

**Manuscript version: Author's Accepted Manuscript**

The version presented in WRAP is the author's accepted manuscript and may differ from the published version or Version of Record.

**Persistent WRAP URL:**

<http://wrap.warwick.ac.uk/115721>

**How to cite:**

Please refer to published version for the most recent bibliographic citation information. If a published version is known of, the repository item page linked to above, will contain details on accessing it.

**Copyright and reuse:**

The Warwick Research Archive Portal (WRAP) makes this work by researchers of the University of Warwick available open access under the following conditions.

© 2019 Elsevier. Licensed under the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International <http://creativecommons.org/licenses/by-nc-nd/4.0/>.



**Publisher's statement:**

Please refer to the repository item page, publisher's statement section, for further information.

For more information, please contact the WRAP Team at: [wrap@warwick.ac.uk](mailto:wrap@warwick.ac.uk).

# Low Temperature Plasma-Catalytic NO<sub>x</sub> Synthesis in a Packed DBD Reactor: Effect of Support Materials and Supported Active Metal Oxides

B. S. Patil<sup>1</sup>, N. Cherkasov<sup>2</sup>, J. Lang<sup>3</sup>, A. O. Ibadon<sup>2</sup>, V. Hessel<sup>1</sup>, Q. Wang<sup>1#</sup>

<sup>1</sup>Micro Flow Chemistry and Process Technology, Eindhoven University of Technology, P. O. Box 513, 5600 MB Eindhoven, Netherlands

<sup>2</sup>Catalysis and Reactor Engineering Research Group, Department of Chemistry and SOBBES, University of Hull, Cottingham Road, Hull, HU6 7RX, United Kingdom

<sup>3</sup>Innovation Management, Verfahrenstechnik & Engineering, Evonik Industries AG, Rodenbacher Chaussee 4, 63457 Hanau-Wolfgang, Germany

#corresponding author: Qi Wang, email: [Q.Wang1@tue.nl](mailto:Q.Wang1@tue.nl), tel. +31(0)40 247 8290

## ABSTRACT

The direct synthesis of NO<sub>x</sub> from N<sub>2</sub> and O<sub>2</sub> by non-thermal plasma at atmospheric pressure and low temperature, is considered to be an attractive option for replacement of the Haber-Bosch process. In this study, the direct synthesis of NO<sub>x</sub> was studied by packing different catalyst support materials particles in a dielectric barrier discharge (DBD) reactor. The support materials and their particle sizes both had a significant effect on the concentration of NO<sub>x</sub>. This is attributed to different surface areas, relative dielectric constants and particles shapes. The nitrogen could be fixed at substantially lowered temperatures by employing non-thermal plasma-catalytic DBD reactor, which can be used as an alternative technology for low temperature synthesis. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with smallest particles size of 250-160  $\mu$ m, gave the highest concentration of NO<sub>x</sub> and the lowest specific energy consumption of all the tested materials and particle sizes. The NO<sub>x</sub> concentration of 5700 ppm was reached at the highest residence time of 0.4 sec investigated and an N<sub>2</sub>/O<sub>2</sub> feed ratio of 1 was found to be the most optimum for NO<sub>x</sub> production. In order to intensify the NO<sub>x</sub> production in plasma, a series of metal oxide catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were tested in a packed DBD reactor. A 5 % WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst increased the NO<sub>x</sub> concentration further by about 10 % compared to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, while oxidation catalysts such as Co<sub>3</sub>O<sub>4</sub> and PbO provided a minor (~5 %) improvement. These data suggest that oxygen activation plays a minor role in plasma catalytic nitrogen fixation under the studied conditions with the main role ascribed to the generation of microdischarges on sharp edges of large-surface area plasma catalysts. However, when the loading of active metal oxides was increased to 10 %, NO selectivity decreased suggesting thermal oxidation of NO into NO<sub>2</sub>.

**Keywords:** plasma catalysis, nitric oxides, catalyst support, support particle size, supported active metal oxides.

## 1. Introduction

Nitrogen, being an important constituent of amino acids, is essential for life on earth [1–3]. However, this abundant element of atmosphere is hardly accessible to most living beings, because of the extremely stable N-N triple bond, which demands unusually high activation energy barrier. To become accessible, nitrogen must be chemically bonded to oxygen or hydrogen through the process of nitrogen fixation [1]. Nitrogen is artificially fixed with hydrogen through the Haber-Bosch process producing ammonia. This process sustains 40 % of today's population and its role will only grow along with the rapidly growing global population [1,4–7]. However, the Haber-Bosch process developed at the beginning of the 20<sup>th</sup> century is notoriously energy-inefficient. It consumes almost 2 % of world's total energy production and emits 300 million metric tons of CO<sub>2</sub> [8,9]. Modern technological and ecological standards require a considerable reduction in its environmental footprint and an increase in its energy efficiency. Nevertheless, the modern Haber-Bosch process has almost reached its theoretical limits on energy efficiency, so further improvements require a thorough search for a totally different approach [10].

Among several alternatives, electricity-driven plasma processes are considered to be very attractive candidates for the Haber-Bosch replacement [11–13]. The idea arises from the thermodynamically non-equilibrium nature of non-thermal plasma (NTP), where electrons have a temperature of thousands of degrees, while the bulk gas is close to room temperature [14,15]. As a result, highly reactive species are formed enabling NTPs to conduct thermodynamically unfavorable reactions at low temperatures [14]. Unfortunately, the reactions taking place in NTP are difficult to control and the selectivity is rarely optimum towards the desired products. Hence, NTP is combined with heterogeneous catalysis through *Plasma Catalysis*, and it is a rapidly growing research area [12,13,16–18]. Plasma catalysis enables reactions at low temperatures and at faster rates, whereas catalysts increase reaction selectivity. When plasma and catalysts are combined, a synergetic effect results in enhancing of the electric field, changing the discharge type, and facilitating micro-discharge formation in catalyst pore. Catalysts can also be altered plasma treatment, for example, change morphology, or chemical composition [19,20]. Non-thermal plasma-catalyst systems have been effectively investigated for a range of processes such as CO<sub>2</sub> conversion to value added products [12,21], CH<sub>4</sub> reforming [22–24], water purification [25], volatile organic compound abatement [26–29] and automotive applications [11,30].

It is striking to note that nitrogen fixation via NTP, has a theoretical energy consumption 3 times lower than the Haber-Bosch process [10], offering a possibility of a fossil-free nitrogen fixation using renewable electricity with a fraction of the current energy costs [31,32]. Compared to the high-pressure Haber-Bosch process, plasma nitrogen fixation offers an opportunity for atmospheric pressure and ambient temperature reactions with substantially improved plant safety, decreased operational and capital costs,

although it will add new (electrical) equipment to the process such as transformer and electrical power supply system which are needed for plasma generation.

The plasma processes are more attractive on a smaller scale such as a container or modular plant [33]. The concept of de-centralized production of chemicals is gradually gaining an acceptance in chemical industry, and hence, opens new doors for containerized plasma nitrogen fixation process [34–36]. This development would benefit remote and stranded areas in enabling them to produce their own fertilizer and fuels, using only renewable energy sources such as solar or wind [31,37–40].

Despite the important advantages, catalytic plasma nitrogen fixation is rather poorly studied [10,31,37]. Plasma catalytic NO<sub>x</sub> synthesis was investigated by Cavadias and Amouroux in inductively coupled high frequency plasma reactor coated with catalysts such as MoO<sub>3</sub> and WO<sub>3</sub> [41]. The yield of NO<sub>x</sub> was about 8 % without catalyst, but increased to 19 % by using the WO<sub>3</sub> catalyst. Mutel *et al.* [42] used the same metal oxides deposited on the plasma reactor wall. The energy consumption for catalytic nitrogen fixation process was found to be 0.93 MJ/mol of N, which provided a 78 % improvement in energy efficiency compared to thermal plasma process [42]. However, this energy consumption numbers are still far away from the energy consumption by Haber-Bosch process (0.48 MJ/mol), which employs thermal catalysis. Belova *et al.* [43,44] investigated plasma catalytic nitric oxide synthesis in a glow discharge reactor and found the following order of catalyst effectiveness Pt>CuO>Cu>Fe>Ag [43,44]. Recently, Cu-ZSM-5 catalyst was investigated by Sun *et al.* [45] for NO<sub>x</sub> formation in DBD reactor with a single stage configuration, where temperatures above 350 °C was found favorable for NO<sub>x</sub> formation [45]. Plasma-catalysis assisted ammonia synthesis in a DBD reactor is also reported in the literature as an alternative to thermal catalysis process, however the energy efficiency and yields are far from the current commercial process [31,46–48]. Nevertheless, to the best of our knowledge, no follow-up literature was published or commercial process developed, acknowledging and explaining the obvious synergetic effect of the catalyst in the results obtained. Similarly, various catalytic materials such as a range of metal oxides and metal-exchange zeolites were patented for plasma nitrogen fixation applications [49,50]. However, no independent studies of these catalysts have been published to assess their suitability for plasma NO<sub>x</sub> synthesis and no systematic work exists covering the performance parameters of the plasma reactor.

The analysis of existing literature shows that very few catalysts have been systematically studied for plasma catalytic NO<sub>x</sub> synthesis in NTP. Moreover, no study has been carried out to explain the reasons for the synergetic effect between plasma and catalyst. In particular, there are a number of overlapping reasons for the synergetic effect between the plasma and catalyst, e.g. influences caused by the different support material, the different active catalyst and process parameters, etc. The decoding of such a complex topic needs a systematic approach in a simplified way. Till now, the information on the effect of

catalyst support materials and reactor performance parameters on NO<sub>x</sub> synthesis are scarce [21,22,51]. Therefore, in this paper, we aim for a systematic study of plasma NO<sub>x</sub> synthesis on supported oxide catalyst in a one-sided DBD reactor. Firstly, the effect of catalyst support, its dielectric properties, porosity, particle size and shape are investigated. Secondly, the main process parameters such as residence time and feed ratio are studied. Finally, a series of active metal oxides supported on the optimal support are tested.

## 2. Experimental section

### 2.1. 1-SDBD Plasma-Catalytic Reactor

Plasma NO<sub>x</sub> synthesis was performed in a one-sided DBD plasma reactor at atmospheric pressure with a bed of catalytic material placed in the discharge zone. The schematic of the experimental set-up is shown in Fig. 1. Two different configurations of 1-SDBD reactor were used. Both reactor configurations consisted of an axial stainless steel (SS) inner high voltage electrode and a ground electrode made of SS mesh tightly wrapped around the quartz reactor body and a support/catalysts were embedded in the plasma zone. The discharge gap of 2 mm and the length of the discharge zone of 60 mm were identical for both reactor configurations. For the catalyst support experiments, the high voltage electrode was 20 mm o.d. and the quartz reactor body was 24 mm i.d. For the supported catalyst experiments, these dimensions were 6 and 10 mm, respectively. In the latter case, the small volume of the reactor allowed for tests with a small amount of the catalyst (about 2 g) compared to ~10-20 g used in the larger reactor. The reactors were placed in a tubular furnace to heat only the plasma discharge (catalyst) zone, while keeping the reactor ends outside of the furnace.

