

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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Plasma-catalytic hybrid reactor concepts

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- Electron collision reactions
- Plasma conversion of noxious compounds
- Plasma Enhanced Selective Catalytic Reduction

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Introduction

- Off-gases from fossil fuelled energy conversion processes and industrial processes: NO_x, 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. $\lambda \sim 1$ for the 3-way catalyst) (+/–)
 - Gas heating may be required for activation (→ 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 NO_x-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
- ⇒ NO_x-reduction in an oxidizing atmosphere
- ⇒ catalytic activity extended to low temperatures
- ⇒ sulfur tolerant

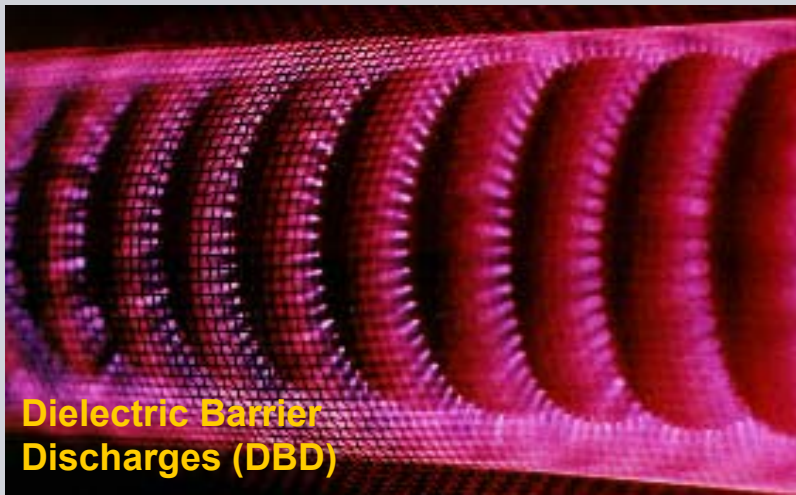
Plasma assisted catalytic oxidation of VOCs for the decontamination of ground water of industrial sites (IUT)

- 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



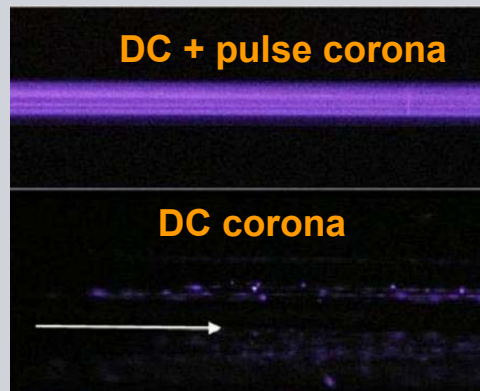
Dielectric Barrier Discharges (DBD)



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)

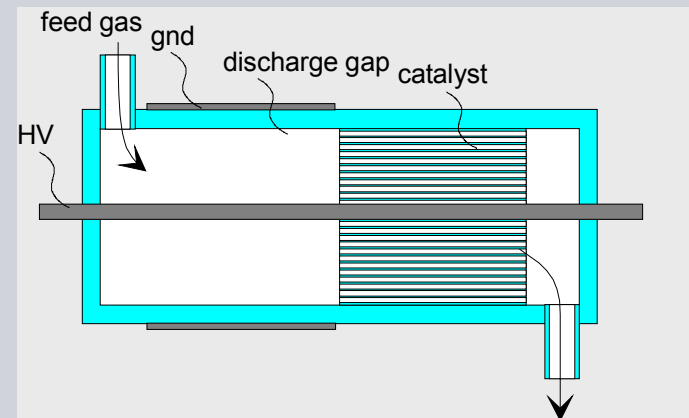
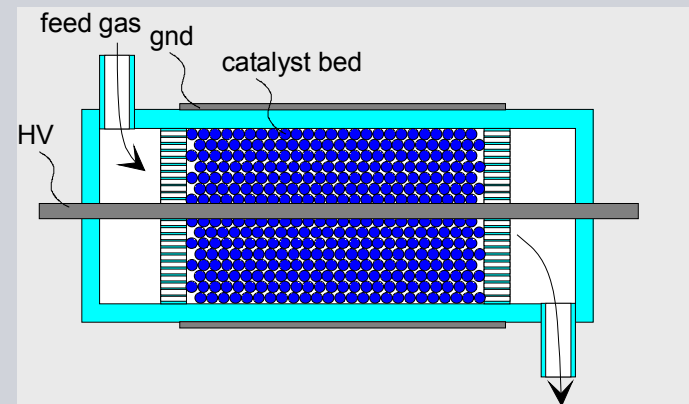
Example: DPB reactor

- 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

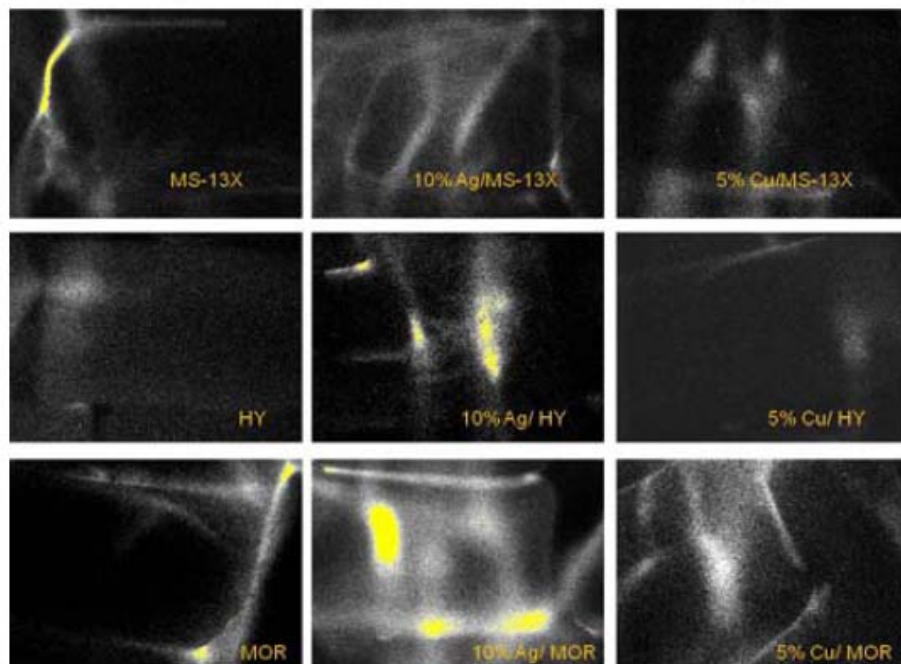


Figure 4. ICCD images of discharge plasmas on the surface of zeolites. (16 kV_{pk-pk} , 50 Hz)

