Plasma-catalytic hybrid methods for gaseous pollutant removal

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Plasma-catalytic hybrid methods for gaseous pollutant removal: Contents

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Introduction

- Off-gases from fossil fuelled energy conversion processes and industrial processes: NOx, CO, HCs, VOCs; concentrations ~ 0.1 % down to < 0.1 ppm
- Gas cleaning: Sorption processes, catalytic conversion, or non-thermal plasmas (NTP).

Advantages and shortcomings:

- Sorption processes:
  - Sorbents available for a wide range of gaseous compounds (+)
  - However, sorbents either need to be regenerated periodically or disposed as special waste when sorption capacity is exhausted (–)
  - Some compounds like elemental mercury do not absorb easily (–)

- Catalytic conversion of noxious compounds:
  - Generates stable, harmless final products if the off-gas fulfills certain requirements (e.g. \( \lambda \approx 1 \) for the 3-way catalyst) (+/–)
  - Gas heating may be required for activation (\( \rightarrow \) energy efficiency) (–)

- Non-thermal plasmas (NTP):
  - Efficient generation of reactive radicals (+)
  - However, the reaction chains induced by these radicals often are neither very selective nor lead to complete conversion of the noxious compound to the desired final product (–)
Plasma-Catalytic Hybrid Processes for Gas Cleaning

Plasma induced/enhanced selective catalytic NOx-reduction for automotive exhaust gases (SAG, Ford, Chrysler, LLNL, PNNL, ...)
- oxidation due to dielectric barrier discharge (DBD) pre-treatment
- non-precious metal catalyst & urea / fuel as a reducing agent
  - NOx-reduction in an oxidizing atmosphere
  - catalytic activity extended to low temperatures
  - sulfur tolerant

Plasma assisted catalytic oxidation of VOCs for the decontamination of ground water of industrial sites (IUT)
- extraction of VOCs from ground water by air stripping:
  - large gas flows, low gas temperature
- efficient plasma pre-treatment using dielectric barrier discharges
  - catalytic oxidation of the VOCs at low temperature (< 100 °C)

Sorption & plasma assisted oxidation of VOCs using oxygen plasma (AIST)
- Sorption of VOC from off-gas
- Regeneration of catalytic sorbent by oxygen plasma
  - Increased efficiency compared to direct plasma-catalytic conversion
Non-Thermal Plasma Reactor Concepts

Dielectric Barrier Discharges (DBD)

μ-Plasmatron Discharge

Dielectric Barrier Discharges inside of a catalytic monolith

DC + pulse corona

DC corona
Plasma-Catalytic Reactor Concepts

1-stage reactor (plasma in contact to catalytic surfaces)
Example: DPB reactor
- Dielectric properties of catalyst need to fit to application
- Direct interaction of plasma & catalyst enabled

2-stage reactor (no direct plasma–catalyst contact)
Example: DBD & catalyst
- Electrical conductivity of the catalyst doesn’t play a role
- Catalytic reactions initiated e.g. by metastable intermediate products
Dielectric Packed Bed Reactor
Influence of Catalyst Properties

Figure 4. ICCD images of discharge plasmas on the surface of zeolites. (16 kV_{\text{pk-pk}}, 50 Hz)

International Symposium on Non-Thermal/Thermal Plasma Pollution Control Technology & Sustainable Energy, ISNTP-7
June 21-25, 2010, St. John’s, Newfoundland, Canada
Hyun-Ha Kim, Atsushi Ogata (National Institute of Advanced Industrial Science and Technology (AIST)):
Catalyst Screening for the VOC Decomposition using Adsorption and Oxygen Plasma
Plasma Activation of Catalytic Reactions

Physical / chemical effects
Gas heating
Catalyst heating
Electric fields
Vibrational excitation
Dissociation
Ionization
UV radiation
Intermediate product formation
Electrical Excitation of NTP-Reactors
Pulsed Excitation of DBDs and PCDs: Thyatron switched Blumlein Circuit

- Max. load voltage 30 kV
- Max. pulse repetition frequency 10 kHz
- Max. pulse energy 126 mJ
- Voltage rise time 100 ns
- Voltage pulse duration 100 ns

- Expensive plasma switch
- Component lifetime limited
- Size and weight not acceptable for automotive applications
Power Modulator for PCD Operation: Electrical Concept

Core material: VAC Vitroperm 500Z
B_{sat} = 1.3 T
L_{us} = 6 mH
L_{sat} = 3.1 µH
Pulsed Electrical Excitation of DBDs: Semiconductor Switched Resonant Circuits

