Removal of hydrocarbons by plasma-catalysis, catalysts regeneration and reuse

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Removal of toluene and naphthalene by dielectric barrier discharge (DBD) reactor filled with various pellet catalysts is discussed with respect with catalyst properties. Regeneration of pellets by various methods (plasma, ozonation, heat) is carried out and regenerated catalysts are repetitively tested. The results show a potential of plasma for effective both removal of hydrocarbons and regeneration of deactivated catalysts.

Plasma catalysis is an effective method for the removal of hydrocarbons. Their removal often leads to formation of various undesirable gaseous and solid products. Solid carbon-containing products (coke deposits) may gradually accumulate on the surface of catalysts and cause their deactivation. Thus their effective regeneration is needed. This work deals with the experimental removal of a model hydrocarbons - toluene and naphthalene - using plasma catalysis in a dielectric barrier discharge (DBD) reactor filled with various pellet catalysts [1,3]. We studied the effect of pellets material properties on removal process [2] and their regeneration by various methods and subsequent re-use [3]. Gaseous and solid products of toluene and naphthalene decomposition were analysed by means of FTIR, TGA, GC-MS, SEM, EDX.

In case of napthalene, the effect of the pellets of various catalytic activity (glass, Al_2O_3, Pt/Al_2O_3, TiO_2, $BaTiO_3$, ZrO_2), shape and size (spherical, cylindrical, 3-8 mm), dielectric constant (5-4000) and specific surface area (35-250 m^2/g) in various carrier gases on removal efficiency and CO_2 selectivity were investigated. The experiments were carried out at low temperature (<150ºC) and with relatively high initial concentrations (5000 ppm). In case of toluene, removal efficiency, accumulation of coke deposits on pellet catalysts (Al_2O_3, Pt/Al_2O_3, Pd/Al_2O_3, TiO_2). followed by their gradual deactivation were investigated. Deactivated catalysts were regenerated using various methods - by plasma generated in a similar DBD reactor filled with the pellets, by ozonation or by heat. The initial concentrations of toluene (2,770 ppm).

With respect to the pellet materials, the highest naphthalene removal efficiency (RE) was obtained with TiO_2 catalyst (88%, 320 J/L), and slightly lower with Pt/Al_2O_3 (78%), but much higher CO_2 selectivity suggesting its best oxidation abilities compared to other materials. The RE for other materials followed a sequence: ZrO_2 (72%)> Al_2O_3 (66%)> glass (64%)> $BaTiO_3$ (51%). The RE increased with increasing material surface area. Shape and size of pellets were found also important: higher RE was found for cylindrical and smaller pellets. Surface analysis of materials revealed differences in distribution of coke deposits on the surface for different pellets as result of dominant discharge mode. Besides the main gaseous products (CO_2, CO, H_2O and HCOOH), several other complex gaseous and solid by-products were identified (phthalic anhydride, maleic anhydride, benzoquinone naphthoquinone, etc).

Toluene removal by plasma catalysis as well as subsequent pellet catalyst regeneration were tested on pellets of various catalytic properties. Removal efficiency, selectivity and carbon balance were evaluated. The RE of toluene followed a sequence: Pd/Al_2O_3 (76%, 760 J/L)> Pt/Al_2O_3 (74%)> Al_2O_3 (65%)> TiO_2 (56%). These results were affected not only by catalytic properties of materials, but also dielectric constant and specific surface area. Pd/Al_2O_3 exhibited the highest toluene RE and the lowest energy demand [kWh/kg]. All catalysts showed the highest selectivity for CO_2 and smaller for CO, HCOOH. Al_2O_3 had the worst carbon balance.

The used pellets materials were regenerated by three different methods - by DBD discharge plasma, by ozone (8,000 ppm) and by heat (at 100ºC). The results show O_3 had negligible effect, and the heat regeneration was completely ineffective. Plasma regeneration was the best although still only partial and spatially non-uniform. It was further improved by mixing pellets in DBD reactor in with several shorter sequences that allow more uniform and effective treatment of the pellet surface with plasma. Regenerated catalysts were further tested exhibiting higher toluene RE after each cycle than those non-regenerated (by 7%, after 3 cycles with Pt/Al_2O_3).

Funded by NextGenerationEU through the Recovery and Resilience Plan projects 09I03-03-V03-00033 and 09I03-03-V04-00092 and APVV-20-0566.

References

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

ICPIG 2025

36th International Conference on Phenomena in Ionized Gases
Aix en Provence (France), July 24, 2025

REMOVAL OF HYDROCARBONS BY PLASMA AND CATALYSTS - CATALYST REGENERATION AND REUSE

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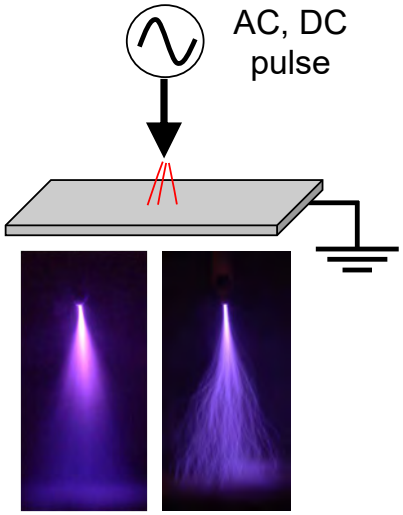
Funded by the European Union
NextGenerationEU

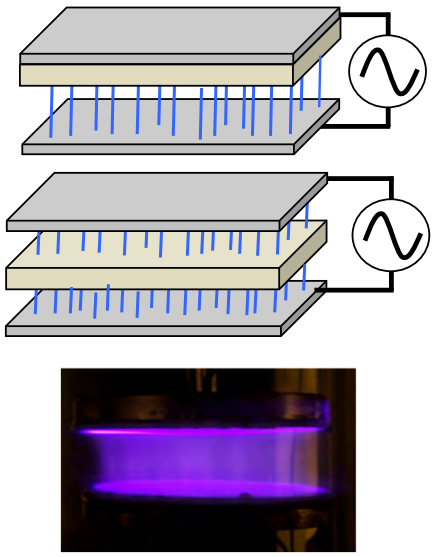
•**Grant support:** EU NextGenerationEU through the Recovery and Resilience Plan, projects No. 09I03-03-V03-00033, 09I03-03-V04-00092 and APVV-20-0566..

