of $E_A$ the Arrhenius equation is inserted in the power law and transposed to the natural logarithmic form (Equation 6.3).

$$\ln(r) = -E_A \cdot (RT)^{-1} + \ln(A) + l \cdot \ln(y_{n\text{-butane}}) + m \cdot \ln(y_{O_2})$$  \hspace{1cm} (6.3)

For low degrees of conversion $\ln(A) + l \cdot \ln(y_{n\text{-butane}}) + m \cdot \ln(y_{O_2})$ is considered constant. Therefore, the slope of the Arrhenius plot ($\ln(r)$ as function of $T^{-1}$) yields the apparent activation energy. The reaction rate is accessible according to Equation 6.4.

$$r_{n\text{-butane}} = \dot{V} \cdot V_m^{-1} \cdot X_{n\text{-butane}} \cdot y_{n\text{-butane},0}$$  \hspace{1cm} (6.4)

Here, $\dot{V}$ is the volumetric flow rate, $V_m$ the molar volume, $X_{n\text{-butane}}$ the degree of n-butane conversion, and $y_{n\text{-butane},0}$ the initial n-butane mole fraction. For the analysis the degrees of n-butane conversion were taken during the heating and not from steady temperature plateaus. As shown in Section 6.1 a heating rate of 5 K min$^{-1}$ was sufficiently low to achieve quasi-steady state. The analysis was carried out in a conversion range of 2% to 10%.

In Figure 6.3a the four plate-reactor and the two packed-bed reactor measurements are shown. The temperatures for degrees of conversion of 95%, 50%, and 5% are summarized in Table 6.1. The four coated-plate measurements show all the same trends: shifts to higher temperatures for the same degree of conversion with decreasing coated area. The measurements of the packed beds show overall higher activities. The 44-plate was coated with the same amount of catalyst as the 37.3 mg packed bed, but the $T_{50}$ shows a difference of 58 °C. The $T_{50}$ of the other packed bed (18.7 mg) is similar to the 44-plate with 4/8 of the catalyst amount. The measurements show a large difference in conversion comparing a plate reactor to a packed-bed reactor. This may indicate a strong influence of the flow conditions. In the packed-bed reactor presumably ideal plug-flow conditions are predominant, whereas in the plate reactor laminar flow over the coating dominates. Furthermore, during the coating overspraying may have led to a different amount of catalyst on the plate than expected and the spraying procedure may have had influence on the catalyst.
Thermocatalytic Conversion of n-Butane

Figure 6.3. (a) Oxidation of n-butane over $\alpha$-MnO$_2$ comparing different coated plates in a plate reactor to a packed-bed reactor. (b) Arrhenius plot of four coated plate and two packed bed measurements.

The Arrhenius plots derived from the measurements are shown in Figure 6.3b. The slopes and the resulting apparent activation energies are summarized in Table 6.1. The apparent activation energies of the coated plates increase with decreasing coated area in a range of 49.3 kJ mol$^{-1}$ to 57.6 kJ mol$^{-1}$. For the packed beds activation energies of 58.3 kJ mol$^{-1}$ and 44.5 kJ mol$^{-1}$ for 37.3 mg and 18.7 mg were found, respectively. The shift to smaller $E_A$ for a higher amounts of catalyst coating for the plate reactor may show the presence of a larger number of more active sites. However, this contradicts the trend for $E_A$ of the packed bed. This evaluation of $E_A$ takes only into account the degrees of conversion below 10%. Therefore, the expected trends for the apparent activation energies considering $T_{50}$ values may not fit the calculated apparent activation energies.

Table 6.1. Temperatures for degrees of conversion of 5%, 50%, and 95% of coated plates with different coverage and different packed beds and the derived apparent activation energies.

<table>
<thead>
<tr>
<th></th>
<th>Plate reactor</th>
<th></th>
<th>Packed bed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4/4</td>
<td>3/4</td>
<td>2/4</td>
</tr>
<tr>
<td>$T_5$ / °C</td>
<td>187</td>
<td>199</td>
<td>207</td>
</tr>
<tr>
<td>$T_{50}$ / °C</td>
<td>274</td>
<td>287</td>
<td>296</td>
</tr>
<tr>
<td>$T_{95}$ / °C</td>
<td>337</td>
<td>374</td>
<td>384</td>
</tr>
<tr>
<td>Slope</td>
<td>$-5933.7$</td>
<td>$-6334.5$</td>
<td>$-6374.1$</td>
</tr>
<tr>
<td>$E_A$ / kJ mol$^{-1}$</td>
<td>49.3</td>
<td>52.7</td>
<td>53.0</td>
</tr>
</tbody>
</table>
7 Catalyst-enhanced Plasma Conversion of Volatile Organic Compounds

The behavior of the discharge was investigated first without catalyst, followed by different coated electrode configurations and measurements at elevated temperature. The results of these basic measurements led gradually to a reliable method for catalyst-enhanced plasma investigations, which are described in the following.

7.1 Identification of Products by Mass Spectrometry

The number of different potential reactions induced by the plasma taking place especially with organic compounds in the gas mixture can lead to a high number of possible by-products. Therefore, mass spectra were recorded by a QMS which are shown in Figure 7.1. These mass spectra may deliver information about formed products by the plasma-induced n-butane oxidation (Equation 7.1). The mass spectra were recorded in a mass-to-charge ratio (m/z) range of m/z = 1 to m/z = 130. Figure 7.1a shows the recorded mass spectra. The first mass spectrum was just of N\textsubscript{2} followed by spectra with added O\textsubscript{2} and n-butane without plasma. The fourth spectrum was measured using N\textsubscript{2}, O\textsubscript{2}, n-butane, and plasma with an applied voltage of 10 kV.

\[
C_4H_{10} + 6.5 O_2 \rightarrow 4 CO_2 + 5 H_2O
\]  

(7.1)

All of these spectra show signals at the expected mass-to-charge ratios for the corresponding gas composition. For the mass spectrum with plasma also peaks are observed indicating product formation e.g. \(m/z = 44\), which were not detected before. Nevertheless, the precise identification of newly occurring peaks is challenging with so many pronounced and different peaks. Therefore, in Figure 7.1b the difference of both spectra is shown. This spectrum can be utilized for the identification of potential products. For the identification only molecules were considered containing N, O, H, and C. Negative peaks which originated from the decreasing mole fraction of N\textsubscript{2}, O\textsubscript{2}, and n-butane were cut off (m/z = 14, 16, 26, 27, 28, 29, 39, 41, 43, and 58). The positive peaks indicate increasing intensities at mass-to-charge ratios by the plasma treatment. Among these mass-to-charge ratios some are unique and indicate the occurrence of specific species like hydrogen (m/z = 1 and m/z = 2), carbon (m/z = 12), and ozone (m/z = 48). The peaks at m/z = 17 and m/z = 18 indicate the formation of water, which is expected for the total oxidation of hydrocarbons in synthetic air. Nevertheless, the intensity ratio of m/z = 17 to m/z = 18 is reported in literature to be 2:10 for water.\[^{183}\] The intensity ratio in Figure 7.1b is 2.5:10.
Figure 7.1. (a) Analog scans of gas streams with pure N$_2$, synthetic air, synthetic air with n-butane, and synthetic air with n-butane and plasma. (b) The positive peaks of a difference scan of synthetic air with n-butane subtracted from synthetic air with n-butane and plasma reveal molecules produced by the plasma.

The higher intensity of $m/z = 17$ may indicate the presence of ammonia in the gas stream, but the second intense peak of ammonia ($m/z = 16$) was cut off and therefore can neither validate nor exclude the formation of NH$_3$. The peak at $m/z = 30$ may indicate the formation of NO or ethane. The other characteristic peaks for both species are cut off and cannot validate the occurrence of either. The occurrence of $m/z = 44$ is obviously due to CO$_2$. NO$_2$ and ethanol are possible molecules for $m/z = 46$. However, the characteristic mass spectrum of ethanol shows the presence of $m/z = 45$ and $m/z = 31$, which both are not observed. Therefore, $m/z = 46$ strongly suggests the presence of NO$_2$. The last occurring peak is $m/z = 76$, which may indicate the presence of dinitrogen trioxide (N$_2$O$_3$). N$_2$O$_3$ is formed in the gas phase in the presence of NO and NO$_2$ according to Equation 7.2, supporting the assumption that $m/z = 30$ indicates the formation of NO.$^{[138]}$ The presence of atomic N and C in the plasma may also lead to the formation of hydrogen cyanide (HCN), but the cut signals are characteristic peaks necessary for the identification of HCN ($m/z = 26$ and $m/z = 27$). The reference spectra used for identification of the characteristic peaks are taken from NIST$^{[183]}$ shown in Appendix A (Figure A.8).

\[
\text{NO}(g) + \text{NO}_2(g) \xrightleftharpoons{} \text{N}_2\text{O}_3(g) \quad (7.2)
\]

The mass spectra reveal that no organic by-products are detected in the range of $m/z = 1$ to $m/z = 130$. It has to be mentioned that by-products with higher mass-to-charge ratios such as long-chain hydrocarbons would not be detected with this measurement settings and presumably not even reach the QMS. The low vapor pressure of such by-products may have led to conden-
sation on the reactor and tubing walls. The influences of NO, NO\textsubscript{2}, or O\textsubscript{3} are discussed further in Section 7.11.

### 7.2 Degrees of n-Butane Conversion under Initial Condition Variations

In addition to the mass spectra the degrees of n-butane conversion were investigated under variation of the initial conditions. In the beginning, measurements were carried out with different mole fractions of n-butane in a range of 50 ppm to 450 ppm n-butane in synthetic air with a pulse repetition frequency of 4 kHz shown in Figure 7.2a. The applied voltage was in the range of 8 kV to 12 kV. Below 8 kV there was no stable ignition of the plasma, and above 12 kV the risk of an electrical breakdown, due to high thermal load was too high. The degree of conversion shows no significant dependence on the mole fraction of n-butane in the investigated range. The degree of conversion is increasing linearly with the applied voltage up to approx. 40\% at 12 kV. In Appendix A the same measurement is shown with a pulse repetition frequency of 2 kHz (Figure A.6). Because of the smaller pulse repetition frequency the maximum applied voltage was increased to 13 kV without risking a electrical breakdown due to high thermal load. There the degree of conversion shows the same behavior, but with smaller degrees of conversion up to approx. 22\% at 13 kV.

In order to further investigate the influence of the plasma on the degradation of n-butane, a near stoichiometric mixture of 450 ppm n-butane and 3700 ppm O\textsubscript{2} was used. The decreased mole fraction of oxygen led to stable ignition of the plasma already at 7 kV. Therefore, the degrees of conversion of n-butane and oxygen were measured for applied voltages of 7 kV to 12 kV and a pulse repetition frequency of 4 kHz. The results are shown in Figure 7.2b. The degree of conversion increases linearly as a function of the applied voltage similar to Figure 7.2a. As also shown by Guo et al.,\cite{99} the degree of conversion increases with lower oxygen mole fractions and therefore a degree of conversion of 53\% was achieved at 12 kV. Comparing the degree of O\textsubscript{2} conversion a large discrepancy is found. The degree of O\textsubscript{2} conversion is only half of the degree of n-butane conversion indicating that part of the achieved conversion originated from decomposition processes and not from total oxidation to CO\textsubscript{2}. The degree of O\textsubscript{2} conversion can only be examined in stoichiometric measurements, because with 20\% O\textsubscript{2} in synthetic air the mole fraction changes disappear in the experimental noise. In order to examine the extent of the decomposition process taking place, n-butane conversion in pure N\textsubscript{2} was measured (Figure 7.2b). There, a degree of conversion of 35\% was achieved.

The measurements shown in Figure 7.2b were carried out consecutively and after dismantling of the used electrode configuration a brown tar-like deposit was found on the surface similar
Figure 7.2. (a) Degree of n-butane conversion for mole fractions of n-butane in the range of 50 ppm to 450 ppm in synthetic air with applied voltages in the range of 8 kV to 12 kV and a pulse repetition frequency of 4 kHz. (b) Degree of conversion of n-butane and oxygen in a near stoichiometric mixture and the degree of conversion of n-butane in pure nitrogen, both with applied voltages of 7 kV to 12 kV and a pulse repetition frequency of 4 kHz.

to the one shown in Figure 7.3b in the following section. It was not possible to investigate the products formed by this decomposition, because these deposits were not observed for synthetic air even after several hours of plasma treatment. In order to prevent further deposition no other measurements were carried out with oxygen mole fraction other than 20%. Based on these results a mole fraction of 300 ppm of n-butane and a pulse repetition frequency of 4 kHz were chosen in the following n-butane oxidation measurements.

7.3 Plasma Treatment of Liquid Volatile Organic Compounds

The set-up was modified for the plasma treatment of liquid VOCs as described in Section 4.4.1. Toluene was chosen as first liquid VOC, because toluene is frequently chosen in literature. Figure 7.3a shows the degree of toluene conversion in synthetic air using 300 ppm toluene with pulse repetition frequencies of 4 kHz, 3 kHz, and 2 kHz and 1000 ppm with 4 kHz. The applied voltages range from 8 kV to 12 kV. The degree of conversion shows the same trends as in the oxidation of n-butane with a linear increase for higher voltages and a decrease in conversion for lower frequencies, but the increase in conversion for higher voltages or frequencies is more pronounced compared with the treatment of n-butane. The conversion at 4 kHz increases from 17% at 8 kV to 69% at 12 kV, which is about 30% higher than for n-butane at 12 kV. The degree of conversion with 2 kHz is in the same range as n-butane at 4 kHz. In contrast to Sec-
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Figure 7.3. (a) Degree of toluene conversion in synthetic air for applied voltages of 8 kV to 12 kV at 2 kHz and 3 kHz with 300 ppm and at 4 kHz with 300 ppm and 1000 ppm. (b) Electrode configuration with tar-like deposit after synthetic air treatment containing toluene with air flow from left to right.

At section 7.2 the degree of conversion decreases with a higher mole fraction of toluene from 69% using 300 ppm to 57% for 1000 ppm, although the total amount of converted toluene is still higher for the 1000 ppm measurement.

After several measurements with toluene, especially with 1000 ppm, there was a significant amount of a brown deposit with a tar-like consistence on the electrode configuration as shown in Figure 7.3b and in the tubing of the set-up. The treated gas passed from left to right over the electrode configuration. It immediately becomes clear that there is an uneven distribution of the deposit on the surface of the electrode configuration. Wherever the electrode configuration is polluted, there is a gap between the deposit and the grid line. This observation may indicate either that the plasma produces such an oxidizing environment next to the grid line in the discharge zone that the deposit is immediately totally oxidized, or the induced flow (Section 5.5) of the plasma prevents the area next to the grid line from polluting it in the first place. The higher degree of pollution in the corners of the squares may indicate the latter, because a deposit flow from two sides may increase the amount of pollution in the converging area. At the entry side of the electrode configuration (left) there is less deposit observed, but it is evenly distributed in patches over the whole width of the electrode configuration. Similar to the unpolluted areas near the grid line, this may indicate a flow behavior influenced by the plasma, which carries away the pollution or the plasma is less oxidizing and therefore leads to less deposits.

The second quarter of the electrode shows the highest amount of deposit, which is most evenly distributed. In the second half of the electrode the amount of deposit is gradually decreasing in the upper right corner of the grid, whereas on the lower right corner the amount of deposit...
stays high. The distribution of the deposition indicates an uneven ignition of the plasma either according to the induced flow or the oxidizing behavior. Furthermore, less oxidizing conditions may have produced the tar-like deposits which then were removed under more oxidizing conditions in a later process. Nevertheless, this electrode configuration was coated by the deposits under uncontrolled conditions and therefore conclusions from the deposits distribution should be taken with care.

The formation of the deposits may originate from the higher tendency of soot formation by aromatics (toluene) than by alkanes (n-butane). Soot formation consists of several steps as shown in Figure 7.4. The formed precursors can react with one another and form tars or decompose further forming nuclei which then agglomerate. A pyrolysis-GC-MS measurement was made of the deposit. The mass spectrometer was not calibrated and only delivered a rough estimation of the components of the deposits. The chromatogram with possible components is shown in Appendix A (Figure A.6b).