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

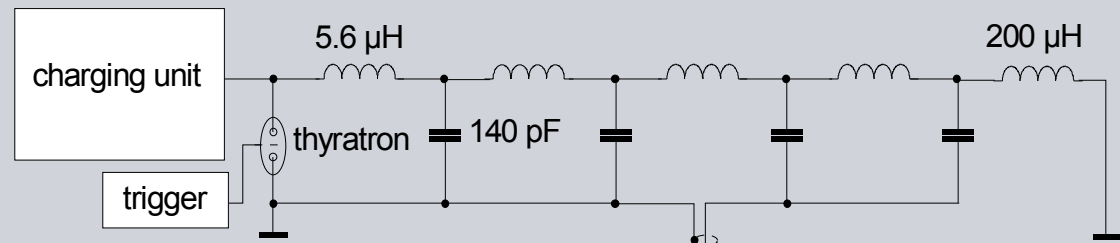
Ionization

UV radiation

Intermediate product formation

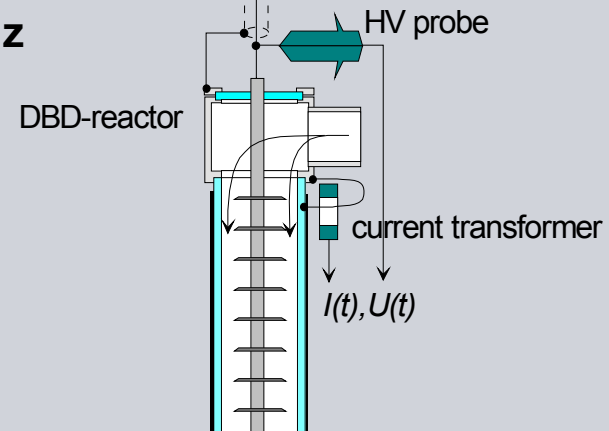
Electrical Excitation of NTP-Reactors

Pulsed Excitation of DBDs and PCDs: Thyatron switched Blumlein Circuit

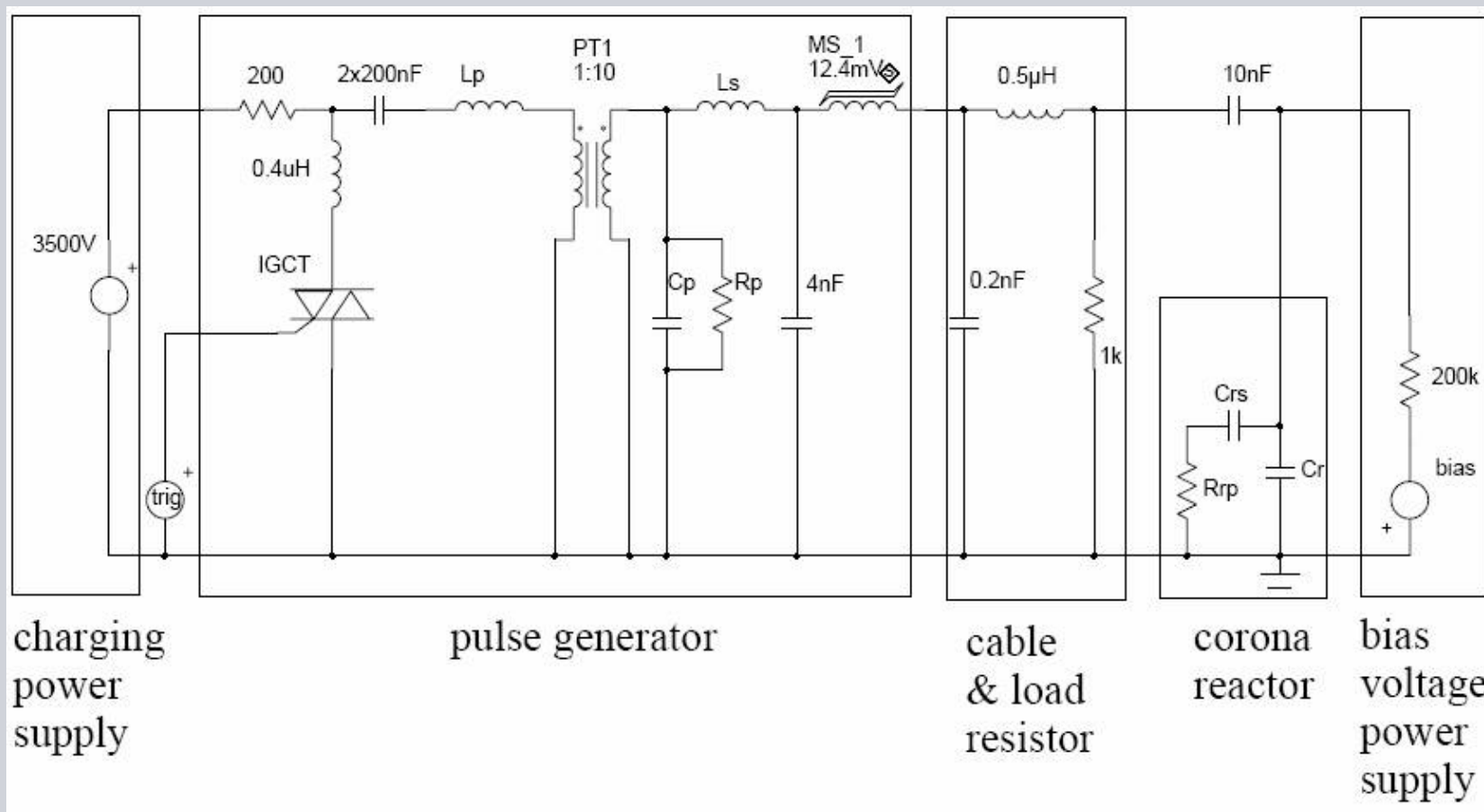


- Max. load voltage 30 kV
- Max. pulse repetition frequency 10 kHz
- Max. pulse energy 126 mJ
- Voltage rise time 100 ns
- Voltage pulse duration 100 ns

- Expensive plasma switch
- Component lifetime limited
- Size and weight not acceptable for automotive applications



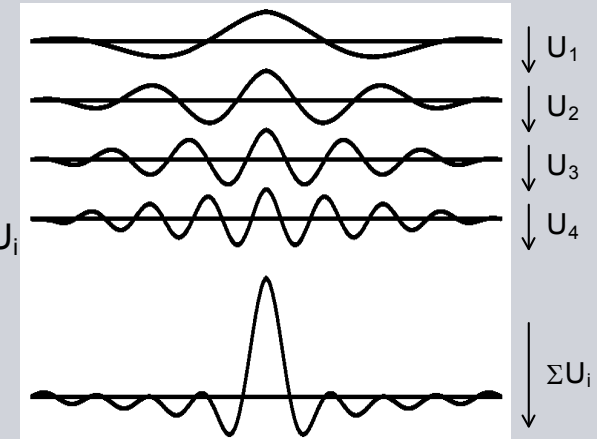
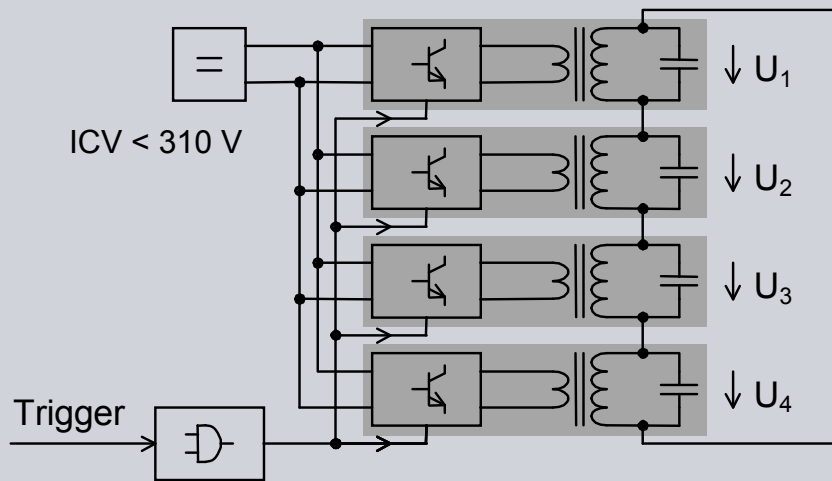
Power Modulator for PCD Operation: Electrical Concept



Core material:
 VAC Vitroperm 500Z
 $B_{sat} = 1.3 \text{ T}$

$L_{us} = 6 \text{ mH}$
 $L_{sat} = 3.1 \mu\text{H}$

Pulsed Electrical Excitation of DBDs: Semiconductor Switched Resonant Circuits



Fourier synthesis of voltage waveforms

- **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**

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NTP Electrical Properties & Chemistry

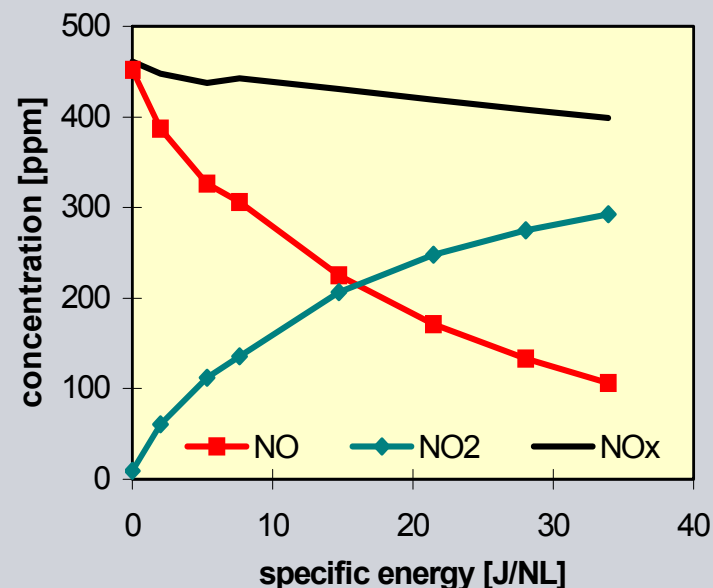
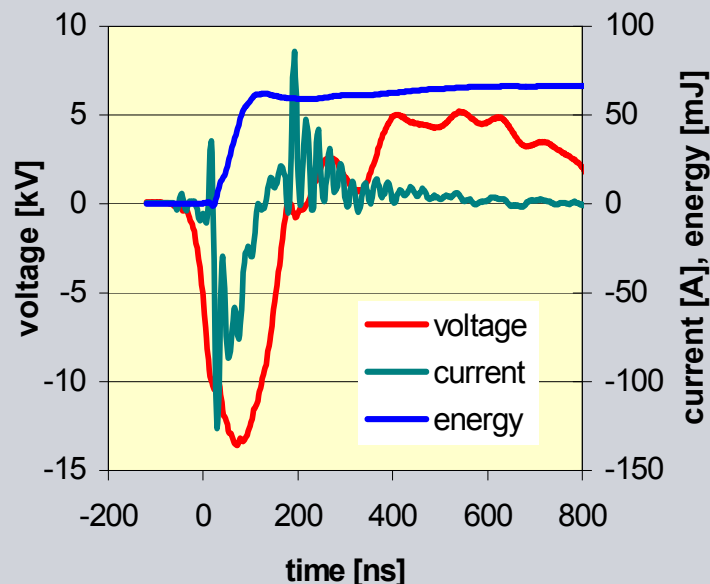
Electrical properties

- 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; **A**tmospheric **P**ressure **G**low **D**ischarge
- 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 \ll discharge current
- reactive power \ll active power
- min. reactor impedance 70 Ohms

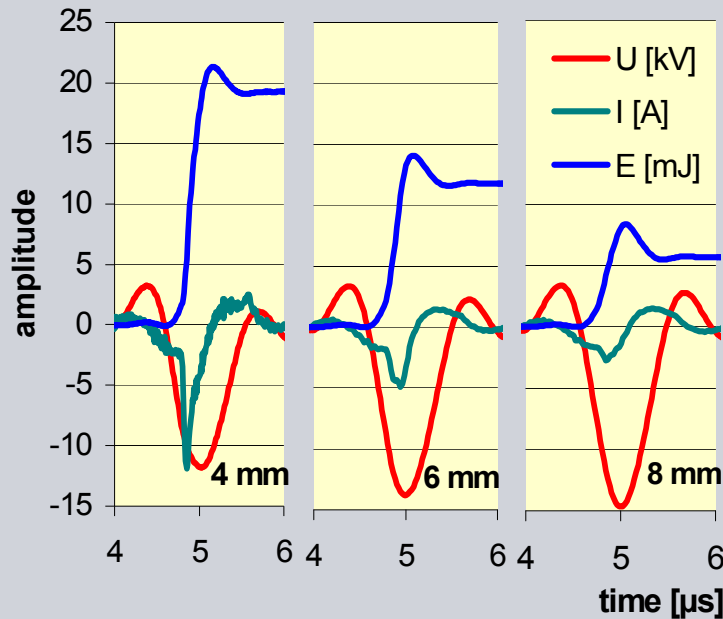
Diesel exhaust: $Q_v = 540$ liters(STP)/min, $T = 220$ °C

