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Dynamic effects in the catalytic treatment of diesel exhaust in non-thermal plasma reactor

Agata Dorosz, Agata Penconek, Katarzyna Jabłczyńska, Arkadiusz Moskal, Tomasz R. Sosnowski\*

Warsaw University of Technology, Faculty of Chemical and Process Engineering, Waryńskiego 1, 00-645 Warsaw, Poland

[Tomasz.Sosnowski@pw.edu.pl](mailto:Tomasz.Sosnowski@pw.edu.pl)

Process intensification concepts benefit from combining two or more phenomena to produce a synergic effect. Additionally, it can be enhanced by non-stationary operation conditions. This work analyses the catalysis in the dielectric barrier discharge non-thermal plasma (DBD-NTP) packed-bed reactor as a method of treatment of diluted diesel exhaust as a model multicomponent gaseous system containing particulate matter (PM). The dynamic changes in gas composition and PM concentration were monitored for a periodic plasma for two catalytic materials (CeO2 and MoS2) immobilized on the surface of glass beads. With the reduction of CO2 concentration, an increase in ozone and CO contents was found in the treated gas mixture at the level dependent on the catalyst. The overall PM content in the exhaust was reduced, although an initial burst of aerosol particles was found shortly after the plasma initiation, probably because of the release of PM from the beads’ coating. This dynamic response of the system was demonstrated to be essential for the overall performance of the exhaust gas treatment system.

* 1. Introduction

In non-thermal plasma (NTP) the gas is activated by highly energetic electrons instead of thermal energy, providing a way to enhance chemical conversion. The NTP has been demonstrated to be efficient in CO2 removal from exhaust gases, both in non-catalytic and catalytic systems (Yap et al. 2015, Mei et al., 2016). Such systems may find automotive, marine, and industrial applications. Heterogeneous reactivity is initiated on the surface of the porous catalytic material under plasma exposure, whereas catalyst morphology and surface properties allow the stabilization of plasma-generated oxidizing species and pollutants in the adsorbed state (Palma et al., 2020). Typically, combustion processes generate aerosol particles (particulate matter, PM) in addition to basic gaseous products such as CO2 and NOx, and PMs may cause problems during the catalytic conversion of exhaust gases. Diesel exhaust is an example of an emission containing PM, mostly composed of carbon soot, which can be oxidized in the NTP environment (Lin et al., 2017). Two main configurations of hybrid setups of NTP-catalyst reactors are used: 'in-plasma configuration’ (for single-stage plasma catalysis or plasma-driven catalysis) and ‘post-plasma configuration’ (for two-stage plasma catalysis). The first involves placing the catalyst inside the plasma chamber in the discharge area, allowing the use of the short-lived intermediates produced by the plasma for reaction on the catalyst surface. This setup is thus advisable for non-thermal plasma sources, such as a dielectric barrier discharge (DBD) or a corona discharge, as a thermal plasma would probably melt the catalyst. The second configuration physically separates the catalyst from the plasma since the catalyst is placed downstream. Here, the lifetime of the intermediates created by the plasma must be sufficiently long to control the reaction on the catalyst surface (Gholami et al., 2017).

There is considerable interest in using NTP-catalytic reactors as a NOx and CO2 converter, as well as a particulate trap, thereby successfully removing these compounds from diesel exhaust. A brief review on this topic can be found elsewhere (Dorosz et al., 2024). Among the common sorbents studied were zeolites, activated carbon and metal oxides: TiO2 (as a photocatalyst), CuO, Al2O3, and more recently, CeO2. Regarding carbon dioxide elimination, NTP catalysis has excellent potential to convert this compound into value-added chemicals, including CO (by CO2 splitting), CH4 and methanol (by CO2 hydrogenation), syngas (by CO2 reforming with CH4) and liquid fuels (Mei et al., 2016; Wang et al., 2017, 2018; van Laer and Bogaerts, 2015). However, deposition and adsorption of PM on the catalyst surface can strongly affect its reactivity and durability. Plasma oxidative action on the exposed surface of PM should not be disregarded, as it may also contribute to the production of secondary gases. When diesel exhaust enters the NTP reaction zone, carbon particles react with oxidative radicals generated by the discharge (Branderburg et al., 2011). This process converts some of them into CO and CO2 (Pan et al., 2010). CO2 splits into CO and O\*.

Considering the above state of knowledge, the current study was dedicated to testing the influence of potential effects on intermittent (on-off) operating conditions of an NTP-DBD catalytic reactor in the simultaneous removal of PMs during catalytic conversion of exhaust gases. The main aim of the research in the laboratory set-up was to check if such an operation regime could intensify the catalytic treatment of PM-contaminated exhaust gases.