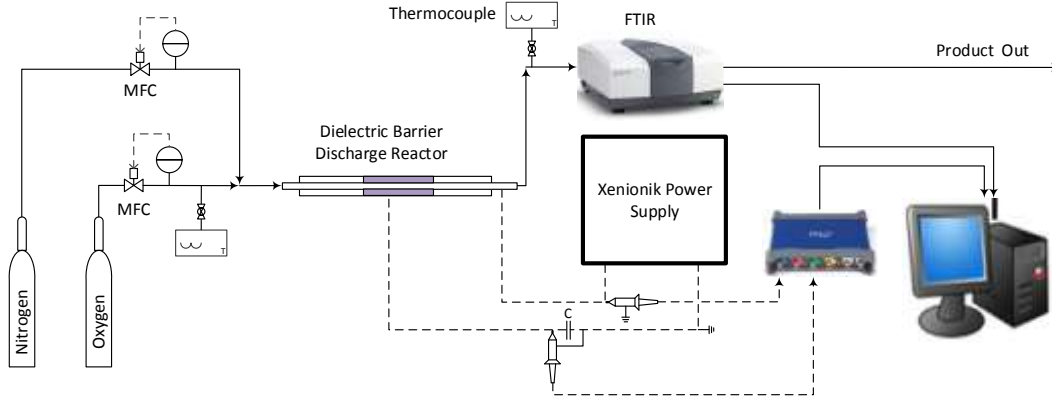
Both reactors were powered by a customized Xenionik EP 4000 alternating current power supply consisting of a signal generator (Siglent SDG 1025), a 4 kW audio amplifier (Behringer EP 4000) and a high voltage transformer (Xenionik). The applied voltage was measured using a high voltage probe (Tektronix P6015A) near the high voltage electrode. The capacitor (100nF) voltage was measured using 1:10 voltage probe on the grounded side as shown in Fig. 1. The power consumed by the DBD plasma reactor was calculated using the Lissajous method [52], based on the area of the plot between the applied and the capacitor voltages. All the electrical signals were recorded using a USB powered 4 channel PC Oscilloscope (PicoScope® 3000). The equations used to calculate the total power ( $P_{tot}$ ), specific energy input (SEI), and the energy consumption per mole of NO<sub>x</sub> ( $E_{NOx}$ ) are shown in Eq. (1-3), respectively.

$$P_{tot} = f C_p \int_{one\ cycle} V(t) dV \quad (1)$$

$$SEI = P_{tot} / Q_{gas} \quad (2)$$

$$E_{NOx} = P_{tot} / (C_{NOx} Q_{gas}) \quad (3)$$

Where  $V$  is the applied voltage,  $C_p$  - capacitance of the capacitor,  $f$  - applied voltage frequency,  $Q_{gas}$  - volumetric gas flow rate,  $C_{NOx}$  - concentration of  $NO_x$  in gas.



**Fig. 1.** A Scheme of the one-sided DBD plasma experimental set-up.

Flow rates of  $N_2$  and  $O_2$  gases (Linde Gases, 99.9%) introduced into the reactor were controlled using mass flow controllers (Bronkhorst). The main impurities in the gases were  $O_2$  and  $N_2$ , respectively, as well as Ar; hence, the amount of impurities in the  $N_2$ - $O_2$  mixture was much lower than 0.1 vol. %. The reaction products were analyzed online in the gas cell with  $CaF_2$  windows (Specac) using a Fourier transform infrared spectrophotometer (Shimadzu IRTracer-100) at the resolution of  $0.5 \text{ cm}^{-1}$ . The concentrations of NO and  $NO_2$  were determined by the adsorption bands at  $1900 \text{ cm}^{-1}$  and  $1630 \text{ cm}^{-1}$ , respectively, using a series of calibration gas mixtures. The concentration of  $NO_x$  was determined as a sum of NO and  $NO_2$  concentrations. In all the experiments, full spectra were recorded and the main products were NO and  $NO_2$ . In a few experiments,  $N_2O$  was detected, but its concentration was negligible ( $N_2O$  intensity was more than 20 times lower than that of  $NO_2$ ). Ozone was not detected because it quickly oxidized NO to  $NO_2$  even if formed. In all the cases,  $N_2$  and  $o_2$  conversion was below 0.5 %. Hence, NO selectivity reported was calculated using Eq. 4.

$$Selectivity \ NO = = C_{NO} / (C_{NO} + C_{NO2}) \quad (4)$$

The operation frequency and the pulse width were optimized in the range of 1–40 kHz and 15–30  $\mu\text{s}$ , respectively, to achieve the highest  $NO_x$  concentration. For the bigger reactor, the frequency of 18 kHz and the pulse width of 20  $\mu\text{s}$  was found to be the optimum. Whereas for the smaller reactor, the

optimum frequency was 21 kHz and the pulse width 25  $\mu$ s. The tested material was kept in-place by quartz wool (Carl Roth GmbH) positioned outside the catalyst bed.

Before every experiment, the reactor was heated to 150 °C with pre-heated nitrogen flow of 1 L/min to dry the tested support/catalysts. All the experiments were performed twice and all reported data were obtained as an average of at least 10 values obtained. The temperatures of the plasma region and the gas outlet were monitored continuously with thermocouples. For monitoring the plasma region temperature, the thermocouple was installed externally 1.5 cm away from the grounding electrode, the maximum temperature was found to be 200 °C. The outlet product stream temperature was always less than 26 °C. Heat transfer estimations based on heat conductivity of the reactor and introduced power showed that temperature inside the reactor was lower than 250°C. Blank experiments with thermal (non-plasma) catalysis were performed up to the temperature of 400 °C and neither NO nor NO<sub>2</sub> were detected. Hence, all NO<sub>x</sub> obtained was formed during plasma and plasma-catalytic processes.

## 2.2. Support and Catalyst Preparation

The support materials investigated in this work,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, MgO, and BaTiO<sub>3</sub> were purchased (Mateck GmbH) in the form of ~3 mm pellets, crushed and sieved into a series of particle fractions for at least 24 h using a mechanical shaker until constant weight.

Supported catalysts were prepared using conventional wet impregnation techniques using pelletized  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. Active materials were selected to study the effect of oxygen binding energy as well as the possible effect of partial catalyst evaporation. About 50 g of the support was placed into a 1 L round-bottom flask, 500 mL of the precursor aqueous solution was added. Water was slowly evaporated by rotavapor for 5 h at 40 °C. The samples were placed in a tube furnace and dried at 110°C for 4 h (heating rate 1 °C/min) and calcined for 2 h at 400 °C in air. The amount of the precursor was taken to obtain the active component (oxide) loading of 5 or 10 wt %. The following precursors were used: cobalt (II) nitrate (Alfa Aesar, >98 wt %) for Co<sub>3</sub>O<sub>4</sub>, oxalic acid dihydrate (Sigma-Aldrich, >99 wt %) and ammonium heptamolybdate (Fluka, >99 wt %) in 3:1 molar ratio for MoO<sub>3</sub>, nickel (II) nitrate hydrate (Alfa Aesar, >98 wt %) for NiO, oxalic acid and ammonium metavanadate (Alfa Aesar, >99 wt %) in 3:1 molar ratio for V<sub>2</sub>O<sub>5</sub>, copper (II) nitrate (Alfa Aesar, >99 wt %) for CuO, ammonium tungsten oxide hydrate (Alfa Aesar, >99 wt %) for WO<sub>3</sub>, lead (II) nitrate (Alfa Aesar, >99 wt %) for PbO.

## 2.3. Characterization of Support and Catalyst

Surface areas and pore distributions were measured by N<sub>2</sub> physisorption using a TriStar 3000 micrometrics surface area and porosity analyser using standard multipoint Brunauer-Emmett-Teller (BET) analysis and Barrett Joyner Halenda (BJH) pore distribution methods. All specimens were dried at 150 °C for 1 h before the measurements in nitrogen flow.



Scanning electron microscopy (SEM) study was performed on the Zeiss EVO 60 instrument equipped with an energy-dispersive X-ray spectrometer Oxford instruments Inca System 350 under the pressure of  $10^{-2}$  Pa and electron acceleration voltage of 20 kV. Powdered samples as well as fractured pellets were studied by applying them on conductive tape followed by carbon-coating before the SEM analysis. The results are presented in Table 1. All the materials except  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> were non-porous ( $V_{\text{pore}} < 0.5$   $\mu\text{L/g}$ ). Average pore diameter for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was 15.5 nm and for TiO<sub>2</sub> – 16.6 nm. Nitrogen adsorption isotherm and a corresponding pore size distribution of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is presented in Fig SI-1, Supplementary Data.

**Table 1.** Properties of support materials.

<b>Support Type</b>	<b>Surface Area(m<sup>2</sup>g<sup>-1</sup>)</b>	<b>Relative dielectric constant</b>
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	112	9.3-11.5
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	0.3	9.3
TiO <sub>2</sub>	34	85
MgO	0.03	9.7
BaTiO <sub>3</sub>	0.1	400-6500
Quartz Wool	0.5	4.6

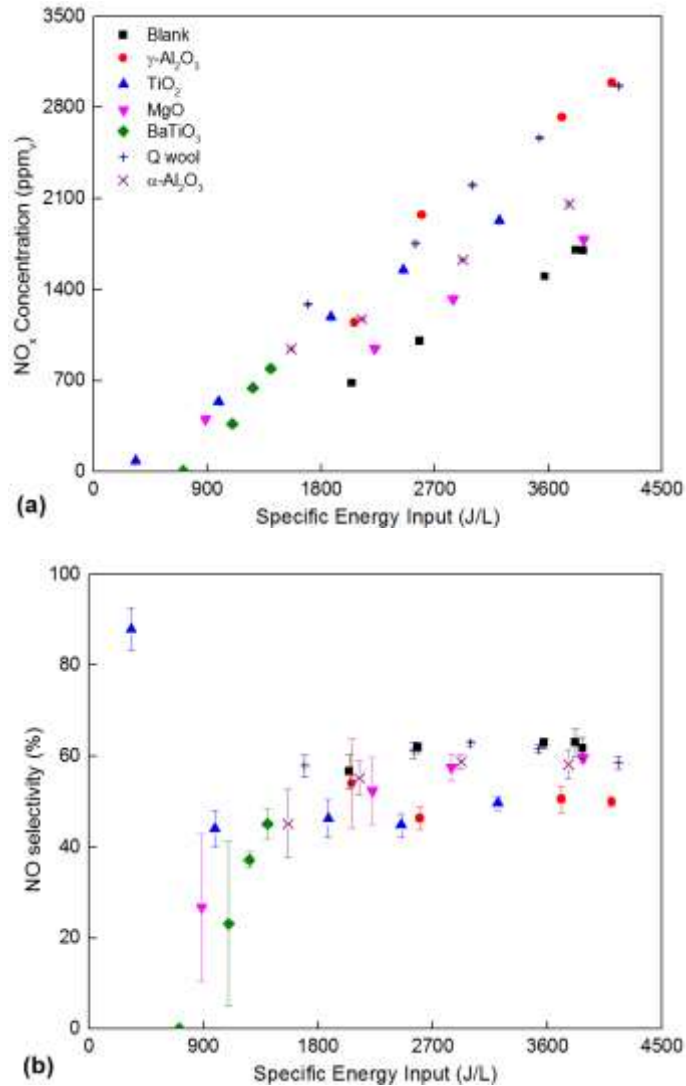
Powder X-ray diffraction measurements of crushed samples were performed using an Empyrean powder X-ray diffractometer equipped with a monochromatic K $\alpha$ -Cu X-ray source in the 2 $\theta$  range of 10-80°, step length 0.026°, step time 147 s. The X-ray diffraction measurements are presented in SI-2. The characterisation was performed before and after the plasma catalytic tests and no differences in either textural and chemical properties of the catalysts were observed.

### **3. Results and discussion**

#### **3.1. Effect of support material**

##### *3.1.1. Effect on NO<sub>x</sub> production*

To understand the effect of the different support materials on NO<sub>x</sub> production, experiments were conducted with 500-630  $\mu\text{m}$  particles (except quartz wool) at varying specific energy input and flow rate of 1 L/min with N<sub>2</sub>:O<sub>2</sub> volume ratio of 1. Support materials studied were  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, MgO, TiO<sub>2</sub>, BaTiO<sub>3</sub> and quartz wool. A blank experiment was also conducted without packing to compare with the packed bed experiments.



**Fig. 2.** (a) The effect of catalyst support on NO<sub>x</sub> concentration. (b) The effect of specific energy input on the NO selectivity.