- Peak voltage 20 kV
- Max. pulse repetition frequency 20 kHz
- Max. pulse energy 45 mJ
- Voltage rise time 300 ns (10 % to 90 %)
- Voltage pulse duration 500 ns (FWHM)
- Reliable, low cost semiconductors
- Small low cost transformers
- Potential for compact design
NTP Electrical Properties & Chemistry

Electrical properties

- Depend on reactor type
  - Pulsed corona – large volume/surface ratio, large discharge gap
  - Dielectric barrier – large surface/volume ratio, small discharge gap; barrier properties; frequency (capacitive coupling)
  - Dielectric packed bed – intermediate surface/volume ratio & discharge gap; dielectric packed be properties; frequency (local capacitive coupling)

Chemistry

- Fast radical & ion formation (E/n) in active discharge region
  - Pulsed corona – streamer head
  - Dielectric barrier – µ-discharges; ionization waves; fully developed streamers; Atmospheric Pressure Glow Discharge

- Slow volume chemistry (chain reactions)
Short Pulse Excitation of DBDs with a Discharge Gap of 4 mm (PVS-1): NO-conversion as a Function of Electrical Energy Input

Voltage, current and pulse energy
- displacement current << discharge current
- reactive power << active power
- min. reactor impedance 70 Ohms

Diesel exhaust: $Q_v = 540$ liters(STP)/min, $T = 220$ °C

NO-conversion
- depends on specific energy only
- energy costs 9.2 Wh/g (50 % conv.)
Pulse Excitation of DBDs (PVS-2)
Influence of the Discharge Gap on Electrical properties

With increasing discharge gap:
- discharge ignition voltage increases
- discharge impedance increases from 1 to 6 kOhms
- pulse energy decreases from 19 to 6 mJ

Voltage, current and pulse energy
ICV = 310 V, T = 180 °C
Pulse Excitation of DBDs (PVS-2)
NO-Conversion as a Function of Specific Energy Input

![Graph showing NO-conversion as a function of specific energy input.](image)

NO-conversion at a discharge gap of 4 mm comparable to short pulse excitation (PVS-1)
- energy costs 9.2 Wh/g (50 % conv.)

At larger discharge gaps the maximum conversion rate is limited by
- reduced pulse energy input
- reduced conversion efficiency

DBD-reactor with a discharge gap of 4 mm, exhaust gas temperature 180 °C
DBD Treatment of Diesel Exhaust
Influence and Conversion of Hydrocarbons

Coaxial DBD-reactor with a structured HV-electrode, discharge gap 4 mm, sinusoidal excitation, frequency 1 kHz (synthetic gas mixture: 72 % N₂, 18 % O₂, 10 % H₂O, 500 ppm NO, 500 ppm C₂H₄, gas temperature 200 °C).

Improved conversion of NO to NO₂ due to HCs
Partial oxidation of hydrocarbons:
formation of aldehydes and CO
Oxidation of soot:

\[
\begin{align*}
O + C(s) &\rightarrow CO(s) \\
O + CO(s) &\rightarrow CO_2 \\
CO(s) &\rightarrow CO \\
NO_2 + C(s) &\rightarrow NO + CO(s)
\end{align*}
\]

Experiment:

- HCs were removed by partial oxidation (aldehydes, CO) and fragmentation
- Efficient oxidation of soot was observed on surfaces

Diesel exhaust: \(Q_v = 540 \, \text{NL/min}, \, T_{\text{gas}} = 220 \, ^\circ\text{C}, \, c(\text{HC}) \approx 500 \, \text{ppm} \, C_1; \, \text{DBD-reactor}: \, d_{\text{gap}} = 4 \, \text{mm}, \, A_{\text{flow}} = 5.15 \, \text{cm}^2, \, Al_2O_3 (5 \, \text{mm}), \, \text{short pulse excitation}, \, E_{\text{pulse}} = 50 \, \text{mJ}\)
DBD Treatment of Diesel Exhaust
Electron Collision Reactions

Simulation of a DBD in Synthetic Diesel exhaust -
13.7 % O₂, 4.5 % CO₂, 5.3 % H₂O, 76.5 % N₂ - at
212 °C; discharge gap 3 mm.