Overall, these measurements show a successful implementation of the saturator for the plasma treatment of liquid VOCs. For toluene a high degree of conversion for a lower mole fraction was achieved. Nevertheless, due to the formation of tar-like deposits, which were deposited on the electrode configuration and the tubing of the set-up, further usage of the saturator and consequently the conversion of toluene was postponed until total oxidation without organic by-products can be ensured.

Figure 7.4. Schematic illustration of the formation of soot particles from gas phase VOCs to agglomerates. During each of the steps total oxidation to CO\textsubscript{2} can take place. Adapted from, with permission from Elsevier.

### 7.4 Computational Fluid Dynamics

Computational fluid dynamics (CFD) is a numerical approach to simulate the flow behavior of fluids. The flow of the liquid is simulated in a 3D model of the investigated component. The 3D model of the plasma reactor was constructed using the computer-aided design (CAD) program "Autodesk® Inventor™". This 3D model then was used by "Autodesk® CFD" to simulate the flow behavior of air. CFD simulations produce images visualizing the flow velocity and direction. The used programs are useful to gain a first impression of the flow behavior, but should be taken with care in terms of detailed insight into the processes.

In Figure 7.5 five different visualizations of the same simulation are shown. This simulation was
carried out at RT and without plasma with 10 L min\(^{-1}\) of air entering the reactor model from a 1/4 inch tubing with a colored scale showing the velocity in a range of 0 cm s\(^{-1}\) to 60 cm s\(^{-1}\). The first two images show a flat cross-section which illustrates the flow velocity and flow direction vectors 5 mm below the electrode configuration as top and side view. The third image is a flat cross-section perpendicular to the electrode configuration in the middle of the reactor, and the last two images show the trajectory of 50 single particles entering the reactor. All these images illustrate high velocity and turbulent behavior of the gas entering the reactor. Especially the trajectory images show several changes in direction. Nevertheless, in all images the calculated velocity is between 5 cm s\(^{-1}\) and 25 cm s\(^{-1}\) in the area of the electrode configuration, and that there is laminar flow behavior until the end of the reactor is reached.

The laminar flow in the area of the electrode configuration suggests that conversion can only take place near the electrode configuration, but as described in Section 5.5 full conversion can be achieved despite the unfavorable flow behavior without plasma. This indicates a significant influence of the plasma on the fluid dynamics in the reactor.

Figure 7.5. CFD images from different angles and in different forms of representation with coloring scale in a range of 0 cm s\(^{-1}\) to 60 cm s\(^{-1}\).
7.5 Influence of the Coating Geometry on the Figures of Merit

7.5.1 Fully Coated and Half-Coated Electrode Configuration

In order to enhance the degree of conversion shown in Section 7.2 the electrode configuration was coated with $\alpha$-MnO$_2$. The straightforward way of coating is a full coverage of both sides of the electrode configuration with catalyst as shown in Figure 7.6a. Three different loadings of catalyst were tested (0.1875 mg cm$^{-2}$, 0.75 mg cm$^{-2}$, and 3 mg cm$^{-2}$). The ignition behav-

![Figure 7.6](image)

Figure 7.6. Fully coated and half-coated electrode configurations with $\alpha$-MnO$_2$. The gas mixture flowed from left to right in all images. (a) Fully coated electrode configuration with 0.75 mg cm$^{-2}$. (b) Fully coated electrode configuration with 0.75 mg cm$^{-2}$ and plasma after several minutes. (c) Fully coated electrode configuration with 3 mg cm$^{-2}$ only showing the spot where plasma ignition takes place. (d) Half-coated electrode configuration with 3 mg cm$^{-2}$. (e) Half-coated electrode configuration with 0.75 mg cm$^{-2}$ with plasma ignition in the coated and the uncoated area. (f) Half-coated electrode configuration with 3 mg cm$^{-2}$ with plasma ignition in the uncoated area and at the edge of the coating.
ior after several minutes of the 0.75 mg cm$^{-2}$ coating is shown in Figure 7.6b. The ignition started first at the far left and far right ends of the grid and then the ignited area grows more and more towards the middle of the grid until the shown state was reached. The 3 mg cm$^{-2}$-coated electrode configuration showed no ignition of plasma except as shown in Figure 7.6c in the contacting area where the catalyst was removed to ensure a conductive connection. The degrees of n-butane conversion and the selectivities to CO$_2$ of the fully coated electrode configurations are shown in Figure 7.7a. The figures of merit are compared to those of an uncoated electrode configuration. The degree of conversion for the uncoated electrode configuration increased linearly from 13% to 53% with a selectivity to CO$_2$ between 46% and 52% for a voltage range of 8 kV to 12 kV. The degree of conversion of the 0.1875 mg cm$^{-2}$ coating was slightly higher at 8 kV, but besides the lowest voltage the degree of conversion for the other applied voltages was about 2% to 8% lower than for the uncoated electrode configuration. In contrast, the selectivity to CO$_2$ increases slightly to a range between 51% and 55%.

With a coating of 0.75 mg cm$^{-2}$ the degree of conversion is about 5% to 8% lower compared with the uncoated electrode configuration with a selectivity to CO$_2$ of 46% to 49% at the lower voltages and 61% at 12 kV. As expected, there was no conversion of n-butane with the 3 mg cm$^{-2}$ coating, because no plasma ignition took place. Figure 7.6b and Figure 7.6c show a significant disturbance of the plasma by the catalyst coating, which obviously leads to lower conversion. Even though conversion is decreased, the selectivity to CO$_2$ tends to increase in the presence of the catalyst. This demonstrates an influence of the catalyst on the process. Other coating geometries besides fully coated electrode configurations were tested in order to reduce the disturbance of the plasma by the catalyst coating.

The fully coated electrode configurations with loads of 0.75 mg cm$^{-2}$ and 3 mg cm$^{-2}$ were chosen for further testing, because the most pronounced effects were expected for the highest load. α-MnO$_2$ on half of the coated area was dissolved in oxalic acid solution as described in Section 4.2. The 3 mg cm$^{-2}$-half-coated electrode configuration is shown in Figure 7.6d. The 0.75 mg cm$^{-2}$-half-coated electrode configuration with plasma shows undisturbed ignition in the first half of the grid and a more filamented ignition in the second half (Figure 7.6e). The brightness of Figure 7.6b and Figure 7.6e cannot be compared directly because of different exposure settings by the camera. The 3 mg cm$^{-2}$-half-coated electrode configuration with plasma (Figure 7.6f) also shows undisturbed plasma ignition for the uncoated grid and no ignition for the coated grid as before in the fully coated case, but on the edge of the coating a plasma ignition can be observed even though there is no grid line. This may indicate conductive behavior of α-MnO$_2$ at high applied voltages and expansion of the electric field.

The degree of n-butane conversion is again compared in Figure 7.7b with the same uncoated electrode configuration as in Figure 7.7a. Surprisingly, the degree of conversion of the
7.5.2 Coated Impinging Plates with an Uncoated Electrode Configuration

In Section 7.5.1 a substantial disturbance of the plasma by the catalyst coating was shown. Therefore, α-MnO$_2$ was coated on impinging plates above and below the uncoated electrode configuration. The impinging plates had a dimension of 190 mm $\times$ 78 mm $\times$ 0.635 mm and two mounting holes for assembling in the reactor. On both sides of the reactor in the outer windows, polyether ether ketone (PEEK) mountings were placed with threaded holes for the assembly instead of quartz glass. The gap between the electrode configuration and the impinging plates was 7 mm on each side. In Figure 7.8a a mounted impinging plate in a dismantled reactor is
shown. The degree of conversion and the selectivity to CO$_2$ are shown in Figure 7.8b. The measurement *uncoated* in Figure 7.8b was performed with the unused and uncoated electrode configuration also used for the impinging plate measurements and therefore cannot directly be compared to the *uncoated* measurements shown in Figure 7.7. Both figures of merit that is, degree of conversion and selectivity to CO$_2$, are very similar for the three measurements for each applied voltage in a range between 1% and 3%, indicating no influence of the catalyst-coated impinging plates on the process. The most obvious explanation for the unchanged figures of merit seems to be that the catalyst coating is too far away from the plasma zone. The absent activity of the catalyst coated on the impinging plates now indicates no reactivity of the plasma in further regions from the electrode configuration, but influence on the flow behavior above and below the electrode configuration.

### 7.5.3 Mask-Coated Electrode Configuration

Both previous chapters show that a catalyst coating must not disturb the plasma ignition, but should be as close as possible to the ignition zone. Therefore, a mask was manufactured made of stainless steel which also generates a gap between the metal grid line and the catalyst coating of 1.0 mm (Figure 4.3) during the coating. The detailed coating procedure is described in Section 4.2. The mask-coated electrode configuration is shown in Figure 7.9a. In Figure 7.9b the degrees of conversion and the selectivity to CO$_2$ are shown for a coating of 0.75 mg cm$^{-2}$ and 3 mg cm$^{-2}$ compared with an uncoated electrode configuration.
The degree of conversion with mask coating compared with the uncoated electrode configuration is still decreased, which is more pronounced for higher loading of catalyst. With a coating of 0.75 mg cm\(^{-2}\) the degree of conversion is 3% to 8% and with 3 mg cm\(^{-2}\) 3% to 13% smaller. The selectivity to CO\(_2\) for the 0.75 mg cm\(^{-2}\) coating was not increased, but for 3 mg cm\(^{-2}\) the selectivity to CO\(_2\) was significantly increased especially at higher applied voltages up to 92%. Despite the decreasing degree of conversion the mask-coated electrode configuration showed the highest beneficial effect of a coated electrode configuration increasing the selectivity to CO\(_2\) above 90%. Therefore, a new mask was manufactured which produced a gap of 1.5 mm. The results are shown in Section 7.8.

### 7.6 Revised Reactor Design

The reactor design described in Section 4.4.2 had several disadvantages. The reactor was originally designed for occasional changes of the electrode configuration and good optical accessibility through windows for optical characterization methods. Therefore, a slim design was chosen. For a change of the electrode configuration, 54 screws had to be unscrewed and the sealing of the main chamber was interrupted on 16 spots. The interrupted sealing enables a space-saving transition to the sealings from the side windows, which are perpendicular to the main sealing, but this led to a more challenging leak-tight assembly of the reactor. The circular glass panes needed for the windows are more expensive to produce than rectangular glass panes.
Furthermore, the reactor contains several small components which are challenging to reproduce and the used high-voltage feed-throughs were expensive. The aim for a revised version of the reactor design was to remove all disadvantages, keep the advantages, and change as little as possible. The result of this redesign is shown in Figure 7.10a. The reactor is made of aluminum with outer dimensions of 540 mm × 170 mm × 51 mm. The design is more bulky and therefore heavier, but the use of interrupted sealing was avoided using only o-ring sealings. There are two lids build into each other (Figure 7.10d). The main lid closes the whole upper side of the reactor with feed-throughs for thermocouples before and after the electrode configuration. The second lid closes the middle part of the first lid and is directly mounted above the electrode configuration. When optical access is needed, the second lid frames a rectangular quartz glass pane allowing overall view on the upper side of the electrode configuration. For measurements without the necessity of optical access, another lid made of aluminum can be used. For changing of the electrode configuration, just the second lid has to be dismantled, reducing the amount of screws needed to be opened from 54 to 20. Both lids are interchangeable and simplify the adaptation to new demands of future measurements (e.g. more thermocouples or different probes). Both small side windows of the old reactor were replaced by one larger side window on each side of the reactor, allowing a broad view on the electrode configuration.
configuration. The inner geometry of the frames of the side windows allows the assembly of rectangular glass panes, which are less expensive and easier to produce than round ones. The lower windows of the old design were removed in order to give a flat bottom for better heat transfer with the heating plate described below. The inner geometry is with exception for the changed windows the same as for the old design (Figure 7.10c).

The new high-voltage feed-through is made out of one piece of PEEK (Figure 7.10b). The feed-through is mounted with a KF flange to the reactor. On the outer side, a thread is installed for the connection of the high-voltage and the grounding cables. This thread is as far as possible enclosed by PEEK to reduce the risk of an electrical breakdown. Both cores of the feed-through are made of stainless steel and are connected by a brass plug (Figure 7.10e). For the connection with the electrode configuration a spring plate is welded on the inner end of the metal core.

### 7.6.1 Tailored Temperature Control

For high volume flows a elaborated temperature control is needed to ensure even and reliable conditions. The first step was a preheater for the gas stream. Therefore, a copper block was made (Figure 7.11a) with a trench for 1.5 m tubing increasing the residence time of the process gas. Seven heating cartridges are used to heat the block to 300 °C. The block is heated about 30 °C above the operating temperature of the reactor to balance insulation losses.

Indirect heating of the reactor just by the preheated gas would be very time-consuming and

![Figure 7.11. (a) Copper block for preheating with heating cartridges and 1.5 m of tubing for sufficient residence time of the process gas. (b) Heating plate with asymmetrically placed heating cartridges. (c) Insulated reactor with heating plate.](image)
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unreliable. Therefore, a heating plate (Figure 7.11b) was made out of aluminum matching the reactor. The heating cartridges were placed asymmetrically in the heating plate. Because the plasma also produces heat, no cartridges were necessary behind the electrode configuration. Five cartridges were placed in the area below the electrode configuration with a thermocouple controlling the heating plate in the middle, and two cartridges were placed in the area before the electrode configuration. Combined with the insulation made for the reactor (Figure 7.11c) the reactor was operated at temperatures of up to 200 °C without and 180 °C with plasma. The elevated temperatures led partly to significant bending of the electrode configurations as can be seen in Appendix A (Figure A.7). Therefore, measurements at elevated temperatures were operated at a maximum applied voltage of 11 kV and for later measurements at a maximum dissipated power of 75 W to prevent breaking of the electrode configuration.

7.7 Flow Rate Variation

The MCA was modified before the following measurements: the mole fraction of CO\textsubscript{2} is now monitored by the MCA, and a CO channel was added (Section 4.4.5). The influence of the flow rate on the figures of merit was investigated at RT. For the calculation of the residence time, the hydrodynamic residence time was used (Equation 4.8). With a gas flow of \(10 \text{ Lmin}^{-1}\) the residence time was 2.3 s in the area of the electrode configuration. For flows of \(7.5 \text{ Lmin}^{-1}\), \(5 \text{ Lmin}^{-1}\), and \(2.5 \text{ Lmin}^{-1}\), residence times of 3.1 s, 4.6 s, and 9.2 s can be calculated, respectively. For all voltages the degrees of conversion (Figure 7.12a) increased as a function of the residence time up to a maximum of 63% at 11 kV with a flow of \(2.5 \text{ Lmin}^{-1}\). A higher carbon balance (Figure 7.12b) was observed for lower flow rates for 11 kV and the

![Figure 7.12](image_url)

Figure 7.12. (a) Conversion, (b) carbon balance, and (c) selectivities to CO and CO\textsubscript{2} of a flow rate variation with a flows of \(10 \text{ Lmin}^{-1}\), \(7.5 \text{ Lmin}^{-1}\), \(5 \text{ Lmin}^{-1}\), and \(2.5 \text{ Lmin}^{-1}\) and residence times of 2.3 s, 3.1 s, 4.6 s, and 9.2 s.

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other way around for 8 kV. The selectivities to CO and CO\textsubscript{2} are shown in Figure 7.12c. At 8 kV the selectivities were all in the same range with slightly increased CO selectivity for smaller flow rate, but for 11 kV both selectivities were higher and decreased with the flow rate. For 2.5 L min\textsuperscript{-1} the selectivities add up to 100\%, which indicates, combined with a carbon balance of 100\%, the absence of formation of organic by-products. A longer residence time had a beneficial effect on all figures of merit at high voltages. The degree of conversion with a flow rate of 2.5 L min\textsuperscript{-1} was more than doubled compared with the conversion of the 10 L min\textsuperscript{-1} measurement, and there were no organic by-products. This demonstrates a higher degree of total oxidation for smaller flow rates. Nevertheless, all further measurements were performed at 10 L min\textsuperscript{-1} in order to prevent overheating of the electrode and to investigate the influence of the catalyst on the selectivities to CO and CO\textsubscript{2}. 
7.8 Catalyst-enhanced Plasma Oxidation of n-Butane over \(\alpha\)-MnO\(_2\) in a Temperature-Controlled Twin Surface Dielectric Barrier Discharge Reactor

Section 7.8 served as basis for the publication "Catalyst-enhanced Plasma Oxidation of n-Butane over \(\alpha\)-MnO\(_2\) in a Temperature-Controlled Twin Surface Dielectric Barrier Discharge Reactor", which was recently accepted by *Plasma Processes and Polymers*. The format was slightly adjusted to the design of this thesis, but the content is unaltered.

