9th Asia-Pacific Conference on Plasma Physics, 21-26 Sep, 2025 at Fukuoka

Effect of pellet catalyst properties on gas cleaning process

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The work deals with gas cleaning process, i.e. removal of model hydrocarbons (toluene and naphthalene) by a dielectric barrier discharge (DBD) reactor filled with various pellet catalysts [1,3]. We studied the effect of pellet material properties on removal efficiency. The plasma reactors were powered by AC high voltage and operated at various specific input energies (SIE) and at the constant gas flow rate (0.5 L/min). After the gas cleaning process, selected pellet catalysts were regenerated by various methods to restore their activity and subsequently re-used again for gas cleaning [3]. Gaseous and solid carbon-containing products (coke deposits) of toluene and naphthalene decomposition were analyzed by means of FTIR, TGA, GC-MS, SEM, EDX analytical methods.

In case of napthalene, the effect of the pellet materials of various catalytic activity (glass, Al2O3, Pt/Al2O3, TiO2, BaTiO3, ZrO2), shape and size (spherical, cylindrical, 3-8 mm), dielectric constant (5-4000) and specific surface area (35-250 m2/g) in various carrier gases (ambient air, oxygen or nitrogen) on removal efficiency and CO2 selectivity were investigated. The experiments were carried out at relatively low temperature (<150°C) and with relatively high initial concentration of naphthalene (5,000 ppm). In case of toluene, its removal efficiency in air, formation of solid products (coke deposits), their accumulation on pellet catalysts followed by their gradual deactivation was investigated. The deactivated pellet catalysts were then regenerated either by plasma, ozonation or heat. The experiments were carried out with four different pellet materials (Al2O3, Pt/Al2O3, Pd/Al2O3, TiO2) at room temperature and with the initial concentration of toluene (2,770 ppm).

The results showed that naphthalene removal efficiency (NRE) increased indeed with the increase of the amplitude and frequency of the applied voltage. The carrier gas had significant effect on the NRE, as different reactive species (N2(A), N, O, O3, OH) and products were formed. In nitrogen, the NRE was the poorest (<25%) with mono-/hetero- N-containing aromatic compounds being main products. In ambient air, the NRE was significantly higher (up to 88%) and accompanied with the formation of CO/CO2 and O-containing hydrocarbons or hydrocarbons with fewer carbon atoms. In oxygen, complete naphthalene removal was achieved. With respect to the pellet materials, the highest NRE was obtained with TiO2 catalyst (88%, 320 J/L), and slightly lower with Pt/Al2O3 (78%), but much higher CO2 selectivity suggesting its best oxidation abilities compared to other materials. The NRE for other materials followed a sequence: ZrO2 (72%)> Al2O3 (66%)> glass (64%)> BaTiO3 (51%). The NRE increased with increasing material surface area, while shape of material was found to be more sensitive and important: higher NRE was found for cylindrical and smaller pellets. Surface analysis of materials revealed differences in distribution of solid carbon products on the surface of various materials, with spherical materials covered almost uniformly, while cylindrical in characteristic circular patterns probably as a result of different discharge modes depending on the used material. Besides the main gaseous products (CO2, CO, H2O and HCOOH), several other complex gaseous and solid by-products were identified (phthalic anhydride, maleic anhydride, benzoquinone naphthoquinone, etc). Toluene removal by plasma combined with pellet catalyst as well as subsequent pellet catalyst regeneration were tested for various materials. Removal efficiency, selectivity and carbon balance of the process were evaluated. The RE of toluene followed a sequence: Pd/Al2O3 (76%, 760 J/L)> Pt/Al2O3 (74%)> Al2O3 (65%)> TiO2 (56%). These results were affected not only by catalytic properties of materials, but also dielectric constant and specific surface area (Al2O3). Pd/Al2O3 exhibited the highest toluene RE and the lowest energy demand [kWh/kg]. All catalysts showed the highest selectivity for CO2 (13–29%) and smaller for CO, HCOOH. For Al2O3 production of other than above species was the highest, resulting in the worst carbon balance.

The used pellets materials were regenerated for 2 hours by three different methods - by DBD plasma, O3 (8,000 ppm), and (at 100°C). The efficiency of regeneration was evaluated based on the production of gaseous products (CO2, CO and HCOOH) in time. Plasma regeneration was the best although still only partial and spatially non-uniform. Regenerated catalysts were re-used for toluene removal and the results showed that regenerated catalysts exhibit higher toluene RE after each cycle than those non-regenerated.

Acknowledgment
Funded by Slovak Research and Development Agency project APVV-20-0566 and EU NextGenerationEU through the Recovery and Resilience Plan projects 09I03-03-V03-00033 and 09I03-03-V04-00092.

References

[1] Cimerman R. et al., J. Phys. D: Appl. Phys. 51, 274003 (2018)
[2] Cimerman R. et al. Catalysts 10 (12), 1476 (2020)
[3] Kšanová J. et al. Hakone XVII, Padova (2024)

9th Asia-Pacific Conference on Plasma Physics, Fukuoka (Japan), Sept 21, 2025

EFFECT OF PELLET CATALYST ON GAS CLEANING BY COLD PLASMA. CATALYST REGENERATION.

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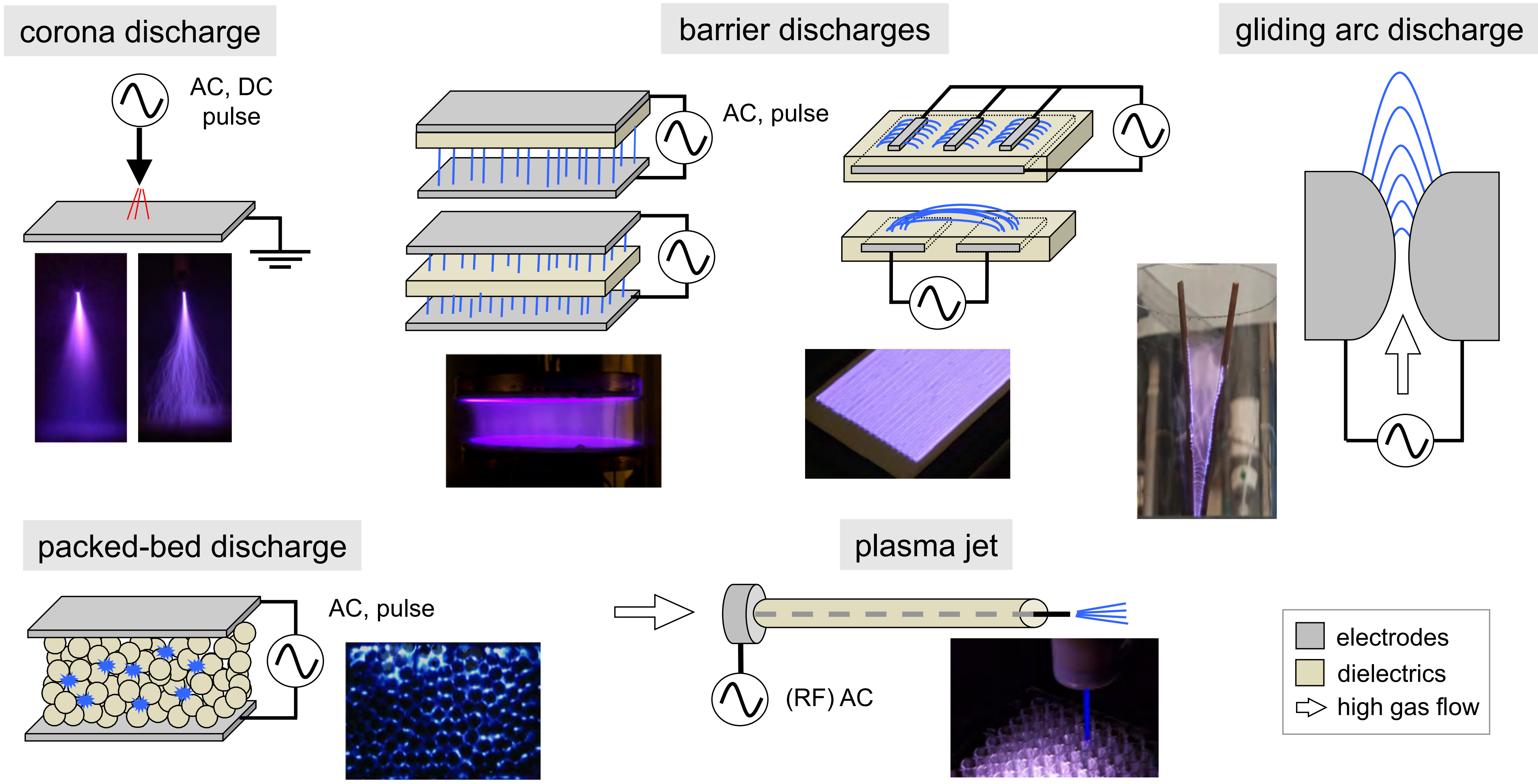
NextGenerationEU

Grant support: Slovak Research and Development Agency and EU NextGenerationEU through the Recovery and Resilience Plan under the project No. 09I03-03-V03-00033