Average electron energy 2-5 eV

Oxygen radical formation
O₂ + e → O + O + e

Oxidation of NO to NO₂, formation of O₃
### DBD Treatment of Diesel Exhaust

#### Summary of the Plasma Chemistry

**Electron collision**

- **dissociation of oxygen**
  
  \[ e + O_2 \rightarrow e + O + O \]  (1)

**Radical attack of HCs**

- \[ O + C_2H_4 \rightarrow HCO + CH_3 + H \]  (2)
- \[ CH_3 + O_2 \rightarrow CH_3O_2 \]  (3)
- \[ H + O_2 \rightarrow HO_2 \]  (4)

**Oxidation of NO**

- \[ RO_2 + NO \rightarrow NO_2 + RO \]  (5)
- \[ O + NO + M \rightarrow NO_2 + M \]  (6)
- \[ O + NO_2 \rightarrow NO + O_2 \]  (7)

**NO-Reduktion?**

- \[ NO + N \rightarrow N_2 + O \]  (8)
- \[ O_2 + N \rightarrow NO + O \]  (T > 450 °C)
Storage of NH$_3$ on the SCR catalyst at T > 140 °C
- Injection of the urea solution
- Evaporation of water
- Thermal decomposition of urea to NH$_3$ and HNCO at T > 130 °C
- Hydrolysis of HNCO to NH$_3$ and CO$_2$ on the SCR-catalyst at T > 140 °C

Conventional SCR-process requires T > 200 °C
• SCR of NO at T > 200 °C
  4 NO + 4 NH$_3$ + O$_2$ → 4 N$_2$ + 6 H$_2$O  \hspace{1cm} (C1)
Plasma Enhanced Selective Catalytic Reduction

- Fast SCR at $T < 200 \, ^\circ\text{C}$
  - NO and NO$_2$

- Slow side reactions of NO$_2$ at $T < 200 \, ^\circ\text{C}$

**DBD-enhanced SCR treatment**

DBD, discharge gap 4 mm, sinusoidal excitation, monolithic 100 cpsi catalyst, 1 % V$_2$O$_5$ in 90 %TiO$_2$, initial gas mixture 500 ppm NO, 500 ppm NH$_3$, in 13 % O$_2$ and 5 % H$_2$O blended with N$_2$.

\[
\begin{align*}
\text{NO + NO}_2 + 2 \text{NH}_3 & \rightarrow 2 \text{N}_2 + 3 \text{H}_2\text{O} \quad \text{(C2)} \\
6 \text{NO}_2 + 8 \text{NH}_3 & \rightarrow 7 \text{N}_2 + 12 \text{H}_2\text{O} \quad \text{(C3)} \\
2 \text{NO}_2 + 2 \text{NH}_3 & \rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{NH}_4\text{NO}_3 \quad \text{(C4)}
\end{align*}
\]
Reaction Rate Coefficients of PE-SCR

Arrhenius plot of the rate coefficients

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

- \( E_A \): activation energy
- \( A \): pre-exponential factor

Mechanistic model (active surface site \( s - (V=O)^{2+} \))

- \( NH_3 + s = [H-s-NH_2] \)
- \( NO + [H-s-NH_2] \rightarrow [H-s-NH_2-NO] \rightarrow N_2 + H_2O + [H-s] \)
- \([H-s] + NO_2 \rightarrow \text{low T re-oxidation of active site}\)
Fast SCR Reaction

- Low T re-oxidation of active catalyst sites can also be achieved using ozone → Yoshioka (Japan) demonstrated efficient plasma enhanced SCR using “indirect” plasma treatment by means of ozonizer.
Test Bench Measurements on Plasma Enhanced SCR

DBD-treatment with $P \approx 250$ W
- NOx-reduction up to 21 g/h
- Energy costs 12 Wh/g NOx

Average values
- NOx-reduction 16.6 g/h
- Energy costs 16 Wh/g NOx
- Power requirements 2.1 % of engine break power
Formation of by-products in Diesel exhaust
Removal of HC (PE-SCR) ↔ Formation of CO

\[ V_2O_5 \cdot WO_3/TiO_2 \text{ works as an oxidation catalyst for HC} \]

\[ \text{it does not enhance the oxidation of CO efficiently} \]

\[ \text{plasma treatment removes HC and generates CO} \]

\[ \text{adding NH}_3 \text{ to the exhaust gas after plasma treatment increases HC-removal and CO-formation rate} \]

Experimental conditions: 2900 rpm, external load 2 kW, volume flow 530 slm, exhaust temperature 220 °C, catalyst temperature 170 °C
Formation of by-products in Diesel exhaust
Removal of NOx (PE-SCR)

- plasma induced NO-removal by oxidation to NO₂
- plasma induced formation of a by-product from NOₓ and HC
- catalytic reduction of NO₂ to NO

Experimental conditions: 2900 rpm, external load 2 kW, volume flow 530 slm, exhaust temperature 220 °C, catalyst temperature 170 °C
Formation of By-Products in Diesel exhaust Particulate Matter

EM picture of the light yellow powder precipitated on the walls of the tubing behind the SCR-reactor.