7.8.1 Experimental Section

Catalyst Preparation and Characterization

The MnO\(_2\) catalyst was prepared by precipitation utilizing the comproportionation of KMnO\(_4\) and Mn(NO\(_3\))\(_2\) as shown by our group before.[24] The precipitate was calcined at 460 °C for 4 h in synthetic air (80% N\(_2\) and 20% O\(_2\)) to produce phase pure \(\alpha\)-MnO\(_2\). The XRD pattern was recorded using a Discover D8 (Bruker, USA) diffractometer with a theta-theta geometry. The powder was investigated with Cu K\(\alpha\) radiation (\(\lambda = 0.15406\) nm, 40 kV, 40 mA) in a range of 5° to 80° 2\(\theta\) with an increment of 0.02°. The pattern was examined using Diffrac Eva Software with access to the International Centre for Diffraction Data (ICDD) database. N\(_2\) physisorption was measured using a BELSORP-mini instrument (BEL Japan Inc., Japan) at 77 K. The catalyst powder was pretreated for 2 h at 250 °C in vacuum to remove adsorbed water. The specific surface area was derived by the BET method and the pore volume by the BJH method.[24]

Coating

For the coating of the targets a custom-made spray coater was used (Figure 7.13). In the following, the procedure for a loading of 3 mg cm\(^{-2}\) is described exemplarily. A suspension of 4 mg mL\(^{-1}\) \(\alpha\)-MnO\(_2\) in a 1:1 mixture of isopropanol and water was prepared and treated for 40 min in an ultra-sonic bath. This suspension was pumped in 30 µL amounts into a nozzle. There, the suspension was atomized with compressed air and sprayed onto the targets. The target surface was heated to 200 °C to evaporate the isopropanol-water mixture immediately. After each coating step the nozzle was moved in 2 mm steps over the length of the target. This procedure was repeated over the whole width of the target with 2 mm wide rows. The spray steps and the movement of the robotic arm were fully computer-controlled. In addition, a mask made of stainless steel was used to prevent coating of the quadratic metal grids used as electrodes. The mask covered an additional area with a width of 1.5 mm on each side of the grid.
lines, preventing the inhibition of plasma ignition next to the metallic grid. The distribution and the height of the coating was examined by a LSM (VK9710, Keyence, Japan).

![Diagram of spray coater](image)

**Figure 7.13.** (a) Scheme of the used spray coater. The catalyst suspension was carried with a syringe pump from the reservoir to the nozzle. The compressed air nebulized the suspension towards the heated target where the liquid phase evaporated instantly. (b) Spray coater with coated twin-SDBD electrode.

**Applied Figures of Merit**

For all measurements the degrees of conversion, the selectivities, and the carbon balance were derived. Conversion (Equation 7.3) is a measure of the converted amount of n-butane relative to the molar amount in the feed.

\[ X = \frac{n_{\text{butane, initial}} - n_{\text{butane}}}{n_{\text{butane, initial}}} \]  \hspace{1cm} (7.3)

Selectivity (Equation 7.4) is the ratio of the amount of a certain reaction product to the amount of converted reactant. CO and CO\(_2\) were the only measured products, and the factor of 4 is based on the stoichiometry of the reaction \( C_4H_{10} + 6.5 O_2 \rightarrow 4 CO_2 + 5 H_2O \).

\[ S_{\text{CO}/CO_2} = \frac{n_{\text{CO}/CO_2}}{4 \cdot (n_{\text{butane, initial}} - n_{\text{butane}})} \]  \hspace{1cm} (7.4)

The carbon balance (Equation 7.5) compares the amount of carbon in the feed with its amount in the effluent. When the carbon balance is smaller than 100%, it is an indication of the formation of organic by products, which were deposited in the reactor as soot or carbonaceous deposits. Carbon balances over 100% could indicate conversion of carbon which had been deposited on
The exposed surfaces beforehand. The carbon balance is derived from the amounts of n-butane, CO, and CO₂.

\[
\text{carbon balance} = \frac{n_{\text{CO}} + n_{\text{CO}_2} + 4 \cdot n_{\text{butane, initial}}}{4 \cdot n_{\text{butane, initial}}} 
\]  

(7.5)

**Thermocatalytic n-Butane Oxidation**

Thermocatalytic n-butane and CO oxidation was performed in a flow set-up with a heated plate reactor as described in detail in Ref.\cite{194}. The reactor temperature was controlled in a range from 40 °C to 450 °C using a heating rate of 5 K min⁻¹. This heating rate was sufficiently slow to achieve quasi-steady state. The set-up was equipped with four gas lines (N₂ 5.0; O₂ 4.8; 1000 ppm C₄H₁₀ 2.5 in N₂ 5.0; 4% CO 4.7 in N₂ 5.0; Air Liquide). These gases were mixed to obtain a gas stream of 78.5% N₂, 20.5% O₂, 1% CO, and 300 ppm n-butane with a volumetric flow rate of 80 mL min⁻¹, which led to the same residence time of 2.3 s as for the plasma-driven measurement series. The catalyst-coated plates were made of aluminum oxide and had dimensions of 50 mm × 100 mm × 0.635 mm. The gas composition was analyzed by an online MCA (CO; 0% - 1%) (ABB, Switzerland) with a non-dispersive IR detector for CO and a QMS (InProcess Instruments GAM 400, Germany) calibrated for n-butane and CO₂.

**(Twin-) Surface Dielectric Barrier Discharge**

The twin-SDBD electrode configuration consisted of an Al₂O₃ plate (190 mm × 88 mm × 0.635 mm) with Ni-coated metal grids screen-printed on either side. The grid lines had a width of 0.45 mm and a square size of 1 cm². On each side 5 × 15 squares were printed. The secondary side inductance of the high-voltage transformer and the capacitance of the twin-SDBD electrode configuration form a series resonant circuit which was excited by high-voltage pulses (0 V - 300 V) provided by the high-voltage pulse generator (G2000, Redline Technologies, Germany). The high-voltage pulses were supplied at pulse repetition frequency of 4000 Hz and excited the resonance circuit, forming a damped sine wave at an eigenfrequency of 86 kHz in the kilovolt range. A high-voltage probe (P6015A, Tektronix, USA) was connected to a digital oscilloscope (DPO5204B, Tektronix, USA) for monitoring of the applied voltage.

**Plasma-driven n-Butane Oxidation**

The plasma-driven experiments were performed in a flow set-up with a custom-made reactor (Figure 7.14). The reactor had outer dimensions of 540 mm × 170 mm × 51 mm and was made from aluminum. The connection with the flow set-up was achieved by KF flanges. The KF flange with a diameter of 25 mm expanded into a rectangular cross section with 105 mm × 19 mm side length. In this rectangular area the twin-SDBD electrode was placed insulated from
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Figure 7.14. (a) Scheme of the custom-made plasma reactor with windows for monitoring of the plasma and high-voltage connectors insulated by PEEK. (b) Photograph of the same plasma reactor on the heating plate with thermal insulation.

The grounded reactor walls using PEEK mountings. The twin-SDBD electrode was centered vertically, horizontally, and laterally in the reactor. The reactor was thermally insulated and heated by a custom-tailored heating plate. In addition, the feed gas was pre-heated to 15 °C above the set temperature by using a resistively heated heat exchanger. The overheating was necessary due to insulation losses. Two thermocouples were installed in the reactor 85 mm before the twin-SDBD electrode (upstream) and 85 mm after the twin-SDBD electrode (downstream) to monitor the bulk gas temperature. For measurements at higher temperatures, the set temperature of the heating plate was chosen as measurement temperature, neglecting the slight heating by the plasma.

The set-up (Figure 7.15) had a gas supply with three gas lines (N₂ 5.0; O₂ 4.8; C₄H₁₀ 2.5; Air Liquide). With these gases a mixture of 79.5% N₂, 20.5% O₂ and 300 ppm n-butane was supplied for all plasma-driven measurements. The gas flow was always 10 L min⁻¹. The gas composition was monitored by an online MCA (Emerson X-stream XEGP, USA). The MCA

Figure 7.15. Scheme of the used set-up with used gases, reactor, SDBD electrode configuration, high-voltage generator, oscilloscope with high-voltage probe, and analytics.
had 3 non-dispersive IR detectors for n-butane (0 ppm - 500 ppm), CO (0 ppm - 1000 ppm), and CO$_2$ (0 ppm - 10000 ppm), and a paramagnetic detector for O$_2$ (0% - 25%).

7.8.2 Results and Discussion

Characterization of MnO$_2$ and the Coating

The synthesis and characterization of the catalyst was described by Ollegott et al.\cite{24} for thermocatalytic CO oxidation. Only N$_2$ physisorption and XRD were repeated after reproducing the synthesis. N$_2$ physisorption measurements provided a specific surface area of the used MnO$_2$ of $37 \text{ m}^2 \text{ g}^{-1}$ and an average pore diameter of 20 nm. The XRD pattern shows the presence of phase-pure $\alpha$-MnO$_2$ (Figure 7.16a). The results indicate a successful reproduction of the synthesis of the $\alpha$-MnO$_2$ catalyst. In Figure 7.16b LSM images of coated twin-SDBD electrodes are provided. On the left side, the light microscope views are shown, and on the right side the corresponding height profiles. The images of $0.75 \text{ mg cm}^{-2}$ MnO$_2$ on the twin-SDBD electrode show well distributed island-like coating on the surface with heights up to 10.7 $\mu$m. The $3 \text{ mg cm}^{-2}$ coating is denser, and fewer gaps can be seen. Heights up to 10.4 $\mu$m were detected. A higher loading led to a denser coating instead of a larger height of the coating on the target.

![Figure 7.16](image.png)

Figure 7.16. (a) XRD pattern of the catalyst. The pattern shows phase-pure $\alpha$-MnO$_2$. (b) LSM images of coated twin-SDBD electrodes with loadings of $0.75 \text{ mg cm}^{-2}$ and $3 \text{ mg cm}^{-2}$.

Thermocatalytic Removal of n-Butane over $\alpha$-MnO$_2$

The thermocatalytic measurement was performed using a plate coated with $3 \text{ mg cm}^{-2}$ of $\alpha$-MnO$_2$. In order to test the performance of the catalyst for the oxidation of CO and n-butane, both gases were added to the feed stream simultaneously. CO was added to simulate produced
CO during plasma operation. Therefore, only one resulting CO$_2$ mole fraction was measured. Figure 7.17 shows the mole fractions for the thermocatalytic measurement. For CO there was a conversion of 5% at a temperature of 86 °C, 50% at 140 °C, and 95% at 175 °C. Furthermore, for n-butane degrees of conversion of 5% at 180%, 50% at 255 °C, and 95% at 319 °C were reached. Since the CO mole fraction remained at 0 ppm above 180 °C, n-butane was totally oxidized to CO$_2$ with no further CO being formed. The carbon balance was higher than 95% indicating total oxidation to CO$_2$ above 320 °C. These results demonstrate a high activity of the catalyst for the oxidation of CO and n-butane under thermocatalytic conditions. The higher activity for CO conversion than for n-butane conversion should be beneficial for the CO$_2$ selectivity of the plasma-assisted catalysis because of the tendency of CO production by plasma-alone VOC oxidation shown later.

![Figure 7.17](image-url)

**Figure 7.17.** Simultaneous thermocatalytic oxidation of CO and n-butane in synthetic air in a temperature range from 40 °C to 450 °C with a heating rate of 5 K min$^{-1}$ and a plate coated with 3 mg cm$^{-2}$ $\alpha$-MnO$_2$.

**Plasma-driven Removal of n-Butane**

**Effect of Applied Voltage**

The following measurement series was performed in the plasma reactor without catalyst as shown in Figure 7.18a. The mole fractions of n-butane, CO, and CO$_2$ as well as the gas temperature before and after the SDBD were monitored and the applied voltage was controlled manually. Since no ignition was observed below voltages of 7.5 kV, all measurements started at a voltage of 8 kV. The voltage was increased up to 11 kV in steps of 1 kV, and the pulse repetition frequency was always set to 4000 Hz. At the beginning of each step the voltage had to be manually readjusted to achieve a stable value before waiting for the n-butane mole fraction to reach steady state. Then, the next voltage step was performed. Due to the applied high voltage the gas temperature increased during each measurement depending on the starting tem-
perature. In the measurement series shown in Figure 7.18a, the downstream temperature after the twin-SDBD electrode increased by 12 °C and the upstream temperature before the twin-SDBD electrode by 5 °C. The increase of the downstream temperature was directly correlated with the energy input of the plasma, which can be seen by the sudden increase at each voltage step, whereas the increase in upstream temperature originated from the gradual warming of the reactor.

The plasma treatment without catalyst at room temperature led to a decrease of the n-butane mole fraction (Figure 7.18b). The conversion of n-butane started with 8% at 8 kV and then rose to 36% at 11 kV. CO$_2$ was the main product with increasing selectivity from 32% to 44% for higher voltages. However, CO as an undesired second main product had an increasing selectivity of 21% to 36% at higher voltages. The differences in selectivity remained the same for all voltages. Since both selectivities were increasing, but still never added up to 100%, the relative amount of undetected organic by-products had to be decreasing. Correspondingly, the carbon balance only reached values above 90%.

The conversion of n-butane increased at higher voltages, but the amount of undetected organic by-products and of CO increased as well. Nevertheless, higher voltages were increasing the selectivity to CO$_2$ as the desired product, demonstrating the production of ROS, which were able to convert a fraction of the VOC to CO$_2$.

![Figure 7.18](image)

Figure 7.18. (a) Plasma treatment of synthetic air with 300 ppm n-butane at RT without catalyst for applied voltages from 8 kV to 11 kV. (b) The mole fractions of n-butane, CO, and CO$_2$ in the effluent and the temperatures in the reactor for applied voltages from 8 kV to 11 kV.

**Influence of the Feed Gas Temperature**

The influence of the feed gas temperature on the plasma-alone abatement of n-butane was investigated in the range from 100 °C to 160 °C in steps of 10 °C as a function of the applied voltage.
Figure 7.19a shows the achieved degrees of conversion. For the measurements with heating significantly higher degrees of conversion for all voltages were reached. Between 100 °C and 160 °C at 8 kV there was no significant difference in conversion, but at 11 kV it increased with rising temperature up to 52%. Furthermore, Figure 7.19a shows minor influences of the temperature on the carbon balance. The selectivities (Figure 7.19b) to CO and CO\textsubscript{2} at 8 kV were all similar with a higher selectivity to CO\textsubscript{2}. For 11 kV the selectivity changed more and more in favor of CO with increasing temperatures. In summary, at high voltages higher temperatures led to higher degrees of conversion and better carbon balances, but higher temperatures favor CO formation at 11 kV. The increased conversion for higher temperatures may be induced by the more rapid decomposition of produced ozone (O\textsubscript{3}), releasing highly reactive atomic oxygen\textsuperscript{[195]} and by change of the discharge itself as shown by Wang et al.\textsuperscript{[196]} Furthermore, the last RT measurement had a lower degree of conversion than the first RT measurement, pointing to an ongoing aging of the twin-SDBD electrode over time under highly oxidizing conditions at higher temperatures during the induction period.