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

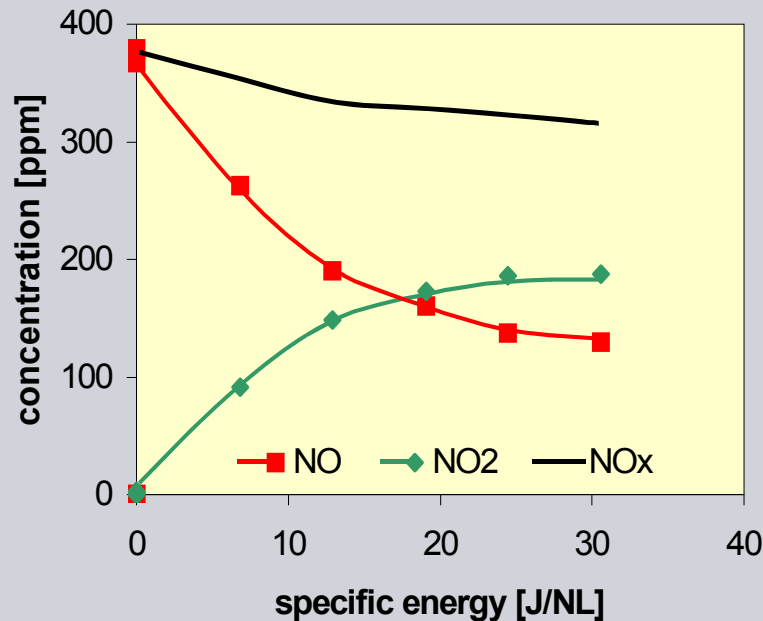


With increasing discharge gap

- 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



NO-conversion at a discharge gap of 4 mm comparable to short pulse excitation (PVS-1)

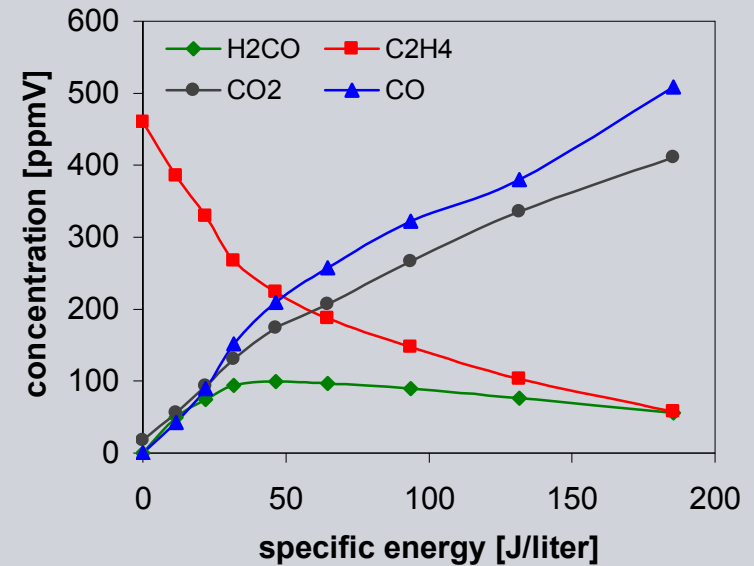
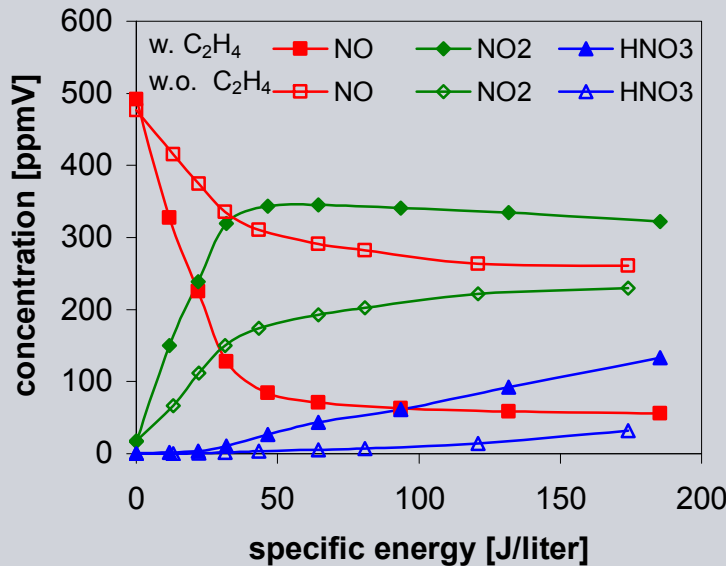
- energy costs 9.2 Wh/g (50 % conv.)

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



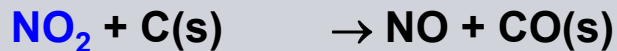
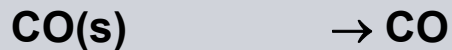
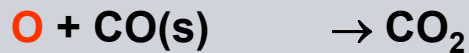
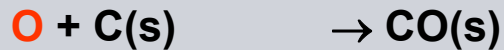
Coaxial DBD-reactor with a structured HV-electrode, discharge gap 4 mm, sinusoidal excitation, frequency 1 kHz (synthetic gas mixture: 72 % N₂, 18 % O₂, 10 % H₂O, 500 ppm NO, 500 ppm C₂H₄, gas temperature 200 °C).

Improved conversion of NO to NO₂ due to HCs

Partial oxidation of hydrocarbons:
formation of aldehydes and CO

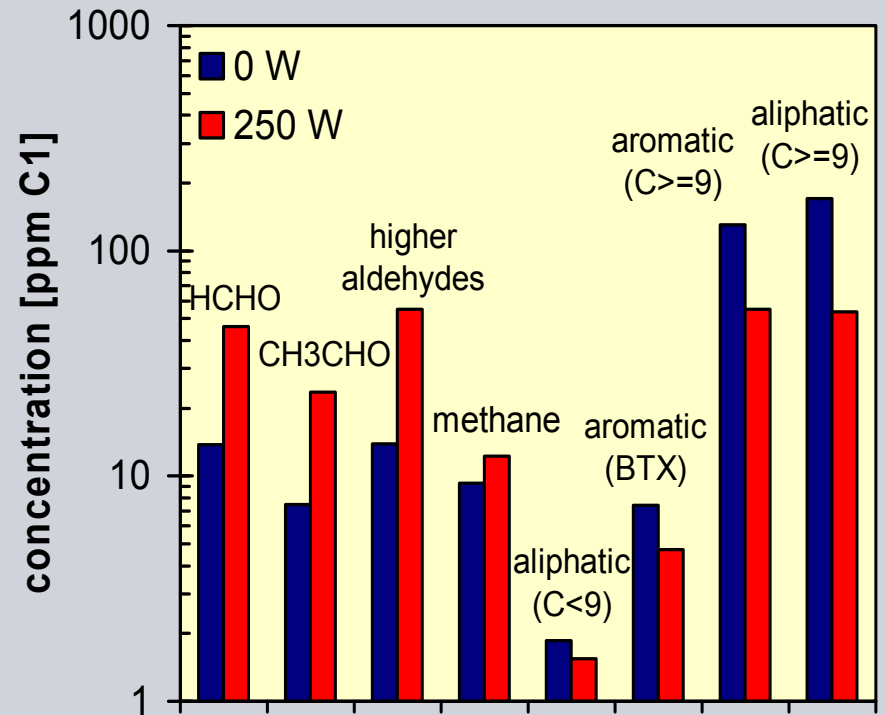
NTP Induced Reactions in Diesel Exhaust: Removal of Soot and HCs

Oxidation of soot:



Experiment:

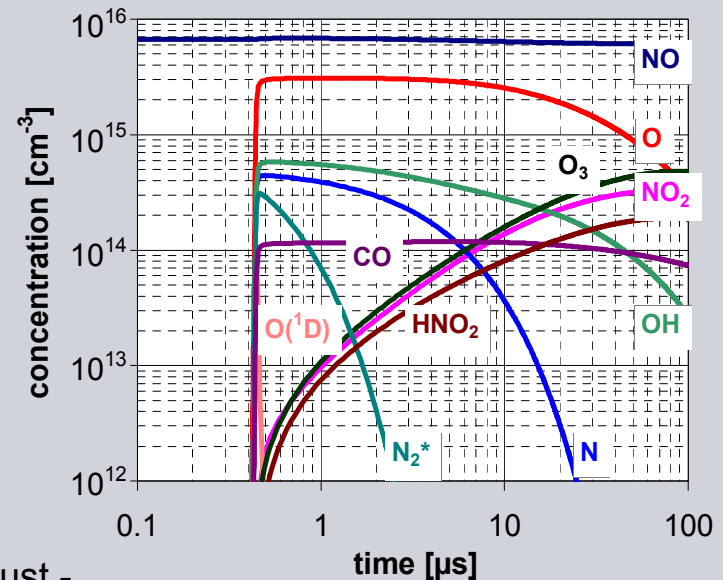
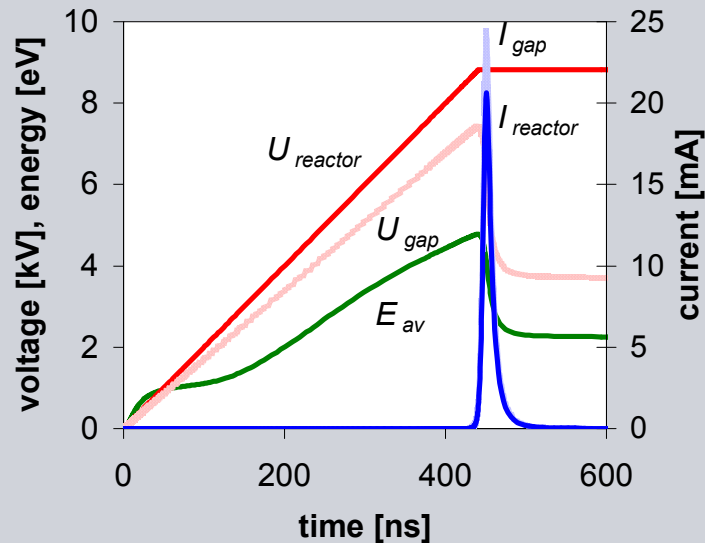
- HCs were removed by partial oxidation (aldehydes, CO) and fragmentation
- Efficient oxidation of soot was observed on surfaces



