

# Importance of plasma discharge characteristics in plasma-catalytic dry reforming of methane and NH<sub>3</sub> synthesis

Robin De Meyer<sup>1,2,3</sup>, Yury Gorbanev<sup>1,3</sup>, Radu-George Ciocarlan<sup>4</sup>, Senne Van Doorslaer<sup>1,4</sup>, Pegie Cool<sup>4</sup>, Sara Bals<sup>2,3</sup> and Annemie Bogaerts<sup>1,3</sup>

<sup>1</sup> Research group PLASMANT, Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Wilrijk-Antwerp, Belgium

<sup>2</sup> Research group EMAT, Department of Physics, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium

<sup>3</sup> Nanolab Centre of Excellence, Groenenborgerlaan 171, 2020 Antwerp, Belgium

<sup>4</sup> Research group LADCA, Department of Chemistry, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium

**Abstract:** While it is known that the packing affects the plasma behaviour in a dielectric barrier discharge (DBD), the effect of the catalysts on the discharge is often neglected. Here, Ni and Co catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are synthesized in two very different ways. These catalysts clearly affect the plasma discharge in a packed-bed DBD used for dry reforming of methane (DRM) and NH<sub>3</sub> synthesis experiments. The altered discharge significantly influences the gas conversion, proving its importance in plasma catalysis research.

**Keywords:** Plasma catalysis, discharge characteristics, ammonia, dry reforming of methane

## 1. Introduction

In order to combat climate change, electrified processes to eliminate greenhouse gases are of great interest. Among them, plasma catalysis is gaining attention and various studies are being dedicated to optimizing the operating conditions and catalyst materials. Plasma is especially interesting as it can be rapidly switched on and off, making it an ideal complement to intermittent electricity production, coming from solar and wind [1].

Often, plasma catalysis is studied in a packed-bed dielectric barrier discharge (DBD) plasma reactor. One of the main advantages of such a configuration is the contact between the plasma and the catalytic material. As the catalyst is packed within the discharge volume, the plasma is generated in between the catalytic packing, optimizing the contact between the reactive plasma species and the catalytically active sites.

Even though it is known that the packing material inside a DBD affects the complicated plasma discharge [2], their effect on the discharge and how that in turn affects the performance in plasma-catalytic research is often ignored [3–5]. As the influence of the discharge characteristics on the gas conversion can be substantial, ignoring it makes it difficult to compare catalytic materials when their effect on the discharge is not acknowledged [6].

In this work, two types of catalysts are synthesized with the aim of deliberately altering the plasma discharge in different ways. The first type was synthesized using the common technique of wet impregnation on porous  $\gamma$ -alumina beads. This technique yields metal nanoparticles scattered throughout the entire bead. The second type of catalyst is synthesized using a technique called spray-coating. Hereby, a thin layer of metal is deposited on the surface of the beads, without any of the metal penetrating the pores. The two types were synthesized for both Ni and Co as the catalytic material.

The synthesized catalysts were used in plasma-catalytic dry reforming of methane (DRM) and NH<sub>3</sub> synthesis. In this way, the effect of the catalyst material on the plasma

discharge can be studied. Furthermore, this allows us to investigate how the effect of the discharge on the performance varies between different reactions.

## 2. Methods

### 2.1 Catalyst synthesis

All catalysts were prepared in duplicate, so that the NH<sub>3</sub> synthesis and DRM experiments could be performed using catalysts from the same synthesis batch, but without having to reuse them. Therefore, all syntheses were carried out for 30 g of dried  $\gamma$ -alumina beads (Sasol), leaving some margin for analysis and losses, as it takes roughly 12.5 g to fill the reactor once.

For the wet impregnation, either Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O or Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was dissolved in water. The amount of salt was chosen to yield a final metal loading of 10 wt%, while the volume of water was chosen to be 0.75 ml per gram of beads, which was determined as the volume that these beads could absorb. Then, the solution was added to the beads, followed by manual stirring, ensuring all beads were saturated with the solution. Next, the beads were left to dry overnight at ambient conditions, after which they were dried thoroughly in a furnace at 120 °C. Further, the beads were calcined in a furnace at 400 °C and finally reduced in a tube furnace at 550 °C for 8 h under an Ar atmosphere containing 2% H<sub>2</sub>.