Atmospheric Discharges



Applications of Plasma Discharges

- **Environmental applications**
  - ✓ air pollution control (exhaust gas treatment – VOC, NOx, CO_2, PM removal)
  - ✓ water cleaning (ozone generation)
- **Biomedical and agricultural applications**
  - ✓ volume and surface decontamination and sterilization …. therapy (cancer, ulcers)
  - ✓ seed germination, plants growth
  - ✓ food and package processing
- **Energy applications**
  - ✓ fuel (CH_4) reforming and H_2 generation (power-to-X)
  - ✓ plasma assisted combustion and ignition
- **Material applications**
  - ✓ plasma cleaning and etching
  - ✓ surface modification and activation
- **Optical applications**
  - ✓ light sources
  - ✓ plasma displays
  - ✓ gas detectors

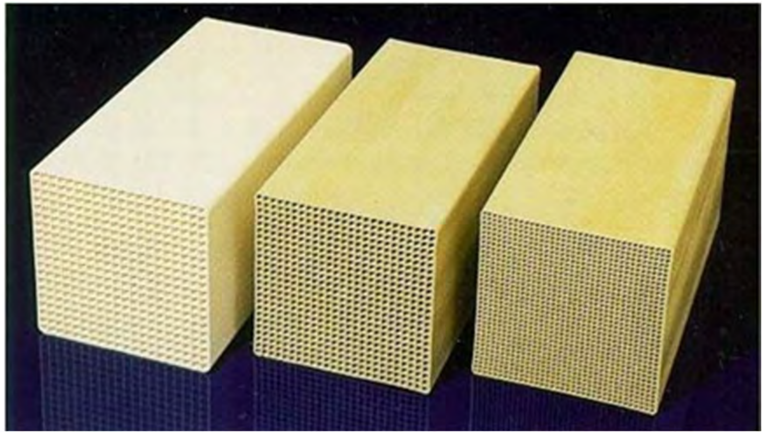
Pros/cons of plasma applications

+ high reactivity
+ efficient gas-phase reactions
- poor selectivity
- high power consumption
- formation of undesired products

Catalysts and ... Combination with Plasma

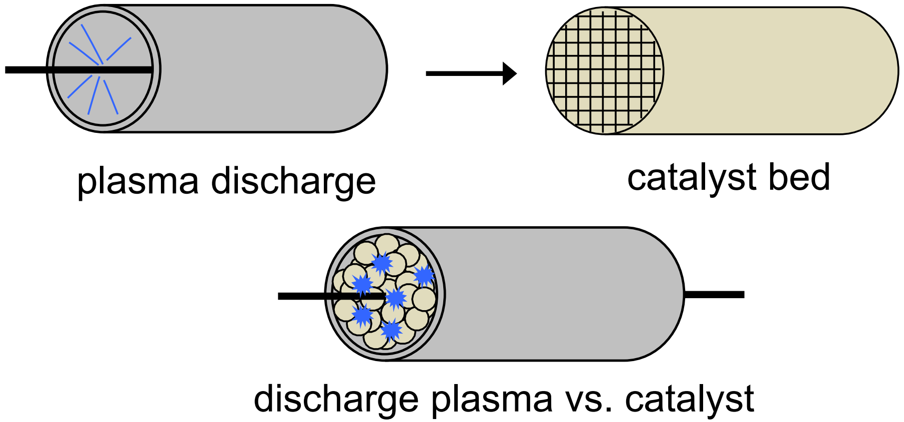
pellets
(size 1 – 5 mm)

foams
(porosity 10 μm – 1 mm)

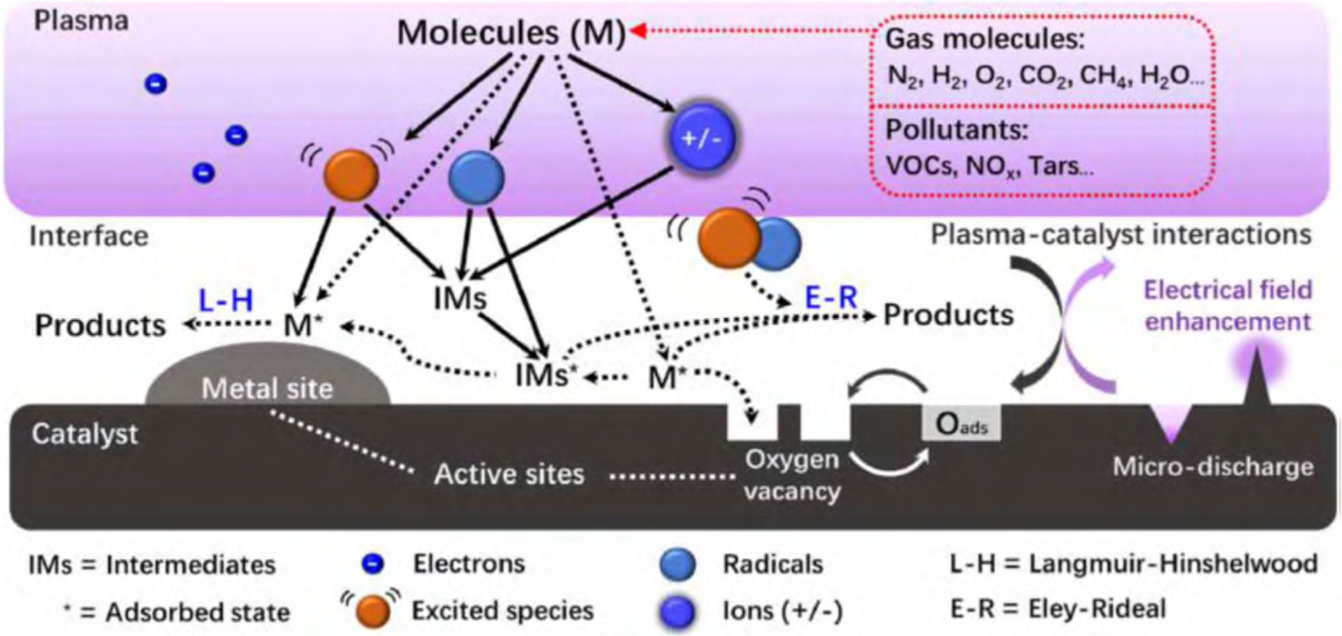


honeycomb monoliths
(diameter 10 μm – 1 mm, CPSI 50-400)

Pros/cons of catalysis
+ high reaction rate
+ high selectivity
+ efficient surface reactions
- high activation temperature
- demand for noble metals
- **limited lifetime**