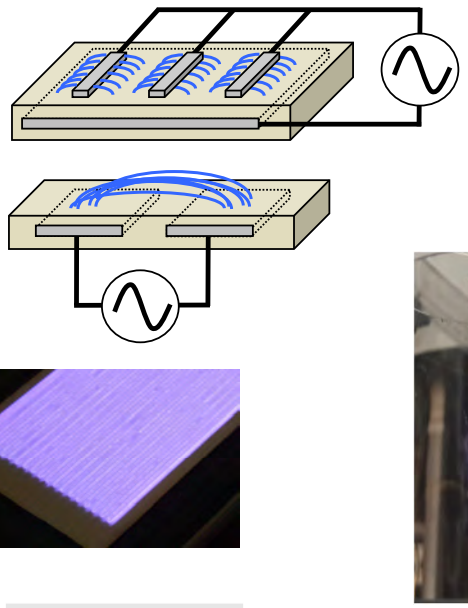
Atmospheric Discharges

corona discharge

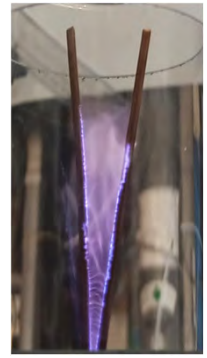


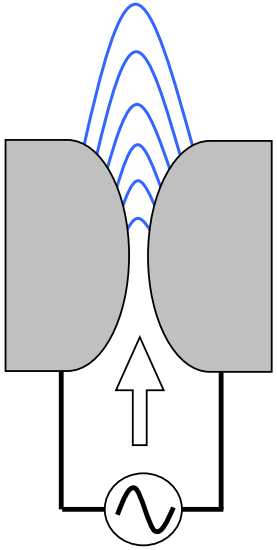
barrier discharges



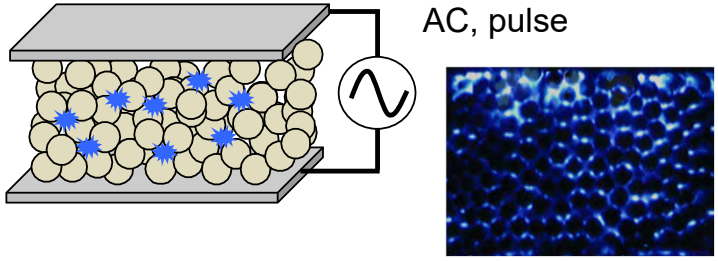


gliding arc discharge

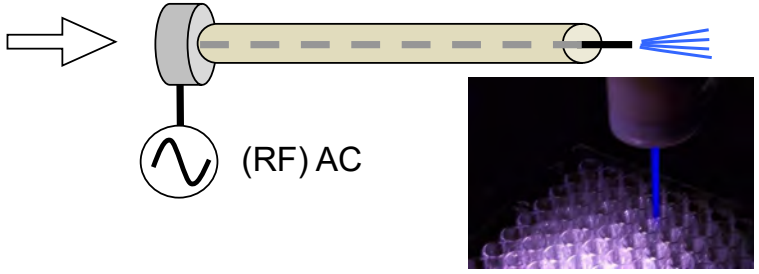


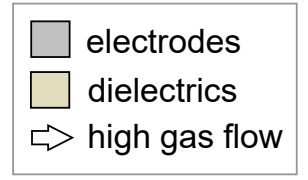


packed-bed discharge



plasma jet





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

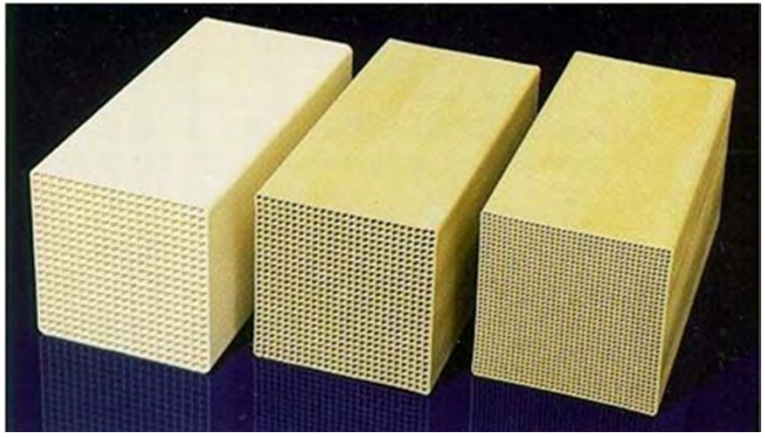
Pros/cons of plasma applications

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

Catalysts and … Combination with Plasma

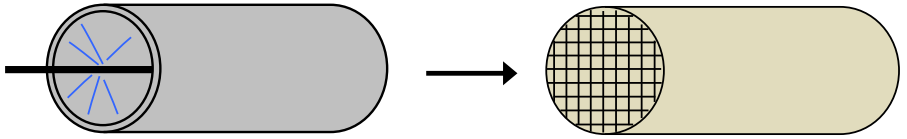
pellets
(size 1 – 5 mm)

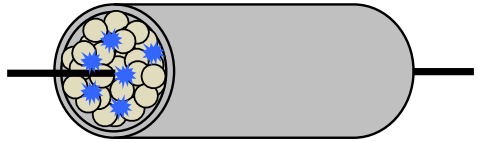
foams
(porosity 10 μm – 1 mm)



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

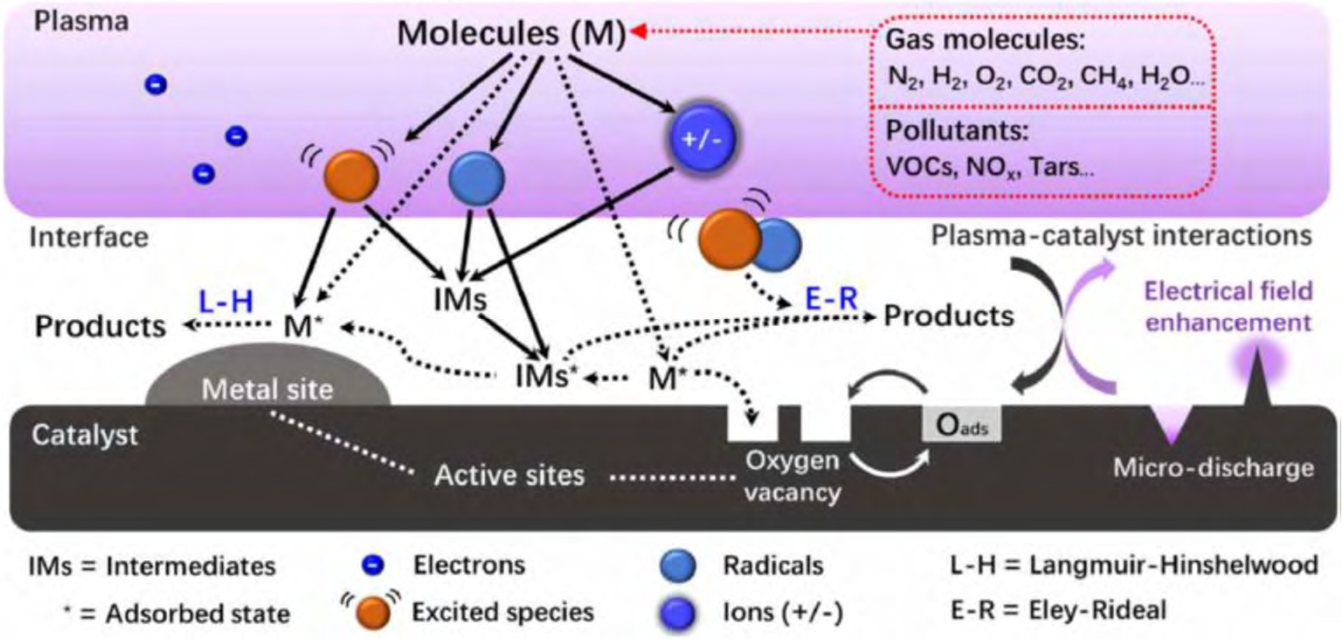
Pros/cons of catalysis
+ high reaction rate
+ high selectivity
+ efficient surface reactions
- high activation temperature
- demand for noble metals
- limited lifetime