For the spray coated catalysts, the goal was to make three sets of catalysts for each metal, with metal loadings of 1, 3.3 and 10 wt%, respectively. However, the 10 wt% catalysts proved too unstable to use in plasma catalysis experiments: the metal layer detached, causing the expected metal loading to no longer be accurate.

The spray coating synthesis again starts with an aqueous solution of either Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O or Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, which was heated in an oil bath to 80 °C. Once the solution reached 80 °C, 125 ml of 3 M NaOH solution was added while stirring continuously, forming a Ni(OH)<sub>2</sub> or Co(OH)<sub>2</sub> precipitate. After continuous stirring at 80 °C for 2 h, the

flask was removed from the oil bath and the precipitate was allowed to settle. Once the supernatant was completely clear, it was removed. 150 ml of deionized water was then added and everything was stirred thoroughly, after which the precipitate again settled. This washing step was repeated three times with water to neutralize the suspension and three times with isopropanol in order to result in a suspension of  $\text{Ni}(\text{OH})_2$  or  $\text{Co}(\text{OH})_2$  in isopropanol. Next, the dried  $\gamma$ -alumina beads were placed in a rotating drum as the suspension was slowly sprayed on the agitated beads. The volume of the suspension was measured to match the desired final metal loading (1 or 3.3 wt%). After spraying the correct amount of suspension on the beads, they were left to dry in ambient conditions overnight. Finally, they were dried, calcined and reduced in the same way as the wet impregnated catalysts. Note that the reduction was done right before the catalysts were used in the plasma catalysis experiment.

## 2.2 Catalyst characterization

The catalysts were characterized using multiple techniques, including scanning electron microscopy (SEM), X-ray diffraction (XRD) and  $\text{N}_2$  sorption. SEM analyses were performed using a FEI Quanta 250 ESEM, which was also equipped with an Oxford Instruments energy dispersive X-ray (EDX) detector. For these analyses, two beads of each sample were embedded in epoxy resin after which they were ground and polished to expose a smooth cross-section of the beads. Then, the cross-sections were attached to a SEM stub and coated with 10 nm of C to improve conductivity and reduce charging. The samples were imaged and EDX maps were acquired. XRD measurements were performed with a Bruker D8 ADVANCE ECO, a few beads were crushed in a mortar and pestle before analysis. The  $\text{N}_2$  sorption measurements were executed by a Quantachrome Quadrasorb SI automated system.

## 2.3 Experimental setup

The plasma catalysis experiments were carried out using a coaxial packed-bed DBD reactor that was described in detail in previous work from our group [7]. The reactor consists of a ceramic tube, wrapped with a metal mesh acting as the powered electrode. A steel rod is placed inside the tube acting as the ground electrode. The gap between the rod and the tube is packed with the catalyst beads, which are held in place with glass wool. For the DRM experiments, a 1:1  $\text{CO}_2$ - $\text{CH}_4$  mixture was sent through the reactor at a flow rate of 100 ml/min. The AC power supply (AFS) generated a 23.5 kHz sine wave with an applied power of 100 W, which resulted in a plasma power of approx. 65 W. The gas coming out of the outlet was analysed by an Agilent MicroGC.

For the  $\text{NH}_3$  synthesis experiments, a 1:1  $\text{N}_2$ - $\text{H}_2$  mixture is sent through the reactor at 100 ml/min. During these experiments, the  $\text{NH}_3$  concentration in the outflow was monitored continuously by the Emerson nondispersive infrared (NDIR) sensor.

During operation of the DBD reactor, the discharge was monitored using a Picoscope 6402d and multiple snapshots were saved to be analysed afterwards.