Plasma Catalysis

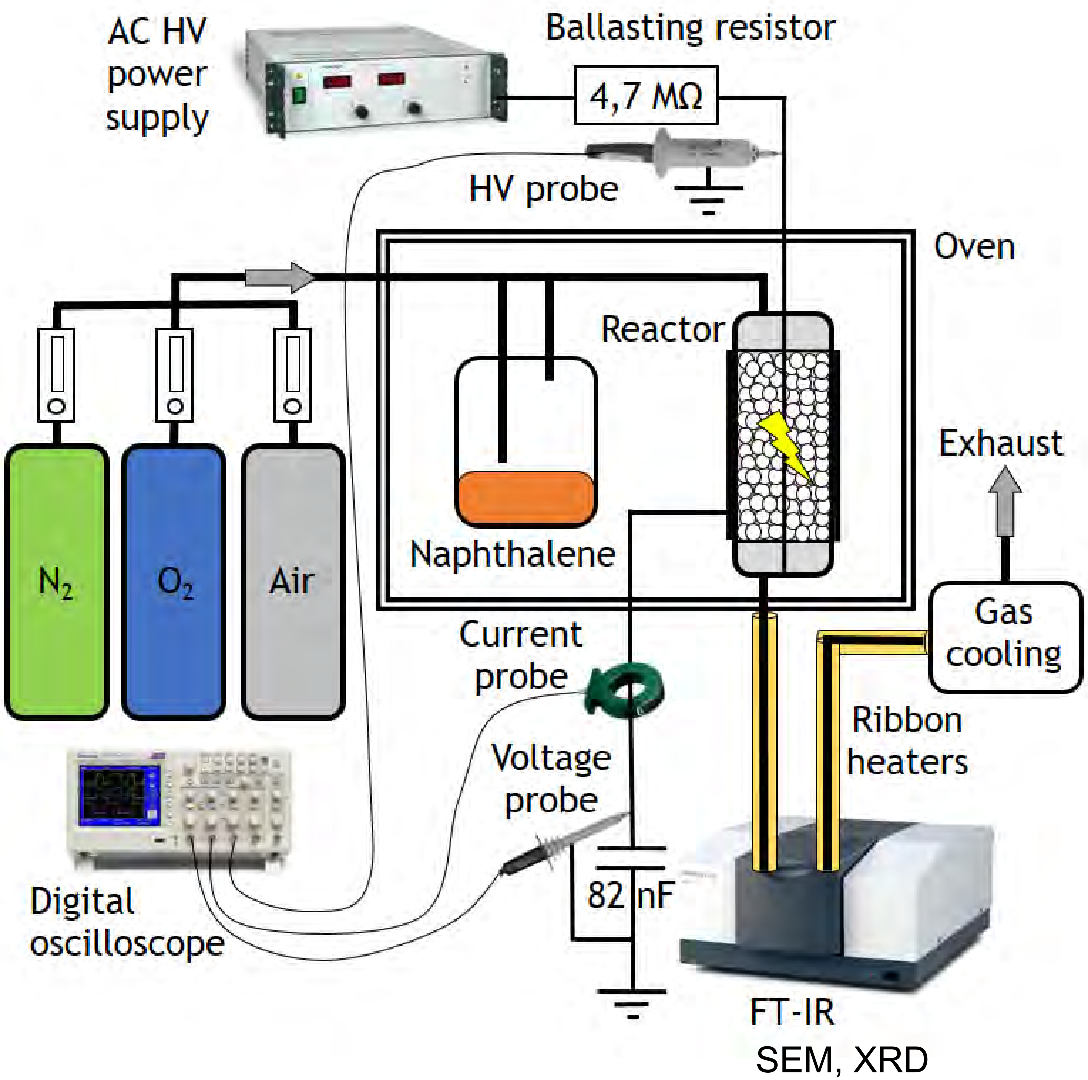


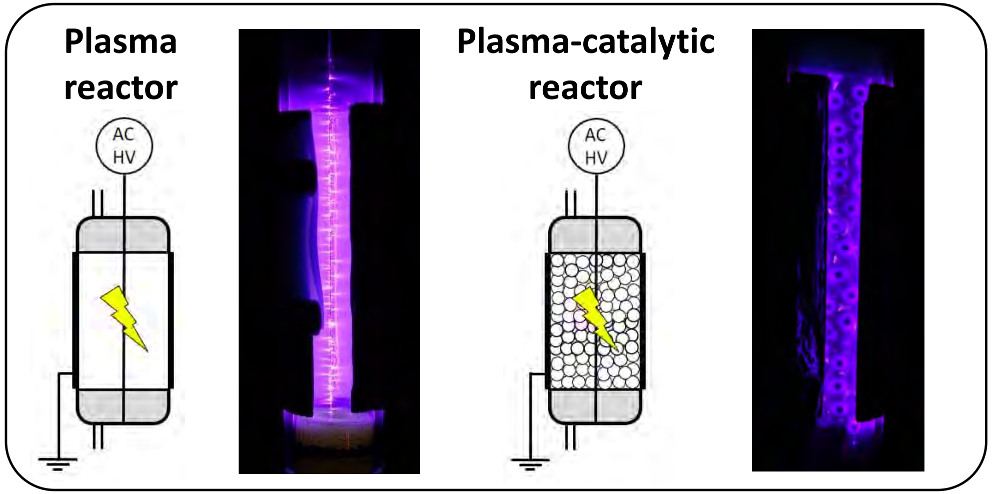
A. Bogaerts, X. Tu, J. C. Whitehead, et al. *J. Phys. D: Appl. Phys.* **53** (2020)

- Their interaction affects the chemical process (removal efficiency, selectivity, carbon balance).
- **Catalyst effect on discharge** → change of electric field; discharge mode and distribution; adsorption of pollutants
- **Discharge effect on catalyst** → UV activation; lattice oxygen activation and catalyst dispersion plasma induced desorption; …

Pros/cons of plasma catalysis
+ higher reaction rate
+ high selectivity and good carbon balance
+ possible synergy
+ low yield of undesired by-products
… **but not always ideal**

Naphthalene Removal by Plasma and Catalysts

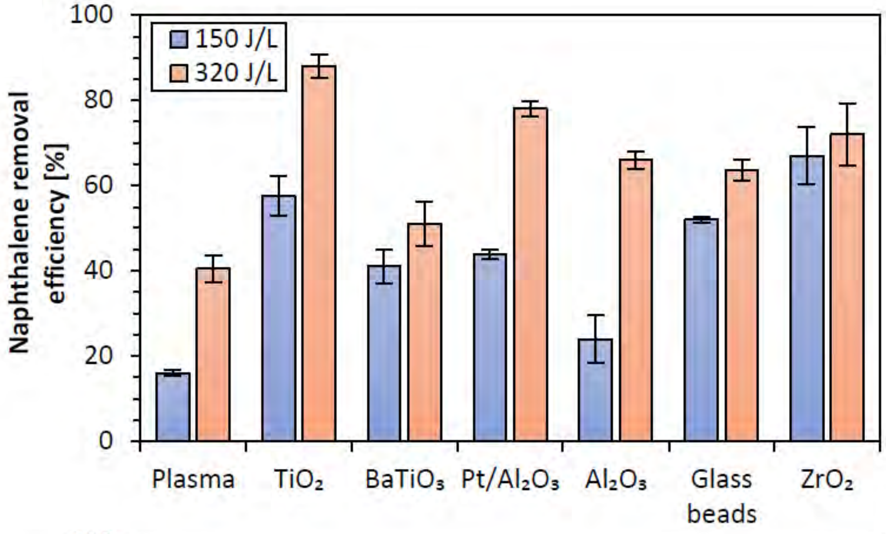


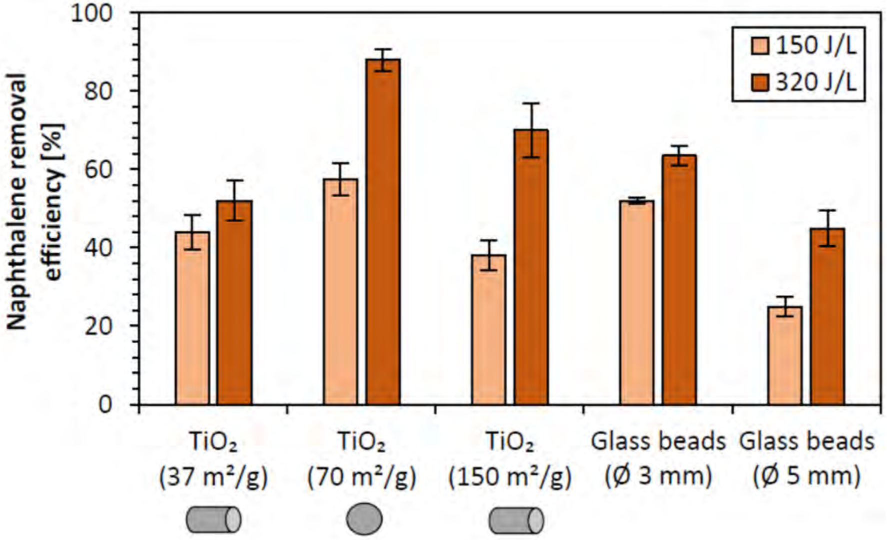


- **Naphthalene concentration:** 3000 ppm
- **Carrier gas:** Air, N_2, O_2 (0.5 L/min)
- **Plasma reactors:** cylindrical DBD (10 cm, Ø15 mm)
- **Catalyst (packing material)**: glass beads, TiO_2, γ-Al_2O_3, Pt/γ-Al_2O_3, $BaTiO_3$, ZrO_2
- ε_r (5–4000), shape (spherical/cylindrical), size (Ø3–5 mm, 3–8 mm long), specific surface area (37–150 m^2/g)
- **Operating temperature** ~ 100°C

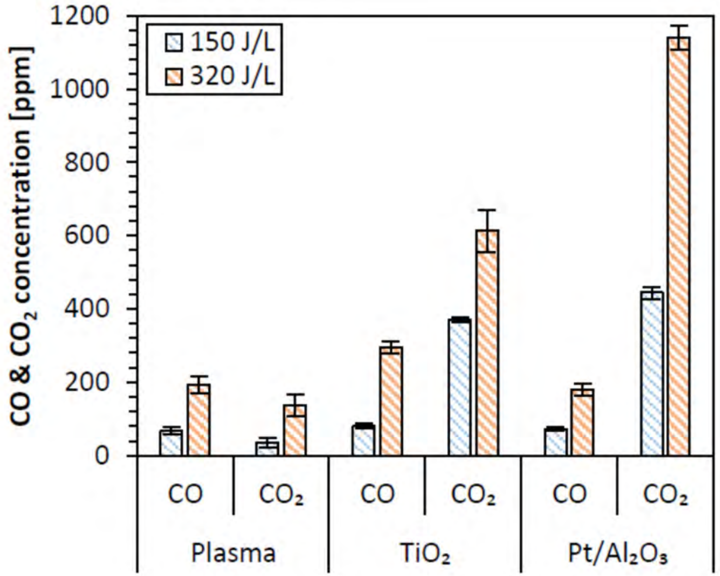
R. Cimerman, D. Račková, K. Hensel, *J. Phys. D: Appl. Phys.* **51** (2018)
R. Cimerman, M. Cíbiková, L. Satrapinskyy, K. Hensel, *Catalysts* **10** (2020)

Effect of Catalyst on Naphthalene Removal





Naphthalene removal efficiency as function of used material



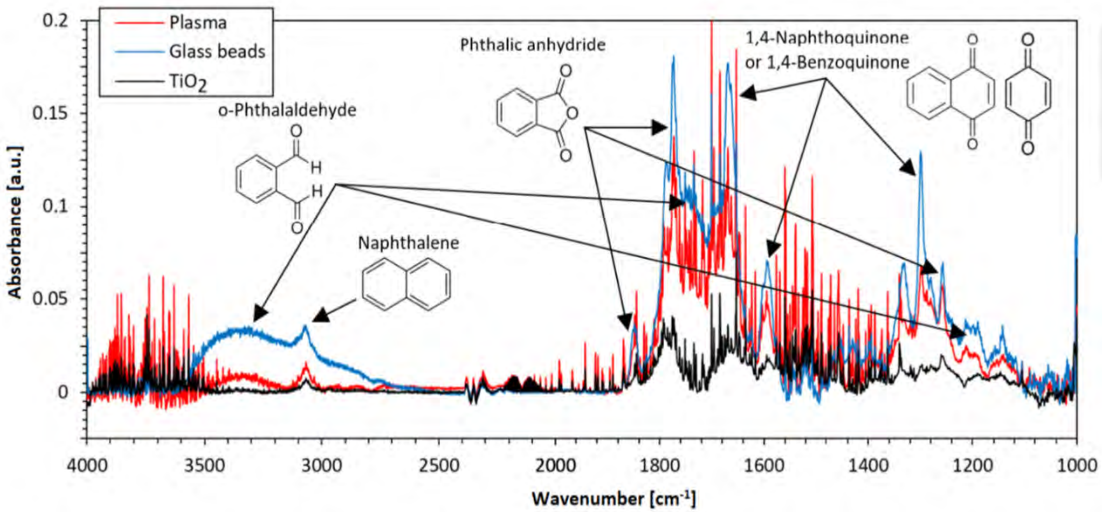
Concentrations of CO and CO_2 as function of used material