In Fig. 2a, the concentration of NO<sub>x</sub> is plotted against the SEI for different supports. The input power was in the same range for all the tested catalyst supports. The effect of the packed catalyst support on NO<sub>x</sub> production is clearly visible, the NO<sub>x</sub> concentration increases proportionally with SEI for all support materials. The SEI for quartz wool, MgO,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and the blank experiment fall in the same range of 2000 to 4000 J/L with varying concentration of the NO<sub>x</sub> from 700 to 3000 ppm. Comparing these catalyst supports shows that the blank experiment without packing any catalyst support always has the lowest NO<sub>x</sub> concentration at the same SEI. Whereas, the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> gave the highest NO<sub>x</sub> concentration. At the SEI of 4000 J/L,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> gives a 100% increase in the NO<sub>x</sub> concentration compared to the blank experiment. Quartz wool was also found to be an efficient catalyst support for NO<sub>x</sub> generation, similar to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

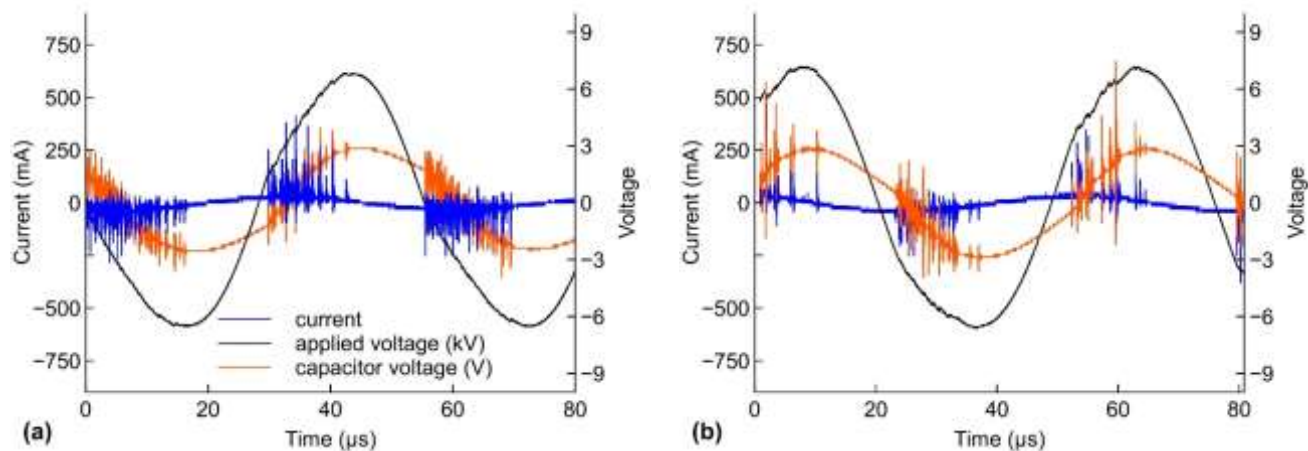
The results obtained for the higher relative dielectric constant supports such as  $\text{TiO}_2$  and  $\text{BaTiO}_3$  are located in a lower range of SEI ( $< 2500 \text{ J/L}$ ). The  $\text{NO}_x$  concentrations for these two packed materials are similar at SEI higher than  $1250 \text{ J/L}$ . However, for these materials at comparable SEI,  $\text{NO}_x$  concentrations are substantially lower, indicating the fact that the plasma discharge might be less intense and was in the form of glow discharge.

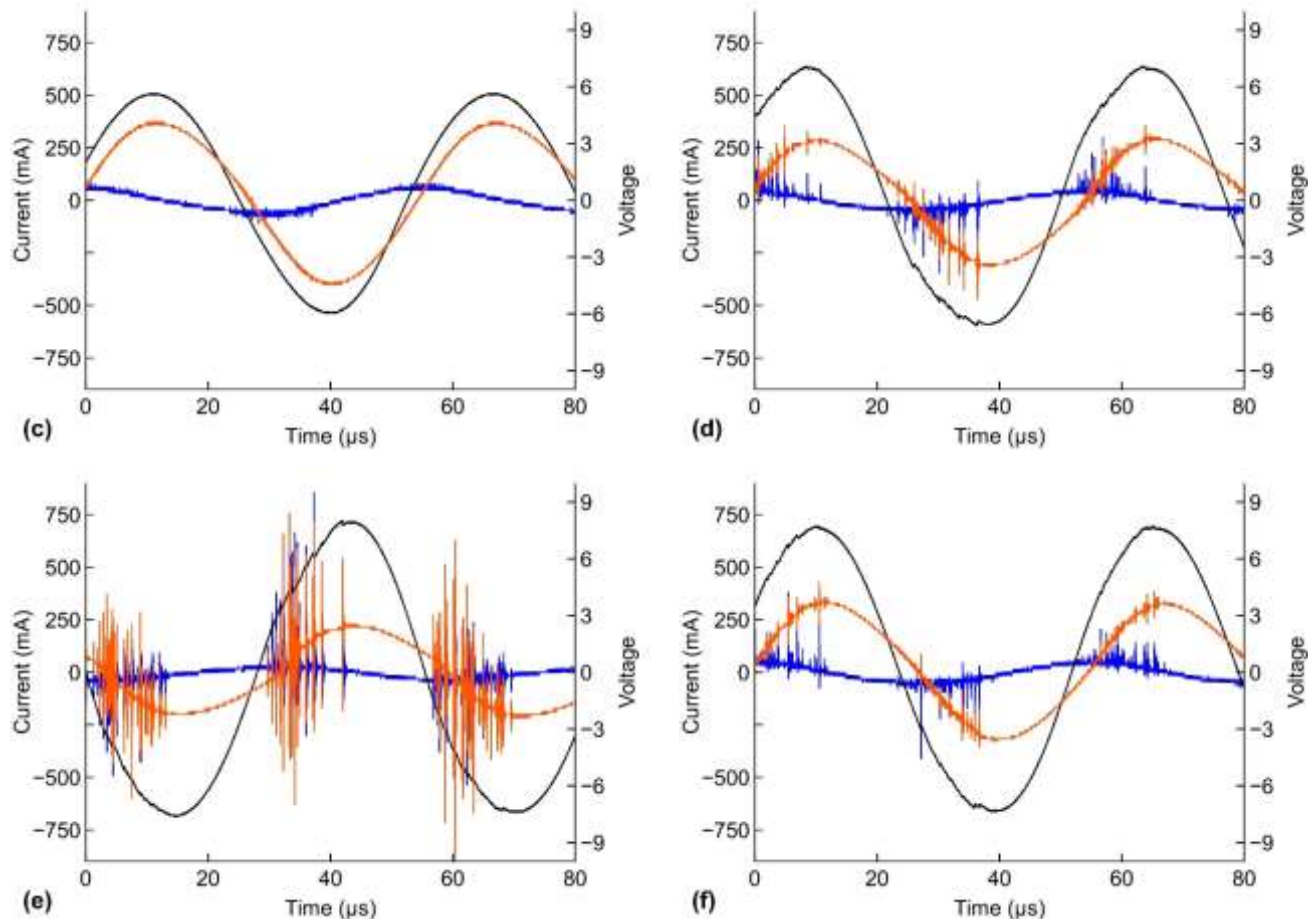
Another important criteria is the selectivity of support materials to produce either  $\text{NO}$  or  $\text{NO}_2$ . In Fig. 2b, the selectivity towards  $\text{NO}$  is plotted against the SEI. The selectivity towards  $\text{NO}$  for all the materials studied lies around 50 % in the SEI range from  $1500$  to  $3800 \text{ J/L}$ , while it changes non-linearly at a lower SEI reaching more than 90 % for  $\text{BaTiO}_3$  and  $\text{TiO}_2$  at the lower SEI studied. On the contrary, at a higher energy input ( $> 3800 \text{ J/L}$ ), the  $\text{NO}$  selectivity slowly decreased. These trends suggest that nitrogen fixation in NTP initially occurs in the form of  $\text{NO}$ . When the energy input increases, chances of  $\text{NO}$  oxidation increase, resulting in the increasing formation of  $\text{NO}_2$ . The  $\text{NO}$  selectivity for  $\gamma\text{-Al}_2\text{O}_3$  is lower than quartz wool, even though both of them produced equally high concentration of  $\text{NO}_x$ . This difference in  $\text{NO}$  selectivity for  $\gamma\text{-Al}_2\text{O}_3$  and quartz wool suggests the possibility of reaction of  $\text{NO}$  species with surface adsorbed oxygen species on  $\gamma\text{-Al}_2\text{O}_3$  to yield higher amount of  $\text{NO}_2$ . Based on the results from this study, one can choose the SEI range and the catalyst support to obtain the desired product.

### 3.1.2. Reasons of varied effect on $\text{NO}_x$ production with different support material

#### Discharge Behavior

The electrical signals for various support materials can provide important information on discharge behavior of the studied systems. Even though the signal generator supplies energy in the form of pulses with a frequency of  $18 \text{ kHz}$  and a pulse width of  $20 \mu\text{s}$ , the voltage and current signal measured on the DBD reactor was quasi-sinusoidal for all the packing materials investigated, as shown in Fig. 3.





**Fig. 3.** Discharge signals for various packing materials at a plasma power of 45 watts; (a) the blank experiment without packing, (b)  $\gamma\text{-Al}_2\text{O}_3$ , (c)  $\text{BaTiO}_3$ , (d)  $\text{MgO}$ , (e) Quartz wool, (f)  $\text{TiO}_2$  (at 18 kHz, 20  $\mu\text{s}$ , flow rate of 1 L/min,  $\text{N}_2/\text{O}_2$  ratio of 1).

However, the spikes on the capacitor voltage and current were different resulting in different discharge behavior with the characteristic photographs presented in SI-7 of the Supplementary Material. These spikes are characteristic for the formation of the microdischarges (filamentary discharges) in DBD reactor [28,53,54]. As reported for the standard one-sided DBD without packing, the microdischarge crosses the complete discharge gap, starting from the inner electrode to the surface of the dielectric. When the discharge gap was packed with support material, the available space for the filamentary microdischarge formation became limited. Thus, only weak microdischarges were generated in-homogeneously in the void space between pellets and between pellets and the dielectric wall as well as pellets and the high voltage electrode. Along with filamentary discharges, surface discharges were formed and propagated over the support material surface [51,55]. Therefore, the filamentary discharge formed in the DBD reactor without packing transits into the combination of localized weak filamentary discharges and surface discharges in case of the packed bed DBD reactor [51].

When the discharge gap is packed with catalyst support, the microdischarges cannot travel on the same tracks any more. It can be noticed from V-I curve of  $\gamma\text{-Al}_2\text{O}_3$  packed DBD and without packed DBD that they are quite similar. Thus, it can be concluded that there were microdischarges generated between the particles surfaces or between the particles and electrode/dielectric in case of  $\gamma\text{-Al}_2\text{O}_3$  packed DBD. However, for  $\text{BaTiO}_3$ , no obvious spikes were identified demonstrating that no microdischarges had been formed. Minor surface discharges might have occurred at the catalyst surface resulting in low  $\text{NO}_x$  formation. For  $\text{MgO}$  and  $\text{TiO}_2$ , the spikes were moderate but weaker than the blank experiment, which demonstrated the formation of weak microdischarges. It is also worth noting that the quartz wool had the highest amplitude for current and capacitor voltage spikes, which mean that the microdischarges generated in case of quartz wool were stronger than the other catalyst supports. Such a difference between discharge behaviors of quartz wool and  $\gamma\text{-Al}_2\text{O}_3$  can explain the difference in  $\text{NO}$  selectivity (Fig. 2b). More intensive plasma generation in case of quartz may have resulted in larger amount of high-energy species to form  $\text{NO}$ . However, it is impossible to rule out other possibilities at this stage.