discharge plasma vs. catalyst

Plasma Catalysis



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

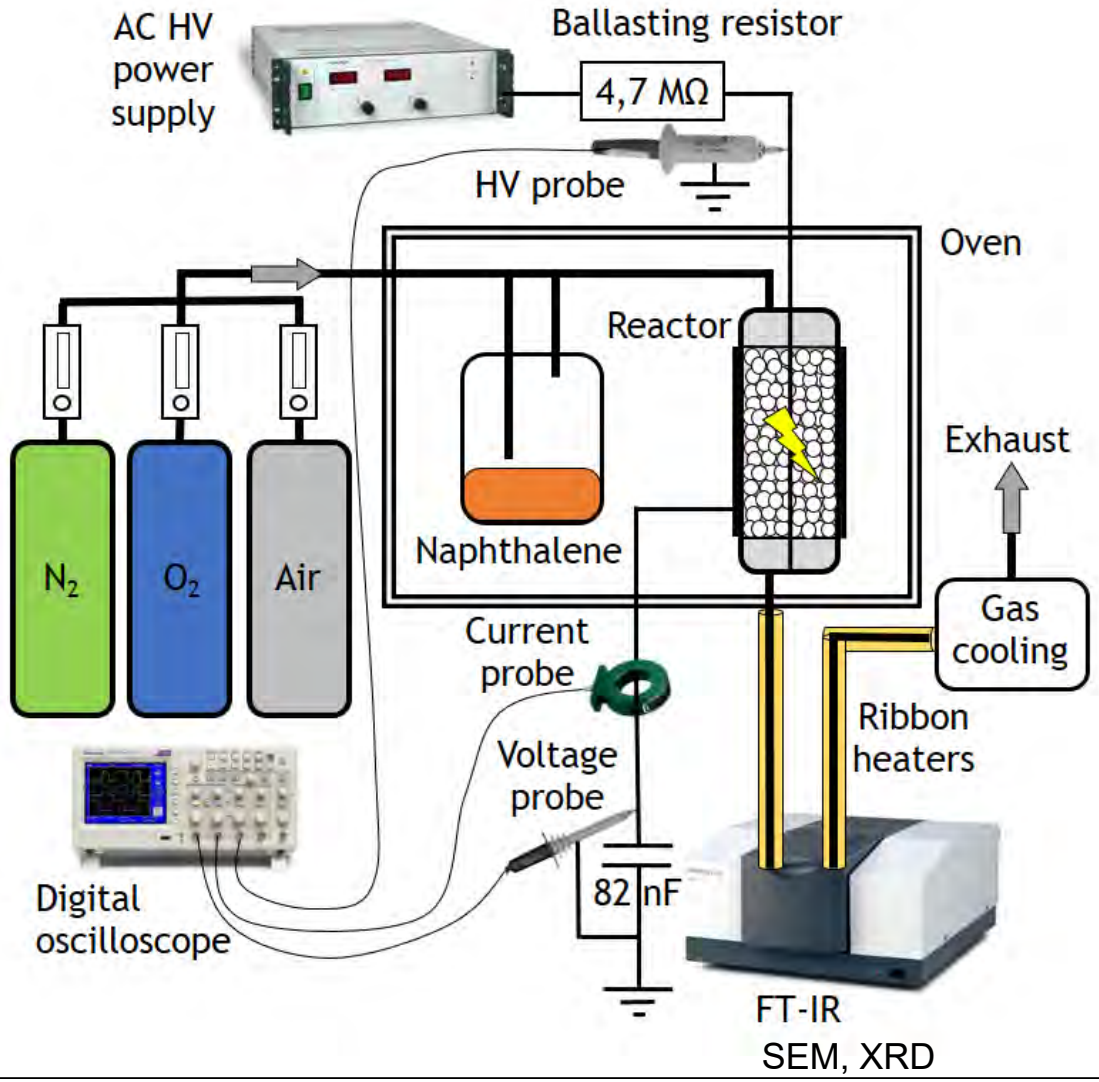
- Their interaction affects the chemical process (removal efficiency, selectivity, carbon balance).
- **Catalyst effect on discharge** → change of electric field; discharge mode and distribution; adsorption of pollutants
- **Discharge effect on catalyst** → UV activation; lattice oxygen activation and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

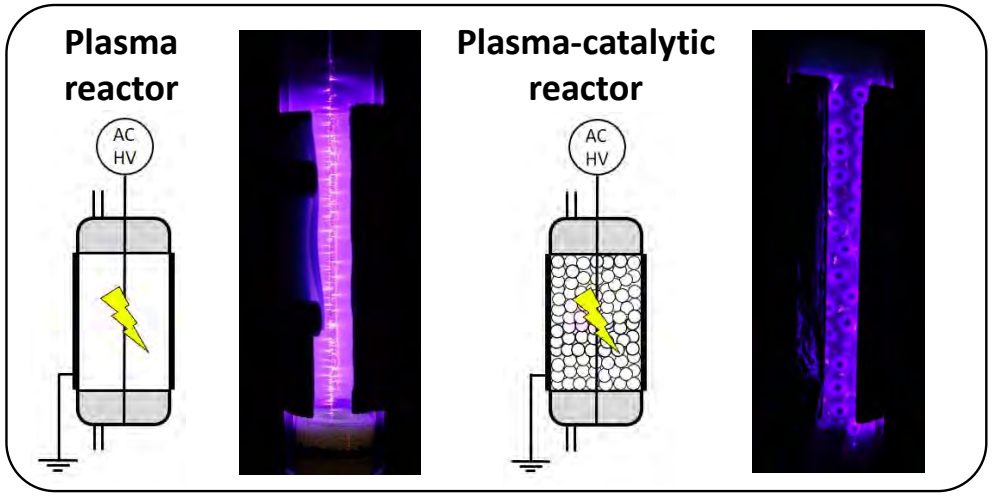
Pros/cons of plasma catalysis

+ 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

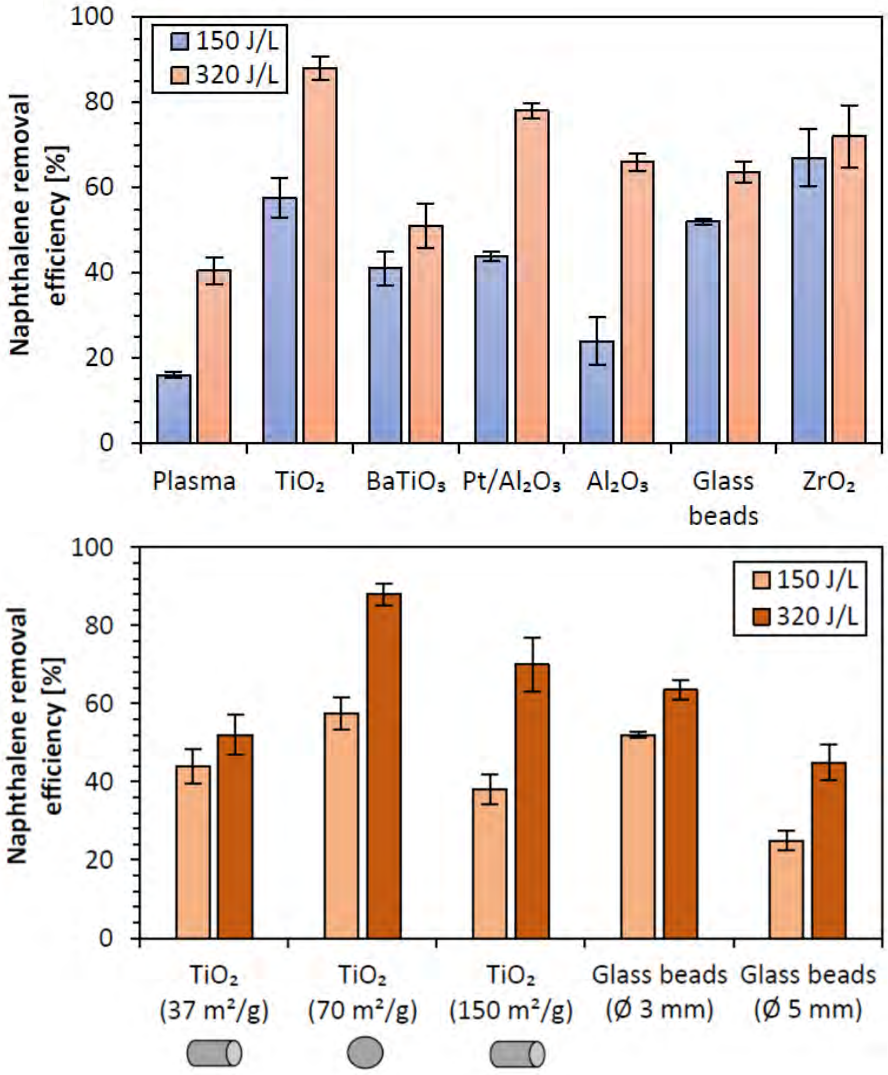




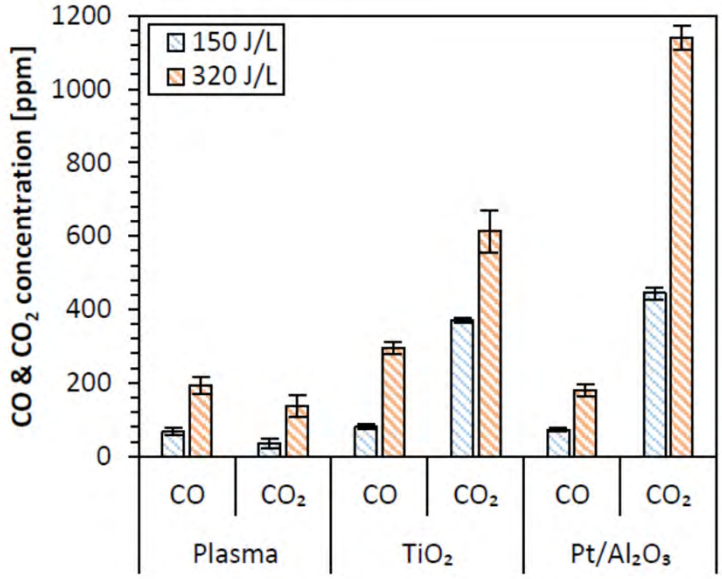
- **Naphthalene concentration:** 3000 ppm
- **Carrier gas:** Air, N_2, O_2 (0.5 L/min)
- **Plasma reactors:** cylindrical DBD (10 cm, Ø15 mm)
- **Catalyst (packing material)**: glass beads, TiO_2, γ-Al_2O_3, Pt/γ-Al_2O_3, $BaTiO_3$, ZrO_2
- ε_r (5–4000), shape (spherical/cylindrical), size (Ø3–5 mm, 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)