Diesel exhaust: $Q_V = 540 \text{ NI/min}$, $T_{\text{gas}} = 220 \text{ }^\circ\text{C}$, $c(\text{HC}) \approx 500 \text{ ppm C1}$; DBD-reactor: $d_{\text{gap}} = 4 \text{ mm}$, $A_{\text{flow}} = 5.15 \text{ cm}^2$, Al_2O_3 (5 mm), short pulse excitation, $E_{\text{pulse}} = 50 \text{ mJ}$

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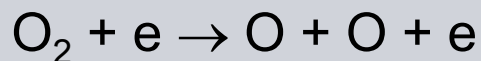
DBD Treatment of Diesel Exhaust Electron Collision Reactions



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



Oxidation of NO to NO₂, formation of O₃

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DBD Treatment of Diesel Exhaust

Summary of the Plasma Chemistry

Electron collision
dissociation of oxygen

$$e + O_2 \rightarrow e + O + O \quad (1)$$

• Radical attack of HCs

$$O + C_2H_4 \rightarrow HCO + CH_3 + H \quad (2)$$
$$CH_3 + O_2 \rightarrow CH_3O_2 \quad (3)$$
$$H + O_2 \rightarrow HO_2 \quad (4)$$

• Oxidation of NO

$$RO_2 + NO \rightarrow NO_2 + RO \quad (5)$$
$$O + NO + M \rightarrow NO_2 + M \quad (6)$$
$$O + NO_2 \rightarrow NO + O_2 \quad (7)$$

• NO-Reduktion?

$$NO + N \rightarrow N_2 + O \quad (8)$$
$$O_2 + N \rightarrow NO + O \quad (T > 450 \text{ °C})$$

Plasma-Enhanced NH₃-SCR

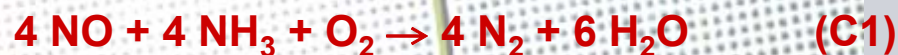
Basics of the Urea SCR-Process

Storage of NH₃ on the SCR catalyst at T > 140 °C

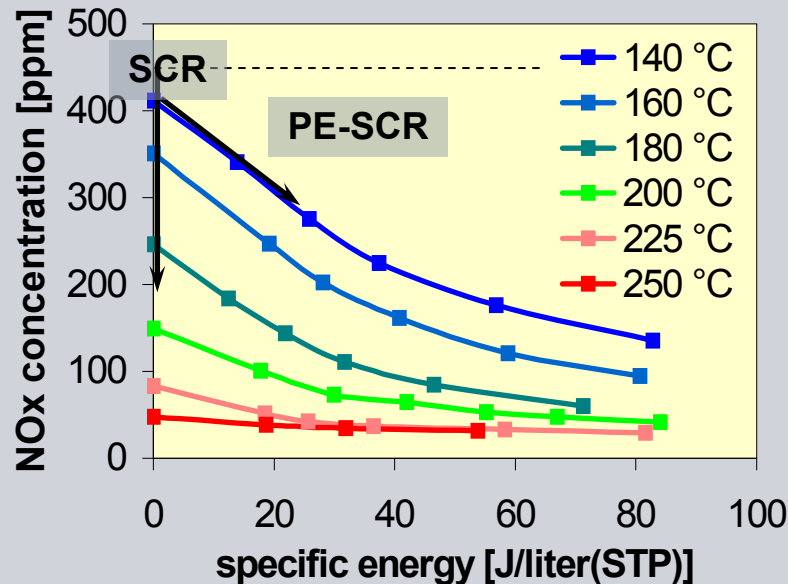
- Injection of the urea solution
- Evaporation of water
- Thermal decomposition of urea to NH₃ and HNCO at T > 130 °C
- Hydrolysis of HNCO to NH₃ and CO₂ on the SCR-catalyst at T > 140 °C

Conventional SCR-process requires T > 200 °C

- SCR of NO at T > 200 °C



Plasma Enhanced Selective Catalytic Reduction



DBD-enhanced SCR treatment

DBD, discharge gap 4 mm, sinusoidal excitation, monolithic 100 cpsi catalyst, 1 % V₂O₅ in 90 %TiO₂, initial gas mixture 500 ppm NO, 500 ppm NH₃ in 13 % O₂ and 5 % H₂O blended with N₂

- **Fast SCR at T < 200 °C** of **NO and NO₂**

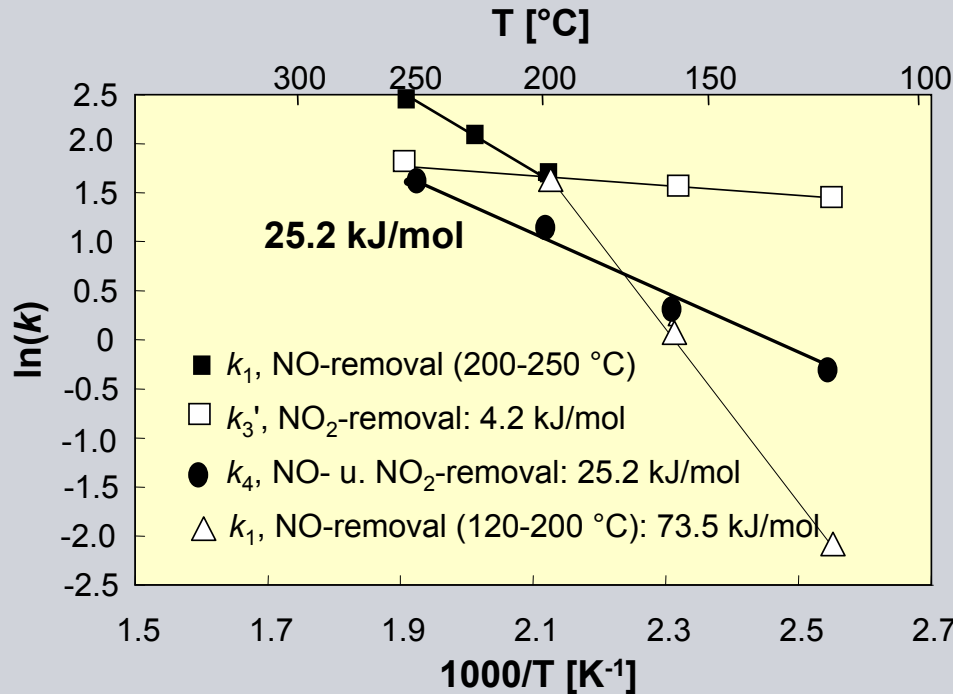


- **Slow side reactions of NO₂ at T < 200 °C**



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Reaction Rate Coefficients of PE-SCR



Arrhenius plot of the rate coefficients

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

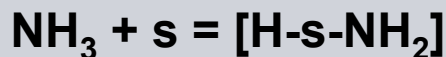
E_A activation energy

A pre-exponential factor

$$-\frac{dn_{NO}}{dt} = k_{C1} \cdot n_{NO} + k_{C4} \cdot n_{NO} \cdot n_{NO2}$$

$$-\frac{dn_{NO2}}{dt} = k_{C2,3} \cdot n_{NO2} + k_{C4} \cdot n_{NO} \cdot n_{NO2}$$

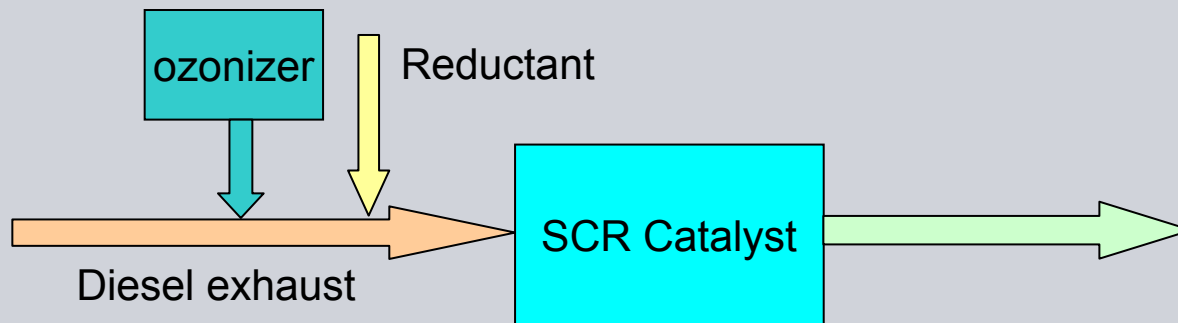
Mechanistic model (active surface site s - $(V=O)^{2+}$)