Gaseous products: mainly CO, CO_2 and HCOOH

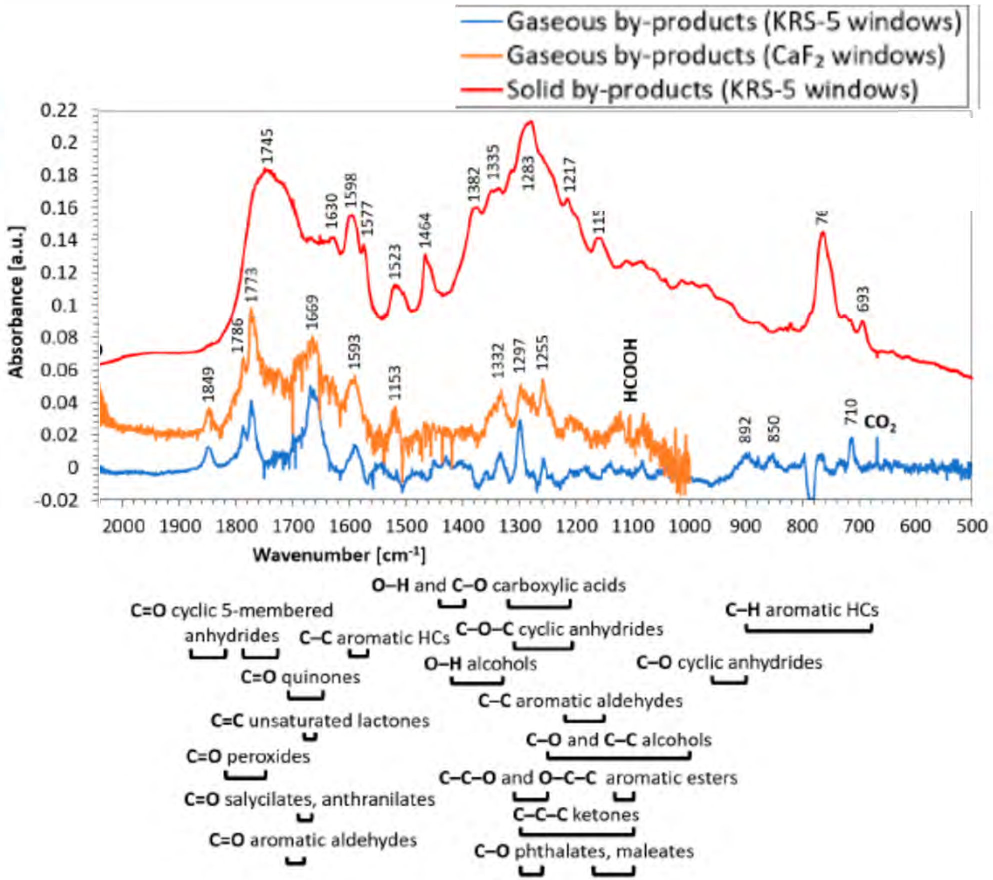
→ very low amount of gaseous products

R. Cimerman, D. Račková, K. Hensel, *J. Phys. D: Appl. Phys.* **51** (2018)

Products of Napthalene Removal



FTIR spectra of gaseous and solid by-products of naphthalene decomposition for a various plasma (catalytic) reactors [ambient air]



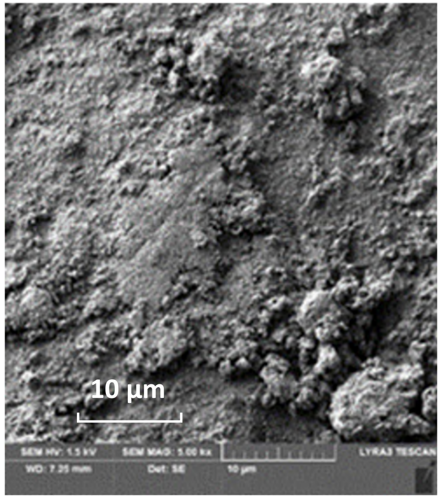
FTIR spectra of gaseous (🟠🔵) and solid (🔴) by-products of naphthalene decomposition

Solid products: C=O, C=C, C–O, C=N, O–H ...
1,4-naphthoquinone, phthalic anhydride, …
→ **high amounts of (undesired) solid products**
i.e. **carbon-containing deposits** (coke)

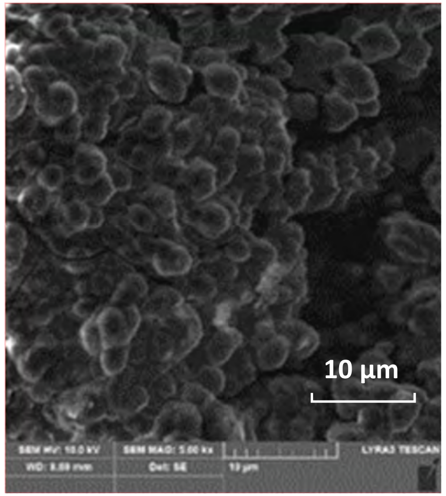
R. Cimerman, D. Račková, K. Hensel, *J. Phys. D: Appl. Phys.* **51** (2018)
R. Cimerman, M. Cíbiková, L. Satrapinskyy, K. Hensel, *Catalysts* **10** (2020)