Naphthalene Removal by Plasma and Catalysts



Naphthalene removal efficiency as function of used material

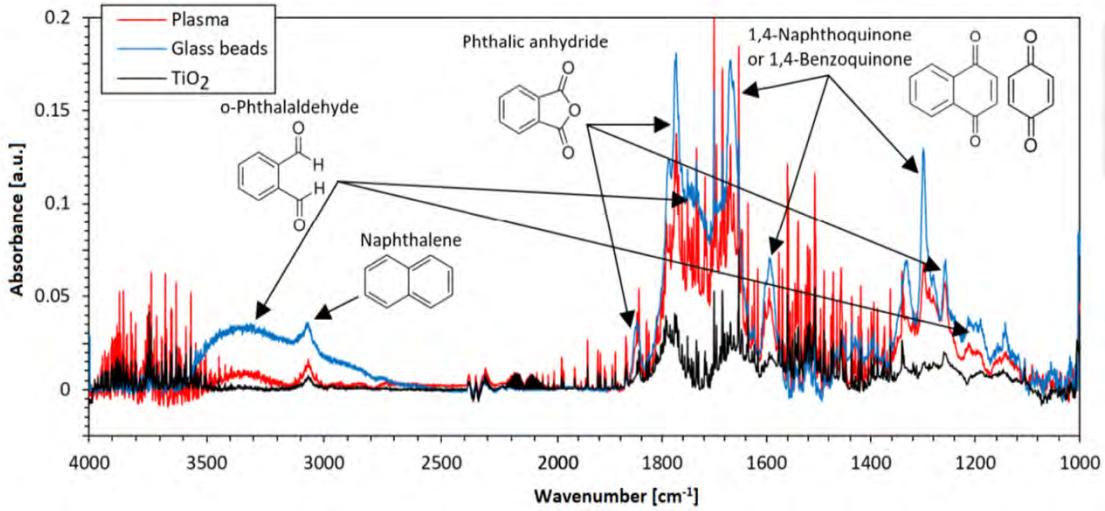


Concentrations of CO and CO_2 as function of used material

Gaseous products: mainly CO, CO_2 and HCOOH
→ **very low amount of gaseous products**

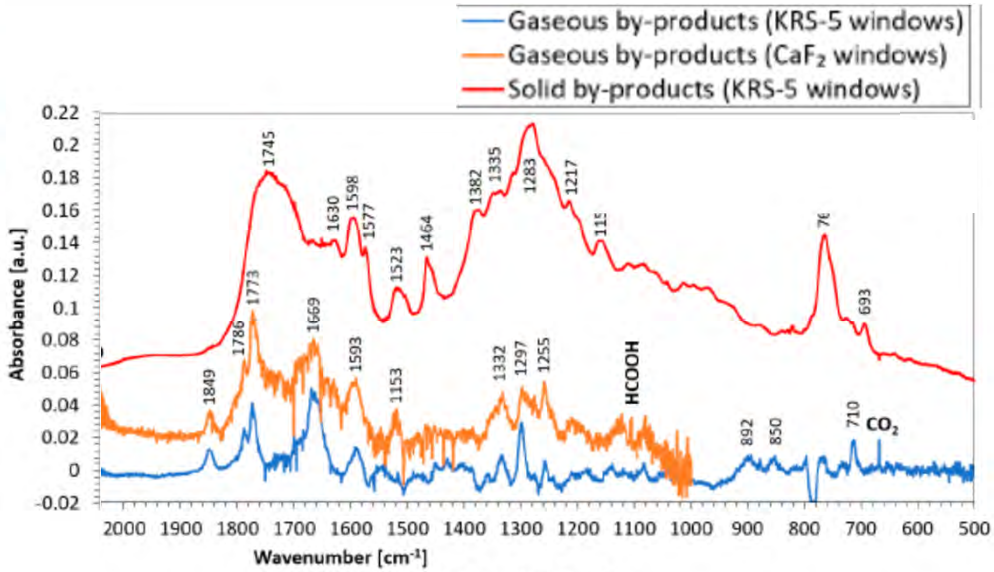
R. Cimerman, D. Račková, K. Hensel, *J. Phys. D: Appl. Phys.* **51** (2018)

Products of Napthalene Removal

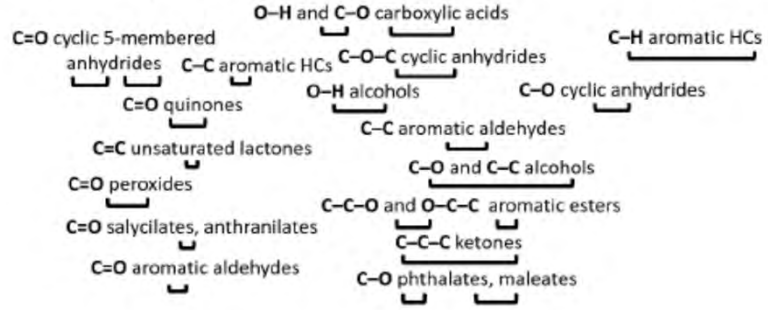


FTIR spectra of gaseous (●●) and solid (●) by-products of naphthalene decomposition

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

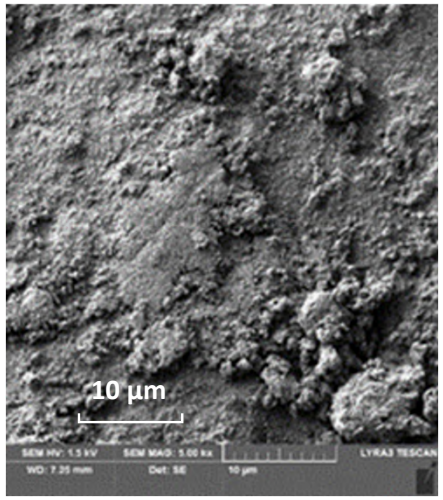


Solid products: C=O, C=C, C–O, C=N, O–H ...
1,4-naphthoquinone, phthalic anhydride, …
→ **high amounts of (undesired) solid products**
i.e. **carbon-containing deposits** (coke)



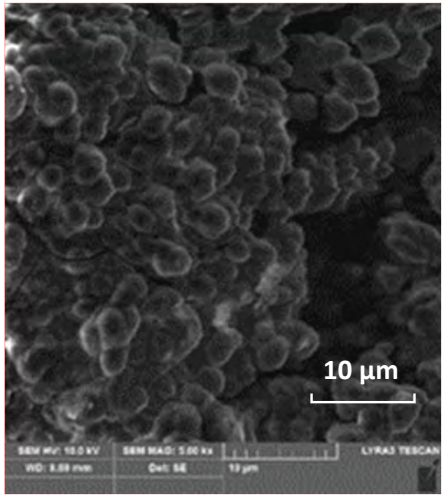
R. Cimerman, D. Račková, K. Hensel, *J. Phys. D: Appl. Phys.* **51** (2018)
R. Cimerman, M. Cíbiková, L. Satrapinskyy, K. Hensel, *Catalysts* **10** (2020)