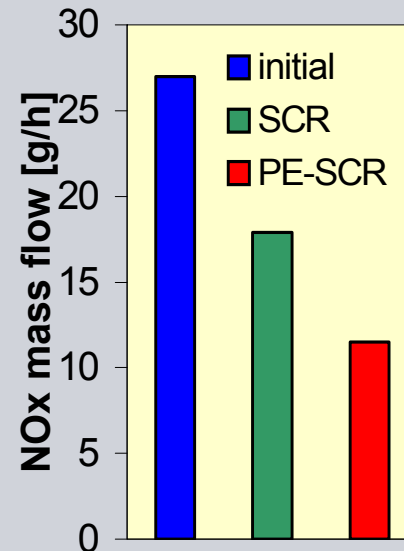
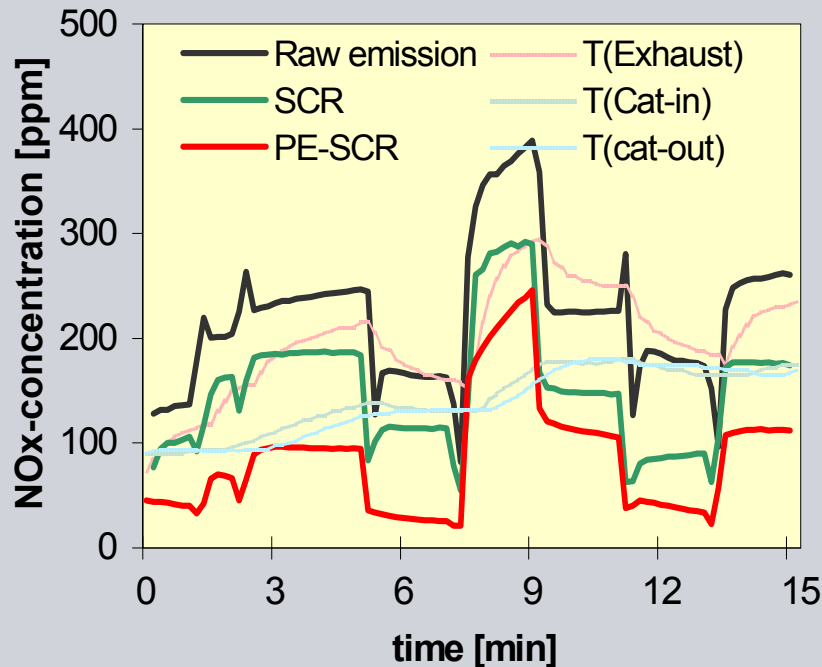
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Fast SCR Reaction

- 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 $P \approx 250 \text{ W}$

- NOx-reduction up to 21 g/h
- Energy costs 12 Wh/g NOx

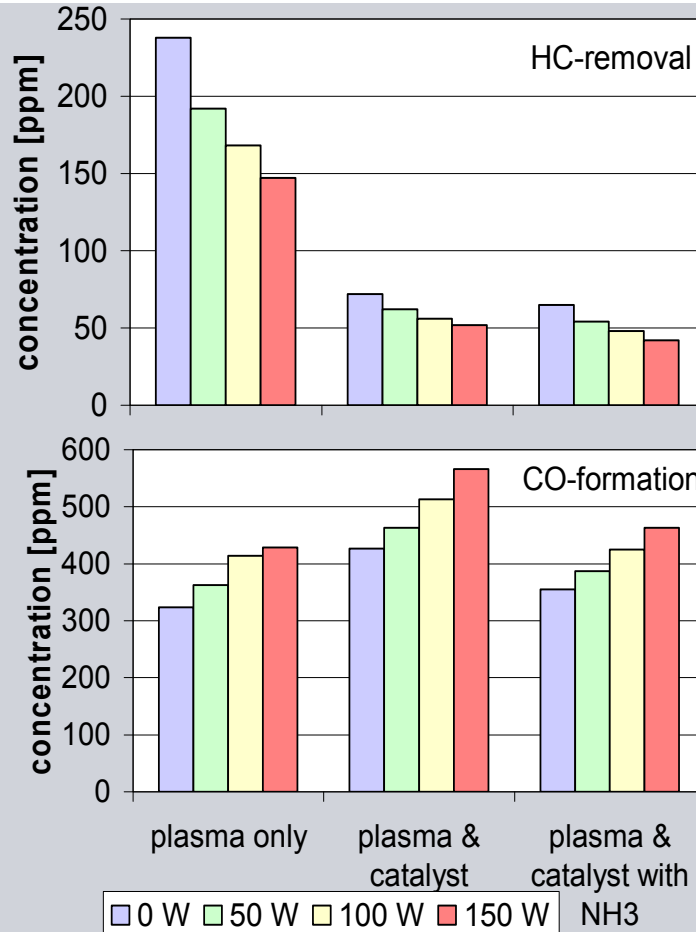
Average values

- NOx-reduction 16.6 g/h
- Energy costs 16 Wh/g NOx
- Power requirements 2.1 % of engine break power

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Formation of by-products in Diesel exhaust

Removal of HC (PE-SCR) ⇔ Formation of CO

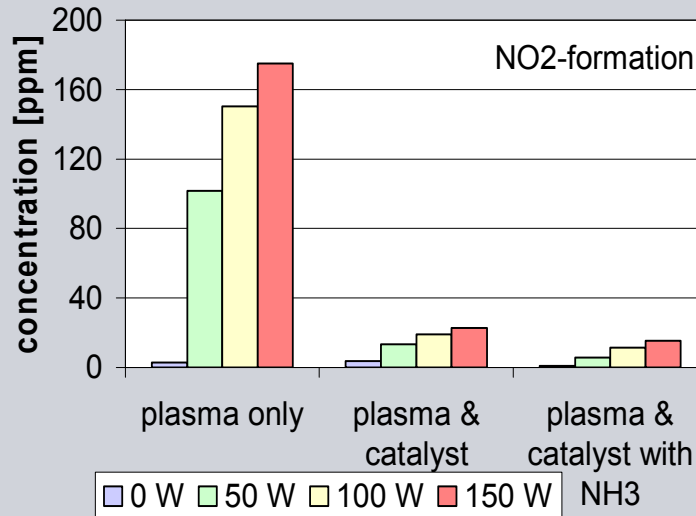
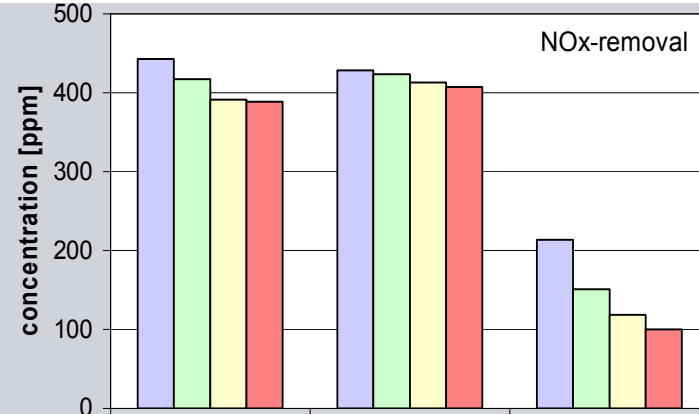
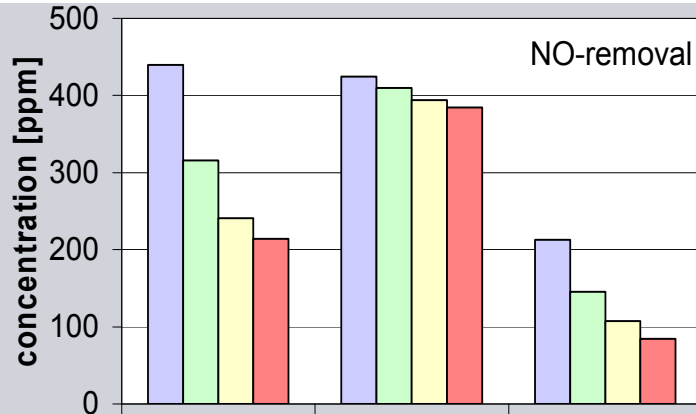


- ⇒ $V_2O_5-WO_3/TiO_2$ works as an oxidation catalyst for HC
- ⇒ it does not enhance the oxidation of CO efficiently
- ⇒ plasma treatment removes HC and generates CO
- ⇒ adding NH_3 to the exhaust gas after plasma treatment increases HC-removal and CO-formation rate

Experimental conditions: 2900 rpm, external load 2 kW, volume flow 530 slm, exhaust temperature 220 °C, catalyst temperature 170 °C

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Formation of by-products in Diesel exhaust Removal of NO_x (PE-SCR)

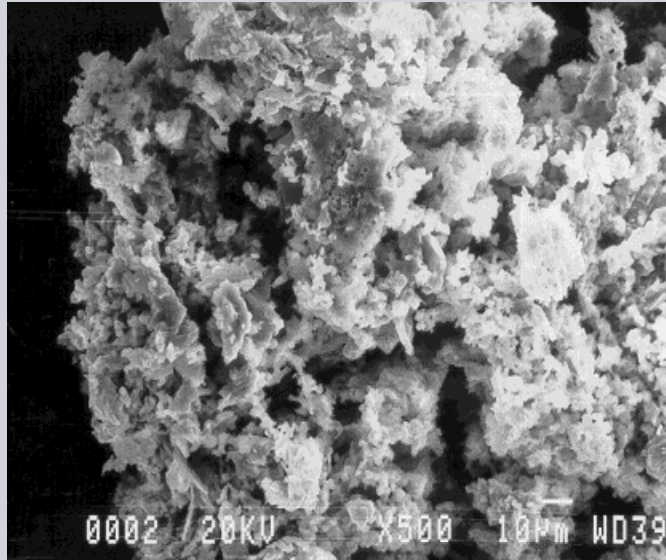


⇒ plasma induced NO-removal by oxidation to NO₂
 ⇒ plasma induced formation of a by-product from NO_x and HC
 ⇒ catalytic reduction of NO₂ to NO