Catalyst-enhanced Plasma Removal of n-Butane over α-MnO\textsubscript{2}

Effect of Catalyst and Coating Geometry

In order to enhance the conversion of n-butane to CO\textsubscript{2}, α-MnO\textsubscript{2} was applied on both sides of the twin-SDBD electrode by spray coating. Figure 7.20 shows the three different tested coating geometries, and in Figure 7.21a the degrees of conversion at 11 kV are compared for all of them. The straightforward way of coating was a full coating with different loadings, and in Figure 7.20b a coating with 0.75 mg cm\textsuperscript{-2} of α-MnO\textsubscript{2} is shown. The contact points for
the applied voltage and for grounding on the other side were cleaned to ensure good electrical contact. The conversion measurements (Figure 7.21a) revealed a degree of conversion of 36% for 0.75 mg cm$^{-2}$, but for 3 mg cm$^{-2}$ it was not possible to achieve plasma ignition. Obviously, the high catalyst loading adds additional dielectric on the metal grid disturbing ignition. To lower the detrimental influence on plasma ignition, in the next step only the downstream half (Figure 7.20c) of the twin-SDBD electrode was coated. Surprisingly, the conversion for 0.75 mg cm$^{-2}$ decreased to 30%, but there was conversion for 3 mg cm$^{-2}$ of 34%. Nevertheless, the degrees of conversion were lower or at the same level as measurements without catalyst at RT (Figure 7.19). For a more efficient coating a mask of stainless steel was made, which prevented the grid and a strip of 1.5 mm width on both sides of the grid from being coated to prevent any interference with plasma ignition. After the coating procedure the mask was removed. The twin-SDBD electrode coated with the grid mask (3 mg cm$^{-2}$) produced a maximum conversion of 46% at RT. Due to the high conversion this coating geometry was chosen for further investigations. All values for the amount of catalyst per area were referred to the actual coated area. Consequently, the total amount of catalyst of the fully coated twin-SDBD electrode (3 mg cm$^{-2}$) was higher than the twin-SDBD electrode (3 mg cm$^{-2}$) coated in the presence of the mask due to the shielding of the electrodes by the mask.

Figure 7.21b shows a comparison of conversion, selectivities, and carbon balances for n-butane oxidation without, with 1 mg cm$^{-2}$, and with 3 mg cm$^{-2}$ catalyst coated in the presence of the
mask to prevent the grid to be coated. The degree of conversion with 1 mg cm\(^{-2}\) catalyst was slightly higher compared with the measurement without catalyst. However, the selectivities to CO and CO\(_2\) were each higher with 1 mg cm\(^{-2}\) of catalyst. Thus, the higher CO and CO\(_2\) selectivities also resulted in a higher carbon balance. With 3 mg cm\(^{-2}\) catalyst loading the degrees of conversion were higher for all tested voltages, and the differences between the measurements were increasing with higher voltages compared with the measurements without catalyst. The absolute increase in conversion was up to 10% in the presence of the catalyst. In the range from 8 kV to 10 kV the CO selectivity was slightly higher with 3 mg cm\(^{-2}\) catalyst than without, but for 11 kV the CO selectivity dropped by 10%. The selectivity to CO\(_2\) at 8 kV was at the same level as with 1 mg cm\(^{-2}\), but with increasing voltage the selectivity increased rapidly up to 79%, and consequently, the carbon balance was also increasing with high voltages up to 100%.

![Figure 7.21](image)

**Figure 7.21.** (a) Comparison of the degrees of n-butane conversion at 11 kV at RT for all tested coating geometries (fully coated, half-coated, and coated with mask) for loadings of 0.75 mg cm\(^{-2}\) and 3 mg cm\(^{-2}\). (b) Comparison of conversion, CO/CO\(_2\) selectivities, and carbon balance for measurements without catalyst and with loadings of 1 mg cm\(^{-2}\) and 3 mg cm\(^{-2}\) \(\alpha\)-MnO\(_2\) coated with the 1.5 mm mask at RT in a range of 8 kV to 11 kV.

**Influence of the Feed Gas Temperature in the Presence of \(\alpha\)-MnO\(_2\)**

The beneficial effect on conversion by heating the reactor and the beneficial effect of the catalyst on the selectivities were combined in the following. For a clear distinction of thermocatalytic and plasma effects on the conversion of n-butane, the measurements were carried out below the thermocatalytic onset temperature for n-butane oxidation of 180 °C. Figure 7.22 shows the degrees of conversion and carbon balances of the measurements at RT, 120 °C, and 140 °C without catalyst and the corresponding measurements with 3 mg cm\(^{-2}\) catalyst. For 8 kV the increase in conversion with catalyst at RT and at 120 °C °C was 4% each and at 140 °C it amounted to 7%
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compared with the case without catalyst. When using a voltage of 11 kV conversion increased for RT, 120 °C, and 140 °C by 10%, 8%, and 9%, respectively. The increase in conversion was rising with temperature for lower voltages and decreasing for higher voltages. Nevertheless, the achieved 58% conversion at 140 °C was still the highest measured conversion at this voltage. The carbon balance at 8 kV shows no clear trend, but the carbon balance at 140 °C with catalyst was slightly better. In contrast, with a voltage of 11 kV the carbon balance was improving with higher temperatures in the presence of the catalyst. For 120 °C and 140 °C carbon balances higher than 100% were measured. This may be due to the conversion of previously deposited carbonaceous species, which had desorbed due to the higher temperature and were converted over the catalyst. The highest impact of the catalyst was found to be on the selectivities summarized in Table 7.1. There was only a small increase in both selectivities with 8 kV at RT, whereas at a temperature of 120 °C the CO selectivity dropped by 7% and the CO\(_2\) selectivity increased by 18%. This trend was stronger at 140 °C resulting in a 8% decrease of CO selectivity and 25% increase of CO\(_2\) selectivity relative to the corresponding 8 kV measurements. The undesirable high CO selectivities at temperatures of 120 °C and 140 °C without catalyst at 11 kV were reversed by the catalyst reaching 10% for CO and 95% for CO\(_2\) at 140 °C. The

![Figure 7.22. Comparison of conversion (opaque) and carbon balance (transparent) of measurements at RT, 120 °C, and 140 °C without coating and with mask-coated catalyst at 8 kV and 11 kV.](image)

high CO\(_2\) and low CO selectivities of the RT measurement were more improved by the catalyst, showing that there are both temperature and voltage effects which have an influence on the performance of the catalyst-enhanced plasma process. The application of \(\alpha\)-MnO\(_2\) as catalyst influenced conversion, selectivities (CO/CO\(_2\)), and the carbon balance in a beneficial way. Because \(\alpha\)-MnO\(_2\) is very active in thermocatalytic CO oxidation reaching 50% CO conversion at 140 °C, the high CO\(_2\) selectivities achieved in the catalyst-enhanced plasma measurements with heated feed gas in the presence of \(\alpha\)-MnO\(_2\) indicate a consecutive catalytic oxidation of the plasma-produced CO over the \(\alpha\)-MnO\(_2\)-coated square-shaped patches between the grid lines.
Since only one mask-coating was fully tested, there is potential for further improvement of the coating geometries to find the optimal gap distance between the metal grid and the deposited catalyst. Furthermore, the applied pulse frequencies and the energy efficiency could be enhanced and investigated for optimal conversion. Also, spectroscopic measurements to derive the O$_3$ densities and those of other ROS will be performed.

Table 7.1. Selectivities of CO and CO$_2$ observed at RT, 120 °C, and 140 °C without coating and with mask-coated catalyst at 8 kV and 11 kV.

<table>
<thead>
<tr>
<th>Selectivity / %</th>
<th>CO 8 kV</th>
<th>CO$_2$ 8 kV</th>
<th>CO 11 kV</th>
<th>CO$_2$ 11 kV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>Without</td>
<td>With</td>
<td>Without</td>
<td>With</td>
</tr>
<tr>
<td>RT</td>
<td>22</td>
<td>27</td>
<td>32</td>
<td>41</td>
</tr>
<tr>
<td>120 °C</td>
<td>33</td>
<td>26</td>
<td>44</td>
<td>62</td>
</tr>
<tr>
<td>140 °C</td>
<td>35</td>
<td>27</td>
<td>45</td>
<td>70</td>
</tr>
</tbody>
</table>

Influence of the Catalyst on the Dissipated Power

For a better insight into the effects leading to the increased degree of conversion at elevated temperatures in the presence of the catalyst, the output power of the high-voltage generator was examined for selected measurements. Table 7.2 summarizes the degrees of conversion and the dissipated power at an applied voltage of 11 kV. Furthermore, the resulting SED and the energy efficiencies based on converted mass of n-butane were derived. There is an increase of the SED with increasing temperature, resulting in similar energy efficiencies in the range from $5 \times 10^{-4}$ mgJ$^{-1}$ to $7 \times 10^{-4}$ mgJ$^{-1}$. Furthermore, the preheated gas stream leads to increased SEDs at the same applied voltage and therefore to increased degrees of conversion. When comparing the measurements without catalyst to the corresponding ones with catalyst, there is an increase of the SEDs both at RT and at 140 °C, but the energy efficiencies seem to decrease in the presence of the catalyst requiring further investigations. For comparison, Gandhi et al.\cite{28} reached a degree of butane conversion of 65% - 90% in 5% O$_2$ with a dissipated power of 40 W to 100 W and a gas flow of 1 L min$^{-1}$ resulting in a SED of up to 6000 JL$^{-1}$. Aubry et al.\cite{197} report degrees of propane conversion up to 100% with a SED of 750 JL$^{-1}$ in air at 300 K. Hill et al.\cite{64} achieved a degree of propane conversion of 63% in air with a SED of 625 JL$^{-1}$ leading to an energy efficiency of approx. $6 \times 10^{-4}$ mgJ$^{-1}$. All these studies applied a volume DBD or packed-bed reactor, and depending on the applied temperatures, similar degrees of conversion at comparable or lower SEDs were achieved in the present study. Although the generator output power is only a rough estimate of the dissipated power, trends and orders of magnitude are considered meaningful. The application of the $\alpha$-Mn$_2$O$_3$ catalyst and elevated temperatures are found to lead to increased SEDs and therefore to higher conversion. Optical
emission spectroscopic measurements are planned to investigate the influence of the catalyst and temperature on electron density and reduced electric field similar to measurements performed by Offerhaus et al.\textsuperscript{[49]} at ambient temperature.

Table 7.2. Degrees of conversion, dissipated power, specific energy densities, and energy efficiencies for selected measurements at an applied voltage of 11 kV.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Degree of conversion</th>
<th>Dissipated power</th>
<th>Specific Energy Density</th>
<th>Energy Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>W</td>
<td>JL(^{-1})</td>
<td>mgJ(^{-1})</td>
</tr>
<tr>
<td>RT without Catalyst</td>
<td>36.0</td>
<td>65</td>
<td>390</td>
<td>6.7 \times 10^{-4}</td>
</tr>
<tr>
<td>140 °C without Catalyst</td>
<td>49.5</td>
<td>86</td>
<td>516</td>
<td>6.9 \times 10^{-4}</td>
</tr>
<tr>
<td>RT with Catalyst</td>
<td>46.3</td>
<td>103</td>
<td>618</td>
<td>5.4 \times 10^{-4}</td>
</tr>
<tr>
<td>140 °C with Catalyst</td>
<td>58.0</td>
<td>146</td>
<td>876</td>
<td>4.7 \times 10^{-4}</td>
</tr>
</tbody>
</table>

### 7.8.3 Conclusion

A twin-surface dielectric barrier discharge was used for the abatement of n-butane as a model volatile organic compound in synthetic air. The plasma-alone treatment of the gas stream decreased the n-butane mole fraction, and the carbon balances reached about 93% - 100%, although the selectivity for undesired CO was rather high. Heating of the reactor in the range from 100 °C to 160 °C led to an increase in conversion and carbon balance. However, the selectivity to CO increased further at high voltages up to 54%. The comparison of the thermocatalytic measurement using a plate coated with 3 mg cm\(^{-2}\) of $\alpha$-MnO\(_2\) with the heated plasma-assisted measurements revealed catalyst-enhanced plasma activity at temperatures too low for thermocatalytic n-butane oxidation. The application of different geometries chosen for $\alpha$-MnO\(_2\) deposition by spray coating showed that the highest conversion and CO\(_2\) selectivity was reached for the electrodes using the mask during coating with a distance of 1.5 mm between the uncoated Ni grid lines and the square patches of 3 mg cm\(^{-2}\) of $\alpha$-MnO\(_2\). Conversion increased by about 10% independent of temperature, but selectivity was strongly shifted to the desired product CO\(_2\) in the presence of the catalyst and at higher temperatures. The application of the $\alpha$-MnO\(_2\) catalyst and elevated temperatures were found to result in increased SEDs. Thus, the application of $\alpha$-MnO\(_2\) in the plasma-driven abatement of n-butane in synthetic air influenced the achieved degrees of conversion, the selectivities, and the carbon balance in a favorable way, indicating a consecutive catalytic oxidation of plasma-produced CO.
7.9 Flow Rate and Temperature Re-Evaluation

A current probe (CP) (Section 4.4.3) was added to the set-up as a final modification. The CP combined with the HVP enables power measurements calculated according to Section 4.4.3. The measurements shown below are plotted as a function of the SED according to Equation 4.9. Additionally, the EE can be calculated according to Equation 4.10. The figures of merit are investigated as a function of the SEDs and the applied voltages are summarized in Appendix B (Tables B.3 – B.8). The SEDs enable an easier comparison with plasma geometries other than the twin-SDBD. Furthermore, temperature or small differences of the electrode configurations such as coating or aging may have more influence on the applied voltages than on the SEDs.

7.9.1 Flow Rate Variation: Re-Evaluation

For the flow rate variation shown in Section 7.7 (Page 73) the figures of merit were evaluated as a function of the applied voltages. Therefore, a re-evaluation of a new series of measurements was carried out as a function of the SED, which also includes the flow rate (Equation 4.9). The degrees of conversion as functions of the SED for flow rates of $2.5 \text{ L min}^{-1}$, $5 \text{ L min}^{-1}$, $7.5 \text{ L min}^{-1}$, and $10 \text{ L min}^{-1}$ are shown in Figure 7.23a. Due to the small flow rate of $2.5 \text{ L min}^{-1}$, the SEDs rapidly increase leading only to a small overlap of the measuring points of all measurements. Nevertheless, the degree of conversion shows the same trend for all four measurements: it is slightly higher for higher flow rates. This may indicate an influence of the plasma on more than just the conversion of n-butane, for instance also on the mole fraction of ROS further illuminated in Section 7.11. Reaching an SED of 400 J L$^{-1}$ the trends are more in line and there is a slower increase in conversion especially for $2.5 \text{ L min}^{-1}$, $5 \text{ L min}^{-1}$, and $7.5 \text{ L min}^{-1}$. This observation suggests that the normalization of the energy input by the flow rate using the SED can be used to predict the degree of conversion at high SEDs, which are experimentally not achievable in the used set-up.

The EEs shown in Figure 7.23b reveal more pronounced differences between the individual measurements than for the degrees of conversion, but for higher SEDs the EEs follow the same trend: for higher flow rates and consequently smaller SEDs, the EEs are higher.

The selectivities to CO$_2$ in the overlapping SED regions show differences up to 10% (Figure 7.23c), especially for the three higher flow rates. For all flow rates the selectivity is increasing with higher SEDs reaching the peak at the highest SEDs with $2.5 \text{ L min}^{-1}$. The smaller increase in selectivity at high SEDs at $2.5 \text{ L min}^{-1}$ is depicted for CO in Figure 7.23d. For smaller SEDs the selectivity to CO in the overlapping SED regions is very similar among the flow rates.

Figure 7.23e shows that the carbon balance is decreasing until approx. 500 J L$^{-1}$ for all flow
Catalyst-enhanced Plasma Conversion of Volatile Organic Compounds

rates. The decrease of the carbon balance is more pronounced for higher flow rates. Above 500 J L$^{-1}$ the carbon balance starts to increase reaching 99% at 1320 J L$^{-1}$.

The introduction of the SED reduces the influence of the flow rates on the figures of merit in contrast to Section 7.7. With smaller flow rates higher SEDs can be achieved with the same dissipated power, which increases the flexibility of the measurements.

Figure 7.23. Degrees of conversion (a), energy efficiencies (b), selectivities to CO$_2$ (c) and CO (d), and carbon balance (e) with power input of 15 W to 55 W in steps of 10 W for flow rates of 2.5 L min$^{-1}$, 5 L min$^{-1}$, 7.5 L min$^{-1}$, and 10 L min$^{-1}$. The applied voltages are summarized in Table B.3. 300 ppm n-butane in synthetic air without catalyst.
7.9.2 Temperature Variation with an Uncoated Electrode Configuration: Re-Evaluation

As in the previous section the following measurements are a re-evaluation of a new series of measurements for a temperature variation, because the measurements in Section 7.8.2 (Page 81) are shown as a function of the applied voltage. The degrees of conversion are shown as a function of SED in Figure 7.24a, but in contrast to Section 7.8.2 in a range of 80 °C to 180 °C in steps of 20 °C. Similar to the results in Section 7.8.2 the conversion increases with SED as well as with temperature. The measurements at RT and 80 °C are 8% and 5% lower, respectively, than the remaining measurements. The increase in conversion between every step in the range of 100 °C to 180 °C is less pronounced. Similar to Section 7.8.2 the highest degree of conversion was achieved at the highest temperature.