Solid Deposits on Catalysts

TiO_2

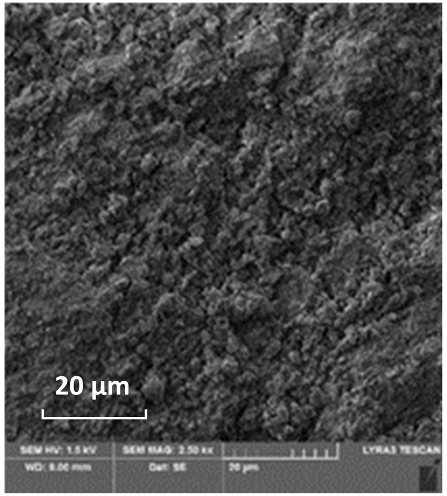


Fresh

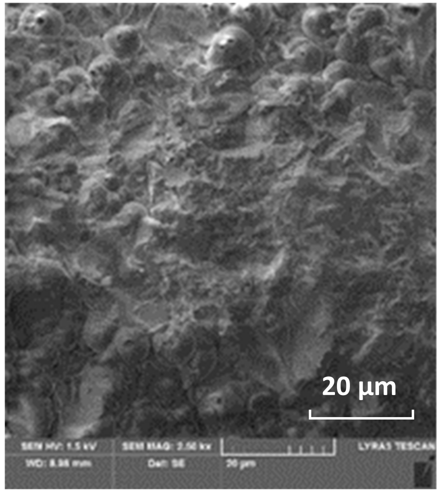


Used

$Pt/\gamma Al_2O_3$



Fresh



Used

SEM and optical microscope images of selected catalysts

R. Cimerman, M. Cíbiková, L. Satrapinskyy, K. Hensel, *Catalysts* **10** (2020)

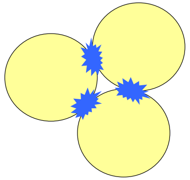
Solid Deposits on Catalysts

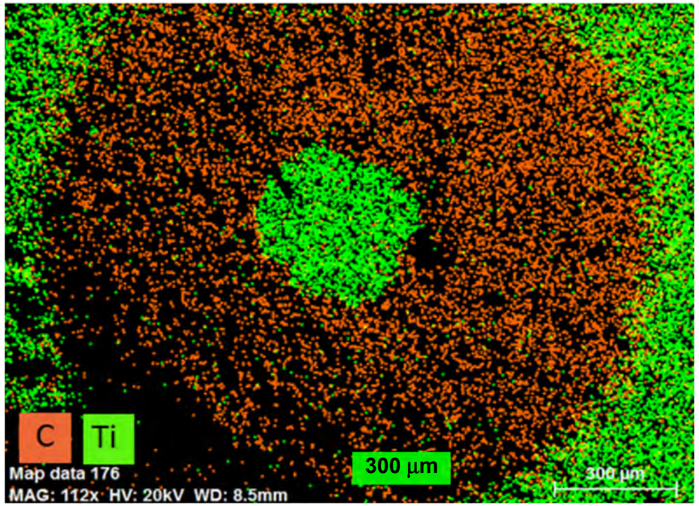
$BaTiO_3$

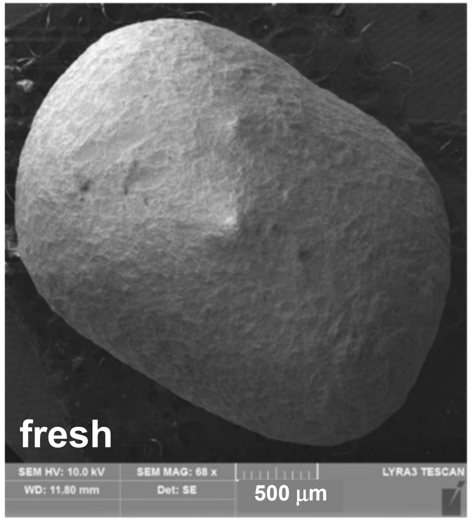
Fresh

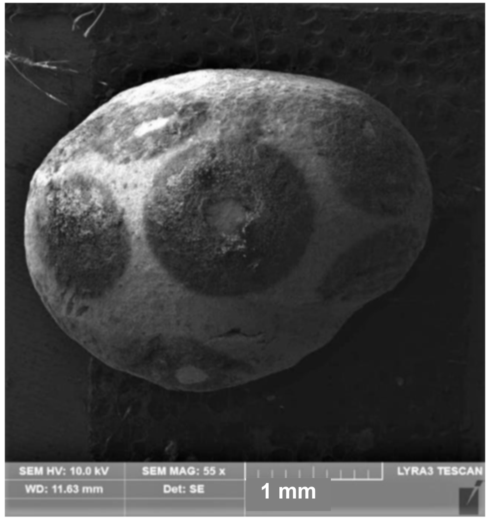
Used

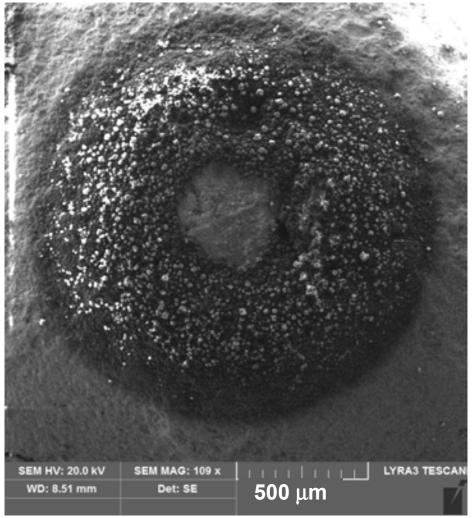
EDX image of $BaTiO_3$.

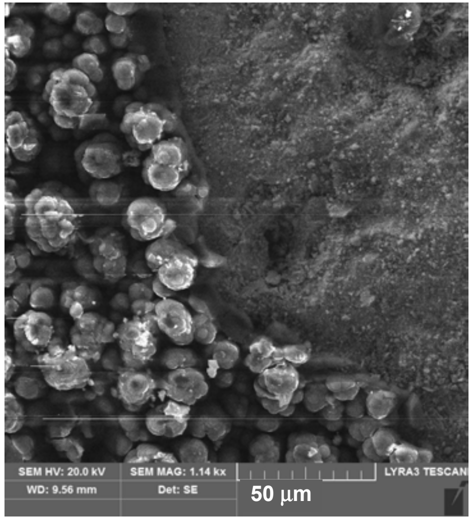












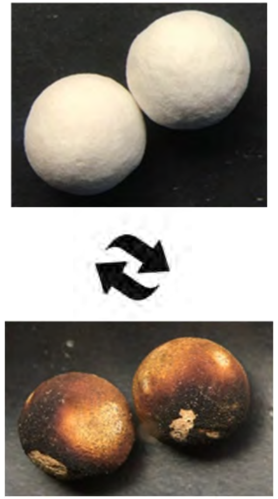
R. Cimerman, M. Cíbiková, L. Satrapinskyy, K. Hensel, *Catalysts* **10** (2020)

Catalyst Deactivation and Regeneration

- **Catalyst deactivation** = loss of catalytic activity and/or selectivity over time → decline of process efficiency
- Deactivation can be chemical, mechanical or thermal.
- Deactivated catalysts can be regenerated/restored, recycled, used for another application, or discarded.
- **Conventional regeneration methods**:
  - ✓ Gasification (oxidation/reduction with a proper reactant, e.g. O_2, H_2, H_2O, CO_2, etc.)
  - ✓ Chemical washing (using chlorobenzene or liquified propane as solvents)
  - ✓ Mechanical treatment
  - ✓ Thermal treatment
- Interest in new, inexpensive, economically, and energetically feasible methods for **catalyst regeneration** that preserve the material of the catalyst without significant changes in surface properties.

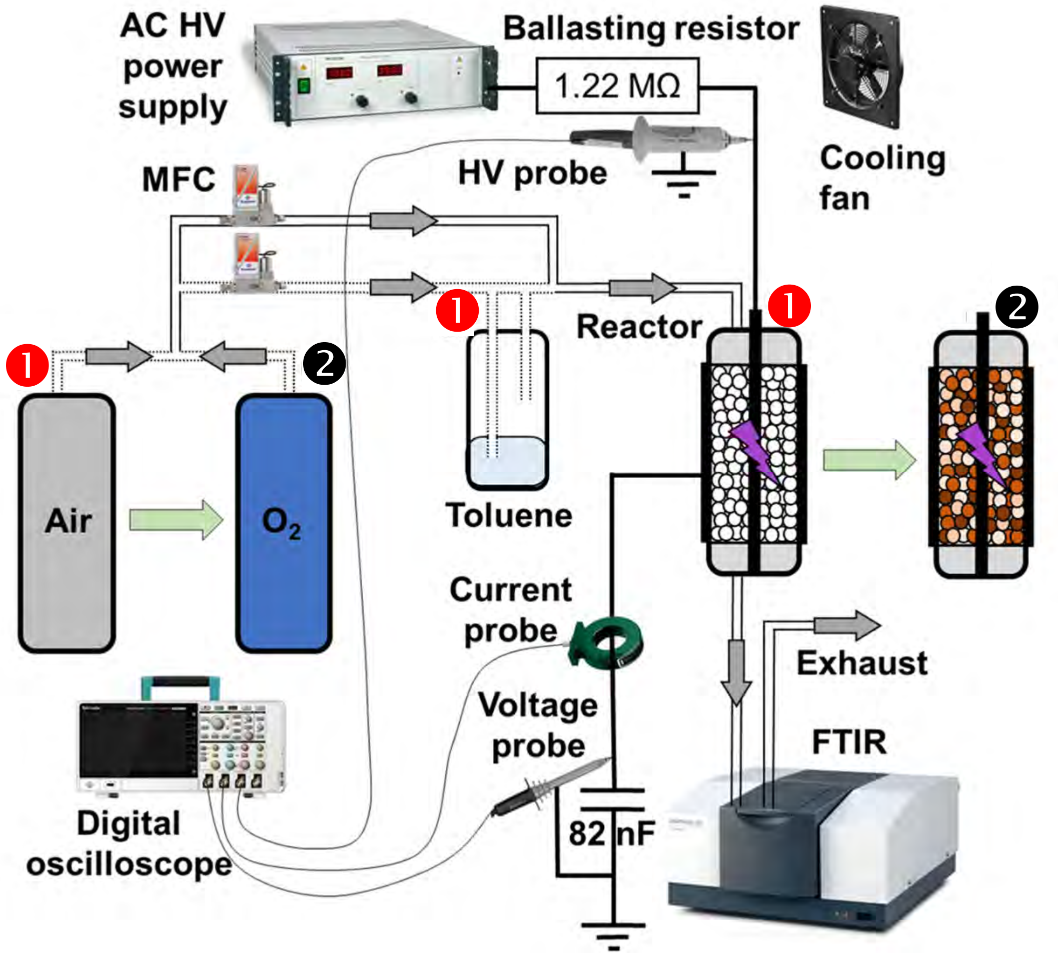
Plasma Regeneration

- Can plasma remove **carbon deposits**, extend or prolong a lifetime of a catalyst?
- Non-thermal plasma → highly reactive environment
- **Principle:** oxidation of undesired deposits usually in oxygen atmosphere, by O, O^-, O_2^+, O_2^-, O_3 and other reactive species (e.g., OH, H, HO_2).
  + minimal damage to original catalyst structure
  + production of species at ambient conditions
- **Regeneration of catalysts:** ❶ deactivated by adsorbed VOCs, ❷ deactivated by coke.



	Pollutant removal		Catalyst regeneration	
Source	**Target**	**Catalyst**	**System**	**Efficiency/Result**
Veerapandian et al. (2021) *J. Hazardous Materials* **402**	toluene	hopcalite	packed-bed DBD reactor	catalyst activity, CO_2 selectivity ▲, surface area ▼
Kuroki et al. (2009) *IEEE Trans. Ind. Appl* **45**	toluene	honeycomb zeolite	pulsed NTP (closed vs. non-closed)	desorption efficiency 53 %, regeneration efficiency 82 %
Wang et al. (2013) 21th ISPC, Cains, Australia	toluene	Ag/, Mn/, Ce/, Ag-Mn/, Ce-Mn /HZSM-5	NTP 2-stage configuration	93 %(Ag-Mn/HZSM-5), 69% (Mn/HZSM-5)
Hossain et al. (2020) *Chem. Eng. Res. Design* **164**	toluene	Pd/ZSM-5 (2 wt. %)	NTP alone, NTP + catalyst (DBD packed-bed reactor)	toluene decomposition ~ 100%
Pinard et al.(2024) *Catalysis Today* **426**	coke	zeolites	NTP (DBD pin-to-plate geometry)	products CO_2, CO, light organics
Di et al. (2023) *Plasma Scie. Technol.* **25**	o-xylene coke	Pt/, Pd/, Au/ /Co3O4	NTP (DBD packed-bed reactor)	
Srour et al. (2021) *Fuel* **306**	coke	hydrodesulfurization (HDS) catalyst	NTP	coke NTP regeneration at 250°C = coke thermal regeneration 500°C.

