Removal of hydrocarbons by non-thermal plasma combined with catalysis, regeneration and re-use of catalysts

K. Hensel, R. Cimerman, G. Selvaraj, J. Kšanová, R. Aripram, R. A. Jangra,
Division of Enviromental Physics, Faculty of Mathematics, Physics and Informaftics, Comenius University Bratislava, Slovakia

Keywords: non-thermal plasma, heterogeneous catalysts, plasma catalysis, volatile organic compunds

Non-thermal plasma generated by atmospheric pressure electric discharges in combination with various catalysts is gaining an increasing interest. It utilizes high plasma reactivity, high catalyst selectivity and as such is often characterized by synergistic effects, when the combined effect of plasma and catalysis may be stronger than their individual. The synergy may lead to higher conversion of reactants, higher selectivity as well as higher energy efficiency. Thanks to this, plasma catalysis has found use in many environmental applications particularly in air pollution control technologies, including removal of nitrogen oxides, volatile organic compounds (VOC), polycyclic aromatic hydrocarbons (PAH), conversion of carbon dioxide CO2, etc. The use of plasma catalysis in the VOC and PAH removal processes has been investigated by many authors and extensive and comprehensive reviews about the topic have been published in several papers. As a model VOC/PAH usually toluene, benzene and naphthalene are being used.

We have investigated removal of VOC/PAH by atmospheric pressure discharges in combination with pellets/beads of various properties and catalytic activities [1,2]. Typically tested materials were glass, Al2O3, Pt/Al2O3, TiO2, and ZrO2. They were characterized by distinct shape (spherical and cylindrical), size (3–5 mm in diameter, 3–8 mm in length), dielectric constant (5–200), and specific surface area (SSA) (37–150 m2/g). In addition, various materials of high dielectric constant (>1000) were tested as they can significantly enhance electric discharge through stronger local electric fields, higher micro discharge density, and improved plasma stability. Among them BaTiO3, relaxor ferroelectrics such as PZN and calcium copper titanate (CCTO) were investigated to assed the role of dielectric response. The results showed the removal efficiency depended on the properties of the catalysts. An improvement was observed with increasing SSA, while the shape of catalyst pellets was found to be even more important. Higher efficiency was also found with smaller size pellets. The products of VOC/PAH decomposition were found both in the gas phase as well as solid deposits (coke) on surfaces of pellets. The absorption spectroscopy (FTIR) and gas chromatography (GC) were used for their identification. In addition to main gaseous products (CO, CO2, H2O and HCOOH), several other complex gaseous and solid by-products were also identified (anhydrides, quinones, carboxylic acids, etc). Surface analysis carried by scanning electron microscopy (SEM/EDS) revealed significant differences in the distribution of deposits on the surface of pellets as the result of different discharge regime (surface discharges vs. filamentary microdischarges) that form depending on the used material.

The experiments also showed that activity and selectivity of the catalysts decreased over time due to gradual accumulation of solid deposits on their surface and their replacement or regeneration was required. Therefore, we also investigated potential of non-thermal plasma regeneration of coke-deactivated pellet catalysts [3]. The plasma regeneration was tested for various catalysts (TiO_2, Al_2O_3, Pt/Al_2O_3, Pd/Al_2O_3) and compared with ozone and thermal regenerations. The results indicated that oxygen plasma regeneration, although not spatially non-uniform, exhibited the highest coke removal efficiency. The effect of ozone and heat

Corresponding author: Karol Hensel (hensel@fmph.uniba.sk)

(100°C) was negligible. GC–MS analysis revealed that coke composed of long-chain alkanes and oxygen- or nitrogen-substituted aromatics was significantly reduced after plasma regeneration, unlike other regeneration techniques. To resolve non-uniform and partial regeneration of the catalyst surface plasma exposure was combined with intermediate pellet mixing and compared to plasma exposure without mixing. The mixing turned out to be effective and lead to enhanced spatial uniformity of regeneration. Despite incomplete coke removal after plasma generation catalysts maintained relatively high removal efficiencies over three repeated removal-deactivation-regeneration cycles. Plasma regeneration was also found strongly catalyst-dependent. Results indicates that primary effect of plasma regeneration is not only the coke removal and restoring the original active sites, but also modifications of catalyst surface. This may include adsorption of oxygen-containing surface species and modifications of the surface properties, which can either enhance or inhibit catalytic performance depending on the catalyst. Overall, our findings highlight the importance of catalyst surface evolution and regeneration strategy in plasma-catalytic systems, and can be implemented when designing systems of cyclic operation of catalyst use, regeneration and reuse.

References

[1] R. Cimerman, et al. J. Phys. D: Appl. Phys. 51 (27), 274003, 13 pp (2018)
[2] R. Cimerman, et al. Catalysts 10 (12), 1476, 22 pp (2020)
[3] J. Kšanová, et al., Plasma Procces. Polym. 23 (4), e70166, 18 pp (2026)

Acknowledgement

The work was supported by Slovak Research and Development Agency grant APVV-20-0566 and the EU NextGenerationEU through the Recovery and Resilience Plan project 09I03-03-V03-00033.

Corresponding author: Karol Hensel (hensel@fmph.uniba.sk)