Energy dispersive X-ray scattering:
- Most of the PM consists of sulfates.
- Only a small fraction of PM can be attributed to $\text{NH}_4\text{NO}_3$. 
Experiments Using Isotopically Marked $^{15}$NO
DBD-Treatment of NO in N$_2$-O$_2$-Mixtures

Plasma induced formation of
O-radicals
$\Rightarrow [^{14,15}NO]/[^{14,15}NO_2]$

N-radicals, N$_2$(A)
$\Rightarrow [^{14}NO_x]/[^{15}NO_x]$

Experimental conditions: DBD-reactor, discharge gap 0.5 mm, electrical excitation 19 kV, 40 Hz, specific energy 90 J/liter, synthetic gas mixture 500 ppm $^{15}$NO, 15 % O$_2$, blended with N$_2$, volume flow 1 slm

$[^{14}NO_x] = 42$ ppm
$[^{15}NO_x] = 61$ ppm
$[N_2O] = 4$ ppm
Plasma-Enhanced HC-SCR
Plasma Enhanced SCR Process

Issues connected to practical application

- Efficiency with higher hydrocarbons (fuel)
- Catalyst temperatures changing within minutes: Influence of plasma treatment on adsorption and desorption effects

adsorption: $T_1$

desorption: $T_2$
Small Scale Laboratory Experiments

Temperature programmed reactions
- temperature ramp applied to the complete PE-SCR system
  - $100 \, ^\circ\mathrm{C} < T < 600 \, ^\circ\mathrm{C}$, rate $\Delta T/\Delta t = +20/-10 \, ^\circ\mathrm{C} /\mathrm{min}$
- gas mixture supplied at constant flow rate (30 Nliters/min)
  - 82 % N$_2$, 8 % O$_2$, 10 % H$_2$O, 1620 ppm C$_{12}$ dodecane, 270 ppm NO
- DBD pre-treatment
  - coaxial DBD-reactor, structured HV-electrode, pulsed excitation
  - specific energy input 16 J/liter, residence time 40 ms
- catalytic after-treatment
  - coated Cordierite carrier (400 cpsi), SV = 50,000 hr$^{-1}$
## Catalysts Tested

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mass coated on carrier [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-NH$_4$ZSM5</td>
<td>9.3</td>
</tr>
<tr>
<td>Pt-Al$_2$O$_3$</td>
<td>8.1</td>
</tr>
<tr>
<td>Pd-Al$_2$O$_3$</td>
<td>9.5</td>
</tr>
<tr>
<td>Cu-NaZSM5</td>
<td>5.2</td>
</tr>
<tr>
<td>CuO-Al$_2$O$_3$</td>
<td>8.1</td>
</tr>
<tr>
<td>Fe-NaZSM5</td>
<td>5.8</td>
</tr>
<tr>
<td>Ag-Al$_2$O$_3$</td>
<td>7.0</td>
</tr>
</tbody>
</table>

\[ V = 36 \text{ cm}^3 \]
\[ D = 25 \text{ mm} \]
\[ D/L = 0.3 \]
Catalytic reduction of NO\textsubscript{x} on Ag-\(\gamma\)-Al\textsubscript{2}O\textsubscript{3} using dodecane as a reducing agent (\(SV = 50,000 \text{ h}^{-1}, \frac{dT}{dt} = +20/-10 \text{ °C/min}, c(\text{HC}) = 3000 \text{ ppm C1}\))
Plasma Induced Catalytic NOx Reduction Using HCs as a Reducing Agent

NOx-reduction: plasma induced conversion of NO to NO₂, formation of aldehydes from dodecane (PNL)
High T: Oxidation of dodecane is the rate limiting step
Adsorption of NO₂ has to be distinguished from NOₓ-reduction
## Maximum NOx-Removal