The resulting EEs (Figure 7.24b) show the same trend with the highest EE for the highest temperature. The EE is decreasing after an initial increase with higher SEDs. It has to be mentioned that the efficiency was calculated based on the dissipated power input and that the power required to increase the temperature was not taken into account. Therefore, the energy input-corrected data were calculated in addition. The EE was adjusted by taking into account the energy required to increase the temperature of the gas stream from 30 °C to the respective experimental measurement temperature. The SED is unaffected by this and still based only on the energy input by the plasma. The corrected EEs indicate an efficiency bias for elevated temperatures. The corrected EEs are very similar to the EE at RT showing a higher apparent EEs for elevated temperatures without correction. This observation demonstrates that the higher degree of conversion at elevated temperatures is more attributed to the additional energy input than to a synergistic effect.

The elevated temperatures also had an influence on the applied voltages required for certain power inputs. As described before, the measurements were carried out either until a power input of 75 W or a applied voltage of 11 kV was reached. With an applied voltage of 11 kV the measurements at RT and 80 °C reach a power input of 55 W and 65 W, respectively. Higher temperatures result in decreased applied voltages for a power input of 75 W. The applied voltages are summarized in Table B.4.

The selectivity to CO$_2$ (Figure 7.24c) increases with higher SED at RT, 80 °C, and 100 °C. The selectivity at RT increases from 30% to 39% and at 80 °C and 100 °C from approx. 35% to approx. 45%. At temperatures above 100 °C the selectivity to CO$_2$ is between 40% to 45% and almost independent of temperature or SED.

The selectivity to CO shown in Figure 7.24d follows a different trend. At RT the selectivity increases from 24% to 30%, which is less rapid than at elevated temperatures. At elevated temperatures the selectivities begin with 90 JL$^{-1}$ between 20% at 80 °C and 28% at 180 °C.
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Figure 7.24. Degree of conversion (a), energy efficiency with experimental data and energy input corrected data (b), selectivities to CO$_2$ (c) and CO (d), and the carbon balance (e) with power input of 15 W to 75 W in steps of 10 W at RT and 80 °C to 180 °C in steps of 20 °C with an uncoated electrode configuration. The applied voltages are summarized in Table B.4. 300 ppm n-butane in synthetic air without catalyst.

For all temperatures the selectivity increases from 20% until 38% at 80 °C and until 48% at 180 °C with 390 J L$^{-1}$ and 450 J L$^{-1}$, respectively.

The carbon balance at RT decreases from 97% to 92% as a function of the SED. At elevated temperatures the carbon balance decreases as well until 210 J L$^{-1}$. For higher SEDs the carbon balance increases again from 94% to 97% and tends to be higher at higher temperature.
In contrast to Section 7.9.1, in this chapter the re-evaluation with SED led to no other trends than described in Section 7.8.2. Conversion as well as the selectivity to CO are increasing as a function of temperature. Only the $RT_{end}$ measurement shows no aging compared with the degree of conversion of the RT measurements shown in Section 7.9.1. However, a higher selectivity to CO$_2$ was achieved for $RT_{end}$ than for $RT_{begin}$.

### 7.10 Gap Width Variation

In Section 7.8 the gap width between electrode grid and catalyst was fixed to 1.5 mm. In the following the influence of the gap width on the figures of merit was investigated to find the optimal distance between the catalyst and the grid line. Gap widths of 0.5 mm, 1.0 mm, 1.5 mm, and 2.0 mm were chosen. The masks used to produce the gaps are shown in Figure 4.3. The coating procedure is described in detail in Section 4.2. In Figure 7.25 images of the coated electrode configurations are displayed. The figures of merit are analyzed as a function of the SED at RT, 120 °C, 140 °C, and 160 °C for the different gap widths and compared to an uncoated electrode configuration. Not all measurements were performed up to a SED of 450 JL$^{-1}$, either because the applied voltage exceeded 11 kV or because the electrode configuration was bent to such an extent that it may be damaged. In Appendix A the figures of merit are shown for a fixed gap width as a function of temperature (0.5 mm Figure A.9; 1.0 mm Figure A.10; 1.5 mm Figure A.11; 2.0 mm Figure A.12).

Figure 7.25. Photographs of the coated electrode configurations with a gap widths between the catalyst coating and the grid line of 0.5 mm (a), 1.0 mm (b), 1.5 mm (c), and 2.0 mm (d). The coating procedure is described in Section 4.2.
7.10.1 Degrees of Conversion and Energy Efficiencies with Different Gap Widths

The degrees of conversion for different gap widths are shown in Figure 7.26 as a function of the SED. The degrees of conversion of the 0.5 mm gap electrode configuration increased linearly up to 20% independent of temperature. At RT the degree of conversion of the remaining measurements (uncoated, 1.0 mm, 1.5 mm, and 2.0 mm) increases linearly as well (Figure 7.26a).

The degree of conversion is in the range of 23% to 26% at 330 J L\(^{-1}\) and increases further for the coated electrodes at higher SEDs. 1.5 mm and 2.0 mm reach 29% and 31% at 390 J L\(^{-1}\), respectively, and the 1.0 mm coating reaches 32% at 450 J L\(^{-1}\). At elevated temperatures the degrees of conversion show a logarithmic-like trend for all but the 0.5 mm coating similar to the uncoated electrode configuration at elevated temperatures in Figure 7.24. The measurements are not as congruent as at RT, but with a maximum difference of approx. 4% they are very similar. The degree of conversion of the 1.0 mm coating is always the lowest in this group and the 2.0 mm coating the highest.

The 0.5 mm coating shows clearly a too narrow gap between grid line and catalyst. As also shown in Section 7.12, ignition is strongly hindered by the coating and therefore conversion is decreased. The applied voltages of the 0.5 mm coating summarized in Table B.5 indicate indirectly that the dissipated power can be strongly increased by coating the electrode configuration with \(\alpha\)-MnO\(_2\). The applied voltages range from 8.4 kV to 9.6 kV for a dissipated power of 65 W. Due to significant bending of the electrode configuration a measurement with 75 W dissipated power was not performed to reduce the risk of damaging it.

For the other gap widths only a minor influence of the gap width is observed. The 1.0 mm gap electrode configuration still shows the lowest degree of conversion, but in a similar range as the other coatings. To reach a dissipated power of 75 W applied voltages in the range of 9.7 kV to 10.6 kV are required (Table B.6). The 1.0 mm coating is the only measurement reaching 75 W without strong bending at RT. The uncoated, the 2.0 mm coating and, the 1.5 mm coating are congruent even at elevated temperature. The applied voltages (Table B.4, Table B.8, and Table B.7) are very similar to one another, indicating no further disturbance of the plasma ignition by the catalyst. The 1.5 mm coating was only measured until 65 W due to significant bending, nevertheless it would probably have withstood higher dissipated powers compared with the measurements of the 1.0 mm and 2.0 mm electrode configurations. However, a prediction of the degree of conversion for 75 W of the 1.5 mm coating may be the same as the 2.0 mm coating considering the congruent trend of the lower SEDs.

The catalyst shows no enhancing influence on the conversion except for lower applied voltages needed for the same dissipated power in contrast to Section 7.8.2 (Page 84). Even elevated temperatures do not lead to an increase in conversion except for the increase already shown...
in Section 7.9.2 (Page 90) demonstrating an implementation of the measurements below the thermocatalytic activity of the catalyst. Still, the gap variation demonstrates the optimal gap width between $\alpha$-MnO$_2$ and the grid line to be slightly above 1.0 mm, considering the degree of conversion.

The comparison of EEs for the gap width variation is shown in Appendix A (Figure A.13). There are no further insights gained besides the observations mentioned in this section and in Section 7.9.2 (Page 90). The trends are the same as observed for the degree of conversion. The EE for the 0.5 mm coating is the lowest, and the remaining EEs are very similar among each other with slight deviations for the 1.0 mm coating. Furthermore, with elevated temperatures the EE is higher.

Figure 7.26. Degrees of conversion for the gap width variation at RT (a), 120 °C (b), 140 °C (c), and 160 °C (d) with power input of 15 W to 75 W in steps of 10 W. The applied voltages are summarized in Tables B.4 – B.8. 300 ppm n-butane in synthetic air with $\alpha$-MnO$_2$. 


7.10.2 Selectivities to CO$_2$ and CO with Different Gap Widths

The influence of the gap width on the selectivity to CO$_2$ is shown in Figure 7.27. At RT (Figure 7.27a) the selectivity at an SED of 90 J/L$^{-1}$ for the uncoated electrode configuration and all coatings is in the narrow range of 30% to 38%. The selectivity of the 0.5 mm coating increases rapidly in a logarithmic-like trend to 80% at 390 J/L$^{-1}$. The selectivity of the uncoated and the other coatings increases slightly until 270 J/L$^{-1}$ to a range of 36% to 44%. From 270 J/L$^{-1}$ the selectivity of the 1.0 mm coating increases linearly to 71% until 460 J/L$^{-1}$, whereas the selectivities of the uncoated, the 2.0 mm coating, and the 1.5 mm coating never exceed 44%.

At elevated temperatures of 120 °C, 140 °C, and 160 °C the selectivity to CO$_2$ decreases for wider gaps. The uncoated electrode configuration is independent of temperature and SED al-

Figure 7.27. Selectivities to CO$_2$ of the gap width variation at RT (a), 120 °C (b), 140 °C (c), and 160 °C (d) with power input of 15 W to 75 W in steps of 10 W. The applied voltages are summarized in Tables B.4 – B.8. 300 ppm n-butane in synthetic air with $\alpha$-MnO$_2$. 

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ways having a selectivity in the range of 40% to 46%. The selectivity of the 0.5 mm coating starting at 96% decreases at 120 °C slightly and increases at 140 °C and 160 °C from 67% and 82%, respectively, reaching 93% at 390 JL⁻¹ for all temperatures. The other coatings show a different trend. The selectivity to CO₂ at 120 °C for 90 JL⁻¹ is approx. 50% and increases until the highest measured SED to 84%, 70%, and 68% for the 1.0 mm coating, the 1.5 mm coating, and the 2.0 mm coating, respectively. For 140 °C and 160 °C the selectivity at 90 JL⁻¹ increases from a range of 52% to 61% to a range of 60% to 67%. The selectivity increases linearly until the highest measured SEDs in a range of 69% to 86% at 140 °C and 72% to 89% at 160 °C. The selectivity to CO is shown in Figure 7.28. A similar trend as shown for CO₂ at RT (Figure 7.28a) can be seen. The selectivity is in a narrow range of 23% to 33% increasing until 330 JL⁻¹ for all electrode configurations except for the 0.5 mm coating. For the 0.5 mm coating

Figure 7.28. Selectivities to CO of the gap width variation at RT (a), 120 °C (b), 140 °C (c), and 160 °C (d) with power input of 15 W to 75 W in steps of 10 W. The applied voltages are summarized in Tables B.4 – B.8. 300 ppm n-butane in synthetic air with α-MnO₂.
selectivity decreases from 28% to 20% and also for the 1.0 mm coating the selectivity decreases above 330 JL$^{-1}$ to 26%.

At elevated temperatures the selectivities to CO at 90 JL$^{-1}$ are in a narrow range of 22% to 28% for all electrode configurations except for the 0.5 mm coating, for which a selectivity to CO in the range of 15% to 32% at 90 JL$^{-1}$ was reached. With increasing SEDs the selectivity to CO for the uncoated electrode configuration increases to a maximum of 47% at 160°C. For the 2.0 mm and 1.5 mm coatings the selectivity remains mostly on the same level independent of temperature and SED. The selectivity to CO of both narrow gap coatings decreases for 120°C, 140°C, and 160°C to 10%, 8%, and 7% for the 0.5 mm coating and 16%, 14%, and 13% for the 1.0 mm coating, respectively. There was no positive effect on conversion by the catalyst, except the achievement of higher SEDs at lower applied voltages for coated electrode configurations. In contrast, in this section a positive effect of the catalyst is found. The selectivity to CO$_2$ is increased and the selectivity to CO is decreased in the presence of the catalyst. Even at RT the selectivities are influenced. This impact of the catalyst decreases for a wider gap or less catalyst. The 0.5 mm coating shows the highest impact on the selectivities, but a diminishing impact on the degree of conversion. For the 1.0 mm coating there is a less pronounced shift of the selectivities observed at RT and at elevated temperatures, and for the 1.5 mm and 2.0 mm coatings it decreases further, but there is still a detectable impact on the selectivities compared with the uncoated electrode configuration.

### 7.10.3 Carbon Balances with Different Gap Widths

The carbon balances for the coating series are shown in Figure 7.29. The uncoated electrode configuration shows a steep decrease of the carbon balance at RT down to 93% at 330 JL$^{-1}$. At elevated temperatures the carbon balance decreases as well to 95% and 93% until 210 JL$^{-1}$ followed by a slight increase until 460 JL$^{-1}$ to approx. 96%. The carbon balance of the 0.5 mm coating is for all temperatures and SEDs in a range of 99% to 101%. The high carbon balance may result from the low degree of conversion, because lower conversion leads to a smaller amount of possible by-products. Furthermore, the high impact of the 0.5 mm coating on the selectivities to CO$_2$ and CO indicates also small selectivities to organic by-products. The carbon balance of the other coated electrode configurations at RT decrease as well until 270 JL$^{-1}$ to 93% to 95%. Then, the carbon balance of the 1.0 mm coating increases again to 99%, and for the 1.5 mm and 2.0 mm coating it stays at 94% and 93%, respectively. For elevated temperatures the carbon balance of the three coatings with a wider gap first decreases and then increases again. However, this is less pronounced compared with RT and the carbon balance is always above 97%. Among these coatings the 1.0 mm coating tends to have the highest carbon balance up to 100% at 160°C, though the difference is approx. 2%.
Figure 7.29. Carbon balances of the gap width variation at RT (a), 120 °C (b), 140 °C (c), and 160 °C (d) with power input of 15 W to 75 W in steps of 10 W. The applied voltages are summarized in Tables B.4 – B.8. 300 ppm n-butane in synthetic air with $\alpha$-MnO$_2$.

The catalyst coating increases the carbon balance especially at elevated temperatures. This observation indicates that fewer by-products are formed in the process.
7.11 Mole fractions of Reactive Oxygen Species

In Section 7.1 NO, NO₂, and O₃ were identified as possible ROS influencing the conversion of n-butane. For the measurements shown in Section 7.9 and Section 7.10 the mole fractions as ion currents \( m/z = 30 \) for NO, \( m/z = 46 \) for NO₂, and \( m/z = 48 \) for O₃ were monitored using a QMS. For each setting two measurements were performed, one with n-butane in synthetic air and one in synthetic air without n-butane. The QMS was not calibrated for the monitored ROS, therefore only a qualitative investigation based on the raw signal from the detector as ion current is displayed.

7.11.1 Influence of the Flow Rate on the Ion Current of Reactive Oxygen Species

The ion currents monitored for the flow rate re-evaluation (Section 7.9.1) are shown in Figure 7.30. The ion current of NO (Figure 7.30a) is in the range of \( 8 \times 10^{-13} \) A to \( 1.2 \times 10^{-12} \) A for all measurements without plasma. The ion currents in synthetic air with n-butane increase linearly with different slopes up to a range of \( 2.8 \times 10^{-12} \) A to \( 3.3 \times 10^{-12} \) A for the three higher flow rates. The \( 2.5 \text{ L.min}^{-1} \) measurement shows a flatter increase until \( 600 \text{ JL}^{-1} \) and then increases more steeply until \( 6.7 \times 10^{-12} \) A. Without n-butane the trends are the same with slightly smaller values.

The ion current of all measurements for NO₂ (Figure 7.30b) begins at 0 A. The difference between the measurements with and without n-butane are more pronounced. The trend of the ion current is similar independent of the presence of n-butane, but without it the ion current of NO₂ is significantly lower. Generally, the increase in NO₂ intensity is steep for all flow rates reaching a maximum at the highest SED for \( 2.5 \text{ L.min}^{-1} \). The higher flow rates tend to have a higher ion current at the same SED.