## 3. Results and discussion

### 3.1 Catalyst characterization

SEM analysis of cross-sections of the various catalyst beads showed significant differences in the distribution of the catalyst metal throughout the support, depending on the synthesis technique. For the spray coated samples (Fig. 1 A, B), a clear shell was observed at the surface of the beads. EDX analyses confirmed that these shells were indeed the catalyst material, while none of the metal penetrated the beads. For the wet impregnated samples (Fig. 1 C-F), EDX maps yielded a radial distribution of the metal throughout the bead, indicating a relatively homogeneous distribution. While the concentration increases slightly near the surface of the bead, plenty of metal is present throughout the entire support.

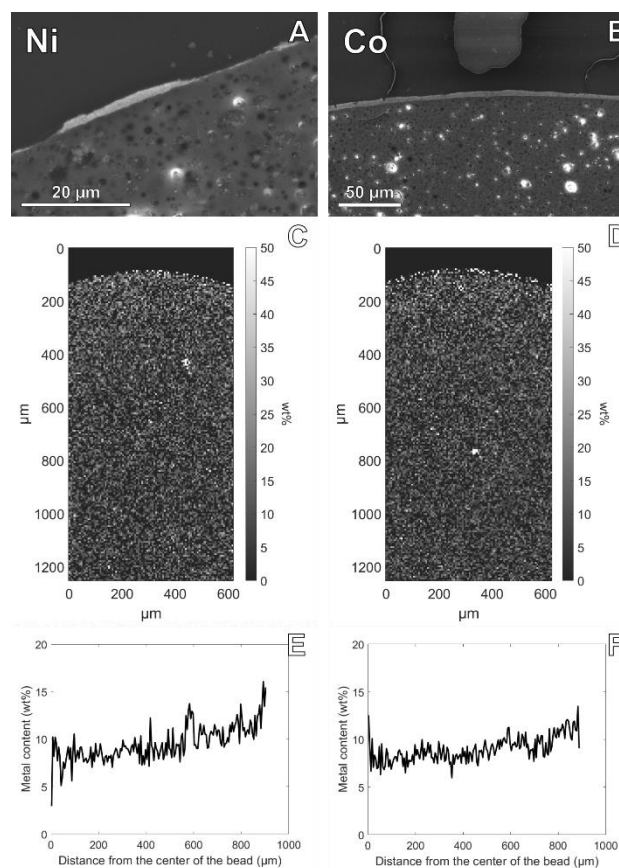


Figure 1: A, B: SEM image of a cross-section of a spray-coated bead with 3.3 wt% Ni (A) and 3.3 wt% Co (B). C, D: EDX map of the cross-section of a wet impregnated bead with 10 wt% Ni (C) and 10 wt% Co (D). E, F: Radial distribution of Ni (E) and Co (F) determined based on the EDX maps shown in C and D.

After the reduction step, some catalysts were crushed to a powder and analysed by XRD. This analysis showed that the reduction of the spray-coated samples was completed, as only Ni or Co metallic phases were detected, while no oxide phases were present in the diffractogram. For the wet impregnated catalysts, however, both metallic and oxide phases were present. This is likely due to the large amount of catalyst particles that were present inside the beads, lacking access to the  $H_2$  in the atmosphere that was needed for reduction.

Based on the  $N_2$  sorption data, BET analyses were done to determine the surface area and porosity of the various catalysts. The blank support material was also analysed to serve as a benchmark. All spray coated catalysts yielded very similar results, with a pore volume similar to the blank support (approx.  $0.54\text{ cm}^3/\text{g}$ ) and a surface area only slightly lower than the support (approx.  $215\text{ m}^2/\text{g}$  versus approx.  $240\text{ m}^2/\text{g}$  for the support). The wet impregnated catalysts, however, yielded a notably lower pore volume ( $0.45\text{ cm}^3/\text{g}$ ) and also showed a slightly lower surface area than the spray coated samples (approx.  $190\text{ m}^2/\text{g}$ ).