Solid Deposits on Catalysts

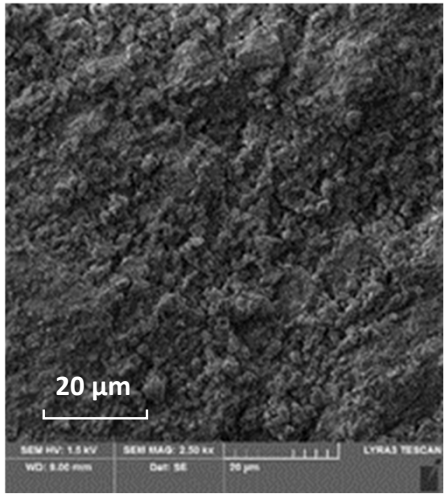


TiO_2

Fresh

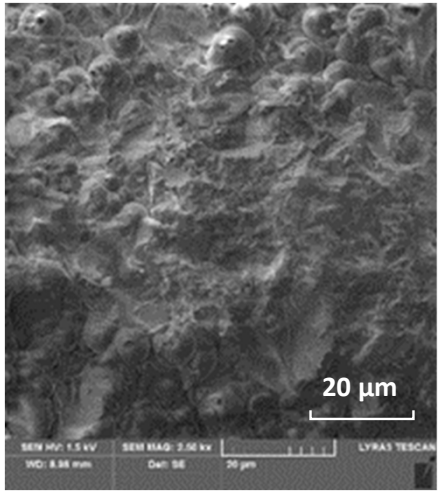


Used



$Pt/\gamma Al_2O_3$

Fresh



Used

SEM and optical microscope images of selected catalysts

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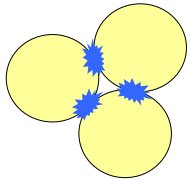
Solid Deposits on Catalysts

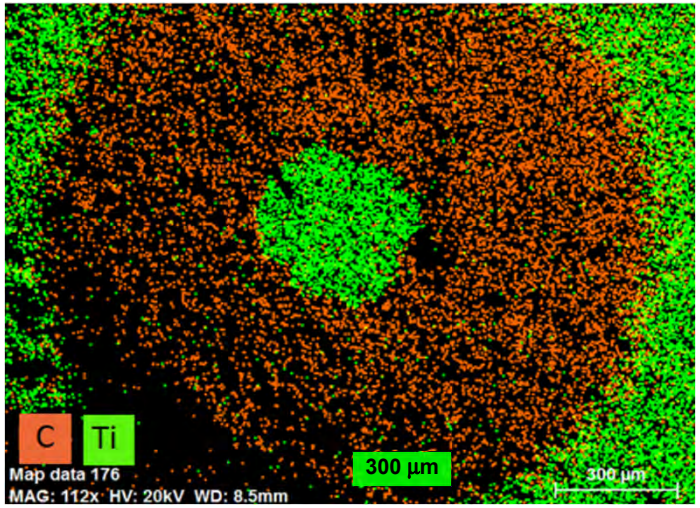
$BaTiO_3$

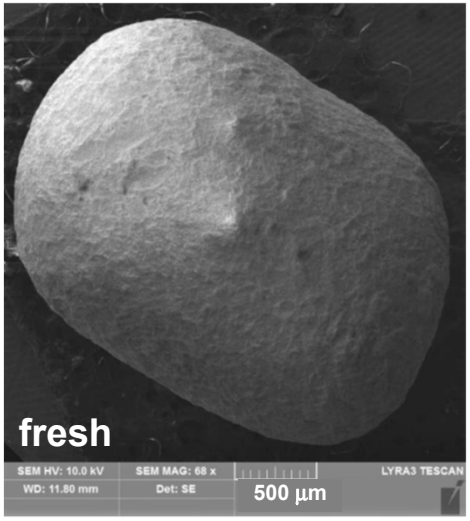
Fresh

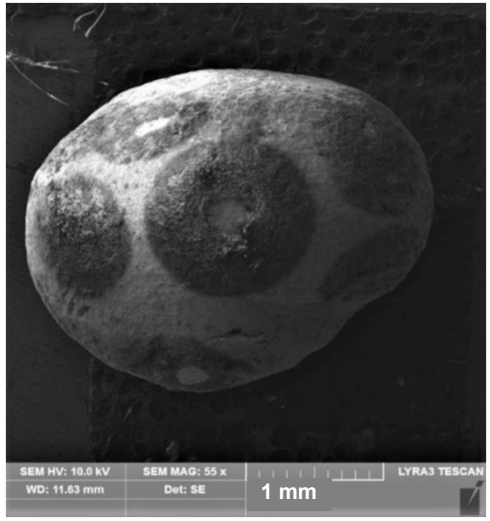
Used

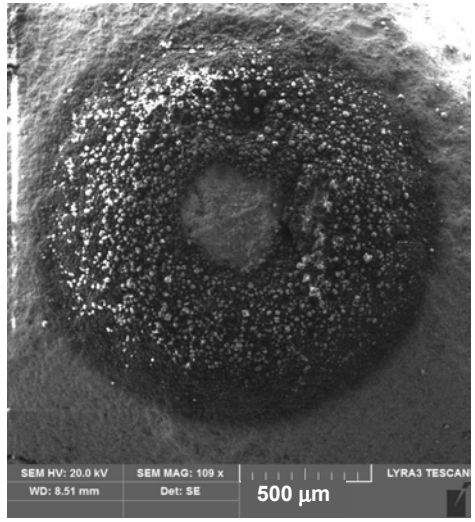


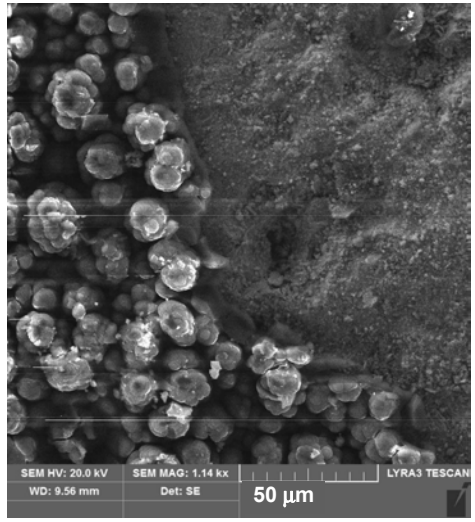
EDX image of $BaTiO_3$.











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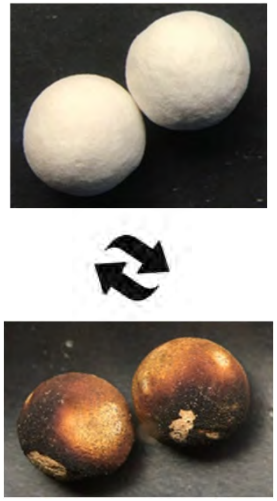
Catalyst Deactivation and Regeneration

- **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.