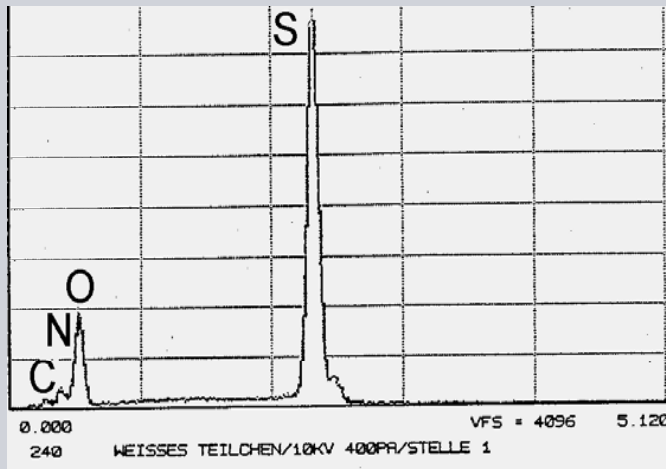
Experimental conditions: 2900 rpm, external load 2 kW, volume flow 530 slm, exhaust temperature 220 °C, catalyst temperature 170 °C

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Formation of By-Products in Diesel exhaust Particulate Matter



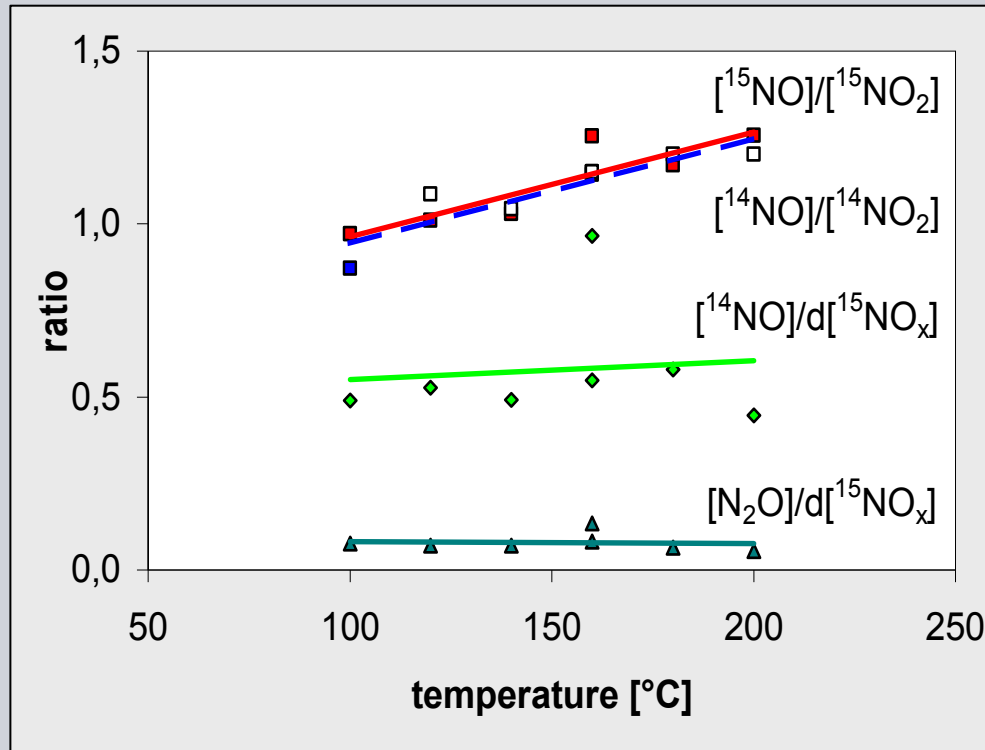
EM picture of the light yellow powder precipitated on the walls of the tubing behind the SCR-reactor.



Energy dispersive X-ray scattering:

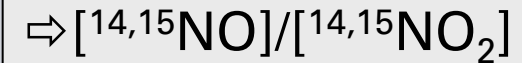
- ⇒ Most of the PM consists of sulfates.
- ⇒ Only a small fraction of PM can be attributed to NH_4NO_3 .

Experiments Using Isotopically Marked ^{15}NO DBD-Treatment of NO in $\text{N}_2\text{-O}_2$ -Mixtures

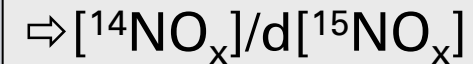


Plasma induced formation of

O-radicals

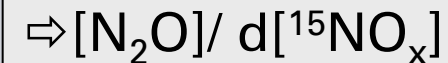


N-radicals, $\text{N}_2(\text{A})$



$$[\text{^{14}NO}_x] = 42 \text{ ppm}$$

$$d[\text{^{15}NO}_x] = 61 \text{ ppm}$$



$$[\text{N}_2\text{O}] = 4 \text{ ppm}$$

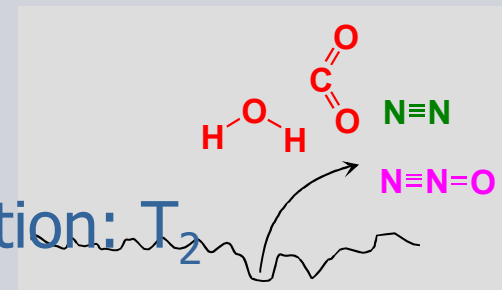
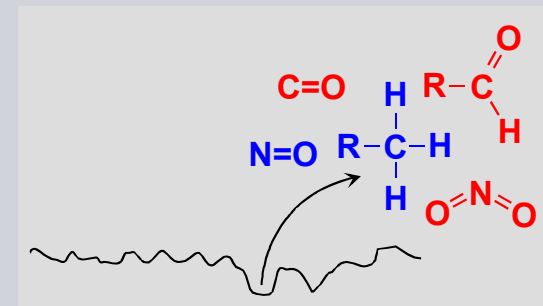
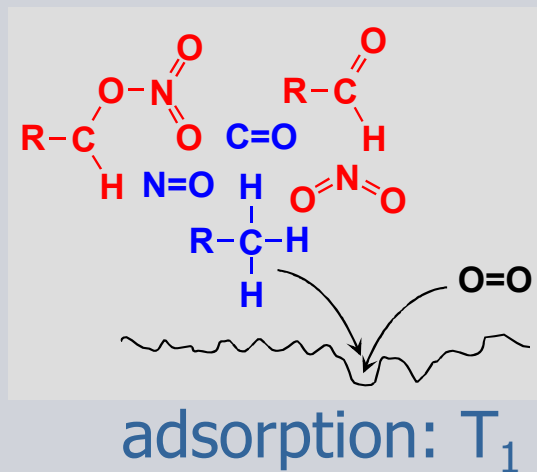
Experimental conditions: DBD-reactor, discharge gap 0.5 mm, electrical excitation 19 kV, 40 Hz, specific energy 90 J/liter, synthetic gas mixture 500 ppm ^{15}NO , 15 % O_2 , blended with N_2 , volume flow 1 slm

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



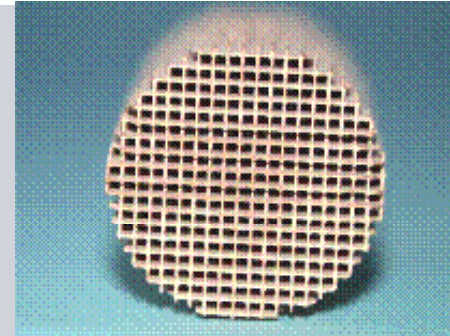
Small Scale Laboratory Experiments

Temperature programmed reactions

- temperature ramp applied to the complete PE-SCR system
 - $100\text{ }^{\circ}\text{C} < T < 600\text{ }^{\circ}\text{C}$, rate $\Delta T/\Delta t = +20/-10\text{ }^{\circ}\text{C}/\text{min}$
- gas mixture supplied at constant flow rate (30 Nliters/min)
 - 82 % N_2 , 8 % O_2 , 10 % H_2O , 1620 ppm C_1 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), $\text{SV} = 50,000\text{ hr}^{-1}$

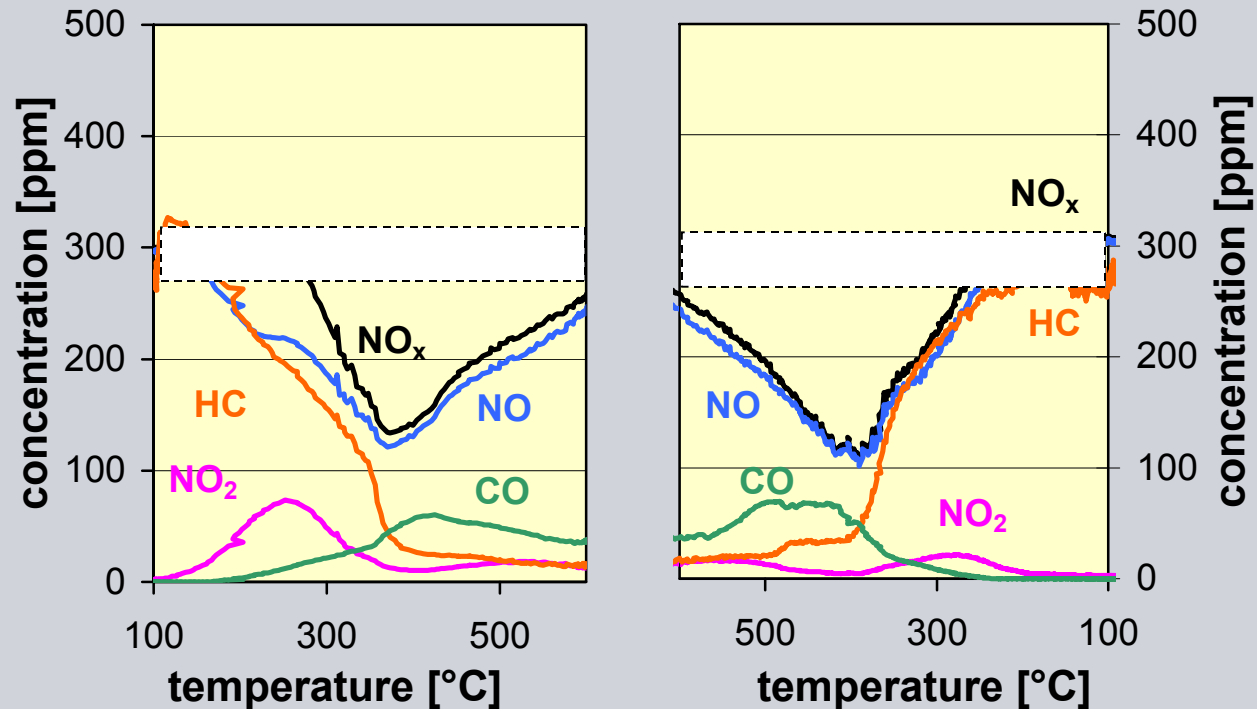
Catalysts Tested

Catalyst	Mass coated on carrier [g]
Pt-NH ₄ ZSM5	9.3
Pt-Al ₂ O ₃	8.1
Pd-Al ₂ O ₃	9.5
Cu-NaZSM5	5.2
CuO-Al ₂ O ₃	8.1
Fe-NaZSM5	5.8
Ag-Al ₂ O ₃	7.0



