Cyclic plasma-catalytic system applied for VOC removal with repetitive deactivation and regeneration of catalysts

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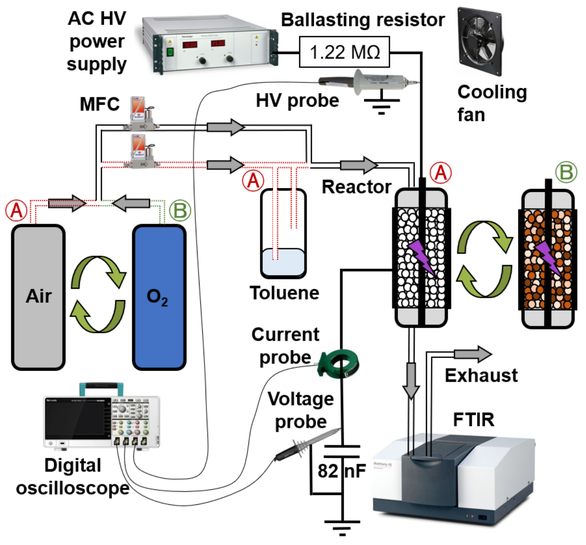
INTRODUCTION

Volatile organic compounds (VOCs) are major contributors to one of the most pressing global environmental issues - air pollution. A promising approach to their removal from the air is through catalysis. However, catalysts often undergo deactivation (i.e., loss of their catalytic activity) as a result of their use. This deactivation of the catalysts is mainly caused by the adsorption of undesired reaction products on their surface resulting in their limited lifetime. As a result, the catalysts need to be regularly replaced or **regenerated**.

Replacement of the catalysts produces waste and conventional (thermal) regeneration techniques require high temperatures (up to 900°C). The conventional techniques are often insufficient and associated with high costs due to high working temperatures and waste production. **The regeneration of the deactivated catalysts** (i.e., restoring their catalytic activity) under ambient conditions would be a more appropriate and cost-effective approach to extend their lifetime. Therefore, it is necessary to search for new or improve existing regeneration techniques. An innovative way of removing VOCs from the gas [1, 2] as well as regeneration of catalysts deactivated by the undesired products such as those from the VOC removal process (for example in the form of a coke) [3], involves utilizing **nonthermal plasma** in these processes.

EXPERIMENTAL SETUP



Nonthermal plasma reactor: atmospheric pressure **packed-bed dielectric barrier discharge (DBD)** reactor in coaxial cylindrical geometry

Each experiment consisted of 2 steps:

Ⓐ **CATALYST DEACTIVATION** = a model VOC (toluene) removal by plasma catalysis in synthetic air; P = 6 W; t = 180 min

- Formation of gaseous and solid products
  ⇒ formation of coke deposits on surface of the catalyst
  ⇒ catalyst deactivation

Ⓑ **PLASMA REGENERATION of previously deactivated catalyst in O_2**; P = 3 W; t = 120 min

- Oxidation of solid coke deposits
  ⇒ formation of gaseous products (CO_2, CO, HCOOH)

- **Repeating of Ⓐ and Ⓑ in cycles:**

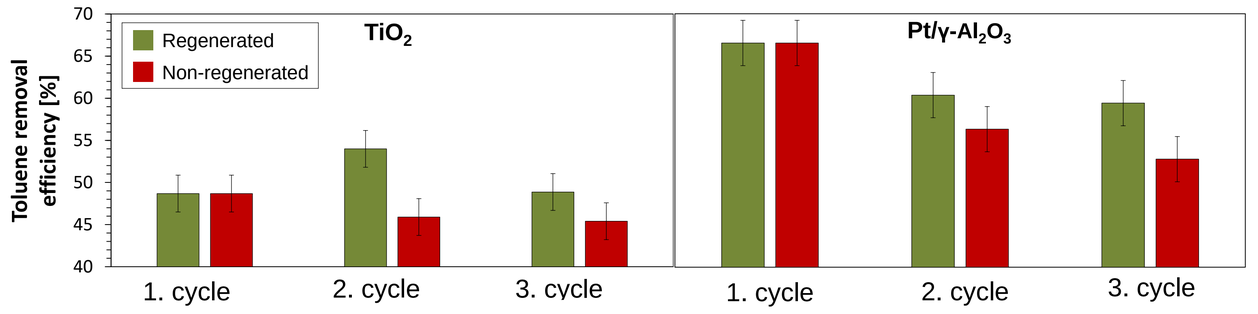
- Other performed methods of regeneration:
  a) Ozone regeneration; $[O_3]$ ~ 8000 ppm; t = 120 min
  b) Thermal regeneration in O_2;T = 100°C; t = 120 min
  c) Sequential plasma regeneration in O_2;
  Δt = 3x40 min of plasma regeneration
  + mixing of catalyst pellets

MAIN OBJECTIVES

The main objectives were:

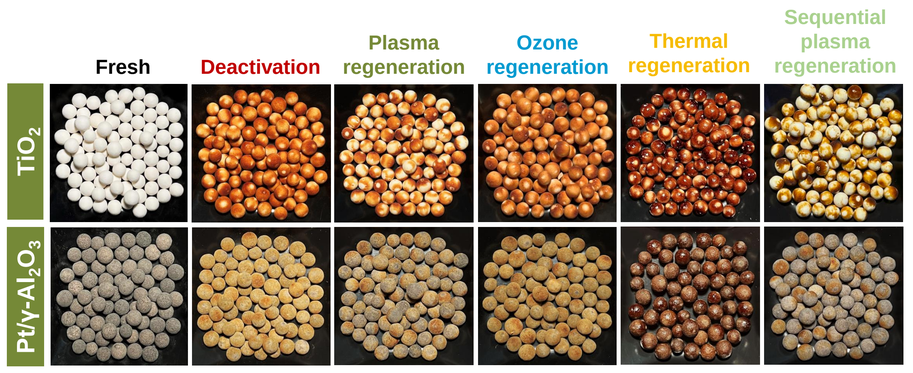
1. To test the plasma-catalytic system in the **toluene removal process** using different catalysts (TiO_2, $Pt/\gamma\text{-}Al_2O_3$).
2. To test the **plasma regeneration** of catalysts.
3. To test the **cyclic system** of catalyst deactivation in the toluene removal process and its subsequent plasma regeneration in **three cycles**.
4. To compare plasma regeneration with other regeneration methods (**ozone and thermal regeneration**).
5. To test **sequential plasma regeneration**, which includes pellet mixing, in order to improve plasma regeneration efficiency.
6. To analyze both the gaseous and solid products of toluene decomposition as well as the catalyst regeneration products by **FTIR and GC-MS**; and to analyze the surface of catalysts by **SEM and TGA**.

TOLUENE REMOVAL EFFICIENCY in each cycle

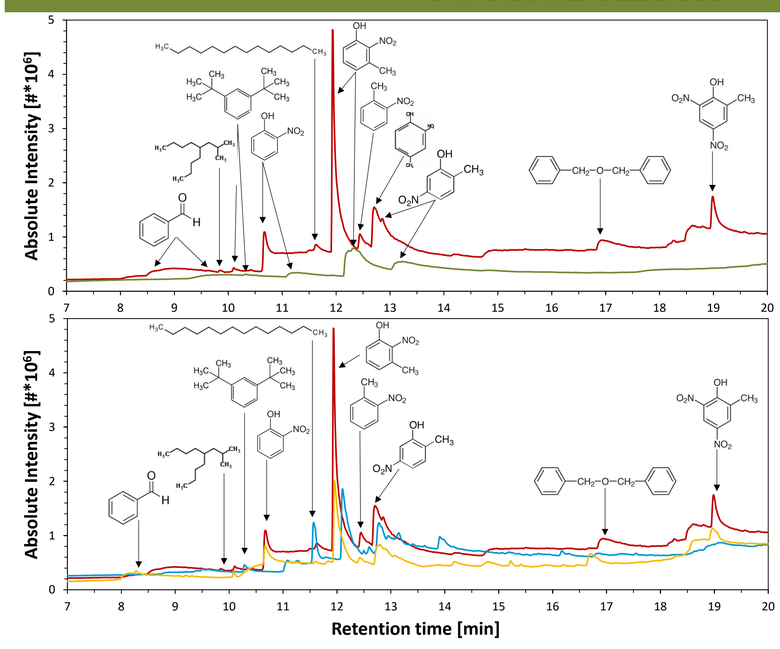


VISUAL COMPARISON of catalysts after each cycle

VISUAL COMPARISON of catalysts after different regeneration methods



GC-MS ANALYSIS

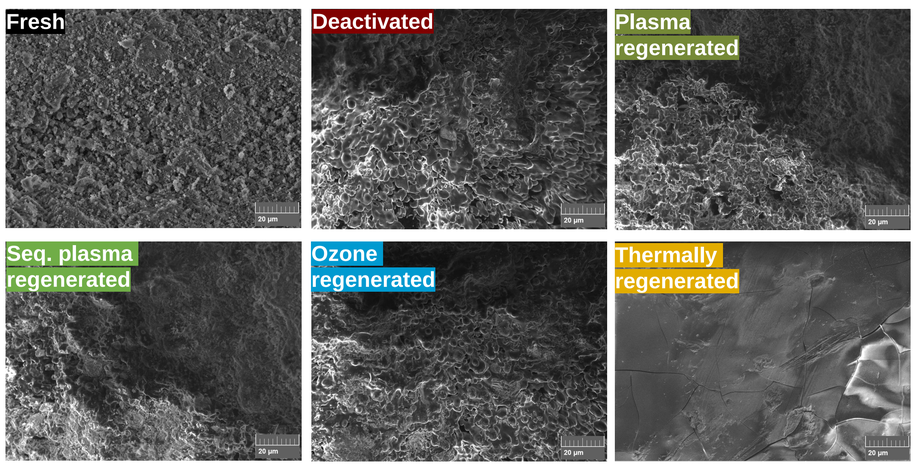


Gas chromatography coupled with mass spectrometry (GC-MS) analysis of deactivated and plasma regenerated **$Pt/\gamma\text{-}Al_2O_3$** catalyst.