Experimental Setup for Catalyst Regeneration



Atmospheric pressure packed-bed dielectric barrier discharge (DBD) reactor in coaxial cylindrical geometry

❶ CATALYST DEACTIVATION

toluene removal by in synthetic **air plasma**
→ formation of gaseous products and solid deposits

Reactor: **cylindrical DBD** (10 cm, Ø15 mm)

Packing material: **γAl_2O_3, Pt/γAl_2O_3, TiO_2**

Gas (flow rate): air + toluene **2770 ppm (0.5 L/min)**

Operating temperature **~ 100°C**

Energy density (discharge power): **320 J/L (6 W)**

Experiment duration: **3 hr**

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❷ CATALYST REGENERATION

removal of solid deposit in **oxygen plasma**
→ formation of gaseous products (CO_2, CO, HCOOH)

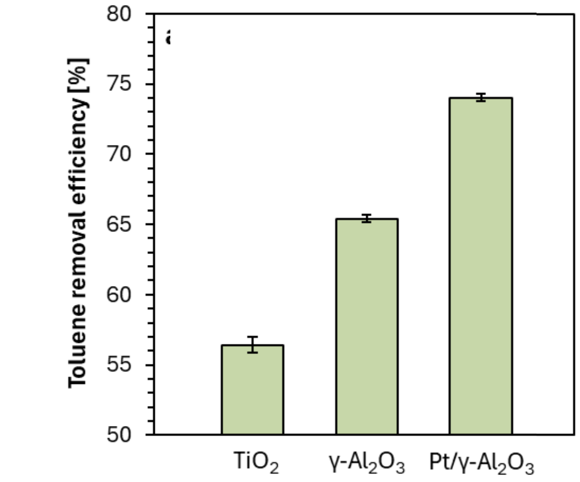
Gas (flow rate): oxygen (0.5 L/min)

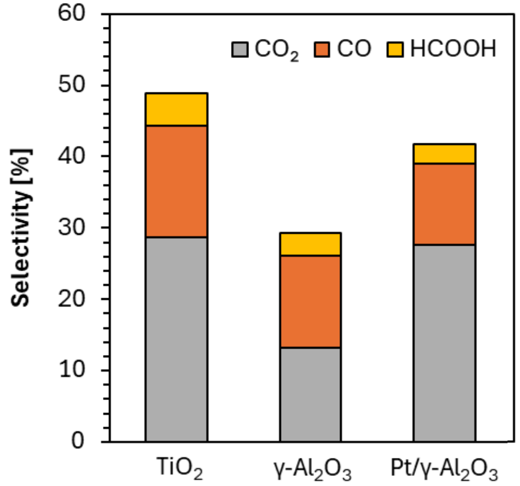
Operating temperature **~ Room**

Energy density (discharge power): **160 J/L (3 W)**

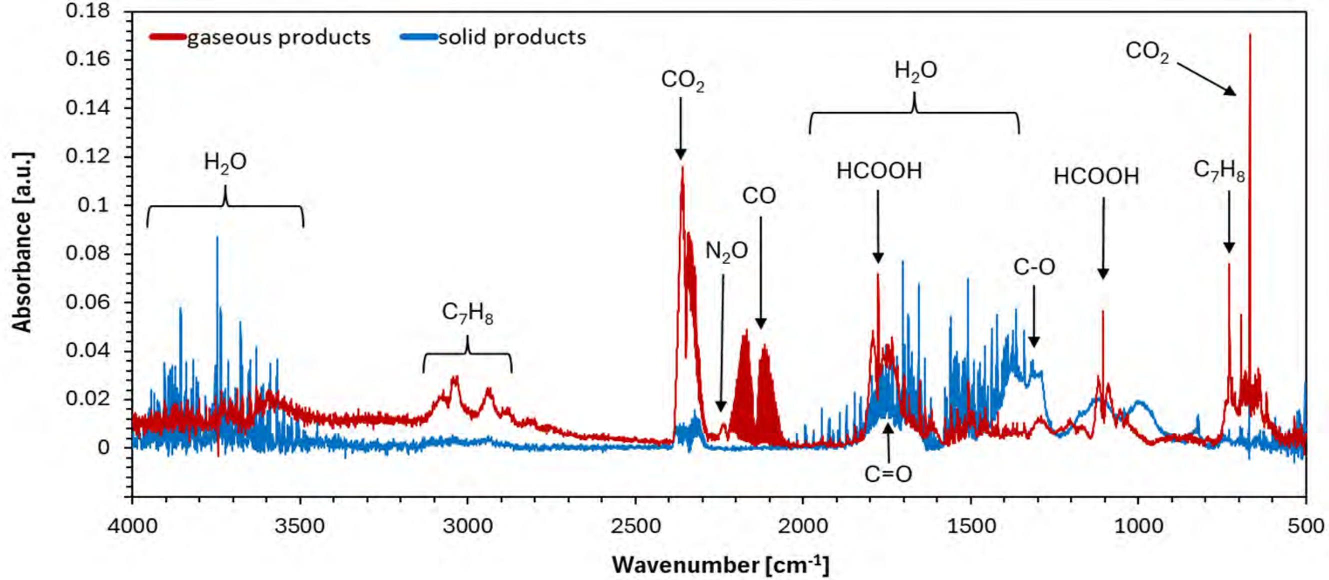
Experiment duration: **2 hr**

Toluene Removal and Catalyst Deactivation





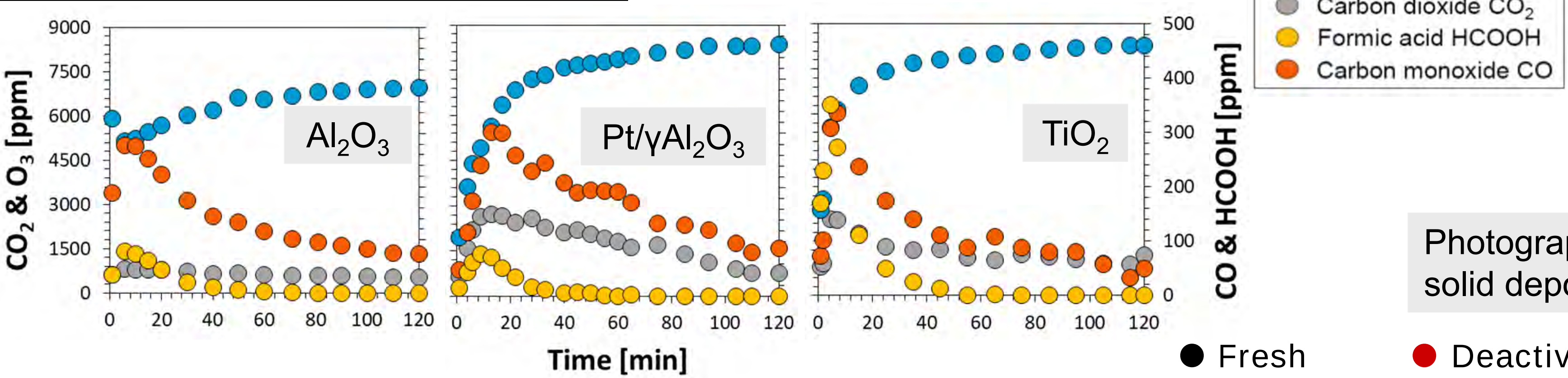
Toluene removal, selectivity (CO_2, CO, HCOOH) and carbon balance for different catalysts (P = 6 W)

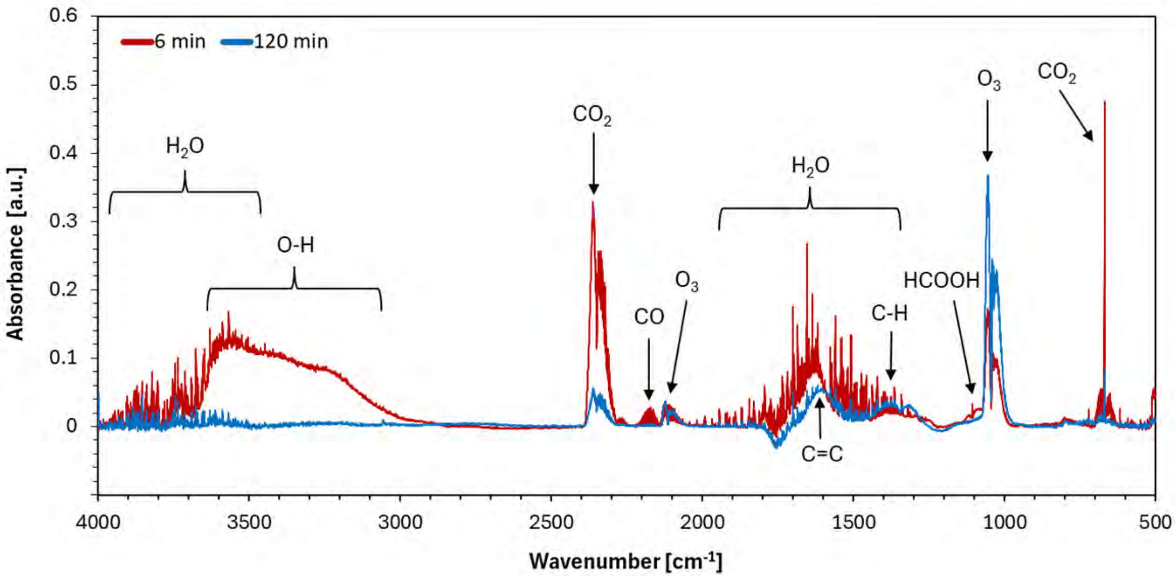


FTIR spectra of gaseous and solid products of toluene removal (Pt/γAl_2O_3)