Bromly et al.\cite{198} reported a promoted oxidation of n-butane in the presence of NO and vice versa of NO in the presence of n-butane. This promoting effect may explain the higher ion current of NO₂ in the presence of n-butane. Although the promoting effect is reported for temperatures above 300 °C, the plasma may induce similar conditions in the ignition area without elevated temperatures.\cite{198,199} However, the higher ion current of NO contradicts this explanation, because the NO mole fraction should be increased in the absence of n-butane.

The ion current of O₃ (Figure 7.30c) shows the highest dependence on the SED. For all flow rates there is a maximum of the ion current between \( 200 \text{ JL}^{-1} \) and \( 400 \text{ JL}^{-1} \). The ion current increases rapidly to a maximum and decreases until it reaches 0 A again in the range of \( 700 \text{ JL}^{-1} \) to \( 800 \text{ JL}^{-1} \). The rapid decrease of the O₃ mole fraction for higher SEDs either indicates a decomposition of O₃ by the plasma-produced reactive species, or the metastable O₃ decomposes...
due to the higher residence time until the QMS is reached.

The difference in the ion currents for both NO and O\textsubscript{3} in the measurements with and without n-butane may be explained by the influence of the different oxidizing potential of the gas mixtures on the filament of the QMS.

The slopes of the ion current may explain trends of conversion (Figure 7.23a) and energy efficiency (Figure 7.23b). The degree of conversion increases more steeply until 400 J/L\textsuperscript{−1} than above 400 J/L\textsuperscript{−1}, which is also the maximum of the O\textsubscript{3} mole fraction. The degree of conversion then increases less steeply than before, but linearly. Also above 800 J/L\textsuperscript{−1} the degree of conversion increases further, which may indicate either the decomposition of O\textsubscript{3} mentioned above providing highly reactive atomic O, or the further increasing NO mole fraction contributes to the degree of conversion, which would support the promoting effect of NO and n-butane mentioned previously. The decreasing EE may indicate a correlation of the process with the O\textsubscript{3} mole fraction, because the EE first increases and then decreases similar to the trend of O\textsubscript{3}.

7.11.2 Influence of the Temperature on the Ion Current of Reactive Oxygen Species

The trends for the ion current of NO shown in Section 7.11.1 are similar for different temperatures (Figure 7.31a). The ion current increases steeply and linearly with higher SED. For n-butane the values are slightly higher than in the absence of n-butane.

The trend of the NO\textsubscript{2} ion current of the n-butane measurements is also steep at the beginning.
For higher temperatures the ion current of NO\(_2\) reaches a maximum for higher SEDs. The higher the temperature is, the lower is the maximum value of the ion current at decreasing SEDs. This may correlate with the increased energy input by the elevated temperature as can be seen in Figure 7.30b for the 2.5 L min\(^{-1}\) measurement reaching an ion current maximum for higher SEDs. The measurements without n-butane also have a significant smaller ion current for NO\(_2\) indicating the promoting effect of NO in the gas mixture as described before.

The highest impact of the temperatures on the ion currents can be seen in Figure 7.31c for O\(_3\). At RT the ion current in the presence of n-butane reaches its maximum between 200 J L\(^{-1}\) and 300 J L\(^{-1}\) and then decreases again, whereas without n-butane the maximum is reached at 150 J L\(^{-1}\). The ion current decreases drastically with increasing temperature. There are still maxima at 90 J L\(^{-1}\), but with higher SED the ion current decreases strongly. At 140 °C the ion current of O\(_3\) is hardly detectable. The increased temperature may increase the decomposition rate of O\(_3\) and the release of atomic oxygen.[195]

This may lead to the increased degree of conversion shown in Figure 7.24a. Also the promoting effect of NO may increase the degree of conversion further, because the effect is reported to be more pronounced at higher temperatures.

Figure 7.31. Ion current of \(m/z = 30\) NO (a), \(m/z = 46\) NO\(_2\) (b), and \(m/z = 48\) O\(_3\) (c) with a power input of 15 W to 75 W in steps of 10 W at RT and 80 °C to 180 °C in steps of 20 °C with an uncoated electrode configuration. The applied voltages are summarized in Table B.4.
7.11.3 Influence of the Gap Width on the Ion Current of Reactive Oxygen Species

The influence of the gap width on the ion currents is shown below at RT and at 160 °C. The influence was measured at 120 °C and 140 °C as well, but the trends were less pronounced and are therefore only shown in Appendix A (Figure A.18 and Figure A.19). The ion currents of NO, NO₂, and O₃ of the RT measurements from Section 7.11.2 are used as comparison and shown as uncoated.

The ion current of NO at RT (Figure 7.32a) shows a moderate increase for all coatings parallel to the uncoated until 270 J L⁻¹. The 0.5 mm and the 1.0 mm coating show a steeper increase for higher SEDs. The uncoated electrode configuration shows a higher NO ion current than the coated electrode configurations until 330 J L⁻¹. For all coated electrode configurations the ion current of NO is only slightly depending on the presence of n-butane. At 160 °C the 0.5 mm coating shows no difference in the NO ion current independent of the presence of n-butane. The other coatings and the uncoated all show increased ion currents. In contrast to RT, at 160 °C the coated electrode configurations show a higher ion current than the uncoated one. Furthermore, the difference caused by the presence of n-butane is more pronounced.

The trends of the NO₂ ion current at RT (Figure 7.33a) shows the influence of narrower gaps on the mole fraction of NOₓ similar to Figure 7.32a. The uncoated electrode configuration with n-butane tends to have higher values for corresponding SEDs. The coated electrode configurations show similar trends until 210 J L⁻¹ with approx. 1.7 × 10⁻¹³ A. For the 0.5 mm coating the ion current then reaches a maximum at 1.9 × 10⁻¹³ A. The ion current of the other coatings

![Figure 7.32. Ion current of m/z = 30 of the gap width variation at RT (a) and 160 °C (b) with power input of 15 W to 75 W in steps of 10 W. The comparisons at 120 °C and 140 °C are shown in Figure A.18. The applied voltages are summarized in Tables B.4 – B.8.](image)

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increases further to a range of $3.3 \times 10^{-13}$ A to $4 \times 10^{-13}$ A until 330 JL$^{-1}$. The ion current of the 1.5 mm and the 2.0 mm coating further increases, whereas for the 1.0 mm it starts to decrease. The ion current was smaller in the absence of n-butane for the uncoated, the 1.5 mm coating, and the 2.0 mm coating. For the uncoated there is the lowest ion current among these measurements. For 0.5 mm and 1.0 mm coatings the ion current without n-butane exceeds the measurements at 270 JL$^{-1}$ and 350 JL$^{-1}$, respectively.

At 160 °C the impact of the catalyst is significantly more pronounced (Figure 7.33b). The uncoated electrode configuration shows a strong increase of the NO$_2$ ion current until its maximum at 330 JL$^{-1}$ of $6.2 \times 10^{-13}$ A with n-butane and $2.6 \times 10^{-13}$ A without. Among the coated electrode configurations the 1.5 mm and 2.0 mm coatings show the highest ion current of NO$_2$ with n-butane, but the ion current barely increases until 150 JL$^{-1}$ in a range of $1.5 \times 10^{-13}$ A to $2.3 \times 10^{-13}$ A. The ion current of the 1.0 mm coating increases as well to $2.3 \times 10^{-13}$ A in a more even way. The smallest ion current was obtained by the 0.5 mm coating reaching $1.0 \times 10^{-13}$ A at its maximum. The trends of the NO$_2$ mole fraction without n-butane show significantly higher values than with n-butane, except for the uncoated electrode configuration. The 0.5 mm coating shows values up to $2.2 \times 10^{-13}$ A and the other coating values in the range of $3.8 \times 10^{-13}$ A to $4.5 \times 10^{-13}$ A.

In Section 7.11.2 elevated temperatures led to increased NO$_2$ mole fractions presumably by the beneficial effect of NO and n-butane in the process. In Figure 7.33 the opposite is shown. Adams et al.[200] demonstrated the oxidizing behavior of NO$_2$ on MnO$_2$ using chemisorption. This process is reported to be more efficient with adsorbed OH on the MnO$_2$ surface, which

![Figure 7.33](image_url)

Figure 7.33. Ion current of $m/z = 46$ of the gap width variation at RT (a) and 160 °C (b) with power input of 15 W to 75 W in steps of 10 W. The comparisons at 120 °C and 140 °C are shown in Figure A.19. The applied voltages are summarized in Tables B.4 – B.8.
is only present during the conversion of n-butane originating from formed H$_2$O. This process would form NO$_3^-$ on the surface of the catalyst. The nitrate ion either forms Mn(NO$_3)_2$ or KNO$_3$ with the residual potassium from the catalyst synthesis. The first one would be decomposed under these reaction conditions forming NO$_2$ again. Therefore, the formation of KNO$_3$ seems plausible which may lead to a deactivation of the NO$_2$-removing behavior after some time, but because of the unknown mole fraction of formed NO$_2$ this cannot be predicted. The small impact of the catalyst on the NO ion current may be explained by the results of Gao et al. showing that among the different manganese oxides $\alpha$-MnO$_2$ is the least capable of oxidizing NO to NO$_2$.

In Figure 7.34 the ion current of O$_3$ at RT is shown. The ion currents for 120 °C, 140 °C, and 160 °C are not displayed, as no O$_3$ was detected because of the high temperature and the catalyst. The ion current of O$_3$ for all measurements with n-butane shows a maximum, which is decreasing with narrower gaps followed by a rapid decrease. The uncoated electrode configuration and the 2.0 mm coating show the highest O$_3$ ion current at 210 JL$^{-1}$ of $1.0 \times 10^{-12}$ A. The 1.5 mm coating at 150 JL$^{-1}$ achieves $8.5 \times 10^{-13}$ A and the 1.0 mm and 0.5 mm coating have the highest ion current of O$_3$ at 90 JL$^{-1}$ amounting to $6.0 \times 10^{-13}$ A and $3.9 \times 10^{-14}$ A, respectively. The decrease in ion current is equally pronounced for all electrode configurations. All measurements without n-butane tend to show higher ion currents of O$_3$ especially for the 1.0 mm and the 2.0 mm coating. The higher O$_3$ ion currents without n-butane may indicate that O$_3$ is consumed by the oxidation of n-butane. The decreasing ion current with narrower gaps indicate a decomposition of O$_3$ by MnO$_2$ as shown by Dhandapani et al. The presence of $\alpha$-MnO$_2$ strongly decreases the mole fractions of NO$_2$ and O$_3$, which were produced by the plasma. This is a significant benefit of the catalyst removing harmful compo-

![Figure 7.34. Ion current of $m/z = 48$ of the gap width variation for RT with power input of 15 W to 75 W in steps of 10 W. The applied voltages are summarized in Tables B.4 – B.8.](image)
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Volatile Organic Compound components produced by the plasma like the oxidation of the produced CO to CO$_2$. Similar effects were shown by Ge et al.[204] removing NO$_2$ and O$_3$ with MnO$_2$ in a corona discharge.

7.12 Ignition Behavior of the Electrode Configuration

The ignition behavior of the uncoated electrode configuration and for the gap variation was investigated using a digital camera as described in Section 4.4.6. Images were recorded for several different conditions. The pictures were not color-corrected, therefore the color of the plasma in all pictures does not necessarily display the real color. For the ignition behavior of the uncoated electrode configuration, images as shown in Figure 7.35a were used. These images were obtained by plasma in N$_2$, in N$_2$ with switched polarity, and in synthetic air. From the N$_2$ images the microdischarges of Figure 7.35b were derived. In synthetic air the ignition was evenly distributed on the metal grid, no single microdischarges were identified, and there was no difference between both N$_2$ measurements. Therefore, only the ignition spots for one measurement series are shown in Figure 7.35b. For this purpose a series of pictures was taken in the range of 7 kV to 12 kV twice, with the plasma switched off in between. One grid line was chosen to be enlarged, and the images were modified to enhance the contrast of the ignition spots. The ignition shows differences in the range of 7 kV to 10 kV, but until 11 kV the ignition behavior is very similar. For a direct comparison of the two series one side of each 12 kV image was separated, and one was mirrored. The combination of these two images is shown in Figure 7.35c. These locations of the ignition spots show a high reproducibility, and even the shape of the ignitions are very similar most of the time.

LSM images of a pristine grid line (Figure 7.35d) and of a used grid line (Figure 7.35e) show the development of nooks on the edge of the grid line, which are marked with red arrows. Enlarged images also show dark areas around these nooks indicating coke may have been produced. To examine if the nooks are formed by the ignition spots, the distance from one nook to another was measured on several nooks and compared to the distance between single ignition spots from Figure 7.35c. The distances are summarized in Table 7.3. Because there was no scale in the images, the grid line width of 450 µm was used as reference. This may have produced a large error of this measurement, but should deliver meaningful orders of magnitude. The average distance between the nooks was 181 µm, and between the ignition spots it was 225 µm. Taking the potentially large error of the distances into account, this observation indicates ignition of the plasma on these nooks. The nooks form more edges and sharp points leading to high local electric fields, which enhance ignition.[29]

The ignition behavior is strongly influenced by the catalyst. In Figure 7.36 the plasma ignition behavior with catalyst of the gap variation series is shown. The images were not always taken
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Figure 7.35. (a) Overall view of the plasma ignition in N\textsubscript{2} at 11 kV. (b) Series of images from one single grid line at different applied voltages in N\textsubscript{2}. (c) Mirrored images of the left side of both 12 kV grid lines from (b). (d) LSM microscope image of a pristine grid line. (e) LSM microscope image of a used grid line.

at the same spot because of experimental limitations. The applied voltage was set to 10 kV, and the ignition took place in synthetic air. Figure 7.36a shows the strongly disturbed ignition for the 0.5 mm gap. This strong disturbance explains the small degree of conversion for the 0.5 mm coating shown in Figure 7.26. Nevertheless, the high selectivity to CO\textsubscript{2} may be induced by the ignition in the few possible spots so close to the catalyst. For the 1.0 mm coating (Figure 7.36b) an undisturbed plasma can be seen. Furthermore, the catalyst is in reach of the plasma, which may have led to such high selectivities to CO\textsubscript{2} (Figure 7.27). For the 1.5 mm and the 2.0 mm coatings there is a gap observed between the plasma and the catalyst. This does not allow the optimal interaction between catalyst and plasma. Moreover, the selectivity to CO\textsubscript{2} decreases in case of larger gaps between plasma and catalyst.
### Table 7.3. Distances of nooks from Figure 7.35e and of ignition spots from Figure 7.35c.

<table>
<thead>
<tr>
<th>Distance / µm</th>
<th>1.</th>
<th>2.</th>
<th>3.</th>
<th>4.</th>
<th>5.</th>
<th>6.</th>
<th>7.</th>
<th>0</th>
</tr>
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<tbody>
<tr>
<td>Used electrode</td>
<td>186</td>
<td>169</td>
<td>184</td>
<td>164</td>
<td>194</td>
<td>183</td>
<td>186</td>
<td>181</td>
</tr>
<tr>
<td>Ignition spots</td>
<td>197</td>
<td>237</td>
<td>242</td>
<td>194</td>
<td>242</td>
<td>203</td>
<td>261</td>
<td>225</td>
</tr>
</tbody>
</table>

Figure 7.36. Ignition behavior in synthetic air with catalyst for 0.5 mm (a), 1.0 mm (b), 1.5 mm (c), and 2.0 mm (d). The color of the plasma can not be compared on the basis of this images because of different color corrections.

In Appendix A the same images are shown with N₂ showing similar behavior for the wider gaps, but for the 0.5 mm coating there is a significant larger ignition area observed demonstrating potential interaction of the plasma with the catalyst coating.

### 7.13 Optical Emission Spectroscopy

The performed OES measurements and the processing of the results were joint experiments with Ryan Thomas Nguyen-Smith and Philipp Wirth (Institute for Electrical Engineering and Plasma Technology, AEPT).