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>maximum NOx-removal [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NTP</td>
</tr>
<tr>
<td></td>
<td>n</td>
</tr>
<tr>
<td></td>
<td>Temp.</td>
</tr>
<tr>
<td>Pt-NH₄ZSM₅</td>
<td>46</td>
</tr>
<tr>
<td>Pt-Al₂O₃</td>
<td>16</td>
</tr>
<tr>
<td>Pd-Al₂O₃</td>
<td>7</td>
</tr>
<tr>
<td>Cu-NaZSM₅</td>
<td>61</td>
</tr>
<tr>
<td>CuO-Al₂O₃</td>
<td>26</td>
</tr>
<tr>
<td>Fe-NaZSM₅</td>
<td>37</td>
</tr>
<tr>
<td>Ag-Al₂O₃</td>
<td>56</td>
</tr>
</tbody>
</table>

Large differences between rise and fall values of deNOx:

- Adsorption and desorption effects are important

NO₂ adsorption

HC adsorption

HC and NO₂ adsorption
## Average NOx-removal

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>average NOₓ-removal [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NTP</td>
</tr>
<tr>
<td></td>
<td>Temp.</td>
</tr>
<tr>
<td>Pt-NH₄ZSM₅</td>
<td>13</td>
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<tr>
<td>Pt-Al₂O₃</td>
<td>13</td>
</tr>
<tr>
<td>Pd-Al₂O₃</td>
<td>0</td>
</tr>
<tr>
<td>Cu-NaZSM₅</td>
<td>21</td>
</tr>
<tr>
<td>CuO-Al₂O₃</td>
<td>2</td>
</tr>
<tr>
<td>Fe-NaZSM₅</td>
<td>16</td>
</tr>
<tr>
<td>Ag-Al₂O₃</td>
<td>20</td>
</tr>
</tbody>
</table>

(determined from time-integrated NOx-balance)

Large difference between rise and fall values:

- Adsorption and desorption effects are important

NO₂ adsorption

HC adsorption

HC and NO₂ adsorption
Plasma catalytic hybrid processes can successfully be applied for the abatement of odorous & noxious compounds from off-gases

- Hybrid processes were demonstrated (Plasma enhanced selective catalytic NOx reduction; Plasma enhanced catalytic oxidation of HCs & VOCs)

Good energy efficiency, low operation costs can be expected

- Specific energies below 15 J/liter were found for automotive applications

Plasma-catalytic hybrid reactor & power supply concepts are available

- 2-stage reactors easy to realize; 1-stage: more R&D required
- Semiconductor power supplies

Sorption properties of catalyst are important

- Catalyst needs to be tailored for application (intermediate product generated by plasma, plasma regeneration of catalyst, ...
Thank you for your attention!

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Measurement of the Plasma Input Power of a DBD-Reactor under Sinusoidal Excitation

Reactor capacity 100 pF, synthetic air 30 Nliter/min, 150 °C

- Measurement of reactor charge and voltage
- Energy input per cycle = Area enclosed by the Lissajous figure
- Smooth edges: Dissipation due to dielectric losses

\[ E_{\text{cycle}} = \int U dQ \]
Measurement of the Plasma Input Power of a DBD-Reactor under Pulsed Excitation

Measurement of reactor voltage and current

Plasma energy input:
Integral of reactor power

\[ E_{\text{pulse}} = \int_{t_0}^{t_1} U(t) \cdot I(t) \, dt \]

Energy dissipation due to dielectric losses: Deviation from voltage-charge relation, before gas discharge breakdown occurs

\[ \frac{1}{C_\text{reactor}} \times \int_{t_0}^{t_1} I(t) \, dt \neq U(t_1) \]
Figure 3 Catalyst mapping in terms of enhancement factor (EF) and adsorption capacity of benzene (100°C, 200 ppm benzene).

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June 21-25, 2010, St. John’s, Newfoundland, Canada
Hyun-Ha Kim, Atsushi Ogata (National Institute of Advanced Industrial Science and Technology (AIST)):
Catalyst Screening for the VOC Decomposition using Adsorption and Oxygen Plasma
Characterization of the DBD

Pulsed electrical excitation using a solid state power supply

Efficient plasma-chemical conversion of NO in N₂
Plasma-Chemical Conversion

Temperature fixed to 200 °C

- at 16 J/liter nearly complete conversion of NO to NO₂
- low conversion of dodecane

Fixed to 16 J/liter
- at 300 °C nearly complete conversion of dodecane
- efficiency of NO-conversion to NO₂ decreases for T > 300 °C