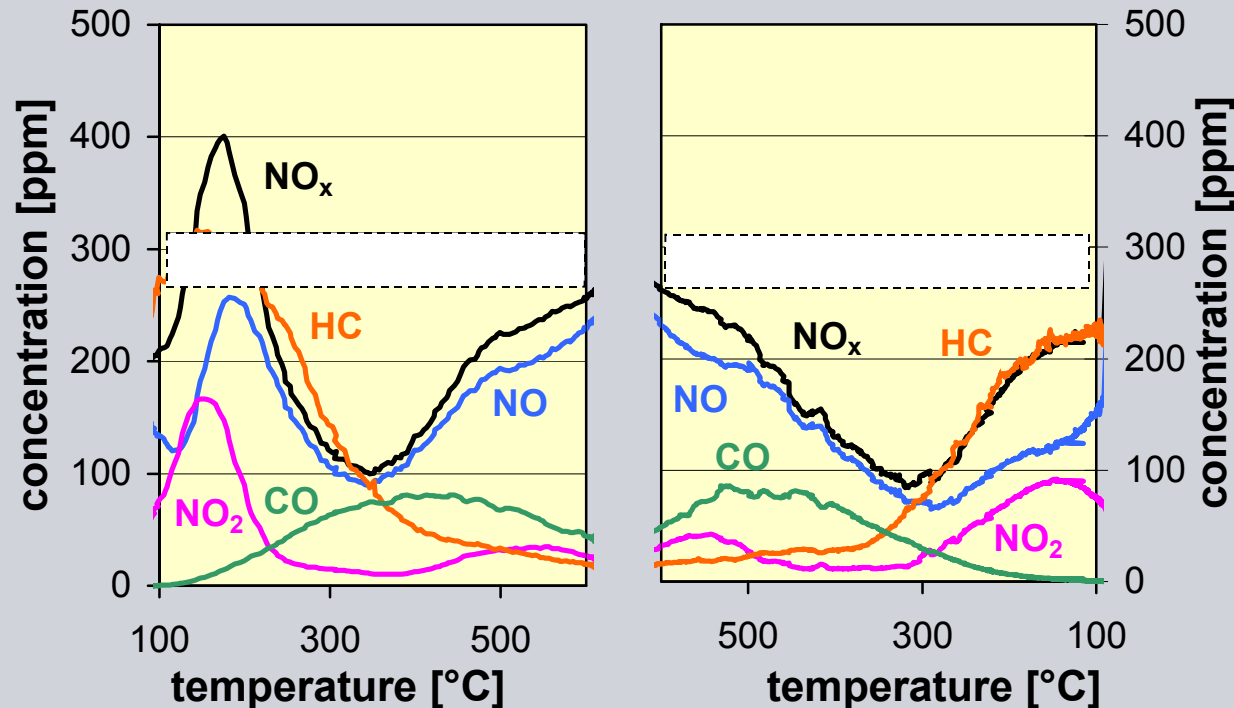
$$V = 36 \text{ cm}^3$$
$$D = 25 \text{ mm}$$
$$D/L = 0.3$$

Catalytic NO_x Reduction Using HCs as a Reducing Agent



Catalytic reduction of NO_x on Ag- γ -Al₂O₃ using dodecane as a reducing agent (SV = 50,000 h⁻¹, dT/dt = +20/-10 °C/min, c(HC) = 3000 ppm C1)

Plasma Induced Catalytic NO_x Reduction Using HCs as a Reducing Agent



NO_x-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 NO_x-reduction

Maximum NO_x-Removal

Catalyst	maximum NO _x -removal [%]					
	n	n	n	y	y	y
Temp.	rise	fall	T _{max} [°C]	rise	fall	T _{max} [°C]
Pt-NH ₄ ZSM ₅	46	44	210	51	40	200
Pt-Al ₂ O ₃	16	45	200	31	39	210
Pd-Al ₂ O ₃	7	7	460	12	12	440
Cu-NaZSM5	61	32	310	76	36	330
CuO-Al ₂ O ₃	26	26	370	29	29	320
Fe-NaZSM5	37	27	400	38	28	440
Ag-Al ₂ O ₃	56	64	390	68	72	310

NO₂ adsorption

HC adsorption

HC and NO₂ adsorption

Large differences between rise and fall values of deNO_x:

⇒ Adsorption and desorption effects are important

Average NOx-removal

Catalyst	average NO _x -removal [%]					
	n	n	n	y	y	y
Temp.	rise	fall	total	rise	fall	total
Pt-NH ₄ ZSM ₅	13	14	14	16	24	20
Pt-Al ₂ O ₃	13	36	29	5	22	18
Pd-Al ₂ O ₃	0	6	4	0	23	18
Cu-NaZSM5	21	12	14	29	28	28
CuO-Al ₂ O ₃	2	10	8	12	23	20
Fe-NaZSM5	16	12	12	20	24	23
Ag-Al ₂ O ₃	20	19	19	25	39	34

NO₂ adsorption

HC adsorption

HC and NO₂ adsorption

(determined from time-integrated NO_x-balance)

Large difference between rise and fall values:

⇔ Adsorption and desorption effects are important

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Plasma Catalytic Hybrid Processes Summary

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 NO_x 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!

Renato Andorf (DC AG)

Rudolf Birckigt

Stefan Bröer

Thomas Hammer

Werner Hartmann

Tetsuo Kishimoto

Bernd Krutzsch (DC AG)

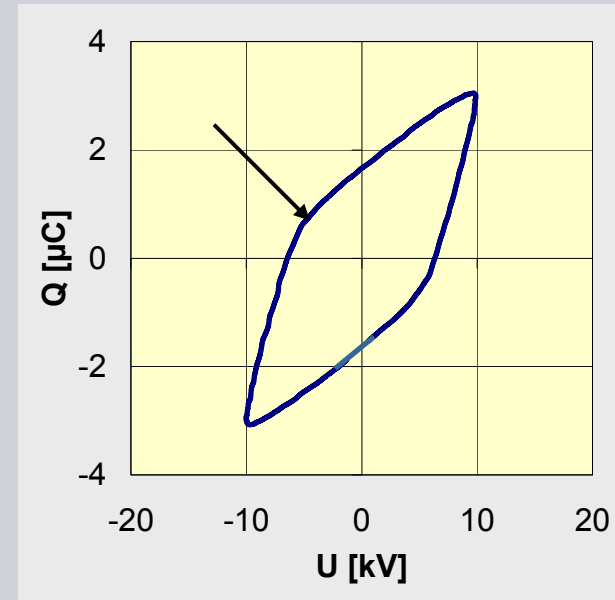
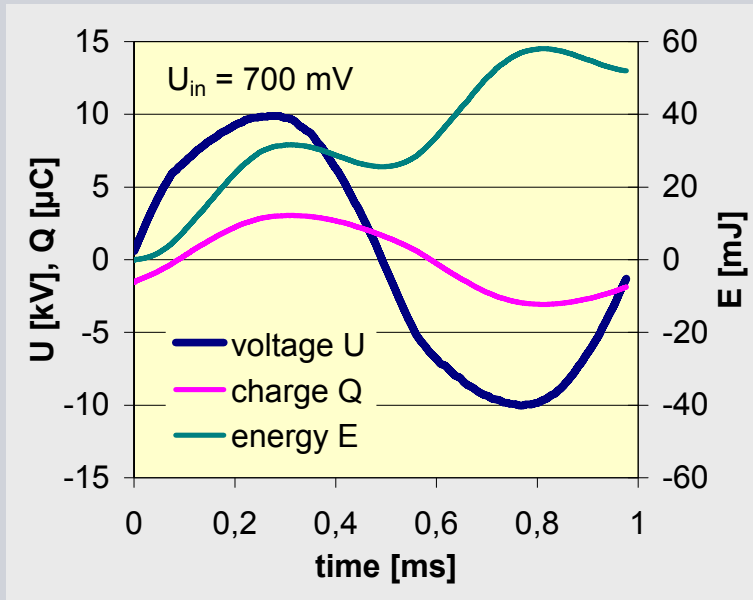
Hans Miessner (IUT)

Rolf Rudolph (IUT)

Carsten Plog (DC AG)