OES was used to determine fundamental plasma parameters (electron density \(n_e\), reduced electric field \((E/N)\)) and the gas temperature \(T_g\) in the discharge area. This measurement series aimed at analyzing the influences of the coatings on the discharge. However, the coating made it challenging to obtain precise values of the expansion of the plasma volume on the electrode configurations. Therefore, the values of the plasma parameters should be taken with care, but nevertheless may deliver insights into trends caused by the coating. All measurements were performed in synthetic air. Offerhaus et al.\(^{[49]}\) found for different excitation parameters \((f_{\text{pul}} = 17 \text{ kHz}; 7 \text{ kV})\) a gas temperature of 380 K, an electron density of \(1.6 \times 10^{11} \text{ cm}^{-3}\), and a reduced electric field of 503 Td.
Figure 7.37 shows the gas temperature, the electron density, and the reduced electric field as a function of the SED of an uncoated electrode configuration compared with coated electrode configurations with gap widths of 1.0 mm, 1.5 mm, and 2.0 mm. The 0.5 mm coating is not shown, because the strongly disturbed ignition prevented reliable measurements (Figure 7.36a). The error bars visualize the standard deviation of the three measurements recorded for each data point. The absolute error of this method is discussed by Offerhaus et al.\cite{49} Generally, the determination of the plasma parameters was challenging because of the undefined plasma volume and the unsteady behavior of the discharge. For the 1.0 mm and the 2.0 mm coatings just one electrode configuration was investigated, but for the uncoated and the 1.5 mm coating three electrode configurations were analyzed. The iterations of all parameters are shown in Figure A.21 revealing a good reproducibility for different electrode configurations (uncoated and 1.5 mm coating).

The gas temperatures (Figure 7.37a) were determined based on the rotational band $N_2(C - B, 0 - 0)$ as described in Section 3.9.\cite{49,171} The uncoated electrode configuration and the ones with 1.5 mm and 2.0 mm coatings show similar gas temperatures increasing from 420 K at 118 $JL^{-1}$ to 553 K at 476 $JL^{-1}$. For the 1.0 mm coating an increase of $T_g$ is observed. For lower SEDs the gas temperature was similar to the other electrode configurations, but with increasing SEDs the deviation of the 1.0 mm coating increases up to a temperature of 610 K. This shows that a coating with narrower gaps results in increasing gas temperature leaving room for much interpretation. The narrower gap may lead to a stronger influence by electron impacts on the nearby molecules and therefore to higher gas temperatures. Furthermore, a more pronounced ion formation on the catalyst surface or recombination processes may increase the gas temperature. For a precise answer further investigations are needed.

The evaluation of the electron density and the reduced electric field were made with the CRM also described in Section 3.9. In contrast to the gas temperature, where coated (1.5 mm and 2 mm) and uncoated electrode configurations showed similar results, for the electron density (Figure 7.37b) a difference between coated and uncoated electrode configurations was observed. The coated electrode configurations showed an electron density between $1 \times 10^{11}$ cm$^{-3}$ and $5 \times 10^{11}$ cm$^{-3}$, whereas the electron density of the uncoated electrode configuration increased more steeply from $1.5 \times 10^{11}$ cm$^{-3}$ to $7.5 \times 10^{11}$ cm$^{-3}$ showing a decrease of electron density for coated electrode configurations. An over-estimated plasma volume for the coated electrode configurations may lead to decreased values.

The reduced electric field (Figure 7.37c) was decreasing for all electrode configurations from 750 Td to 690 Td, but none of the electrode configurations showed a separated behavior. This may indicate that the electron energy distribution function (EEDF) was not shifted over the course of the SED.
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Figure 7.37. Plots of the gas temperature (a), the electron density (b), and the reduced electric field (c) as a function of the SED with different electrode configurations. All measurements were carried out in synthetic air without n-butane. The applied voltages are summarized in Table B.9.

### 7.14 Photocatalytic Conversion of n-Butane

The plasma discharge emits light in the ultraviolet (UV) range.\(^{[49]}\) Therefore, the possibility of contribution to the conversion of n-butane of this UV radiation was investigated. The activity of the known photocatalyst SrTiO\(_3\) was compared to the activity of α-MnO\(_2\) in plasma-assisted oxidation of n-butane. First the photocatalytic activity of the SrTiO\(_3\) was validated with the set-up described in Section 4.5, then its plasma-catalytic activity was compared to the photocatalytically inactive catalyst of this study (α-MnO\(_2\)) as well as to an uncoated electrode configuration. The activity was investigated at RT, 120 °C, and 140 °C with a total light power of 2.22 W resulting in an SED of 132 J L\(^{-1}\). The elevated temperatures were necessary, because the desorption of the product is known to limit the efficiency of SrTiO\(_3\).\(^{[205,206]}\) The degrees
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of n-butane conversion are summarized in Table 7.4. At RT there was a degree of n-butane conversion of 0.6% and at elevated temperatures of 1.9%. For the plasma-catalytic investigations SrTiO$_3$ was coated on an electrode configuration with a gap of 1.5 mm and a loading of 3 mg cm$^{-2}$. This electrode configuration was compared to an electrode configuration with $\alpha$-MnO$_2$ coated in the same way and an uncoated one. The degrees of conversion at RT, 120 °C, and 140 °C of these measurements are shown in Figure 7.38a as a function of the SED. The degree of conversion at RT was the highest for the SrTiO$_3$ electrode configuration. At elevated temperatures a difference was challenging to observe. Therefore, in Figure 7.38b the degrees of conversion are shown for 330 J L$^{-1}$ only. The degree of conversion at RT of the SrTiO$_3$ coating was 7% higher than that of the other electrode configurations. This difference decreases with increasing temperature down to 1%. The other figures of merit are not shown here, because for them the SrTiO$_3$ coating shows similar behavior as the uncoated electrode configuration. These result may suggest a beneficial effect of the photocatalyst utilizing the emitted UV radiation. However, the light power emitted by the plasma was measured with the photosensor used in

Table 7.4. Degrees of n-butane conversion of a photocatalytic application in synthetic air at a flow rate of 1 L min$^{-1}$ over SrTiO$_3$ at different temperatures with a total light power of 2.22 W.

<table>
<thead>
<tr>
<th></th>
<th>RT</th>
<th>120 °C</th>
<th>140 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butane</td>
<td>0.6%</td>
<td>1.9%</td>
<td>1.9%</td>
</tr>
</tbody>
</table>

Figure 7.38. (a) Degrees of n-butane conversion of three electrode configurations with a flow of 10 L min$^{-1}$ and 300 ppm n-butane in synthetic air: two coated with SrTiO$_3$ and $\alpha$-MnO$_2$ with a gap width of 1.5 mm and a loading of 3 mg cm$^{-2}$ and one uncoated. The applied voltages are summarized in Table B.10. (b) Detailed comparison of the measurements of (a) with a SED of 330 J L$^{-1}$.
Section 4.5 for determination of light power of the LED array. Therefore, the synthetic quartz window (Section 4.4.2) was used to ensure a maximum transmission. With this sensor there was no measurable amount of light power. This indicates that no photocatalysis can take place by the UV radiation of the plasma. Similar results were found by Mei et al.\textsuperscript{[207]} The increased degree of conversion may originate from different dielectric behavior of SrTiO\textsubscript{3} compared to $\alpha$-MnO\textsubscript{2}.
8 Summary and Conclusion

In this work an $\alpha$-MnO$_2$-enhanced twin-surface dielectric barrier discharge driven plasma oxidation for the abatement of n-butane in synthetic air was investigated. The used set-up and the reactor were optimized in the course of this work to obtain deeper insights into the process. First measurements showed that a total oxidation of n-butane to CO$_2$ and H$_2$O takes place without significant formation of organic by-products. The independence of the degree of n-butane conversion from the n-butane mole fraction was demonstrated. Basic CFD simulations showed laminar flow behavior above and below the electrode configuration without plasma ignition, but the results of Schlieren imaging and formation of deposits on the reactor walls demonstrated an influence of the plasma on the flow conditions. Elevated temperatures had a beneficial effect on n-butane conversion, but selectivity shifted in favor of CO instead of CO$_2$. The increase of the CO mole fraction, while the CO$_2$ mole fraction stayed constant may indicate two separate formation pathways, which are independent from each other. The enrichment of synthetic air with liquid VOCs was established, and a degree of toluene conversion of up to 69% was achieved. However, further investigations of the abatement of toluene or other liquid VOCs were postponed because of a distinct formation of tar-like deposits in the reactor.

Thermocatalytic investigations of the $\alpha$-MnO$_2$ catalyst for the simultaneous conversion of n-butane and CO were carried out. High activity for the conversion of n-butane with a $T_{50}$ of 253 °C and even higher for the conversion of CO with a $T_{50}$ of 153 °C were observed. The degree of n-butane conversion was increased in the presence of CO, but on the other hand the degree of CO conversion was decreased in presence of n-butane. For CO conversion the presence of two different active sites was discussed. All of the thermocatalytic measurements achieved a carbon balance of over 95% at the highest achieved degree of conversion. The high activity for the oxidation of CO was beneficial to convert the formed CO during plasma operations in a consecutive oxidation step to CO$_2$.

Several coating geometries of the electrode configuration showed a detrimental effect on the performance of the process. The plasma ignition of these coatings was disturbed and therefore n-butane conversion was decreased, but the selectivity to CO$_2$ was increased. To overcome the negative influence on the conversion a mask was developed, which prevented the electrode grid lines to be coated, thus lowering the disturbance of plasma ignition. The first version of this mask produced a gap of 1.5 mm between the grid line and the catalyst coating. This coating geometry increased the degree of n-butane conversion at the same applied voltage between 8% and 10%. The influence of the catalyst on the selectivities was more pronounced. At 11 kV and 140 °C the selectivity to CO decreased from 52% to 10% and the selectivity to CO$_2$ increased from 44% to 95%. The application of the $\alpha$-MnO$_2$ catalyst at elevated temperatures was found...
Summary and Conclusion

to result in increased SEDs and therefore decreasing EE. The application of $\alpha$-MnO$_2$ in the plasma-driven abatement of n-butane in synthetic air at constant applied voltage influenced the achieved degrees of conversion, the selectivities, and the carbon balance in a favorable way, indicating a consecutive catalytic oxidation of plasma-produced CO.

The introduction of all figures of merit as a function of the SED instead of the applied voltage removed the influence of flow rate and enabled a better comparison of the used set-up to similar applications. Based on the SED also the energy efficiency was calculated. The energy efficiency indicates an efficiency bias for elevated temperatures demonstrating that the higher degrees of conversion at elevated temperatures were more likely attributed to the additional energy input than to synergistic effects of temperature and plasma.

The SEDs also revealed that the beneficial effect on the degree of n-butane conversion of the catalyst for the same applied voltage vanished for the same SED compared with an uncoated electrode configuration. Nevertheless, the variation of the gap width revealed the 1 mm gap width as best performing. The degree of conversion was very similar to the uncoated electrode configuration and the selectivities were shifted in favor of CO$_2$. Furthermore, the carbon balance was higher at elevated temperatures with catalyst, which decreased the amount of undetected by-products. Photographs of the ignition on the different coatings showed plasma in contact with the catalyst for the 1.0 mm gap width, strong disturbance of the plasma for the 0.5 mm gap width, and gaps between plasma and the catalyst for the 1.5 mm and the 2.0 mm coatings.

The mole fractions of NO, NO$_2$, and O$_3$ were also influenced by temperature and the presence of the catalyst and of n-butane. The NO mole fraction increased as a function of temperature and in the presence of n-butane. The influence of the catalyst was minor, with a slightly stronger increase of the NO mole fraction in the presence of n-butane compared with the uncoated electrode configuration. NO$_2$ showed a more pronounced dependence on the presence of n-butane. The mole fraction was doubled by the presence of n-butane without catalyst, but halved with n-butane and catalyst. The strongest temperature dependence was found for the mole fraction of O$_3$ with a strong decrease at elevated temperatures indicating its faster decomposition. The presence of catalyst and n-butane led to a minor decrease of the O$_3$ mole fraction except for the 0.5 mm coating, but this was more attributed to the strong disturbance of the plasma.

The catalyst also showed an influence on the fundamental plasma parameters. The gas temperature was slightly increased for the 1.0 mm coating, and the electron density was decreased for all coatings. However, this has to be taken with care, because of rough estimations made for the plasma volume, which has an influence on these parameters. And at last, emitted UV light was investigated for possible utilization, but no measurable amount of UV radiation was found with the used sensor. Nevertheless, the SrTiO$_3$ photocatalyst showed a higher degree of
n-butane conversion in plasma application than $\alpha$-MnO$_2$ and the uncoated electrode configuration, which may originate from the different dielectric behavior in comparison to $\alpha$-MnO$_2$. However, the selectivities were similar to the uncoated electrode configuration. The application of $\alpha$-MnO$_2$ on the twin-SDBD was successfully accomplished. Although n-butane conversion was not increased by the catalyst, the selectivity was shifted towards CO$_2$ and the mole fraction of the ROS was lowered with as little disturbance of the plasma as possible. The described method enables a rapid investigation of other catalysts. Even when the conversion of VOCs with this twin-SDBD may not be competitive with other plasma applications or common VOC abatement methods until now, the investigations of new pathways may lead to more sustainable solutions in the future, and the set-up’s spectroscopic accessibility makes it highly valuable for further academic research.
Summary and Conclusion
9 Outlook

In future measurements the plasma-catalyst interaction should be increased and investigated more deeply. High-resolution high-speed photography may show the propagation of the streamer on the catalyst surface. Knowledge about formed or decomposed ROS on the catalyst surface and their formation in the plasma may enable tailored catalyst composition. This may be achieved with (two atom) laser induced fluorescence ((TA)LIF) or a molecular beam mass spectrometer (MBMS). Furthermore, identification of the processes responsible for the strong increased gas temperature with and without catalyst measured with OES may deliver more control over the entire process and an optimized high voltage generator may lead to more elaborated control over the applied voltages and pulses.

The determination of the mole fractions of NO and NO\textsubscript{2} using a calibrated MS is expected to deliver insight into the order of magnitude of NO\textsubscript{x} species, which have to be removed. This removal may be achieved by SCR reacting with n-butane according to Equation 2.26. The direct validation of the activity of a SCR catalyst will be challenging. In thermocatalysis the activity may be proven by the formation of N\textsubscript{2} in an inert gas atmosphere such as He. However, for plasma applications there are no inert gases, because noble gases have a strong influence on the ignition behavior.

The catalyst may be optimized in terms of electrical behavior such as dielectric constant (LaMnO\textsubscript{3}, Pt/SrTiO\textsubscript{3}), but also in terms of thermocatalytic activity and selectivity (Pt, Cu/MnO\textsubscript{2}, SCR catalysts). At last, the flow behavior in the reactor influenced by the plasma should be investigated further. Therefore, particle image velocimetry (PIV) may deliver insights without the necessity of making assumptions needed for simulations. These investigations may lead to new findings for an optimized electrode configuration.
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Figure A.4. Transmission in range of 200 nm to 400 nm for natural and synthetic quartz glass.
Figure A.5. Alumina plates for thermocatalytic oxidation with different areas coated with $\alpha$-MnO$_2$.

Figure A.6. (a) Degree of n-butane conversion for mole fractions of n-butane in a range of 50 ppm to 450 ppm in synthetic air with applied voltages in a range of 8 kV to 13 kV and a pulse repetition frequency of 2 kHz in addition to Figure 7.2a. (b) Pyrolysis-GC-MS measurement of the tar-like precipitate shown in Figure 7.3b.