### 3.2 Plasma-catalytic performance

For the DRM experiments, the total conversion is shown in Fig. 2 A. The first interesting observation is that the blank support material performed best out of all tested materials. The spray-coated (SC) Co samples performed slightly worse than the blank support, with minimal difference between the 3.3 wt% and 1 wt% catalysts. The other catalysts all performed significantly worse than the blank support.

For the  $NH_3$  synthesis experiments, the  $NH_3$  concentration in the outflow of the reactor is shown in Fig. 2 B. Here, the blank support performed worst, together with the SC Ni 1 wt% catalyst. All other catalysts performed significantly better, with the other spray-coated catalysts vastly outperforming any other packing.

### 3.3 Discharge characterization and discussion

During the plasma experiments, the voltage over the reactor and the current flowing through was monitored. Based on these electrical measurements, various properties of the plasma discharge were determined. First, the number and intensity of microdischarges was quantified. This microdischarge quantity was obtained by integrating the FFT of the current signal over a frequency range of 10 – 100 MHz, corresponding to realistic time-scales for microdischarges. In Fig. 2 (right axis), it is clear that the microdischarge quantity can vary greatly, which is illustrated in Fig. 3 A-B. The clearest correlation between microdischarges and performance was observed for the  $NH_3$  synthesis experiments, where a high quantity of microdischarges clearly corresponds to a low yield of  $NH_3$ .

Further, the electrical properties of the system and the plasma discharge vary greatly depending on the catalyst, as is shown in Fig. 3 C. The Lissajous figures change drastically in shape when different catalysts are used. A number of physical properties can be extracted from these

Lissajous figures, including the effective dielectric capacitance, a measure of partial discharging, burning voltage, conductively transferred charge and more [8]. Interesting insights can be obtained, most notably the change in discharge regime induced by the catalysts and how this affects the gas conversion. The spray-coated catalysts (except for 1 wt% Ni in  $NH_3$  synthesis, possibly something went wrong) drastically reduced the microdischarge quantity and at the same time decreased the non-discharging fraction  $\alpha$  as defined by Peeters and van de Sanden [8]. This more uniform plasma discharge is notably better for  $NH_3$  synthesis, as  $NH_3$  is decomposed in microdischarges [9]. For DRM on the other hand, the less uniform plasma with plenty of microdischarges performs better because most conversion takes place in these more intense plasma discharges [10].

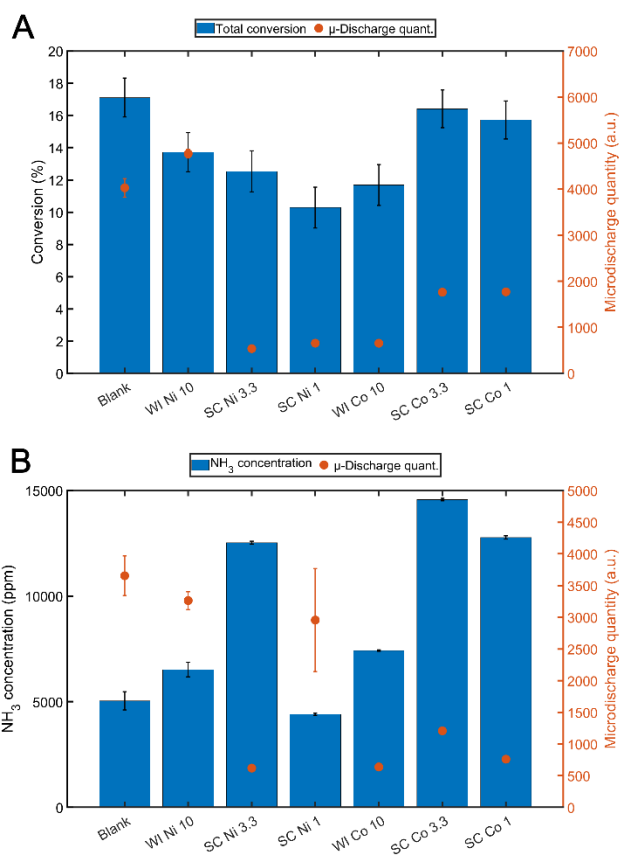


Figure 2: A: Total conversion of  $CO_2$  and  $CH_4$ , and B:  $NH_3$  concentration in the outflow of the reactor, using the various catalysts and blank  $Al_2O_3$ . Microdischarge quantity is also shown for every catalyst. Experiments were all performed for the same conditions.