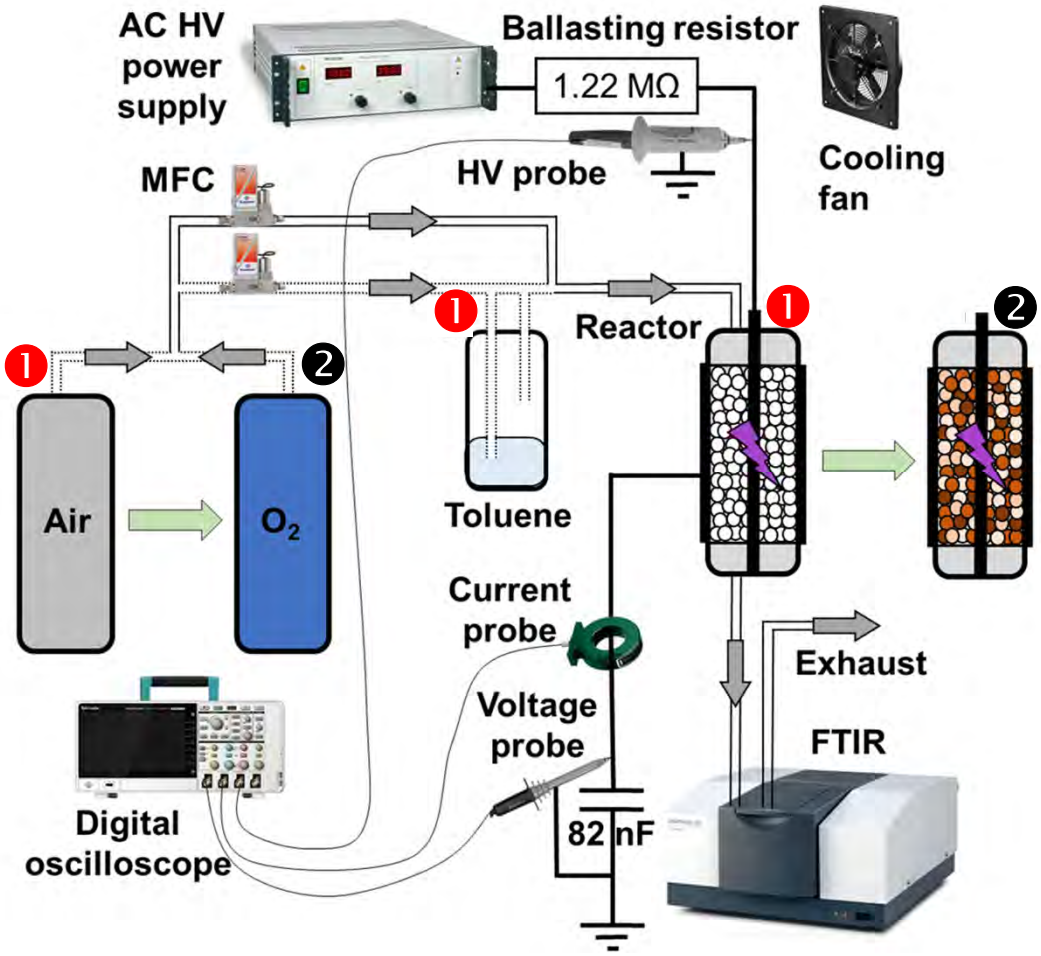
Plasma Regeneration

- 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
  + potential increase of average pore size
  + 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, $Pt/\gamma Al_2O_3$, 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)**

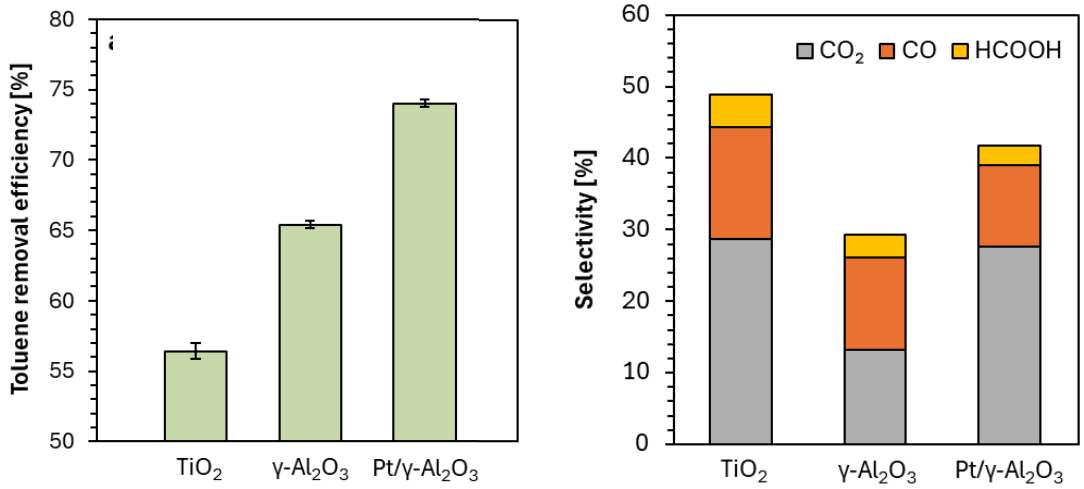
Experiment duration: **3 hr**

❷ CATALYST REGENERATION

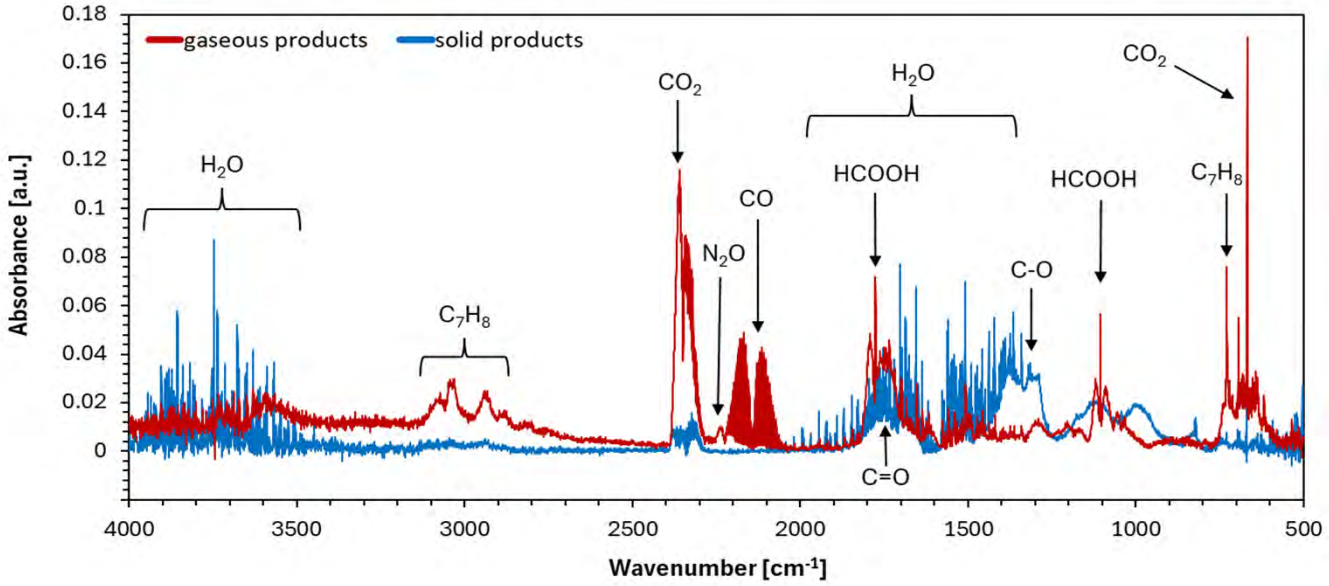
removal of solid deposit in oxygen plasma
→ formation of gaseous products (CO_2, CO, HCOOH)

- Plasma regeneration: **P = 3 W** for 2 hr
- Ozone regeneration: **O_3 ~ 8000 ppm** for 2 hr
- Thermal regeneration: **T = 100°C** for 2 hr

Toluene Removal and Catalyst Deactivation



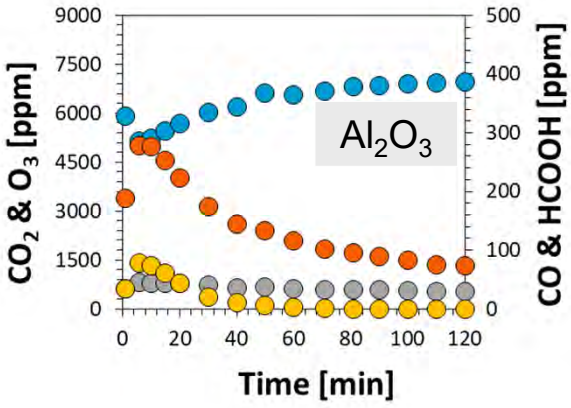
Toluene removal, selectivity (CO_2, CO, HCOOH) and carbon balance for different catalysts (P = 6 W)

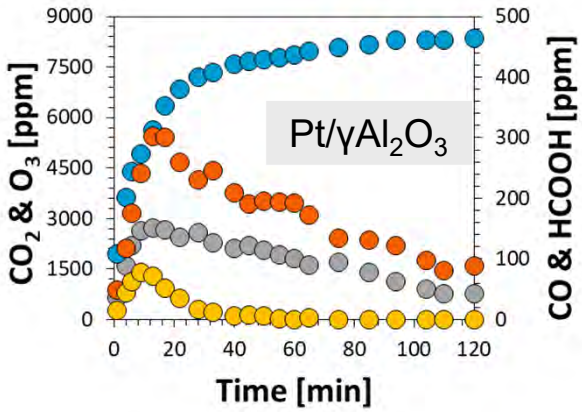


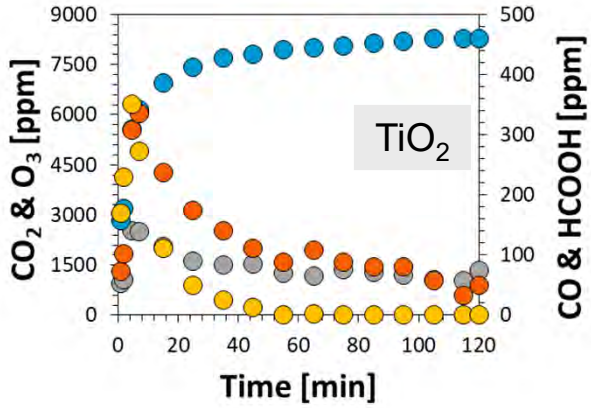
FTIR spectra of gaseous and solid products of toluene removal ($Pt/\gamma Al_2O_3$)