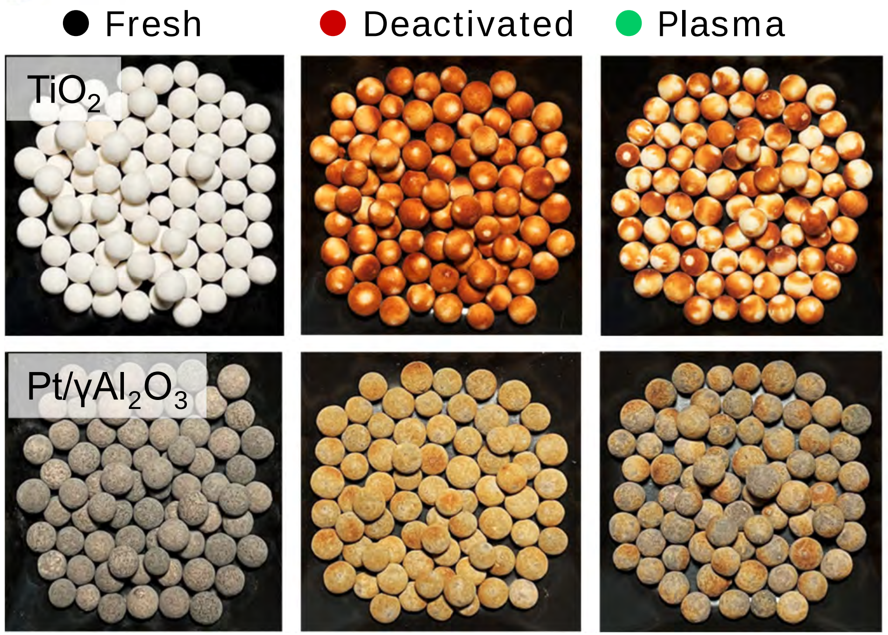
Catalyst Regeneration by Oxygen Plasma

Plasma regeneration (P = 3 W for 2h)



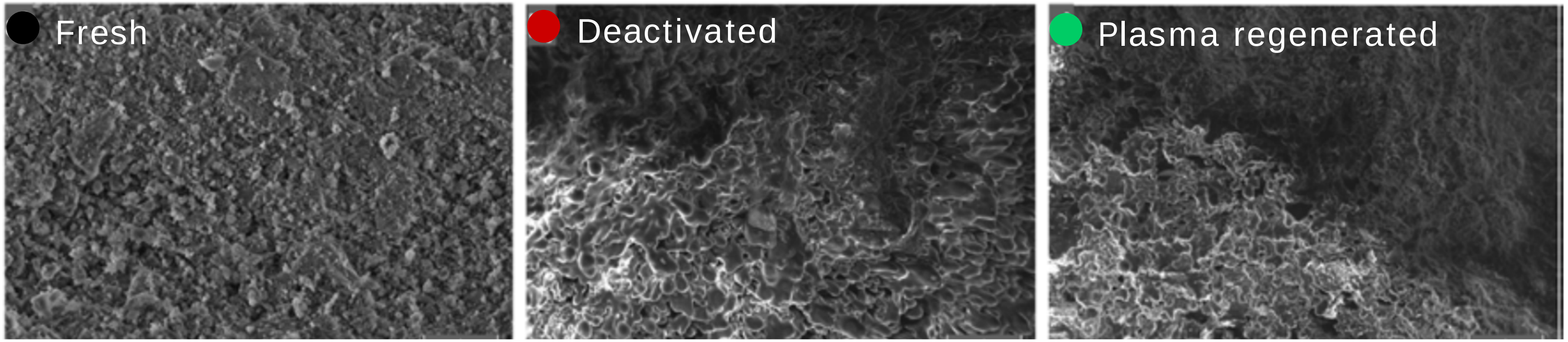


Photographs of catalysts and solid deposits on their surface

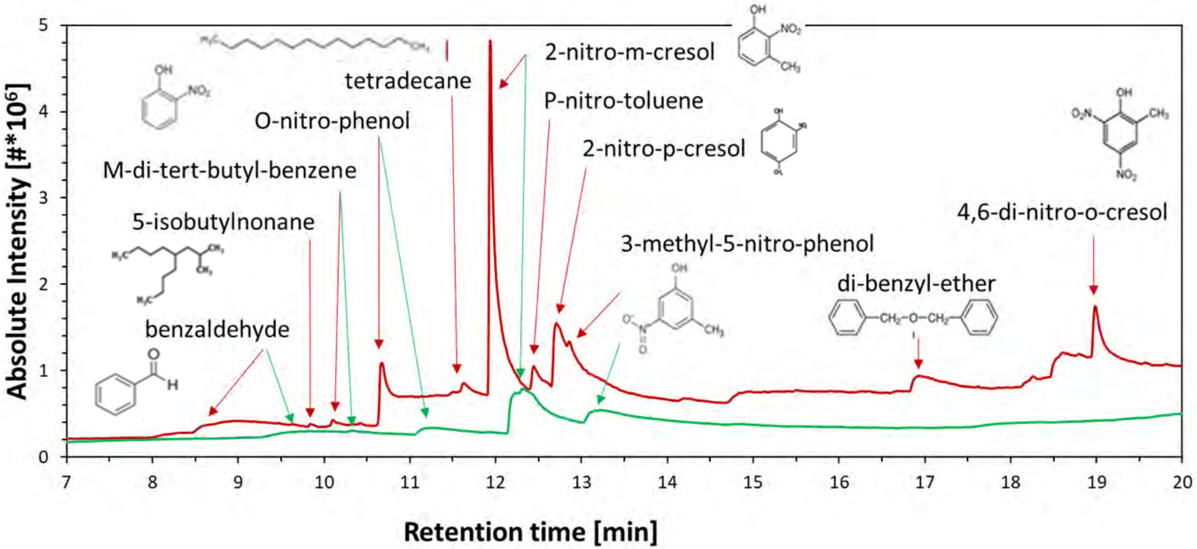


K. HENSEL, et al. Effect of pellet catalyst on gas cleaning process by cold plasma, Catalyst regeneration.

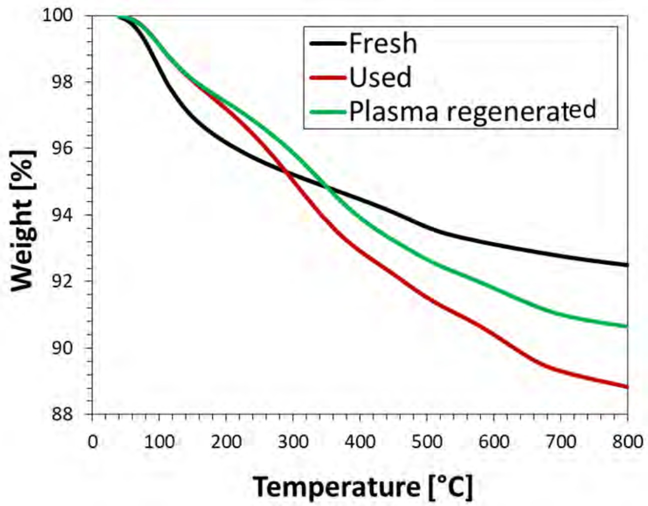
Analysis of Solid Products (Pt/Al_2O_3 Catalyst)



Scanning electron microscopy (SEM) of catalysts



GC-MS analysis of solid products on catalyst



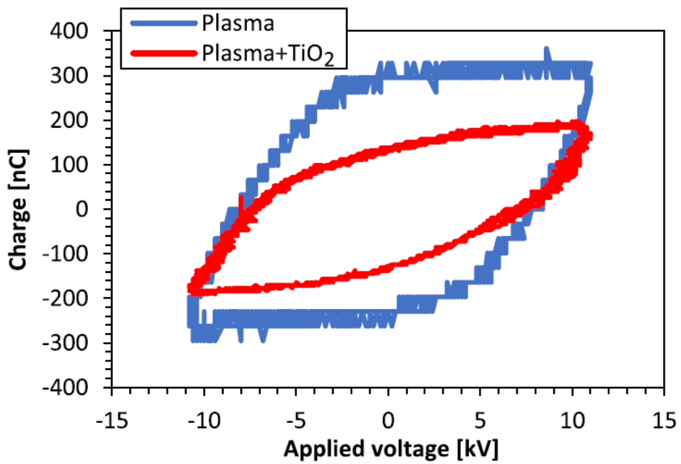
Thermogravimetric analysis (TGA) of catalyst