As a result, various materials provide substantially different discharge behavior, either improving or suppressing the formation of microdischarges. From the comparison of the V-I signals and  $\text{NO}_x$  concentration data, it is clear that the formation of microdischarges is essential for the nitrogen fixation. The possible reasons for the different V-I behavior of the materials studied are the differences in relative dielectric constant, surface area, or particle shape. The detailed analysis of these factors is provided below. However, it should be mentioned that other parameters such as surface electrical conductivity, presence of nanofeatures generating high electric field may also contribute and further controlled experiments are required to elucidate these parameters.

### Surface area

As shown in Fig. 2a, the  $\gamma\text{-Al}_2\text{O}_3$  catalyst support, with the highest surface area, gave the highest  $\text{NO}_x$  concentration (Table 1). A more direct comparison between  $\gamma\text{-Al}_2\text{O}_3$  and  $\alpha\text{-Al}_2\text{O}_3$ , which have a similar chemical functionality and close dielectric constants, shows that the surface area is crucial for plasma nitrogen fixation.

Surface area is known to be essential for conventional (thermal) heterogeneous catalysis for extensive reasons. A high surface area in a catalyst provides more active sites; or alternatively, a catalyst support with a higher area generally holds smaller metal nanoparticles with larger active (metal) area. In the case of plasma catalysis, the reaction is activated by the microdischarges between the particles or between particles and electrode/dielectric. The discharge area without any packing material is only the area of the reactor walls. In the presence of the packing particles, the discharges happen mainly on the surface of the particles as observed in other studies[55]. Hence, the higher surface area is considered to lead to higher frequency of discharges resulting in higher  $\text{NO}_x$  concentration. Similarly, an empty DBD reactor

has a negligible geometric area of its walls and is the reason for the lowest NO<sub>x</sub> concentration observed (Fig. 2a).

#### Relative dielectric constant

As described in the section 3.1.1, at the same input power, the NO<sub>x</sub> concentration obtained with TiO<sub>2</sub> and BaTiO<sub>3</sub> catalyst supports was much lower compared even to the blank experiment. The relative dielectric constants of TiO<sub>2</sub> and BaTiO<sub>3</sub> are much higher than that of other materials (Table 1), which suggests an important role of the relative dielectric constant on NO<sub>x</sub> plasma synthesis. For a comparison, the blank experiment can be considered as an experiment with a relative dielectric constant of 1 for the *packing material*, which is the mixture of N<sub>2</sub> and O<sub>2</sub>. All the other materials have a relative dielectric constant lower than 10, while TiO<sub>2</sub> has 85 and BaTiO<sub>3</sub> has in the range of 600-4500 depending on temperature [56].

The relative dielectric constant is an indication about how easily a material can be polarized when an electric field is applied. A higher dielectric constant means a material can polarize more easily when an electric field is applied and a polarized material creates an internal electric field which opposes the overall electric field. This gives a lower overall electric field and results in decreased energy of electrons. In other words, the voltage on the packing material ( $U_p$ ) depends on the relative dielectric constants of the gas phase ( $\epsilon_g$ ) and packing material ( $\epsilon_p$ ) as well as mean gap thicknesses in the gas ( $d_g$ ) and the solid respectively ( $d_p$ ) as shown in Eq. 5 [57].

$$U_p = U_g \frac{\epsilon_g}{\epsilon_p} \frac{d_p}{d_g} \quad (5)$$

Thus, with a higher relative dielectric constant, a lower voltage will be added to the packing material because the sum of  $U_p$  and  $U_g$  is the total voltage applied to the packed DBD reactor. In case of BaTiO<sub>3</sub>, which has a very high relative dielectric constant, plasma ignition is very easy. As a result of lower voltage on the packaging material, electrons have lower acceleration and carry smaller energy. Smaller electron energy leads not only to a decrease in the energy of the reactive species, but also to decreased gas ionization as well. The latter happens because in a higher electric field, shorter distance is required for electrons to reach the ionization energy resulting in larger number of ionizations inside the fixed discharge gap. In our case, only very low plasma current could be observed when BaTiO<sub>3</sub> was used as support. Also, BaTiO<sub>3</sub> does not show the spikes in current or capacitor voltage signals, indicating the presence of glow (uniform discharge) instead of filamentary discharges. As a result, it was difficult to increase the SEI to BaTiO<sub>3</sub> packed DBD, even though the input energy was of the same magnitude as other supports. Thus, the results from BaTiO<sub>3</sub> are located in the lowest range in Figure 2a. When alumina, with a lower relative dielectric constant, was used as support for the reaction, intense plasma was visible. This also resulted in a higher concentration of NO<sub>x</sub> (Fig. 2a).

### Shape of the catalyst support

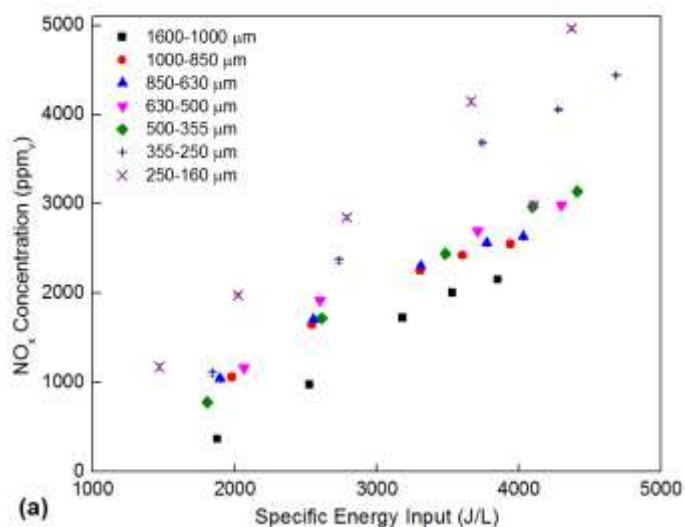
The surface area and the relative dielectric constant are not the only factors that affect NO<sub>x</sub> formation because the quartz wool has shown very high NO<sub>x</sub> concentration as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. A possible explanation for this effect is the increase in electric field in places with higher curvatures [58]. Quartz wool has a fine fibrous structure with the rigid sharp edges which induces very high electric fields as reflected by the sharpest V-I spikes (Fig. 3e). Chen *et al.* [59] proved that the sharp edges of packing material led to higher local electric fields and highly energetic electrons [21]. Thus, the superior performance of quartz wool for NO<sub>x</sub> production can be explained by fibrous sharp edge morphology.

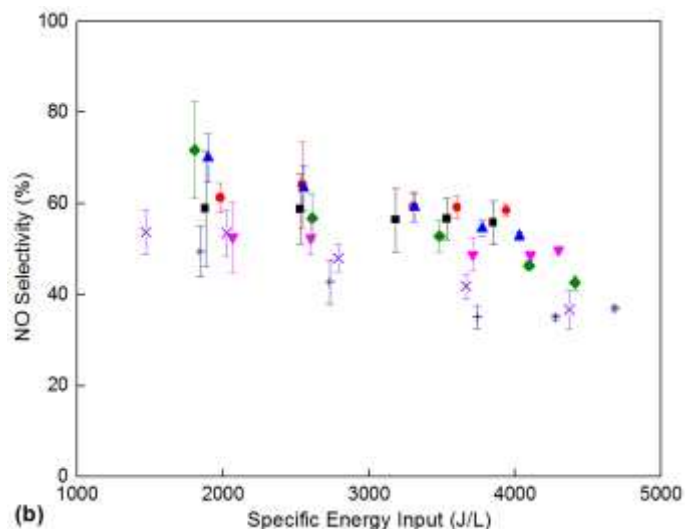
Similarly,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> also showed considerable number of high intensity peaks for current and voltage, which could be the result of the sharp edges on the particles as can be seen from the SEM pictures in (Figure SI-3). Analogous sharp edges can also be seen in case of BaTiO<sub>3</sub>. For BaTiO<sub>3</sub>, the effect of electric field enhancement by sharp edges could have been nullified by its comparatively high relative dielectric constant. Similarly, the shape considerations also worked for other materials. For example, the SEM shows that MgO and TiO<sub>2</sub> have much smoother edges in agreement with lower microdischarges and NO<sub>x</sub> formation.

## 3.2. Effect of particle size

### 3.2.1. Effect on NO<sub>x</sub> production

Results from this work show that particle shape has substantial effect on NO<sub>x</sub> formation and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was found to be the most efficient catalyst support. As a result of this, the effect of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particle size on NO<sub>x</sub> formation was studied further.





**Fig. 4.** The effect of the catalyst support ( $\gamma$ - $\text{Al}_2\text{O}_3$ ) particle size (a) on  $\text{NO}_x$  concentration and (b) the selectivity towards NO. (Flow rate of 1 L/min and  $\text{N}_2/\text{O}_2=1$  at frequency of 18 kHz and pulse width of 20  $\mu\text{s}$ .)

The concentration of  $\text{NO}_x$  increases proportionally with SEI for all particle sizes investigated as shown in Fig. 4a. There is a marked effect of particle size on the  $\text{NO}_x$  concentration. The smaller support particles gave higher concentration of  $\text{NO}_x$  as compared to the corresponding larger support particle. The highest  $\text{NO}_x$  concentration of 5000 ppm was achieved with smallest support particle (250-160  $\mu\text{m}$ ) tested. The reasons could be the changes in discharge behavior and void fraction which are discussed in the next section.

For all particle sizes, the NO selectivity decreased with the increasing SEI, as shown in Fig. 4b. The chances of NO oxidation increased with the corresponding increase in energy input, yielding higher amounts of  $\text{NO}_2$ . Although not linearly, but generally smaller particles favored  $\text{NO}_2$  formation than NO formation. This is because the smaller particles exhibit higher discharge and surface area, which increases the electron energy as well as influences the residence time. These two factors contribute to the oxidation of NO to  $\text{NO}_2$  during the course of the reaction. A previous study showed that the SEI and residence time are the two factors that lead to further oxidation of NO to  $\text{NO}_2$  [60]. Here, the residence time is influenced by the void fraction which will be discussed below.

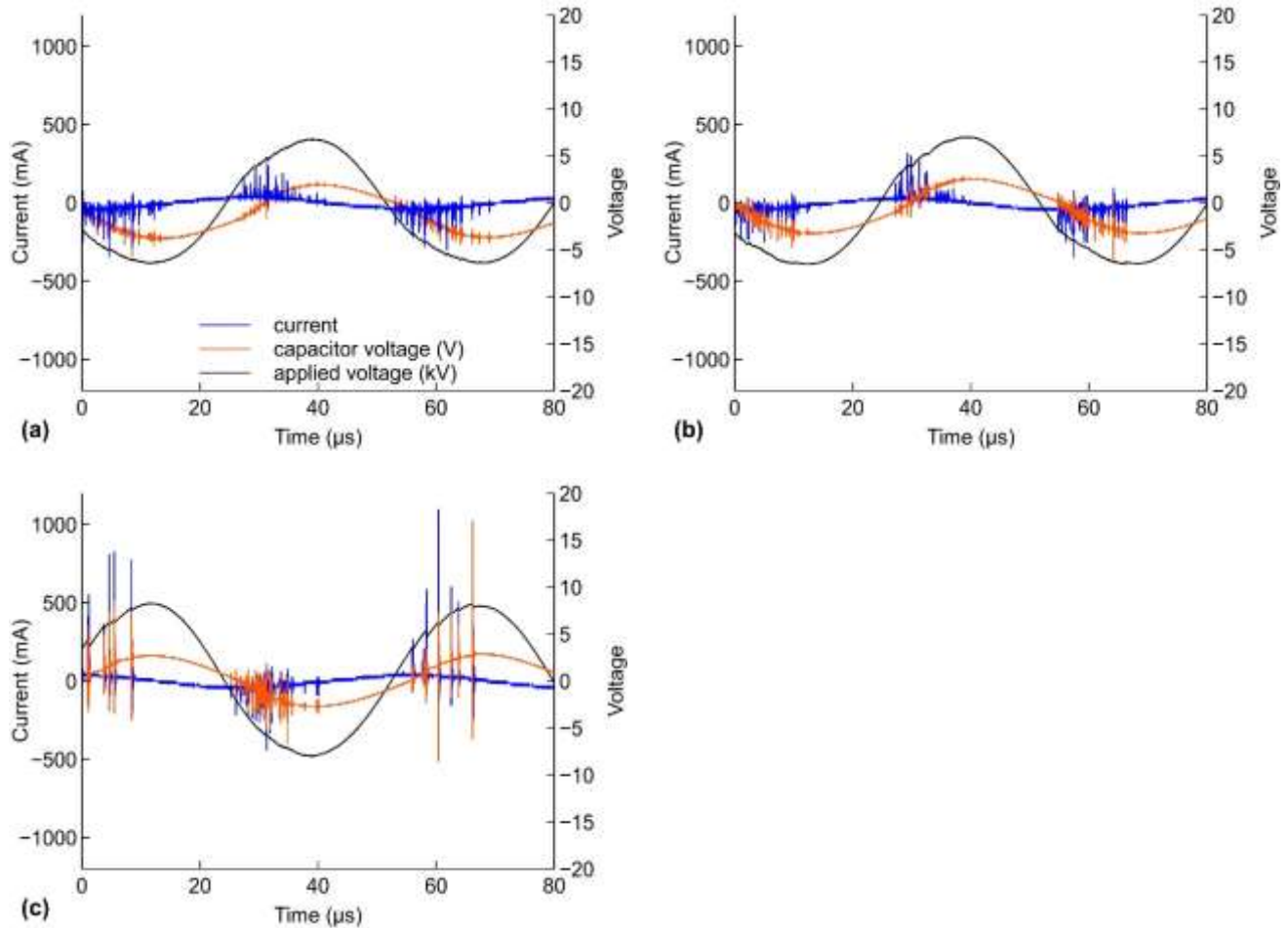
### 3.2.2. Reasons of varied effect on $\text{NO}_x$ production with different particle sizes