Catalyst Regeneration – Plasma / Ozone

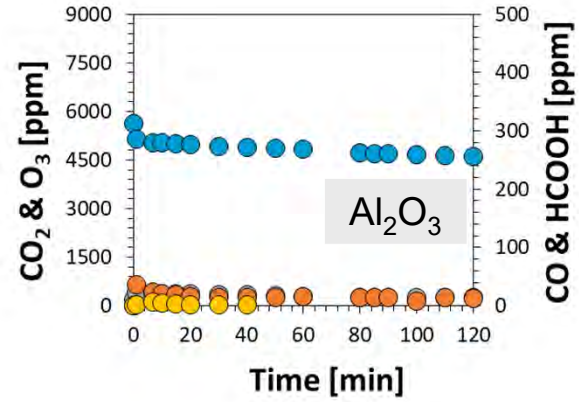
Plasma regeneration (P = 3 W for 2h)

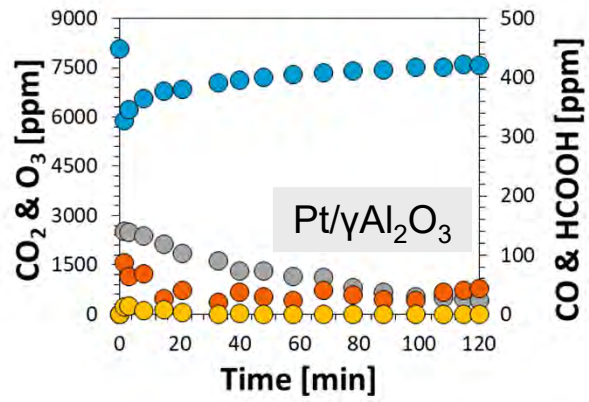


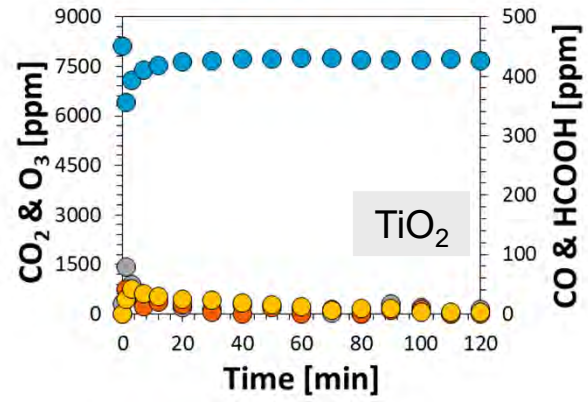


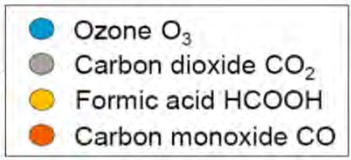


Ozone regeneration (O_3 ~ 8000 ppm for 2h)









Temporal evolution of concentration of gaseous products as analysed by FTIR spectroscopy

Photos of Catalysts

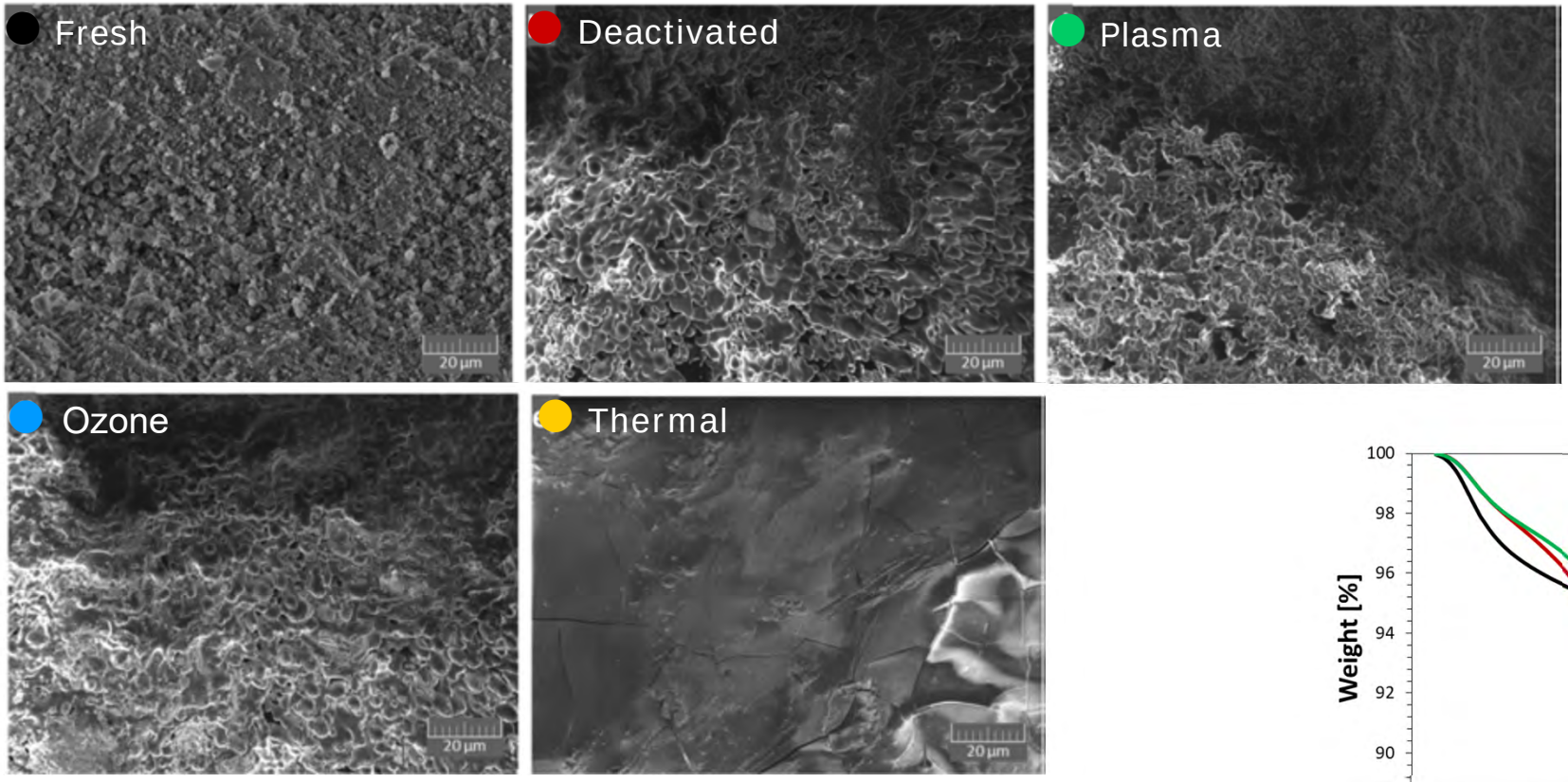
TiO_2

$Pt/\gamma Al_2O_3$

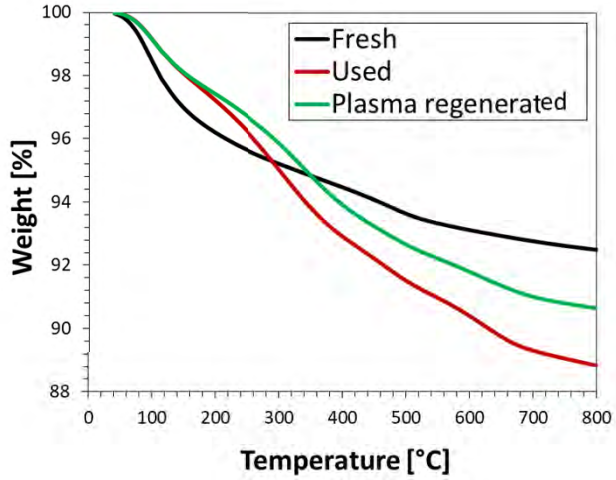
● Fresh ● Deactivated ● Plasma ● Ozone ● Thermal