Figure A.7. Bending of the electrode configuration at elevated temperatures without and with plasma ignition as described in Section 7.6.1.
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Temperature Variation with a 0.5 mm Gap Coating

Figure A.9. Degree of conversion (a), energy efficiency (b), selectivities to CO\textsubscript{2} (c), CO (d), and the carbon balance (e) with power input of 15 W to 75 W in steps of 10 W at RT and 120 °C to 160 °C in steps of 20 °C with an electrode configuration coated with a gap of 0.5 mm between catalyst and grid line. The applied voltages are summarized in Table B.5.
Temperature Variation with a 1.0 mm Gap Coating

Figure A.10. Degree of conversion (a), energy efficiency (b), selectivities to CO₂ (c), CO (d), and the carbon balance (e) with power input of 15 W to 75 W in steps of 10 W at RT and 120 °C to 160 °C in steps of 20 °C with an electrode configuration coated with a gap of 1.0 mm between catalyst and grid line. The applied voltages are summarized in Table B.6.
Appendix

Temperature Variation with a 1.5 mm Gap Coating

Figure A.11. Degree of conversion (a), energy efficiency (b), selectivities for CO\textsubscript{2} (c), CO (d), and the carbon balance (e) with power input of 15 W to 75 W in steps of 10 W at RT and 120 °C to 160 °C in steps of 20 °C with an electrode configuration coated with a gap of 1.5 mm between catalyst and grid line. The applied voltages are summarized in Table B.7.
Appendix

Temperature Variation with a 2.0 mm Gap Coating

Figure A.12. Degree of conversion (a), energy efficiency (b), selectivities to CO₂ (c), CO (d), and the carbon balance (e) with power input of 15 W to 75 W in steps of 10 W at RT and 120 °C to 160 °C in steps of 20 °C with an electrode configuration coated with a gap of 2.0 mm between catalyst and grid line. The applied voltages are summarized in Table B.8.
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Appendix

Ion Currents at different Temperatures and Gap Widths

Figure A.14. Ion current of m/z 30 (a) and m/z 46 (b) of a 0.5 mm coating at RT, 120 °C, 140 °C, and 160 °C with n-butane in synthetic air and without n-butane in synthetic air in a range of 90 J/L⁻¹ to 460 J/L⁻¹. The applied voltages are summarized in Table B.5.

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Figure A.18. Ion current of \textit{m/z} 30 of the gap width variation at RT (a), 120 °C (b), 140 °C (c), and 160 °C (d) with power input of 15 W to 75 W in steps of 10 W. The applied voltages are summarized in Tables B.4 – B.8.

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B Appendix

Table B.1. Settings of the QMS for different modes.

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<th>Calibrated settings</th>
<th>Ion current setting</th>
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<td>Range L</td>
<td>$1 \times 10^{-9}$</td>
<td>[–]</td>
<td>$1 \times 10^{-10}$</td>
</tr>
<tr>
<td>Pause Cal.</td>
<td>5.0</td>
<td>5.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Speed</td>
<td>[–]</td>
<td>[–]</td>
<td>1 s</td>
</tr>
<tr>
<td>Steps</td>
<td>[–]</td>
<td>[–]</td>
<td>64</td>
</tr>
</tbody>
</table>

Table B.2. Paschen coefficients A and B used from ref.\cite{36,38} for the plot of Figure 2.1 with Equation 2.1.

<table>
<thead>
<tr>
<th>Unit</th>
<th>N\textsubscript{2}</th>
<th>Ar</th>
<th>CO\textsubscript{2}</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Pa\textsuperscript{-1} m\textsuperscript{-1}</td>
<td>9.00</td>
<td>10.2</td>
<td>15.00</td>
</tr>
<tr>
<td>B</td>
<td>Pam</td>
<td>256.5</td>
<td>176.3</td>
<td>349.5</td>
</tr>
</tbody>
</table>

Table B.3. Applied voltages for the measurements shown in Section 7.9.1.

<table>
<thead>
<tr>
<th></th>
<th>15 W</th>
<th>25 W</th>
<th>35 W</th>
<th>45 W</th>
<th>55 W</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 L\text{min}\textsuperscript{-1}</td>
<td>8.0 kV</td>
<td>8.8 kV</td>
<td>9.8 kV</td>
<td>10.5 kV</td>
<td>11.2 kV</td>
</tr>
<tr>
<td>7.5 L\text{min}\textsuperscript{-1}</td>
<td>9.2 kV</td>
<td>9.4 kV</td>
<td>9.9 kV</td>
<td>10.0 kV</td>
<td>11.2 kV</td>
</tr>
<tr>
<td>5 L\text{min}\textsuperscript{-1}</td>
<td>8.9 kV</td>
<td>9.4 kV</td>
<td>10.0 kV</td>
<td>10.7 kV</td>
<td>11.2 kV</td>
</tr>
<tr>
<td>2.5 L\text{min}\textsuperscript{-1}</td>
<td>8.7 kV</td>
<td>9.2 kV</td>
<td>9.7 kV</td>
<td>10.3 kV</td>
<td>10.8 kV</td>
</tr>
</tbody>
</table>
Table B.4. Applied voltages for the measurements shown in Section 7.9.2 and Section 7.10.

<table>
<thead>
<tr>
<th></th>
<th>15 W</th>
<th>25 W</th>
<th>35 W</th>
<th>45 W</th>
<th>55 W</th>
<th>65 W</th>
<th>75 W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic air with n-butane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RT begin</td>
<td>8.0 kV</td>
<td>8.8 kV</td>
<td>9.8 kV</td>
<td>10.5 kV</td>
<td>11.2 kV</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>80 °C</td>
<td>8.5 kV</td>
<td>8.7 kV</td>
<td>9.5 kV</td>
<td>10.3 kV</td>
<td>10.7 kV</td>
<td>11.2 kV</td>
<td>–</td>
</tr>
<tr>
<td>100 °C</td>
<td>7.3 kV</td>
<td>8.2 kV</td>
<td>9.0 kV</td>
<td>9.6 kV</td>
<td>10.3 kV</td>
<td>10.8 kV</td>
<td>11.1 kV</td>
</tr>
<tr>
<td>120 °C</td>
<td>7.9 kV</td>
<td>8.2 kV</td>
<td>8.8 kV</td>
<td>9.7 kV</td>
<td>10.2 kV</td>
<td>10.6 kV</td>
<td>10.8 kV</td>
</tr>
<tr>
<td>140 °C</td>
<td>7.9 kV</td>
<td>8.3 kV</td>
<td>8.9 kV</td>
<td>9.6 kV</td>
<td>10.1 kV</td>
<td>10.4 kV</td>
<td>10.7 kV</td>
</tr>
<tr>
<td>160 °C</td>
<td>8.0 kV</td>
<td>8.2 kV</td>
<td>8.9 kV</td>
<td>9.7 kV</td>
<td>10.0 kV</td>
<td>10.3 kV</td>
<td>10.6 kV</td>
</tr>
<tr>
<td>180 °C</td>
<td>7.9 kV</td>
<td>8.2 kV</td>
<td>8.8 kV</td>
<td>9.6 kV</td>
<td>10.0 kV</td>
<td>10.2 kV</td>
<td>10.5 kV</td>
</tr>
<tr>
<td>RT end</td>
<td>8.6 kV</td>
<td>9.2 kV</td>
<td>10 kV</td>
<td>10.6 kV</td>
<td>11.2 kV</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Table B.5. Applied voltages for the measurements shown in Section 7.10 for the 0.5 mm gap coating.

<table>
<thead>
<tr>
<th></th>
<th>15 W</th>
<th>25 W</th>
<th>35 W</th>
<th>45 W</th>
<th>55 W</th>
<th>65 W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic air with n-butane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RT</td>
<td>7.4 kV</td>
<td>7.8 kV</td>
<td>8.1 kV</td>
<td>8.5 kV</td>
<td>9.1 kV</td>
<td>9.6 kV</td>
</tr>
<tr>
<td>120 °C</td>
<td>6.9 kV</td>
<td>7.2 kV</td>
<td>7.4 kV</td>
<td>7.7 kV</td>
<td>8.0 kV</td>
<td>8.5 kV</td>
</tr>
<tr>
<td>140 °C</td>
<td>6.9 kV</td>
<td>7.4 kV</td>
<td>7.5 kV</td>
<td>7.8 kV</td>
<td>7.9 kV</td>
<td>8.4 kV</td>
</tr>
<tr>
<td>160 °C</td>
<td>6.9 kV</td>
<td>7.3 kV</td>
<td>7.6 kV</td>
<td>7.8 kV</td>
<td>8.1 kV</td>
<td>8.5 kV</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>15 W</th>
<th>25 W</th>
<th>35 W</th>
<th>45 W</th>
<th>55 W</th>
<th>65 W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic air without n-butane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RT</td>
<td>7.7 kV</td>
<td>7.7 kV</td>
<td>7.9 kV</td>
<td>8.2 kV</td>
<td>8.5 kV</td>
<td>8.9 kV</td>
</tr>
<tr>
<td>120 °C</td>
<td>8.0 kV</td>
<td>8.4 kV</td>
<td>8.9 kV</td>
<td>9.6 kV</td>
<td>9.8 kV</td>
<td>10.2 kV</td>
</tr>
<tr>
<td>140 °C</td>
<td>7.0 kV</td>
<td>7.4 kV</td>
<td>7.6 kV</td>
<td>7.9 kV</td>
<td>8.3 kV</td>
<td>8.6 kV</td>
</tr>
<tr>
<td>160 °C</td>
<td>7.0 kV</td>
<td>7.4 kV</td>
<td>7.5 kV</td>
<td>7.7 kV</td>
<td>7.9 kV</td>
<td>8.3 kV</td>
</tr>
</tbody>
</table>
Table B.6. Applied voltages for the measurements shown in Section 7.10 for the 1.0 mm gap coating.

<table>
<thead>
<tr>
<th></th>
<th>15 W</th>
<th>25 W</th>
<th>35 W</th>
<th>45 W</th>
<th>55 W</th>
<th>65 W</th>
<th>75 W</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>8.0 kV</td>
<td>8.6 kV</td>
<td>9.4 kV</td>
<td>10.1 kV</td>
<td>10.3 kV</td>
<td>10.5 kV</td>
<td>10.6 kV</td>
</tr>
<tr>
<td>120 °C</td>
<td>7.5 kV</td>
<td>8.0 kV</td>
<td>8.7 kV</td>
<td>9.2 kV</td>
<td>9.5 kV</td>
<td>9.7 kV</td>
<td>9.8 kV</td>
</tr>
<tr>
<td>140 °C</td>
<td>7.5 kV</td>
<td>8.1 kV</td>
<td>8.8 kV</td>
<td>9.3 kV</td>
<td>9.5 kV</td>
<td>9.6 kV</td>
<td>9.8 kV</td>
</tr>
<tr>
<td>160 °C</td>
<td>7.4 kV</td>
<td>8.0 kV</td>
<td>8.8 kV</td>
<td>9.2 kV</td>
<td>9.4 kV</td>
<td>9.5 kV</td>
<td>9.7 kV</td>
</tr>
</tbody>
</table>

Table B.7. Applied voltages for the measurements shown in Section 7.10 for the 1.5 mm gap coating.

<table>
<thead>
<tr>
<th></th>
<th>15 W</th>
<th>25 W</th>
<th>35 W</th>
<th>45 W</th>
<th>55 W</th>
<th>65 W</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>8.1 kV</td>
<td>8.5 kV</td>
<td>9.5 kV</td>
<td>10.1 kV</td>
<td>10.6 kV</td>
<td>11.0 kV</td>
</tr>
<tr>
<td>120 °C</td>
<td>7.4 kV</td>
<td>7.9 kV</td>
<td>8.6 kV</td>
<td>9.3 kV</td>
<td>9.7 kV</td>
<td>10.1 kV</td>
</tr>
<tr>
<td>140 °C</td>
<td>7.8 kV</td>
<td>8.2 kV</td>
<td>9.0 kV</td>
<td>9.7 kV</td>
<td>10.0 kV</td>
<td>10.3 kV</td>
</tr>
<tr>
<td>160 °C</td>
<td>7.8 kV</td>
<td>8.1 kV</td>
<td>8.9 kV</td>
<td>9.6 kV</td>
<td>9.9 kV</td>
<td>10.2 kV</td>
</tr>
</tbody>
</table>

Appendix
Table B.8. Applied voltages for the measurements shown in Section 7.10 for the 2.0 mm gap coating.

<table>
<thead>
<tr>
<th></th>
<th>15 W</th>
<th>25 W</th>
<th>35 W</th>
<th>45 W</th>
<th>55 W</th>
<th>65 W</th>
<th>75 W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic air with n-butane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RT</td>
<td>8.1 kV</td>
<td>8.7 kV</td>
<td>9.6 kV</td>
<td>10.3 kV</td>
<td>10.7 kV</td>
<td>11.3 kV</td>
<td>–</td>
</tr>
<tr>
<td>120 °C</td>
<td>7.6 kV</td>
<td>8.1 kV</td>
<td>8.8 kV</td>
<td>9.6 kV</td>
<td>10.0 kV</td>
<td>10.4 kV</td>
<td>10.6 kV</td>
</tr>
<tr>
<td>140 °C</td>
<td>7.9 kV</td>
<td>8.2 kV</td>
<td>8.6 kV</td>
<td>9.5 kV</td>
<td>9.9 kV</td>
<td>10.3 kV</td>
<td>10.6 kV</td>
</tr>
<tr>
<td>160 °C</td>
<td>7.9 kV</td>
<td>8.2 kV</td>
<td>8.8 kV</td>
<td>9.4 kV</td>
<td>9.8 kV</td>
<td>10.2 kV</td>
<td>10.4 kV</td>
</tr>
<tr>
<td>Synthetic air without n-butane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RT</td>
<td>8.4 kV</td>
<td>8.9 kV</td>
<td>9.7 kV</td>
<td>10.4 kV</td>
<td>10.7 kV</td>
<td>11.1 kV</td>
<td>–</td>
</tr>
<tr>
<td>120 °C</td>
<td>8.1 kV</td>
<td>8.5 kV</td>
<td>8.9 kV</td>
<td>9.4 kV</td>
<td>9.9 kV</td>
<td>10.3 kV</td>
<td>10.5 kV</td>
</tr>
<tr>
<td>140 °C</td>
<td>8.1 kV</td>
<td>8.4 kV</td>
<td>8.8 kV</td>
<td>9.4 kV</td>
<td>9.9 kV</td>
<td>10.3 kV</td>
<td>10.5 kV</td>
</tr>
<tr>
<td>160 °C</td>
<td>8.0 kV</td>
<td>8.3 kV</td>
<td>8.7 kV</td>
<td>9.4 kV</td>
<td>9.9 kV</td>
<td>10.2 kV</td>
<td>10.4 kV</td>
</tr>
</tbody>
</table>

Table B.9. Applied voltages for the measurements shown in Figure 7.37. In contrast to the other summarized applied voltages the voltages are written by measuring sequence, due to the deviant measurement procedure.

1. uncoated 8.0 kV, 8.2 kV, 9.0 kV, 9.2 kV, 10.0 kV, 10.5 kV, 11.0 kV, and 11.2 kV
2. uncoated 7.9 kV, 8.7 kV, 9.0 kV, 10.0 kV, 10.6 kV, and 11.0 kV
3. uncoated 7.9 kV, 9.0 kV, 10.0 kV, 10.7 kV, and 11 kV
   1.0 mm 8.1 kV, 8.0 kV, 8.4 kV, 9.0 kV, 9.4 kV, and 10.0 kV
1. 1.5 mm 8.0 kV, 8.7 kV, 9.0 kV, 10.0 kV, 10.8 kV, and 11.0 kV
2. 1.5 mm 8.0 kV, 8.6 kV, 9.0 kV, 10.0 kV, 10.1 kV, 10.8 kV, and 10.8 kV
3. 1.5 mm 7.9 kV, 8.0 kV, 8.8 kV, 9.0 kV, 10.0 kV, 10.3 kV, and 10.5 kV
2.0 mm 8.0 kV, 8.8 kV, 9.0 kV, 9.9 kV, 10.8 kV, and 11.0 kV

Table B.10. Applied voltages for the measurements shown in Figure 7.38.

<table>
<thead>
<tr>
<th></th>
<th>15 W</th>
<th>25 W</th>
<th>35 W</th>
<th>45 W</th>
<th>55 W</th>
<th>65 W</th>
<th>75 W</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>8.1 kV</td>
<td>9.0 kV</td>
<td>9.8 kV</td>
<td>10.4 kV</td>
<td>10.8 kV</td>
<td>11.3 kV</td>
<td>–</td>
</tr>
<tr>
<td>120 °C</td>
<td>7.4 kV</td>
<td>8.1 kV</td>
<td>8.7 kV</td>
<td>9.4 kV</td>
<td>10.0 kV</td>
<td>10.5 kV</td>
<td>11.1 kV</td>
</tr>
<tr>
<td>140 °C</td>
<td>7.4 kV</td>
<td>8.2 kV</td>
<td>8.8 kV</td>
<td>9.4 kV</td>
<td>9.8 kV</td>
<td>10.6 kV</td>
<td>11.0 kV</td>
</tr>
</tbody>
</table>