#### Discharge behavior

First of all, the change of discharge behavior is the most straightforward explanation of particle size effect as can be seen from the V-I curves (Fig. 5). Comparing the current and voltage curves for various particle sizes, it can be noted that the particle size has a considerable effect on the intensity of spikes. For the smaller particles sizes, a higher amplitude of current fluctuations was observed demonstrating higher intensity of microdischarges formed. As discussed in section 3.1.2, these high intensity spikes are the



reason for the higher amount of NO<sub>x</sub> produced. The smaller particles with sizes of 355-250 and 250-160 μm, generated a higher amount of NO<sub>x</sub> likely due to the high intensity localized electric field generated at particle-particle, particle-electrode and particle-dielectric contact points. The decrease in the particle size also increases the exposed surface area of particle to the plasma discharge. These combinations of effects are responsible for higher amount of NO<sub>x</sub> produced in smaller size particles.



**Fig. 5.** Discharge signals at a plasma power of 45 watts, 18 kHz, 20 μs, flow rate of 1 L/min and N<sub>2</sub>/O<sub>2</sub> ratio of 1 for the DBD reactor packed with γ-Al<sub>2</sub>O<sub>3</sub> with the particle diameters of (a) 1600-1000 μm, (b) 850-630 μm, (c) 350-250 μm. The following designations are used: (blue) current, (black) applied voltage, (orange) capacitor voltage.

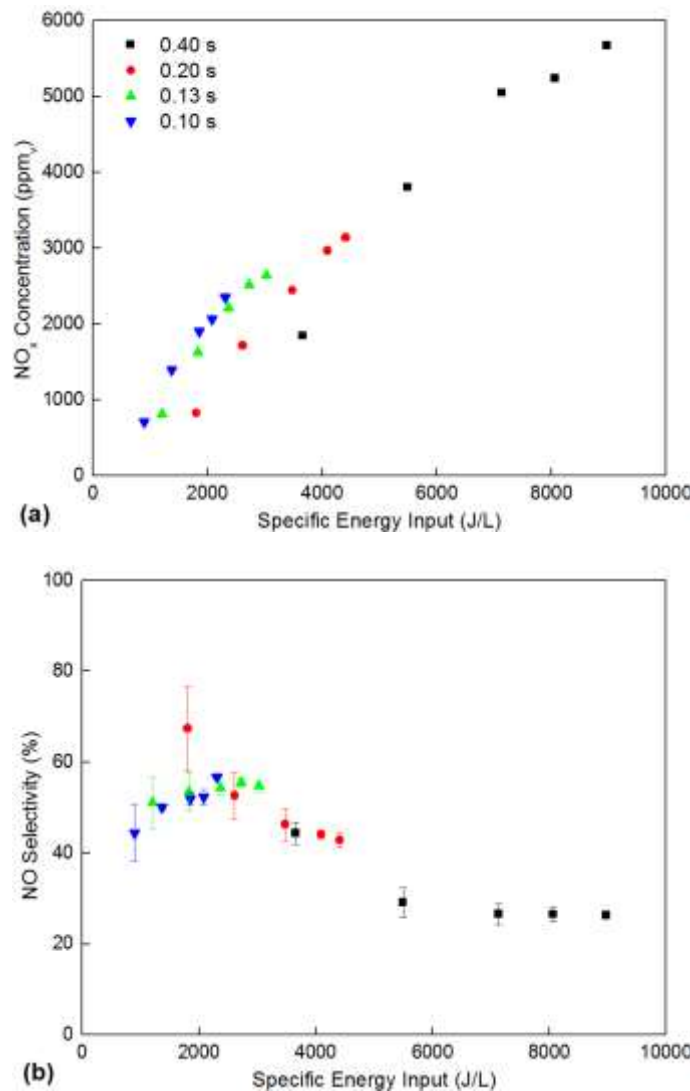
### Void fraction

Except for the discharge behavior, the void fraction was also changed. For the same reactor volume, the void fraction decreases with the decrease in particle size. This decrease in void fraction results in the higher number of contact points between support particles and between particle and electrode/dielectric, the points where electric field is stronger than the mean value in the reactor [22]. Hence, the discharge area must have been much higher and intense in case of DBD reactor packed with smaller particles than

with the larger particle sizes. As a result,  $\text{NO}_x$  formation increased with the smaller particles, which is in good agreement with the results obtained for  $\text{CO}_2$  conversion [21,22,57].

### 3.3. Effect of residence time

The mean residence time will affect the extent of the reaction in conventional thermal catalysis. Thus, the performance of DBD reactor with varying residence time was investigated with particles of  $\gamma\text{-Al}_2\text{O}_3$  (500-355  $\mu\text{m}$ ) up to an acceptable pressure drop. Therefore, four residence times were investigated with a feed ratio ( $\text{N}_2/\text{O}_2$ ) of 1 (Fig. 6). The residence time of 0.1 s, 0.13 s, 0.2 s and 0.4 s were achieved by changing the gas feed flowrate to 2, 1.5, 1, to 0.5 L/min, respectively.



**Fig. 6.** The effect of the residence time for  $\gamma\text{-Al}_2\text{O}_3$  packed DBD reactor on (a)  $\text{NO}_x$  concentration and (b) the selectivity towards NO. (Particle size= 500-355 micron, 18 kHz, 20  $\mu\text{s}$ ).

Fig. 6a shows the effect of residence time and SEI on  $\text{NO}_x$  concentration. Concentration of  $\text{NO}_x$  increases proportionally to SEI for all residence times investigated. The highest concentration of 5670 ppm was achieved with SEI of 8980 J/L for residence time of 0.4 s.

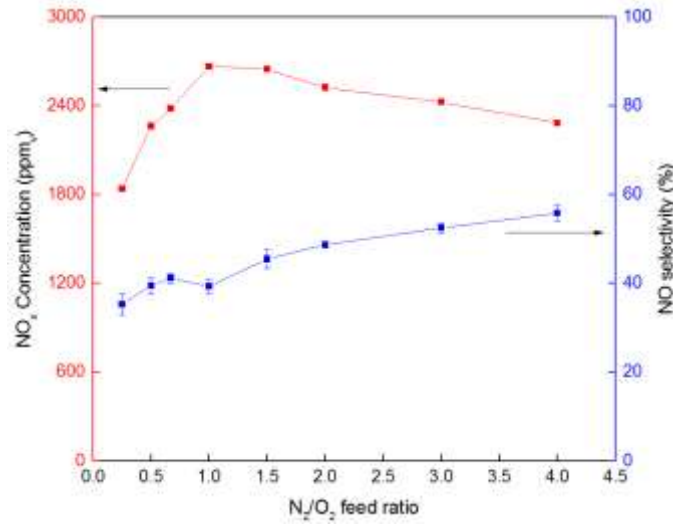
Longer residence times results in a higher concentration of  $\text{NO}_x$  because of longer reaction times and the higher SEI per unit volume of the feed gases. Increase in residence time helps in the ionization and reaction of the maximum number of reactant species. Supplying a higher SEI per unit volume of reactants gives high mean energy to electrons to react and produces the reaction species, which lead to reaction to produce nitric oxide and  $\text{NO}_2$ .

Fig. 6b shows the selectivity to produce NO over  $\text{NO}_2$ . For the highest residence time, 0.4 s, the selectivity for NO decreases with the increased SEI, therefore  $\text{NO}_2$  formation is favored over NO formation. At short residence time, i.e. 0.1 s, selectivity for NO formation increases. Thus, the  $\text{NO}_2$  formation is favored over NO formation at lower residence time. With a long residence time inside the discharge zone, NO is further oxidized to  $\text{NO}_2$ . Whereas with a short residence time, it is not sufficient for oxidation of NO to  $\text{NO}_2$ , therefore NO leaves in higher amount as final product.

### **3.4. Effect of Feed Ratio**

The effect of feed ratio on  $\text{NO}_x$  synthesis was investigated by varying the feed ratio of  $\text{N}_2$  to  $\text{O}_2$  from 0 to 4. The effect of feed ratio on the concentration of  $\text{NO}_x$  and the selectivity of NO is shown in Fig. 7. A feed ratio of 1 to 1.5 was found to be optimum to produce higher amount of  $\text{NO}_x$ , similar to our previously published study on gliding arc reactor [60]. At a feed ratio of 1, reactive species of nitrogen and oxygen have equal probability to combine with adjacent oxygen and nitrogen species, respectively. The combination reaction gives NO first and then further oxidation yields  $\text{NO}_2$ .

As the ratio of  $\text{N}_2$  to  $\text{O}_2$  increases, NO is produced in higher amount than  $\text{NO}_2$ . For a ratio of 4, the selectivity of NO is 56 % and at the feed ratio of 0.25 the selectivity of NO is 35%. At a lower feed ratio meaning a higher feed rate of oxygen, the formation of  $\text{NO}_2$  is favored more as the NO produced is readily further oxidized to  $\text{NO}_2$  because of the higher proportion of  $\text{O}_2$  in the feed.



**Fig. 7.** The effect of feed ratio on  $NO_x$  concentration and NO selectivity in a DBD packed with  $\gamma-Al_2O_3$  particles 500-355  $\mu m$  at the total gas flow rate of 1 L/min.

### 3.5. Active Metal Oxides Supported Catalysts

In order to study the effect of catalyst in plasma nitrogen fixation, the best performing  $\gamma$ - $\text{Al}_2\text{O}_3$  support was selected and various metal oxides were deposited on it. Supported rather than single-phase catalysts were used, so the overall physical properties of the particles such as relative dielectric constant and shape were constant, apart from catalyst surface chemical properties which are determined by the supported active oxide. This combination provided a direct comparison of the plasma catalytic properties of the active metal oxide, rather than a combination of physical and chemical properties as has been previously performed.