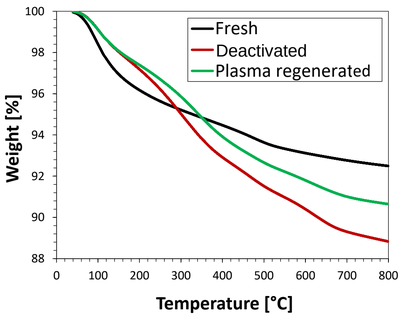
GC-MS analysis of deactivated, ozone and thermally regenerated of **$Pt/\gamma\text{-}Al_2O_3$** catalyst.

- Deactivated
- Plasma regenerated
- Ozone regenerated
- Thermally regenerated

SEM & TGA ANALYSIS

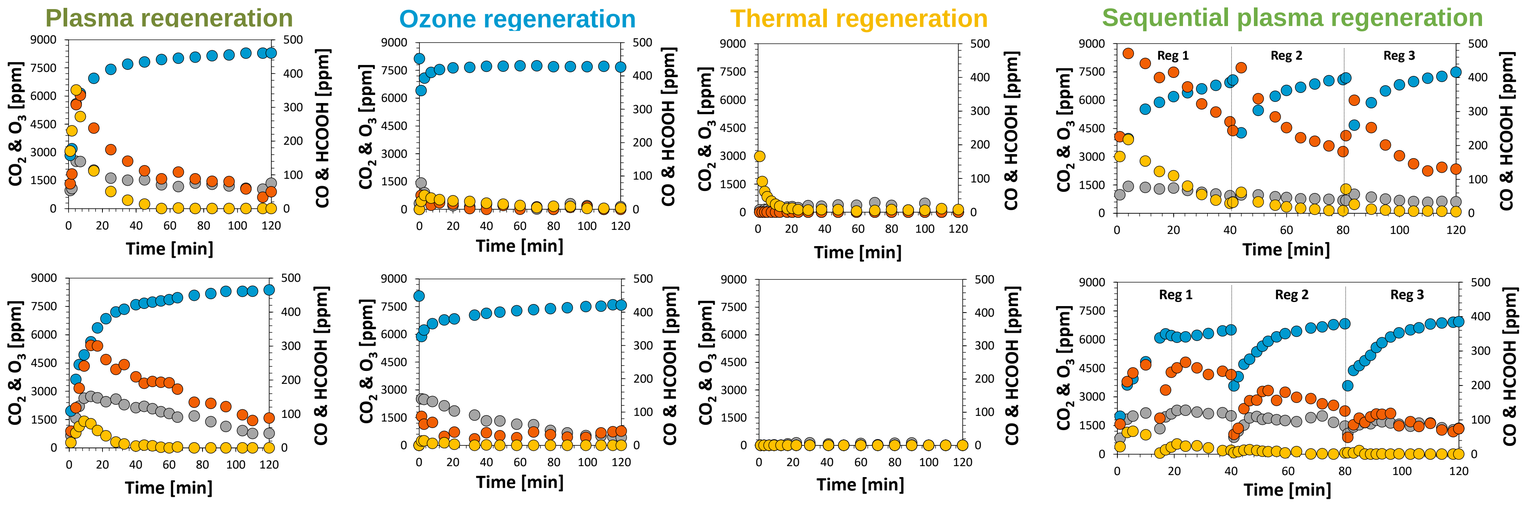


Scanning electron microscopy (SEM) of fresh, deactivated, plasma regenerated, sequential plasma regenerated, ozone regenerated and thermally regenerated **$Pt/\gamma\text{-}Al_2O_3$** catalyst.



Thermogravimetric analysis (TGA) of fresh, deactivated and plasma regenerated **$Pt/\gamma\text{-}Al_2O_3$** catalyst.

FTIR ANALYSIS – gaseous products of regeneration



- Ozone O_3
- Carbon dioxide CO_2
- Formic acid HCOOH
- Carbon monoxide CO

Temporal evolution of concentration of **gaseous products for various regeneration methods** analysed by **Fourier-transformed infrared (FTIR) absorption spectroscopy**

CONCLUSIONS

Investigation of a **cyclic system** consisting of catalyst deactivation by plasma catalytic removal of toluene and its regeneration demonstrates that plasma-regenerated catalysts maintain **higher toluene removal efficiency in each cycle**, compared to those non-regenerated. This indicates that plasma regeneration restored catalytic activity, offering an efficient alternative to conventional techniques.

Regenerations using **plasma showed significantly higher efficiency** than other regeneration methods (ozone and thermal regeneration).

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