Michael Römheld

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

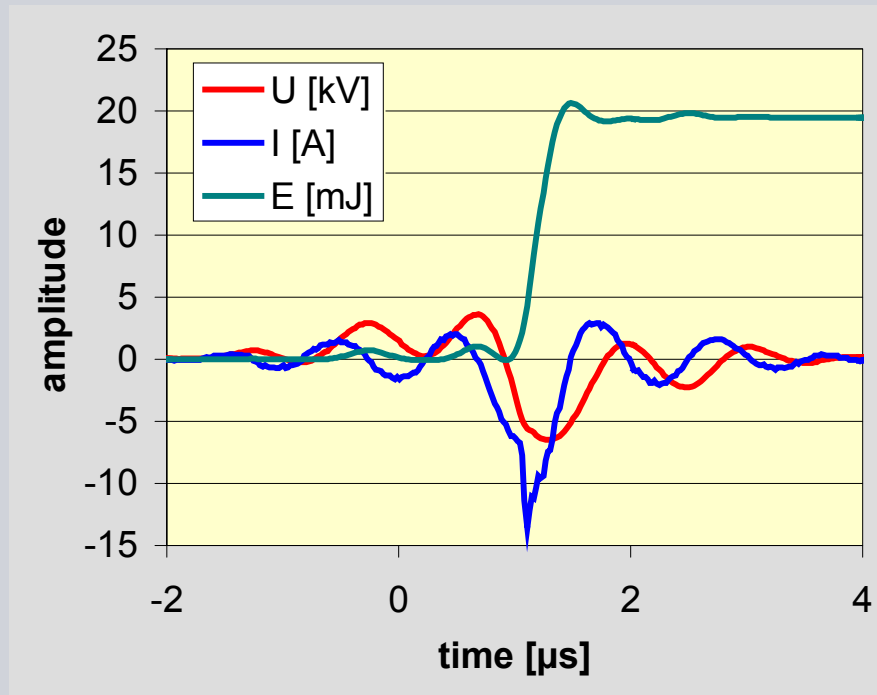


Reactor capacity 100 pF, synthetic air 30 Nl/min, 150 °C

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

$$E_{cycle} = \oint_{cycle} U dQ$$

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

$$E_{pulse} = \int_{pulse} U(t) \cdot I(t) dt$$

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

$$\frac{1}{C_{reactor}} \times \int_{t_0}^{t_1} I(t) dt \neq U(t_1)$$

Catalyst Screening for the VOC Decomposition using Adsorption and Oxygen Plasma

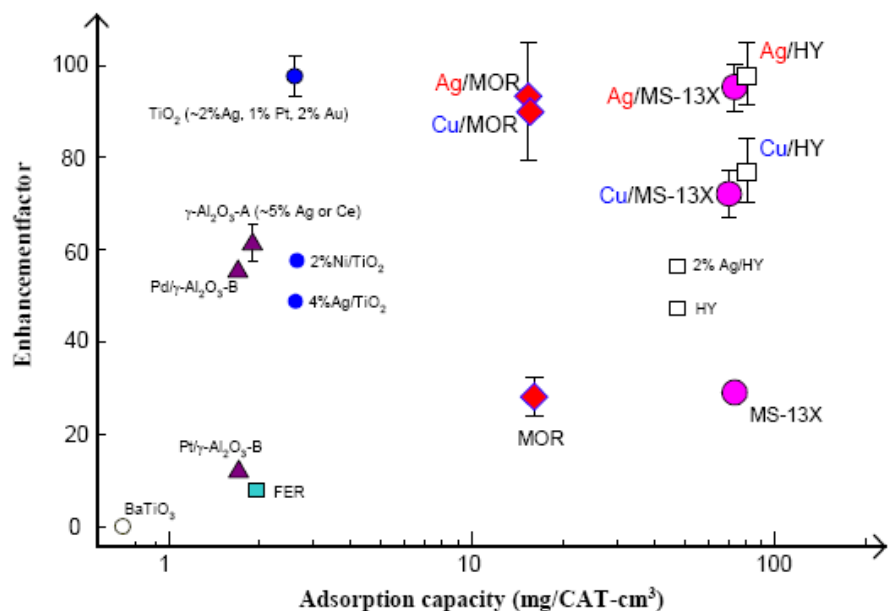
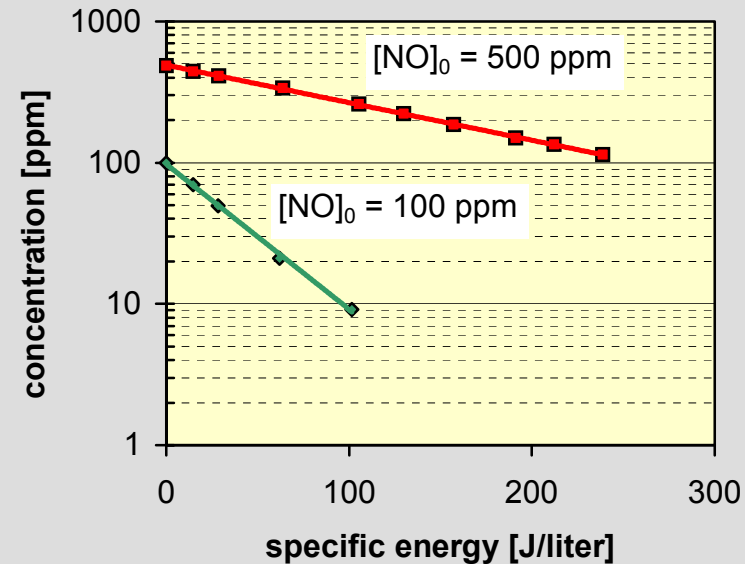
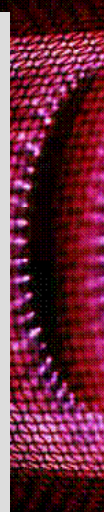
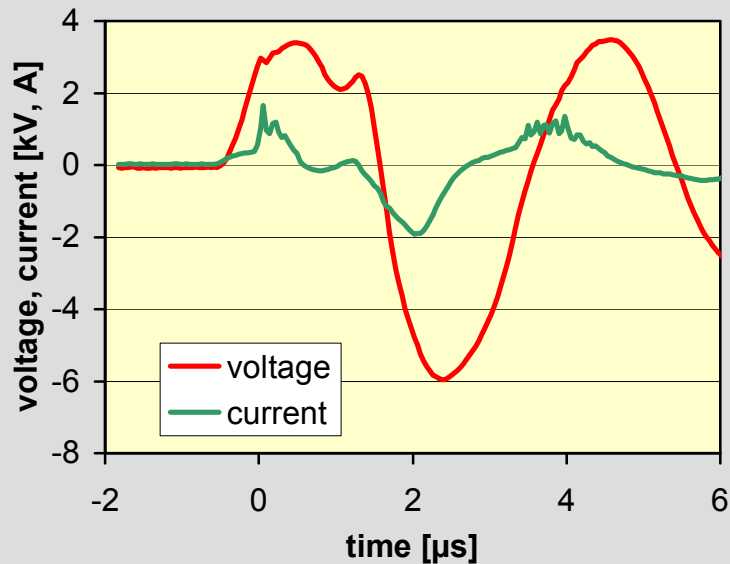


Figure 3 Catalyst mapping in terms of enhancement factor (EF) and adsorption capacity of benzene (100°C, 200 ppm benzene).

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

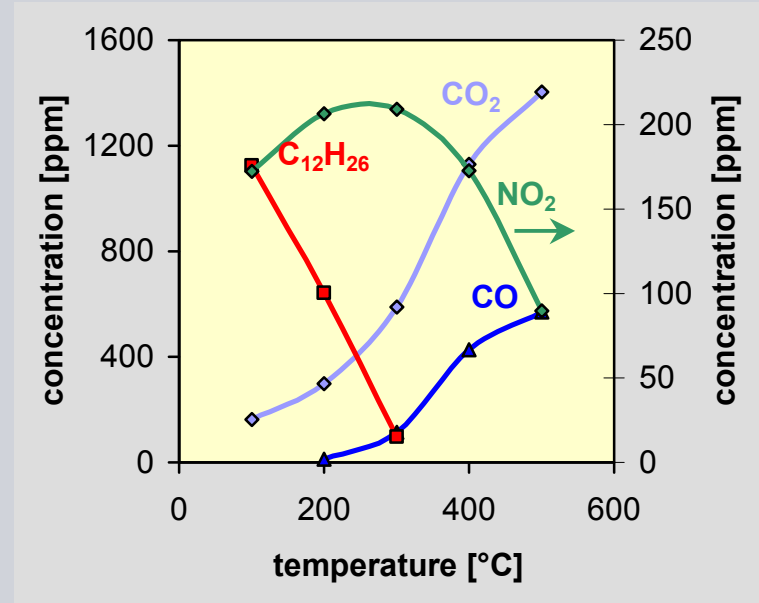
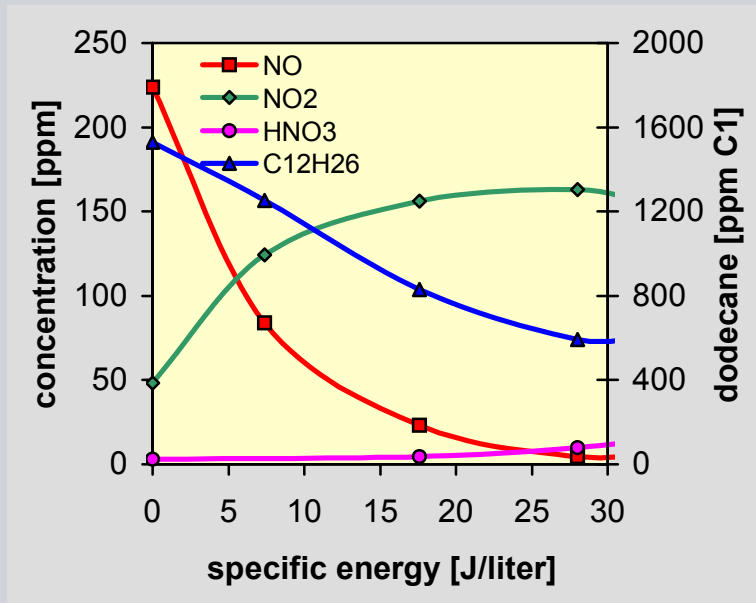
Characterization of the DBD



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

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