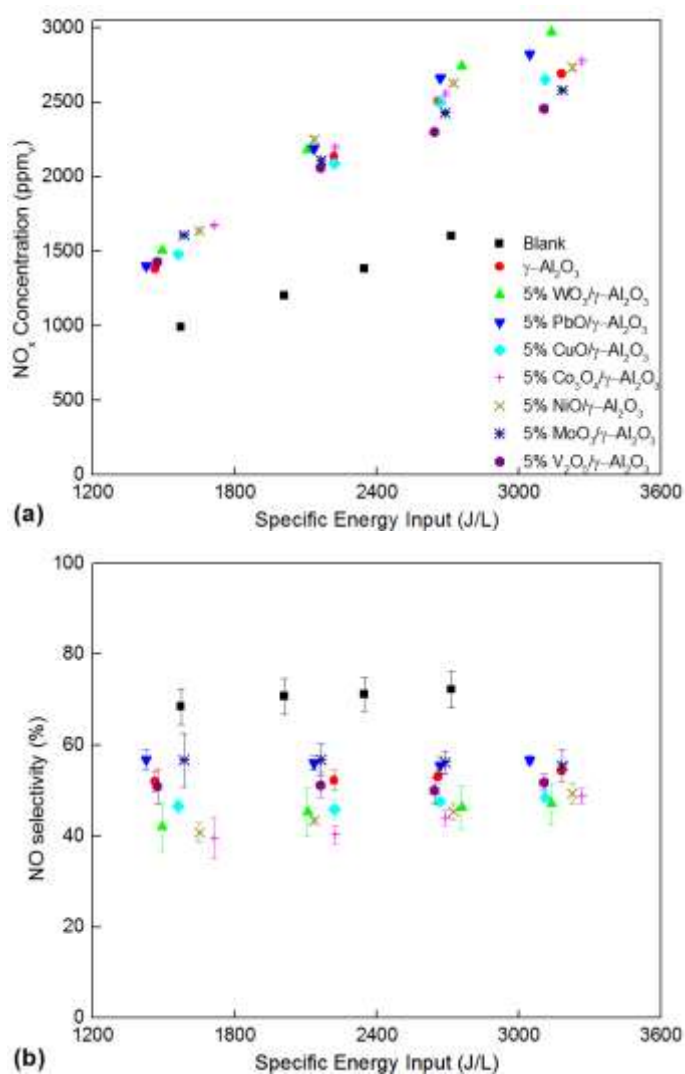
The conventional catalysts for complete oxidation of hydrocarbons were selected for the study, because their main role in the thermal activation of oxygen species is thoroughly studied [61,62]. It is expected that in the plasma-catalytic nitrogen fixation, nitrogen species will be activated by the high-energy plasma species, then these species should react with the oxygen species either thermally activated by the catalysts or by plasma. An alternative hypothesis is that the most essential catalyst property is a high vapor pressure under plasma conditions (such as  $\text{MoO}_3$  reported by Mutel *et al.* [42]) to allow for, in effect, homogeneous catalysis in gas phase [10].

To study these hypotheses, a wide range of oxides with various degrees of oxygen activation abilities were supported. For example, alumina is almost inactive in oxygen activation, while  $\text{PbO}$ ,  $\text{CuO}$  and  $\text{Co}_3\text{O}_4$  provide quick oxidation of hydrocarbons with the activity inferior only to noble metals (Fig. SI-5 in the Supplementary Data) [61]. Noble metals were not considered in the current work, because highly conductive metallic particles have different electronic properties. In such a case, it would be impossible to attribute any observed differences in activity to the factor of chemical properties. Other oxides such as  $\text{NiO}$ ,  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$  and  $\text{WO}_3$  are expected to be of intermediate activity between  $\text{Al}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$ , if oxygen activation step is crucial for nitrogen fixation. Also, these oxides have various volatility ( $\text{V}_2\text{O}_5$  and  $\text{MoO}_3$  have the highest vapor pressure). Rather high vapor pressure was expected to facilitate plasma-catalyst interactions allowing for heterogeneous catalysts to act as gas phase homogeneous catalysis. The effect of increased total pressure on plasma behavior should be negligible as the maximum increase in total pressure was expected to be below  $10^{-3}$  mbar, which is far smaller than the change in pressure caused by various gas flow rates (Fig. 6).

These catalysts were characterized by nitrogen physisorption, powder X-ray diffraction and SEM. These results are given in Fig. SI-1, SI-2, SI-3 and SI-4 respectively in the Supplementary Data. They showed that the introduction of the active oxide on alumina did not affect its overall physical properties. Elemental mapping confirmed a uniform distribution of the oxides over the support.

### 3.5.1. Influence of Active Metal Oxides

Packing catalyst support or supported metal oxides in DBD clearly shows a considerable improvement in the amount of  $\text{NO}_x$  produced compared to the blank experiment conducted as shown in Fig. 8a. Also the SEI for all the performed experiments was the same, demonstrating that the assumption of supported metal oxides did not change the physical properties of the catalyst support is valid. The comparison of  $\gamma\text{-Al}_2\text{O}_3$  with the supported catalysts does not show a large increase in  $\text{NO}_x$  concentration. However, the trends are in excellent agreement with the results of Gicquiel et al. [63], who showed that  $\text{WO}_3$  provided the highest nitrogen fixation activity in plasma followed by  $\text{MoO}_3$  and empty microwave discharge reactor.

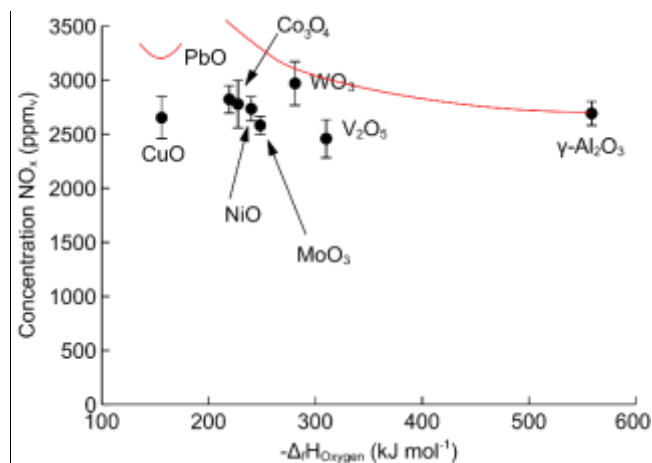


**Fig. 8.** The effect of metal oxides supported over  $\gamma\text{-Al}_2\text{O}_3$  on (a)  $\text{NO}_x$  concentration and (b) the selectivity towards NO.

The catalysts also affected the selectivity towards NO (Fig. 8b). For the blank experiment, the NO selectivity was the highest suggesting that the primary product of plasma nitrogen fixation, NO, had lower chances of further oxidation to form NO<sub>2</sub>. For the plasma-catalytic nitrogen fixation, however, the results were unexpected. In particular, the most active 5% WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst showed the lowest activity suggesting that it increased either NO oxidation or provided an alternative direct route towards NO<sub>2</sub> formation. Surprisingly, the other two active catalysts 5% Co<sub>3</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> and 5% PbO/Al<sub>2</sub>O<sub>3</sub> which showed similar NO<sub>x</sub> concentrations demonstrated the different NO selectivities, 48 and 56 % respectively. Conversely, it was expected to obtain very similar results due to very similar oxygen activation properties of these two catalysts. Such a difference indicates that there exists a separate channel for NO<sub>2</sub> formation on certain catalysts. However, the mechanistic studies do not support the possibility of NO<sub>2</sub> formation as a product of plasma oxidation of N<sub>2</sub> [64,65]. As a result, the effect of the catalyst on NO selectivity could be explained in terms of localized discharge formation, i.e. enhancement of plasma formation in the catalyst vicinity allowing for higher plasma density, resulting in higher chances of secondary oxidation of NO either with plasma-activated oxygen species or with surface adsorbed oxygen species. The catalyst-dependent plasma formation near the surface was reported by Durme et al. [28].

Further comparison of the catalytic results has been performed following the known trends in complete catalytic oxidation of hydrocarbons, i.e. studying the effect of catalyst activity depending on oxygen "binding" energy [61]. Interestingly, there is only a minor correlation between the nitrogen fixation activity in plasma and the activity in oxygen activation (Fig. 9). For example, PbO and Co<sub>3</sub>O<sub>4</sub>, which are the most active in oxygen activation, demonstrated only slightly higher NO<sub>x</sub> concentration compared to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Also, the WO<sub>3</sub> catalyst showed NO<sub>x</sub> concentration noticeably higher than expected based on its oxygen activation activity. These observations suggest that oxygen activation on the catalysts plays a role in plasma-catalytic nitrogen fixation. However, this role is much less important compared to thermal oxidation reaction probably because oxygen activation under the studied conditions takes place mostly in plasma as shown by the results obtained with all the supported catalysts which were closely similar. This means that the main role of plasma catalyst in nitrogen fixation is in the facilitation of microdischarge formation rather than the chemical interaction with the plasma-activated species.

Complete hydrocarbon oxidation usually takes place at elevated temperatures of 300-500 °C, but the studied reactions were performed at a reactor temperature of about 250 °C. As a result, it may result in insufficient oxygen activation on the catalyst surface and this may affect the conclusions drawn regarding the catalytic activity. This possibility and the influence of temperature between 200 and 400 °C for a selected NiO/Al<sub>2</sub>O<sub>3</sub> catalyst has been studied and reported in supplementary information section SI-5. The results presented in Fig. SI-8 of the Supplementary information show that NO<sub>x</sub> concentration slightly decreases at a higher temperature, which confirms that oxygen activation in plasma nitrogen fixation does not play an important role.

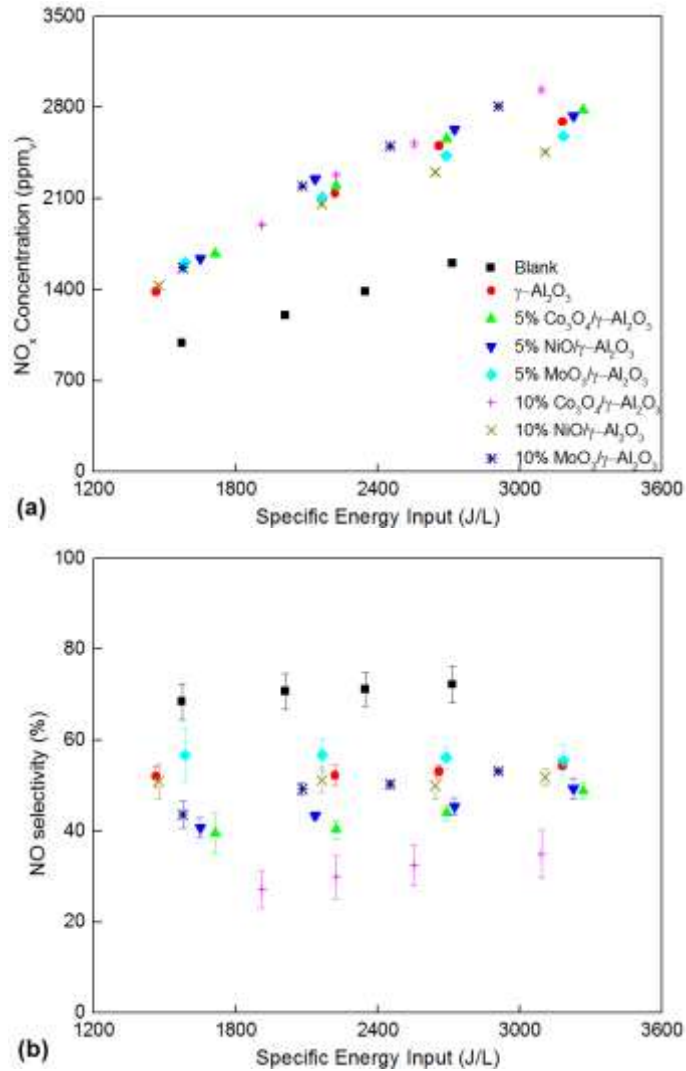


**Fig. 9.** NO<sub>x</sub> concentration for the studied 5% alumina-supported catalysts at the highest specific energy input as a function of oxygen "binding" energy (standard enthalpy of oxide formation per oxygen atom) with the (red) general trend on the expected concentration in case of a limiting step of oxygen activation.