* 1. Methods
  2. Experimental system with dielectric barrier discharge (DBD) catalytic reactor and gas analysis

The schematic of the experimental system is shown in Figure 1a. Diluted diesel exhaust was used as a model multicomponent gas mixture containing particulate matter (PM). The diesel exhaust was obtained from the combustion of sulphur-free diesel oil in the Mercedes Benz 240D (1982) four-cylinder diesel engine, adapted to laboratory use. The basic engine parameters were as follows: engine capacity 2399 cm3, engine power 53 kW at 4200 rpm, and torque 137 Nm at 2400 rpm. The emissions were generated under idle speed conditions. The DBD plasma reactor uses high AC voltage between electrodes (one covered by a dielectric material) to generate non-thermal plasma. It creates microdischarges in the gas, producing chemically reactive species. The cylindrical, coaxial reactor was made of glass (Din = 16 mm, L = 450 mm) with a 5 mm steel rod acting as a cylindrical collecting electrode and copper foil as a discharge electrode. The reactor was packed with 4 mm glass beads: without a catalyst (in experiment A), coated with CeO2 particles (cerium dioxide - experiment B), or coated with MoS2 particles (molybdenum disulfide – experiment C). Diluted exhaust entered the NTP-DBD reactor, and after the treatment, it flew to the second tank (sampling chamber), where the concentration of gases (O3, CO2, CO) and aerosol particles were assessed by gas and PM sensors. The pressure drop across the reactor was monitored with a digital differential micromanometer 8710 DP-CALC (TSI Inc., Shoreview, USA).

b)

a)

 Obraz zawierający zrzut ekranu, krąg, design

Opis wygenerowany automatycznie

*Figure 1: a) the schematic of the whole experimental system, b) the NTP-DBD packed bed catalytic reactor.*

Plasma was generated using a high-voltage power source (15 and 19 kV peak-to-peak at 5130 Hz). Plasma discharge was monitored in situ by monitoring the applied voltage and the electrical current. The measuring system allowed to record the temporary plasma power and calculate the time-averaged plasma power Pav:

(1)

where *V*(t) is the temporary high voltage supplied to the system, *Cm* is the capacitance of the test capacitor (85 pF), *T* – is the total time, and *Vm*is the voltage across the test capacitor. The power at maximum voltage in this system was about 35 W for DBD, providing 0.117 J per dm3 of treated gas (gas flow rate: 5 dm3/min).

* 1. Glass beads coating by catalysts

Technical grade CeO2 (MRM Chemicals, Gdańsk, Poland) and MoS2 particles (EVIL Lubricants, Raszyn, Poland) have been used. The coating of glass beads with the catalyst was done by the gelation process of 40% water glass (sodium silicate) (Farkom, Wilga, Poland) with acetic acid (Sigma-Aldrich, Poznań, Poland). This solution served as the precursor for forming the silica network that constitutes the base of the coating. Firstly, 100 grams of glass beads were stirred with 6 mL of the 40% sodium silicate solution for 2 minutes to ensure an even distribution of the solution over the glass spheres. Subsequently, 5 g of powder, either CeO2 or MoS2, was added, and the suspension was stirred for 2 minutes to ensure thorough dispersion of the particles. After adding 6 mL of the 8% acetic acid solution and completing the mixing process, the coated beads were placed on a flat surface for 24 hours for gelation and initial drying. After resting, the coated beads underwent a two-step heat treatment to stabilize and densify the coating by heating to 60°C for 1 hour and, next, heating to 300°C for 15 minutes.

* 1. Catalyst characterization

X-ray diffraction (XRD) analysis was conducted to characterize the crystalline structure and phase composition of the CeO2 and MoS2 catalyst particles. The measurements were performed using a diffractometer (XRDynamic 500, Anton Paar Poland, Warsaw, Poland) equipped with a Cu-Kα radiation source operating at 40 kV and 50 mA. Data were collected over a 2θ range from 10° to 80° with a step size of 0.01° and a counting time of 10 s per step. The crystalline phases present in the sample were identified by comparing the obtained diffraction patterns with the reference data from the Crystallography Open Database (COD) (entries 1531960 and 1562989). The crystallite size was estimated using the Scherrer equation (Patterson, 1939), considering the full width at half maximum (FWHM) of the most intense diffraction peak. All analyses were conducted under ambient conditions.

Scanning electron microscopy (SEM) was used to analyse the size and morphology of the catalyst particles, as well as to investigate the surface characteristics of the coated glass beads. Prior to imaging using a scanning electron microscope FEI Phenom FP 3950/00 (Thermo Fisher Scientific Poland, Warsaw, Poland), the samples were coated with a thin layer of gold to enhance conductivity and prevent charging. Catalyst particle size and morphology observations were done at a magnification of 12,000x.