Summary

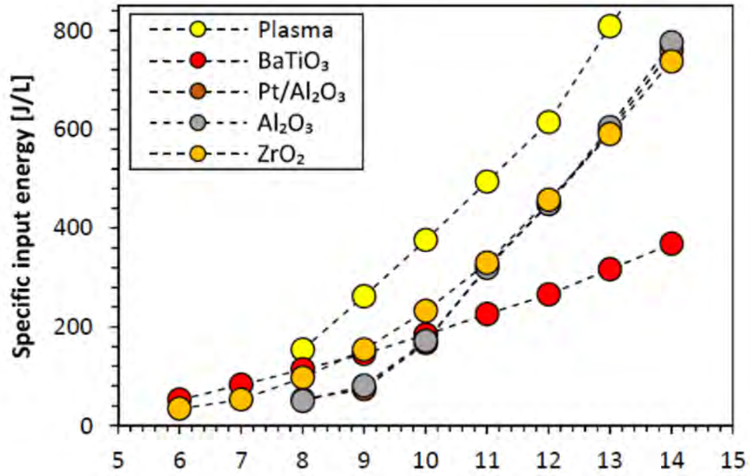
- **Removal of hydrocarbons** by **plasma combined with catalyst** is usually effective process due to high reaction rates, selectivity and carbon balance and possible synergy.
- The catalytic pellets affects the removal efficiency and formation of by-products. In case of naphthalene removal an **improvement of efficiency** was observed for increasing surface area, for smaller diameter and spherically rather than cylindrically shaped catalysts.
- However, if the removal process is not fully optimized, the efficiency and selectivity can still be low. It can lead to **formation of undesired by-products** that accumulate on catalyst and **deactivate it**. Distribution of these carbon containing deposits (coke) on surfaces depends on properties of the catalyst.
- We assume it is the result of **different discharge modes** (surface discharge mode vs. filamentary microdischarge mode) that depends on the used catalysts and mostly its dielectric constant.
- **Oxygen plasma** can be used for effective regeneration of deactivated pellet catalysts. It can **carbon deposits** to CO_2, CO, HCOOH, leading to gradual regeneration of the catalyst.
- **Plasma regeneration** showed significantly higher efficiency than ozone and thermal regeneration.
- Alike removal, the regeneration efficiency also **depends on the catalyst properties** linked with an exhibiting discharge mode.
- Regeneration by plasma is promising method but **requires further optimization** (e.g. by mixing catalytic pellets during regeneration).

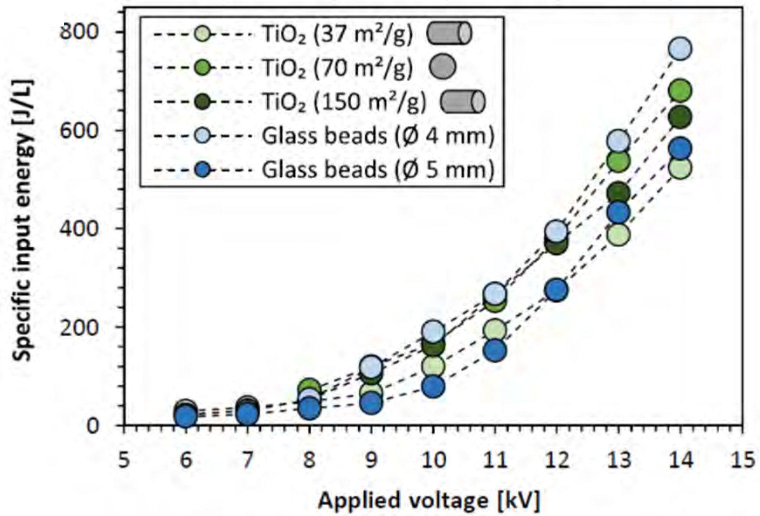
Effect of Catalyst on Electrical Properties

	TiO_2	$BaTiO_3$	$Pt/\gamma Al_2O_3$	γAl_2O_3	Glass beads	ZrO_2
Dielectric constant	20–100 (~85)	400–10000 (~4000)	8–11 (~9)	8–11 (~9)	~5	12–25
Shape	Spherical, cylindrical	Spherical/ cylindrical	Spherical	Spherical	Spherical	Cylindrical
Size [mm] (Ø = diameter; L=length)	Ø 2–3 (sphere) Ø 2, L 3–5 (cylinder)	Ø 2–4	Ø 2–3	Ø 2–3	Ø 3 Ø 5	Ø 2, L 3–5
SSA [m^2/g]	37 (cylinder), 70 (sphere), 150 (cylinder)	<1 [195]	N/A	~250 [195]	N/A	90



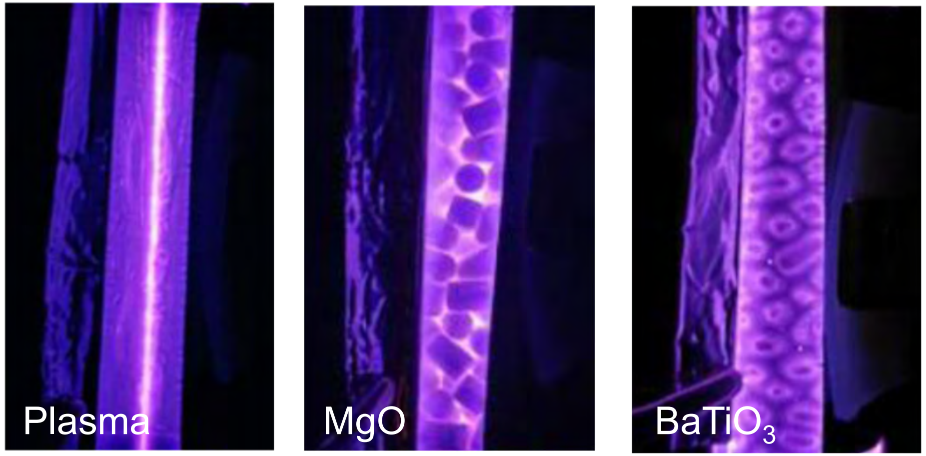
Lissajous figures [air, 11 kV, 500 Hz]



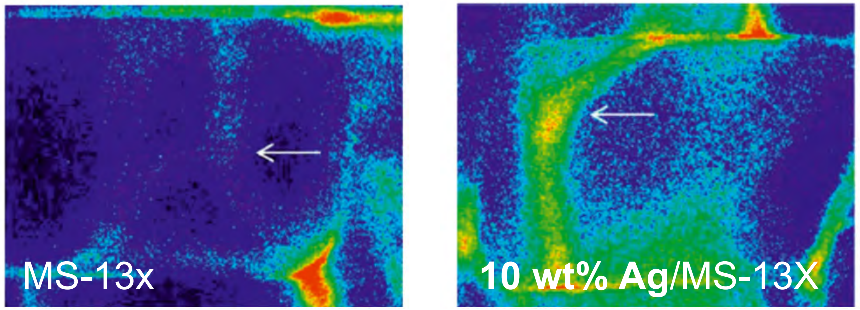


Input energy as function of applied voltage [air, 500 Hz]

Effect of Catalyst on Optical Properties

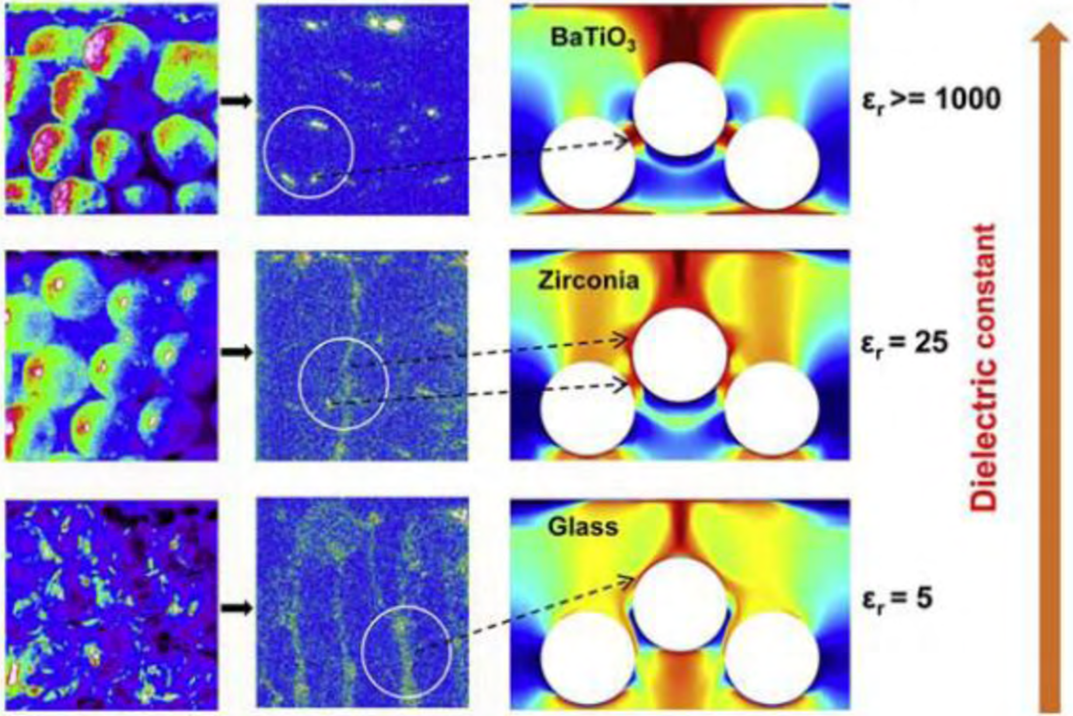


Discharges with various catalysts [14 kV, 500 Hz]



ICCD camera images of discharges [19 kV, 50 Hz]

H. H. Kim, A. Ogata, *Eur. Phys. J. Appl. Phys.* **55** (2011)



Streamer propagation in a packed bed plasma reactor

W. Wang W. et al., *Chem. Eng. J.* 334 (2018)