### 3.5.2. Influence of Active Metal Oxide Loading

To study the effect of the supported oxide on plasma nitrogen fixation, several selected catalysts with higher active metal contents were prepared. Fig. 10a shows that the NO<sub>x</sub> concentrations for the 5 and 10 % active metal oxide loaded catalysts in plasma are very close, which supports the conclusion that active metal oxides play a minor role in plasma nitrogen fixation. Furthermore, the catalyst that contain 10 % of the active oxides is shifted to a lower SEI compared to that containing 5%, which indicates that for these catalysts not only surface chemical properties, but bulk physical properties discussed in 3.1 (e.g., relative dielectric constant), were substantially affected. Interestingly, the MoO<sub>3</sub> catalyst which was reported by several authors to be efficient in plasma nitrogen fixation showed rather marginal improvement compared to γ-Al<sub>2</sub>O<sub>3</sub> [42,63]. However, the difference in catalyst performance was most clear while considering NO selectivity. Because, a well-known active oxidation catalyst, 10% Co<sub>3</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>, provided enough active species for oxidation of NO into NO<sub>2</sub> (Fig. 10b).





**Fig. 10.** The effect of the supported oxide loading on (a) on NO<sub>x</sub> concentration and (b) the selectivity towards NO.

## 4. Conclusions

A systematic study of the plasma catalytic nitrogen oxidation has been performed in a one-sided DBD reactor. A range of catalyst supports,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, MgO, BaTiO<sub>3</sub> and quartz wool were studied, which showed completely different behavior. Quartz wool and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed almost twofold increase in NO<sub>x</sub> concentration compared to the blank experiment, while BaTiO<sub>3</sub> provided much lower concentration due to the formation of glowing discharge compared to numerous filamentous microdischarges that were obtained using other supports. Electrical characteristics of the microdischarges were studied and showed a direct correlation between the formation of microdischarges and NO<sub>x</sub> formation. Hence, maximizing the formation of microdischarges seems to be an appropriate means of increasing nitrogen fixation in plasma.

The comparison of the physical properties of the investigated catalyst supports indicated that 3 characteristics contribute in facilitating microdischarges formation. Firstly, high surface area provides large area for the generation of the microdischarges because  $\gamma\text{-Al}_2\text{O}_3$  ( $\sim 100 \text{ m}^2/\text{g}$ ) showed about 30 % higher  $\text{NO}_x$  concentration compared to  $\alpha\text{-Al}_2\text{O}_3$  ( $< 1 \text{ m}^2/\text{g}$ ). Secondly, moderate relative dielectric constant ( $< 10$ ), provides high voltage in the packing material and results in high  $\text{NO}_x$  concentration. In case of higher dielectric constants, the glowing discharge was observed for  $\text{BaTiO}_3$ , producing lower  $\text{NO}_x$  concentration. Thirdly, the presence of sharp edges where the electric field is high was an important factor. Rigid fibrous quartz wool provided enough sharp edges, where the electric field is stronger to generate high intensity microdischarges, which gave higher  $\text{NO}_x$  concentration similar to  $\gamma\text{-Al}_2\text{O}_3$ . Similarly, smaller particles provided lower curvature radii, which increased  $\text{NO}_x$  formation by almost twofold when comparing  $\gamma\text{-Al}_2\text{O}_3$  particles of 0.2 and 1.3 mm average diameter. However, at this stage it is impossible to rule out contribution of other effects such as surface electrical conductivity of presence of nanofeatures on the catalyst surface.

Results of gas residence time study in a plasma reactor packed with  $\gamma\text{-Al}_2\text{O}_3$  showed that a higher gas flow rate increases energy efficiency by about 50 %, but decreases total  $\text{NO}_x$  concentration considerably in the gas. The gas ratio,  $\text{N}_2/\text{O}_2$ , of 1, was found to be optimum, with the other ratio in the range of 0.2–4 providing about 17 % decreased  $\text{NO}_x$  formation due to the preferential formation of the primary NO products from such a gas mixture.

The most important factors that increase the nitrogen fixation efficiency by almost 60 % compared to the blank experiment are catalyst's geometrical factors such as particle sizes and shapes. Hence, the main role of the plasma catalyst seems to be the facilitation of the formation of microdischarges in plasma via large surface area and a large amount of sharp edges. Therefore, the catalyst supports which have high surface area in combination with sharp edges, such as 3D printed, could yield higher concentrations in plasma catalytic nitrogen fixation.

A range of metal oxides were supported on  $\gamma\text{-Al}_2\text{O}_3$ , which provided comparable physical properties of the catalysts and allowed for direct comparison of the effect of surface chemistry on the plasma nitrogen fixation. The supported catalysts showed rather marginal (at most 10 %) increase compared to the catalyst support used ( $\gamma\text{-Al}_2\text{O}_3$ ). Interestingly,  $\text{WO}_3$  was found to be the most active, while well-known oxygen activation catalyst such as  $\text{PbO}$  or  $\text{Co}_3\text{O}_4$  showed much lower improvement of below 5 %. These data show that oxygen activation on complete combustion catalysts plays a role. It is likely that the vibrationally excited nitrogen species, which are known to be formed in plasma [63,64], have a higher probability of reaction with the mobile oxygen species on the catalyst surface. The marginal increase in selectivity shows that the non-catalytic route via direct gas-phase interaction of excited  $\text{N}_2$  with  $\text{O}_2$  species prevails. When the loading of active metal oxide was increased from 5% to 10%, the difference

in catalysts activity was the most evident in case of 10%  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ , a well-known oxidation catalyst, which likely provided a large amount of activated oxygen to oxidize plasma-formed NO into  $\text{NO}_2$ .

Based on the results of the study, it is clear that further efforts are required to make plasma nitrogen fixation commercially feasible. Firstly,  $\text{NO}_x$  yield should reach an order of 1 vol. % for ease of separation. Secondly, the energy efficiency should be increased to a level comparable to that of the Haber-Bosch process of 0.48 MJ/mol. Even having the same energy efficiency, plasma nitrogen fixation could be a compelling business case provided by off-the-grid economy opportunities. For example, synthesis of nitrogen fertilizers in container-scale miniplants can be performed using local renewable energy resources such as wind and solar. At an industrial scale, plasma synthesis is promising by significant simplification of the plant equipment required.

## **Acknowledgement**

This research is funded by the EU project MAPSYN: Microwave, Acoustic and Plasma SYNtheses, under the grant agreement no. CP-IP 309376 of the European Community's Seventh Framework Program.

## ***Appendix A. Supplementary Data***

Supplementary Data associated with this paper can be found in the online version of the paper and contains the following information: Nitrogen adsorption isotherm of pristine  $\gamma$ -alumina support, Powder X-ray diffraction patterns of the catalysts synthesized, SEM Images of catalyst supports and the supported active metal oxides, Volcano plot of catalytic activity for propylene oxidation on oxide catalysts, Temperature of catalyst bed and its effect on the  $\text{NO}_x$  concentration and NO selectivity, Energy Efficiency for Plasma  $\text{NO}_x$  Synthesis

## References

- [1] J.N. Galloway, E.B. Cowling, Reactive nitrogen and the world: 200 years of change., *Ambio*. 31 (2002) 64–71. doi:10.2307/4315217.
- [2] V. Smil, Global Population and the Nitrogen Cycle, *Sci. Am.* 76 (1997).
- [3] D.E. Canfield, A.N. Glazer, P.G. Falkowski, The evolution and future of Earth's nitrogen cycle., *Science*. 330 (2010) 192–6. doi:10.1126/science.1186120.
- [4] E. Cowling, J. Galloway, C. Furiness, M. Barber, T. Bresser, K. Cassman, et al., Optimizing nitrogen management in food and energy production and environmental protection: summary statement from the Second International Nitrogen Conference., *Sci. World J.* 1 (2001) 1–9. doi:10.1100/tsw.2001.481.
- [5] V. Smil, *Enriching the Earth: Fritz Haber, Carl Bosch, and the Transformation of World Food Production*, MIT Press, 2004.
- [6] M. Appl, Ammonia, 2. Production Processes, *Ullmann's Encycl. Ind. Chem.* (2012) 139–225. doi:10.1002/14356007.o02.
- [7] M. Appl, The Haber-Bosch Heritage: The Ammonia Production Technology, in: 50th Anniv. IFA Tech. Conf., 1997: p. 25.
- [8] R.R. Schrock, Reduction of dinitrogen., *Proc. Natl. Acad. Sci. U. S. A.* 103 (2006) 17087. doi:10.1073/pnas.0603633103.
- [9] J.W. Erisman, M.A. Sutton, J. Galloway, Z. Klimont, W. Winiwarter, How a century of ammonia synthesis changed the world, *Nat. Geosci.* 1 (2008) 636–9.
- [10] N. Cherkasov, A.O. Ibhaddon, P. Fitzpatrick, A review of the existing and alternative methods for greener nitrogen fixation, *Chem. Eng. Process. Process Intensif.* 90 (2015) 24–33. doi:10.1016/j.cep.2015.02.004.
- [11] C.E. Stere, W. Adress, R. Burch, S. Chansai, A. Goguet, W.G. Graham, et al., Ambient Temperature Hydrocarbon Selective Catalytic Reduction of NO<sub>x</sub> Using Atmospheric Pressure Nonthermal Plasma Activation of a Ag/Al<sub>2</sub>O<sub>3</sub> Catalyst, *ACS Catal.* 4 (2014) 666–673.
- [12] A. Gómez-Ramírez, V.J. Rico, J. Cotrino, A.R. González-Elipse, R.M. Lambert, Low temperature production of formaldehyde from carbon dioxide and ethane by plasma-Assisted catalysis in a ferroelectrically moderated dielectric barrier discharge reactor, *ACS Catal.* 4 (2014) 402–408. doi:10.1021/cs4008528.
- [13] L. Wang, Y. Yi, Y. Zhao, R. Zhang, J. Zhang, H. Guo, NH<sub>3</sub> Decomposition for H<sub>2</sub> Generation: Effects of Cheap Metals and Supports on Plasma–Catalyst Synergy, *ACS Catal.* (2015) 4167–4174. doi:10.1021/acscatal.5b00728.
- [14] A. Fridman, *Plasma Chemistry*, Cambridge University Press, New York, 2008.
- [15] M.A. Lieberman, A.J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing*, Wiley, 2005.
- [16] C.E. Stere, W. Adress, R. Burch, S. Chansai, a. Goguet, W.G. Graham, et al., Probing a Non-Thermal Plasma Activated Heterogeneously Catalyzed Reaction Using in Situ DRIFTS-MS, *ACS Catal.* 5 (2015) 956–964. doi:10.1021/cs5019265.
- [17] J.C. Whitehead, Plasma catalysis: A solution for environmental problems, *Pure Appl. Chem.* 82 (2010) 1329–1336. doi:10.1351/PAC-CON-10-02-39.
- [18] Y.-R. Zhang, K. Van Laer, E.C. Neyts, A. Bogaerts, Can plasma be formed in catalyst pores? A modeling investigation, *Appl. Catal. B Environ.* 185 (2016) 56–67. doi:10.1016/j.apcatb.2015.12.009.