Photographs of catalysts and solid deposits on their surface

Analysis of Solid Products by SEM and TGA

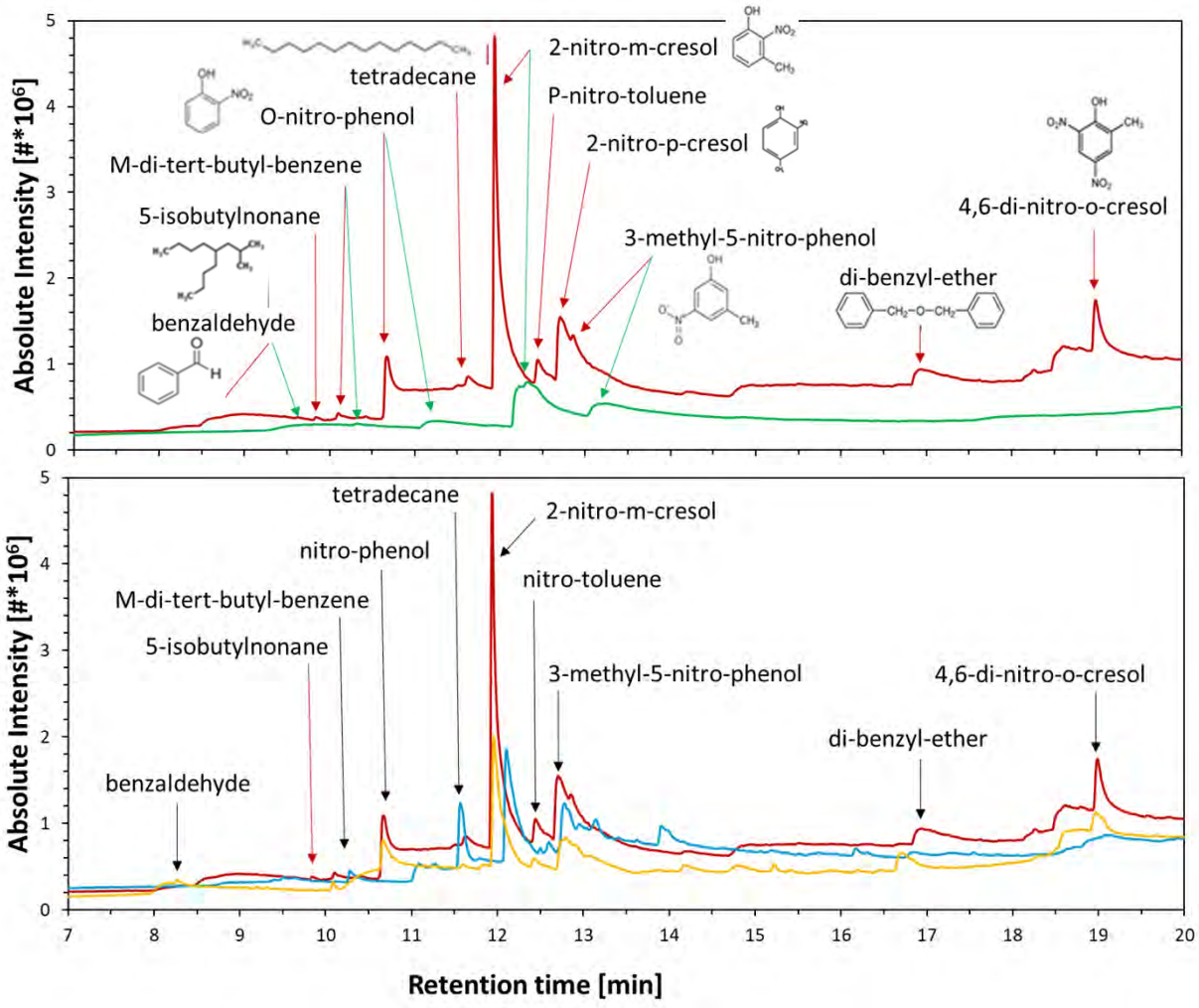


Scanning electron microscopy (SEM) analysis of catalysts ($Pt/\gamma Al_2O_3$)



Thermogravimetric analysis (TGA) of ● fresh catalyst,
● deactivated catalyst and ● plasma regenerated catalyst ($Pt/\gamma Al_2O_3$).

Analysis of Solid Products by GC-MS



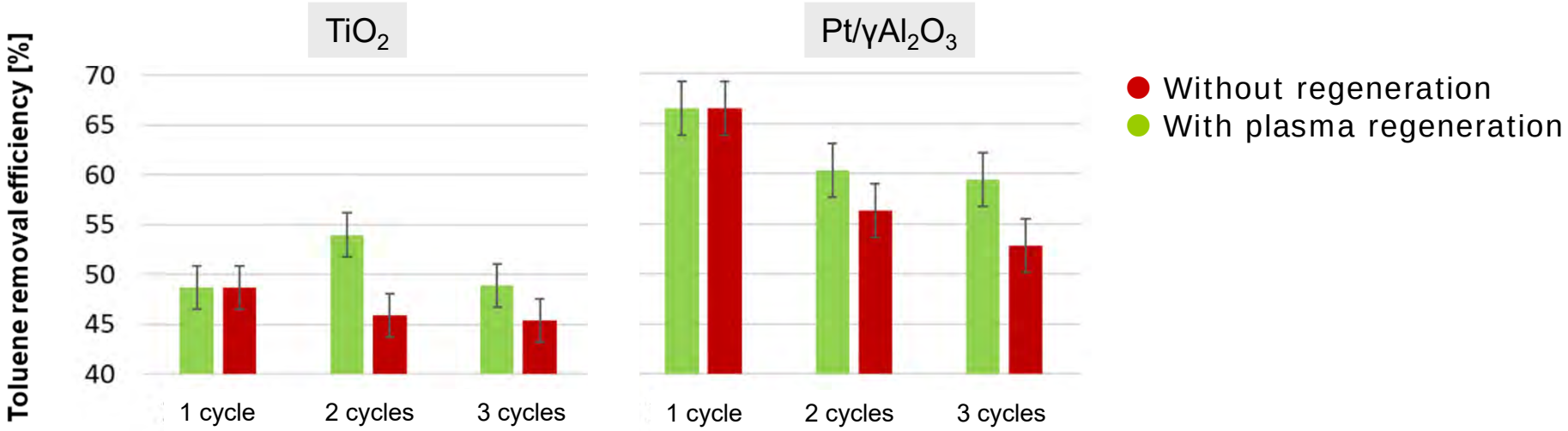
- deactivated catalyst
- plasma regenerated catalyst ($Pt/\gamma Al_2O_3$)

- deactivated catalyst
- ozone regenerated catalyst
- thermally regenerated catalyst ($Pt/\gamma Al_2O_3$)

GC-MS analysis of solid products on catalysts surface

Repetitive Use of Regenerated Catalyst

- Toluene removal experiments
  = 3 cycles (i.e. the same catalyst was re-used 3 times)
  - ✓ non-regenerated catalyst (i.e. without previous regeneration)
  - ✓ regenerated catalyst (i.e. with previous regeneration)



Toluene removal efficiency with non-regenerated and plasma regenerated catalysts

- Regenerated catalysts showed higher efficiency than non-regenerated ones

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.
- However, if 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**.
- We investigated a potential of **oxygen plasma** generated by packed-bed DBD reactor for regeneration of deactivated pellet catalysts, and compared it with other methods.
- The effect of regeneration was monitored by FTIR, GC-MS, SEM and TGA analysis.
- The results show that the plasma can **effectively oxidize carbon containing deposits** (coke) to CO_2, CO, HCOOH, leading to gradual regeneration of the catalyst.
- **Plasma regeneration** showed significantly higher efficiency than ozone and thermal regeneration.
- Brief test of regenerated catalyst showed improved removal efficiency when compared to non-regenerated.
- Regeneration efficiency of **depends on the catalyst properties** linked with an exhibiting discharge mode (surface discharge vs. localised filamentary discharges).
- Regeneration by plasma is promising method but **requires further optimization** (e.g. by mixing catalytic pellets during regeneration).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Thank you for your attention

K. Hensel, R. Cimerman, J. Kšanová, et al.: Removal of hydrocarbons by plasma and catalysts. Their regeneration and reuse.