* 1. Results and discussion
  2. Catalyst and coating characterization

The XRD analysis of the CeO₂ and MoS₂ catalysts revealed well-defined diffraction peaks that closely matched the reference patterns (Figure 2a), indicating high crystallinity and purity of both materials. From the Scherrer equation (Patterson, 1939), applied to the most intense peak, the calculated crystallite size for CeO₂ was 101 nm, while for MoS₂, it was slightly larger (122 nm). These sizes suggest a high degree of structural organization. The comparison with SEM images (Figure 2b and Figure 2c) revealed that the catalyst grains are significantly larger than the crystal-lite sizes, suggesting that each grain was typically an aggregate of multiple smaller crystallites. This catalyst structure is beneficial since larger grain sizes should enhance structural stability, reducing the likelihood of catalyst sintering and deactivation. On the other hand, the smaller crystallites within the grains provide numerous active sites. The difference in grain and crystallite size may contribute to the distinct catalytic behaviours of CeO2 (Wang et al., 2020) and MoS2 (Ghanashyam and Jeong, 2022), as it affects both the exposure and accessibility of active sites within the catalyst structure.

3.2. Intermittent reactor operation

Depending on the catalyst, different degrees of reduction in CO2 and an increase in ozone, CO, and NOx were found. The examples of time variation in CO2, CO, and O3 concentrations at the reactor outlet without a catalyst and with a MoS2 catalyst are shown in Figures 3 and 4. It is seen that MoS2 facilitated CO2 splitting, leading to higher CO concentrations during ‘plasma-on’ periods.

The overall PM content in the exhaust was reduced to zero after the second on-off plasma cycle in the non-catalytic system (Figure 5). In the catalytic NTP-DBD reactor, initial bursts in PM concentration were always found during the initial switching period of the plasma (Figures 6-7). After two cycles, PM concentration dropped in the CeO2 NTP-DBD reactor but was still elevated when MoS2 was used as a catalyst. This dynamic response, essential for the overall system’s performance as a PM trap, may be attributed to the partial release of fine catalyst particles from the glass beads coating layer caused by the interactions with plasma, but also by an increase in the pressure drop in the reactor after plasma initiation (Table 1).

**Obraz zawierający Czarno-biała fotografia, monochromatyzm, kwiat, czarne i białe

Opis wygenerowany automatycznieObraz zawierający czarne i białe, monochromatyzm

Opis wygenerowany automatycznie**Obraz zawierający tekst, zrzut ekranu, diagram, linia

Opis wygenerowany automatycznie

a)

b)

c)

Figure 2: a) Diffraction patterns of CeO2 and MoS₂, with characteristic peaks corresponding to their crystalline phases. b) *SEM image of CeO₂ catalyst particles (scale bar: 10 μm), c) SEM image of MoS₂ catalyst particles (scale bar: 8 μm).*



*Figure 3: Variations in the outflow CO2, CO and ozone concentration. Experiment A (no catalyst).*



*Figure 4: Variations in the outflow CO2, CO and ozone concentration. Experiment C (MoS2).*

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*Figure 5: Variations in the outflow PM2.5, PM10, and ozone concentration. Experiment A (no catalyst).*



*Figure 6: Variations in the outflow PM2.5, PM10, and ozone concentration. Experiment B (Ce2O).*



Figure 7: *Variations in the outflow PM2.5, PM10, and ozone concentration. Experiment C (MoS2).*

Table 1: Pressure drop in the reactor after switching the plasma for non-coated glass beads (experiments A) and the beads coated with the catalysts: CeO2 or MoS2 (experiments B and C, respectively).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Experiment A | Experiment B | Experiment C |  |
| Average value, Pa | 13.3 | 25.3 | 15.3 |  |
| Relative increase, % | - | + 90.2 | + 15.0 |  |

3.3. Limitations and future work

This work contributes to a better understanding of CeO2 and provides the first quantitative data for MoS2 in plasma reactors, highlighting the need for better catalysts. Potential improvements could include more stable coatings, alternative catalyst structures, and scale-up to pilot reactors.

* 1. Conclusions

The study demonstrated the complex dynamics of an NTP-DBD catalytic reactor during intentionally intermittent operation in the treatment of a model exhaust gas-PM mixture. The applicability of this system for simultaneous PM removal and exhaust gas conversion to potentially valuable products was demonstrated even when inexpensive technical-grade catalysts, CeO2 and MoS2,were used as a coating of glass beds forming the reactor packing. However, some unexpected effects were revealed that should be considered when such a strategy of process intensification is considered.

Nomenclature

Cm – capacitance of the test capacitator, pF

Din – reactor inner diameter, mm

P – plasma power, W

L – reactor length, mm

t – time, s

Vm – voltage across the test capacitator, V

T – total time of the process, s

V – temporary high voltage, V

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