- [19] E.C. Neyts, a Bogaerts, Understanding plasma catalysis through modelling and simulation—a review, *J. Phys. D. Appl. Phys.* 47 (2014) 224010. doi:10.1088/0022-3727/47/22/224010.
- [20] E.C. Neyts, K. (Ken) Ostrikov, M.K. Sunkara, A. Bogaerts, Plasma Catalysis: Synergistic Effects at the Nanoscale, *Chem. Rev.* 115 (2015) 13408–13446. doi:10.1021/acs.chemrev.5b00362.
- [21] X. Duan, Z. Hu, Y. Li, B. Wang, Effect of Dielectric Packing Materials on the Decomposition of Carbon Dioxide Using DBD Microplasma Reactor, *AIChE J.* (2014). doi:10.1002/aic.
- [22] H.J. Gallon, X. Tu, J.C. Whitehead, Effects of Reactor Packing Materials on H<sub>2</sub> Production by CO<sub>2</sub> Reforming of CH<sub>4</sub> in a Dielectric Barrier Discharge, *Plasma Process. Polym.* 9 (2012) 90–97. doi:10.1002/ppap.201100130.
- [23] Q. Wang, B.-H. Yan, Y. Jin, Y. Cheng, Investigation of Dry Reforming of Methane in a Dielectric Barrier Discharge Reactor, *Plasma Chem. Plasma Process.* 29 (2009) 217–228. doi:10.1007/s11090-009-9173-3.
- [24] X. Tu, H.J. Gallon, M. V Twigg, P. a Gorry, J.C. Whitehead, Dry reforming of methane over a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst in a coaxial dielectric barrier discharge reactor, *J. Phys. D. Appl. Phys.* 44 (2011) 274007. doi:10.1088/0022-3727/44/27/274007.
- [25] J.M. Cormier, O. Aubry, a. Khacef, Degradation of organics compounds and production of activated species in dielectric barrier discharges and glidarc reactors, *NATO Secur. through Sci. Ser. A Chem. Biol.* (2008) 125–134. doi:10.1007/978-1-4020-8439-3\_10.
- [26] H.L. Chen, H.M. Lee, S.H. Chen, M.B. Chang, S.J. Yu, S.N. Li, Removal of volatile organic compounds by single-stage and two-stage plasma catalysis systems: a review of the performance enhancement mechanisms, current status, and suitable applications., *Environ. Sci. Technol.* 43 (2009) 2216–27. <http://www.ncbi.nlm.nih.gov/pubmed/19452866>.
- [27] A.M. Vandenbroucke, R. Morent, N. De Geyter, C. Leys, Non-thermal plasmas for non-catalytic and catalytic VOC abatement., *J. Hazard. Mater.* 195 (2011) 30–54. doi:10.1016/j.jhazmat.2011.08.060.
- [28] J. Van Durme, J. Dewulf, C. Leys, H. Van Langenhove, Combining non-thermal plasma with heterogeneous catalysis in waste gas treatment: A review, *Appl. Catal. B Environ.* 78 (2008) 324–333. doi:10.1016/j.apcatb.2007.09.035.
- [29] F. Thevenet, L. Sivachandiran, O. Guaitella, C. Barakat, a Rousseau, Plasma–catalyst coupling for volatile organic compound removal and indoor air treatment: a review, *J. Phys. D. Appl. Phys.* 47 (2014) 224011. doi:10.1088/0022-3727/47/22/224011.
- [30] M.B. Kizling, S.G. Jaras, A review of the use of plasma techniques in catalyst preparation and catalytic reactions, *Appl. Catal. A Gen.* 147 (1996) 1–21.
- [31] B.S. Patil, Q. Wang, V. Hessel, J. Lang, Plasma N<sub>2</sub>-fixation: 1900–2014, *Catal. Today.* 256 (2015) 49–66. doi:10.1016/j.cattod.2015.05.005.
- [32] V. Hessel, G. Cravotto, P. Fitzpatrick, B.S. Patil, J. Lang, W. Bonrath, Industrial applications of plasma, microwave and ultrasound techniques: Nitrogen-fixation and hydrogenation reactions, *Chem. Eng. Process. Process Intensif.* 71 (2013) 19–30. doi:10.1016/j.cep.2013.02.002.
- [33] S. Samukawa, M. Hori, S. Rauf, K. Tachibana, P. Bruggeman, G. Kroesen, et al., The 2012 Plasma Roadmap, *J. Phys. D. Appl. Phys.* 45 (2012) 253001. doi:10.1088/0022-3727/45/25/253001.
- [34] C. Bramsiepe, S. Sievers, T. Seifert, G.D. Stefanidis, D.G. Vlachos, H. Schnitzer, et al., Low-cost small scale processing technologies for production applications in various environments — Mass produced factories, *Chem. Eng. Process. Process Intensif.* 51 (2012) 32–52. doi:10.1016/j.cep.2011.08.005.
- [35] N. Krasberg, L. Hohmann, T. Bieringer, C. Bramsiepe, N. Kockmann, Selection of Technical

- Reactor Equipment for Modular, Continuous Small-Scale Plants, Processes. 2 (2014) 265–292. doi:10.3390/pr2010265.
- [36] T. Seifert, S. Sievers, C. Bramsiepe, G. Schembecker, Small scale , modular and continuous : A new approach in plant design, *Chem. Eng. Process. Process Intensif.* 52 (2012) 140–150. doi:10.1016/j.cep.2011.10.007.
- [37] B.S. Patil, Q. Wang, V. Hessel, J. Lang, Plasma Assisted Nitrogen Fixation Reactions, in: *Altern. Energy Sources Green Chem.*, Royal Society of Chemistry, 2016.
- [38] R. Ingels, D. Graves, S. Anderson, R. Koller, Modern Plasma Technology for Nitrogen Fixation: New Opportunities?, in: *Int. Fertil. Soc., International Fertiliser Society, London, UK, 2015: pp. 1–27.* <http://fertiliser-society.org/proceedings/uk/Prc771.HTM>.
- [39] W. Avery, A role for ammonia in the hydrogen economy, *Int. J. Hydrogen Energy.* 13 (1988) 761–773. doi:10.1016/0360-3199(88)90037-7.
- [40] E. Morgan, J. Manwell, J. McGowan, Wind-powered ammonia fuel production for remote islands: A case study, *Renew. Energy.* 72 (2014) 51–61. doi:10.1016/j.renene.2014.06.034.
- [41] D. Rapakoulias, S. Cavadias, J. Amouroux, Processus catalytiques dans un reacteur a plasma hors d'équilibre II . Fixation de l'azote dans le système N<sub>2</sub>-O<sub>2</sub>., *Rev. Phys. Appl.* 15 (1980) 1261–1265.
- [42] B. Mutel, O. Dessaux, P. Goudmand, Energy Cost Improvement of The Nitrogen Oxides Synthesis in a Low Pressure Plasma, *Rev. Phys. Appl.* 19 (1984) 461–464.
- [43] V.M. Belova, E.N. Eremin, A.N. Mal'tsev, Heterogeneous catalytic oxidation of nitrogen in a glow discharge II 1:1 nitrogen-oxygen mixture, *Russ. J. Phys. Chem.* 52 (1978) 968–970.
- [44] E.N. Eremin, V.M. Belova, A.N. Maltsev, Heterogeneous catalytic oxidation of nitrogen inglow discharge III. N<sub>2</sub>:O<sub>2</sub>~1:4 Nitrogen-Oxygen mixture, *Russ. J. Phys. Chem.* 52 (1978) 970–972.
- [45] Q. Sun, A. Zhu, X. Yang, J. Niu, Y. Xu, Formation of NO<sub>x</sub> from N<sub>2</sub> and O<sub>2</sub> in catalyst-pellet filled dielectric barrier discharges at atmospheric pressure., *Chem. Commun. (Camb).* 5 (2003) 1418–9.
- [46] T. Mizushima, K. Matsumoto, J. Sugoh, H. Ohkita, N. Kakuta, Tubular membrane-like catalyst for reactor with dielectric-barrier-discharge plasma and its performance in ammonia synthesis, *Appl. Catal. A Gen.* 265 (2004) 53–59. doi:10.1016/j.apcata.2004.01.002.
- [47] B. Mingdong, B. Xiyao, Z. Zhitao, Synthesis of Ammonia in a Strong Electric Field Discharge at Ambient Pressure, *Plasma Chem. Plasma Process.* 20 (2000) 511–520.
- [48] M. Bai, Z. Zhang, M. Bai, X. Bai, H. Gao, Synthesis of Ammonia Using CH<sub>4</sub>/N<sub>2</sub> Plasmas Based on Micro-Gap Discharge under Environmentally Friendly Condition, *Plasma Chem. Plasma Process.* 28 (2008) 405–414. doi:10.1007/s11090-008-9132-4.
- [49] L.R. O`Hare, Nitrogen fixation by plasma and catalyst, US 4451436, 1984.
- [50] L.R. O`Hare, Nitrogen fixation by electric arc and catalyst, US 4877589, 1989.
- [51] X. Tu, H.J. Gallon, J.C. Whitehead, Electrical and spectroscopic diagnostics of a single-stage plasma-catalysis system: effect of packing with TiO<sub>2</sub>, *J. Phys. D. Appl. Phys.* 44 (2011) 482003. doi:10.1088/0022-3727/44/48/482003.
- [52] T.C. Manley, No Title, *Trans Electrochem. Soc.* 84 (1943) 83–96.
- [53] M. Bai, Z. Zhang, X. Bai, M. Bai, W. Ning, Plasma synthesis of ammonia with a microgap dielectric barrier discharge at ambient pressure, *IEEE Trans. Plasma Sci.* 31 (2003) 1285–1291. doi:10.1109/TPS.2003.818761.
- [54] U. Kogelschatz, Dielectric-barrier Discharges : Their History , Discharge Physics , and Industrial Applications, *Plasma Chem. Plasma Process.* 23 (2003) 1–46.

- [55] H.H. Kim, A. Ogata, Interaction of Nonthermal Plasma with Catalyst for the Air Pollution Control, *Int. J. Plasma Environ. Sci. Technol.* 6 (2012) 43–48.
- [56] G. Arlt, D. Hennings, G. De With, Dielectric properties of fine-grained barium titanate ceramics, *J. Appl. Phys.* 58 (1985) 1619–1625. doi:10.1063/1.336051.
- [57] D. Mei, X. Zhu, Y.-L. He, J.D. Yan, X. Tu, Plasma-assisted conversion of CO<sub>2</sub> in a dielectric barrier discharge reactor: understanding the effect of packing materials, *Plasma Sources Sci. Technol.* 24 (2015) 015011. doi:10.1088/0963-0252/24/1/015011.
- [58] Z. Yao, C.L. Kane, C. Dekker, High-field electrical transport in single-wall carbon nanotubes, *Phys. Rev. Lett.* 84 (2000) 2941–4. doi:10.1103/PhysRevLett.84.2941.
- [59] H.L. Chen, H.M. Lee, S.H. Chen, M.B. Chang, Review of Packed-Bed Plasma Reactor for Ozone Generation and Air Pollution Control, *Ind. Eng. Chem. Res.* 47 (2008) 2130.
- [60] B.S. Patil, J. Rovira Palau, V. Hessel, J. Lang, Q. Wang, Plasma Nitrogen Oxides Synthesis in a Milli-Scale Gliding Arc Reactor: Investigating the Electrical and Process Parameters, *Plasma Chem Sirc Plasma Process.* 36 (2016) 241–257. doi:10.1007/s11090-015-9671-4.
- [61] V.D. Sokolovskii, Principles of Oxidative Catalysis on Solid Oxides, *Catal. Rev.* 32 (1990) 1–49. doi:10.1080/01614949009349939.
- [62] J.P.A. Neeft, M. Makkee, J.A. Moulijn, Catalysts for the oxidation of soot from diesel exhaust gases. I. An exploratory study, *Appl. Catal. B Environ.* 8 (1996) 57–78. doi:10.1016/0926-3373(95)00057-7.
- [63] A. Gicquel, S. Cavadas, J. Amouroux, Heterogeneous catalysis in low-pressure plasmas, *J. Phys. D. Appl. Phys.* 19 (1986) 2013–2042.
- [64] V.D. Rusanov, A.A. Fridman, G. V Sholin, The physics of a chemically active plasma with nonequilibrium vibrational excitation of molecules, *Sov. Phys. Uspekhi.* 24 (1981) 447–474. doi:10.1070/PU1981v024n06ABEH004884.
- [65] V.D. Rusanov, A.A. Fridman, G. V Sholin, Physics of chemically active plasma with nonequilibrium vibrational excitation of molecules, *Usp. Phys. Nauk.* 134 (1981) 185–231.