Generally, it is clear that the introduction of a catalyst packing, especially the spray coated ones, drastically modifies the plasma discharge. This altered discharge in turn has a significant impact on the gas conversion that is achieved in the reactor. This indicates that a substantial part of the gas conversion is happening in the plasma phase, rather than at the surface of the catalysts. Note that this

effect of the plasma discharge on the performance is very pronounced for the  $\text{NH}_3$  synthesis, but less so for the DRM experiments.

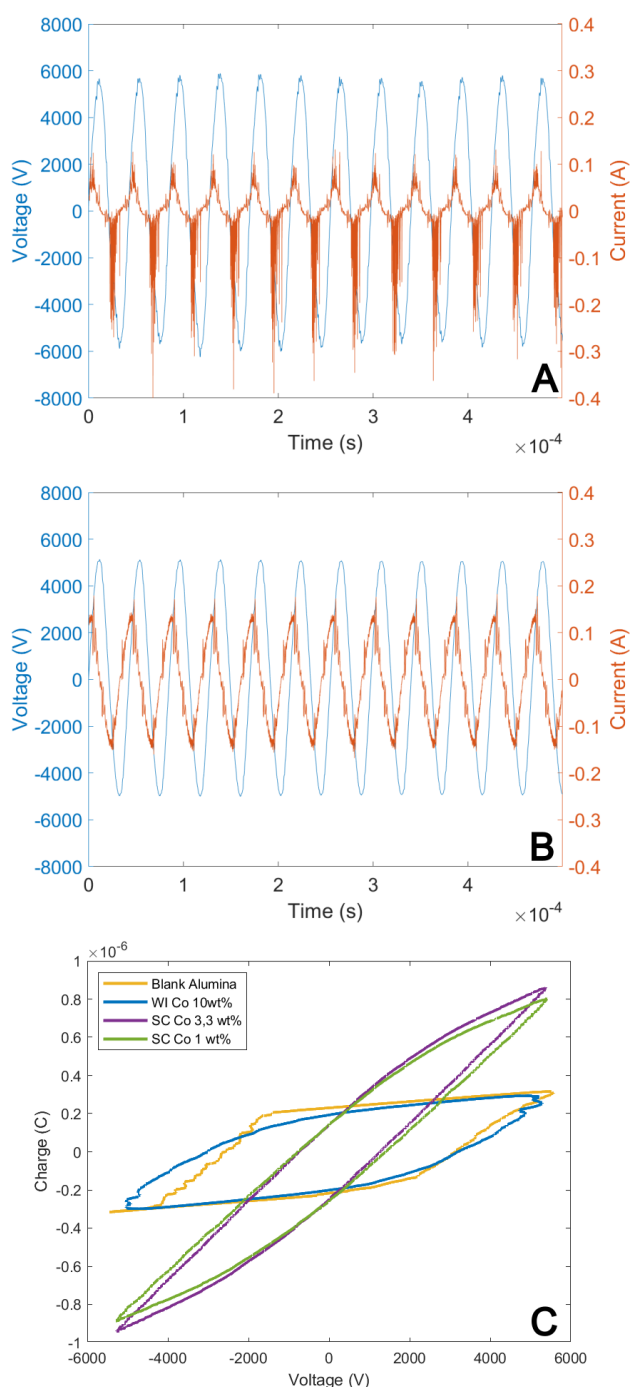


Figure 3: Electrical measurements of the various plasma discharges. Voltage and current signal during plasma discharge with 10 wt% Ni wet impregnated (A) and 3.3 wt% Ni spray coated (B) catalysts in an  $\text{NH}_3$  synthesis experiment. (C) Lissajous figures of discharges using various Co catalysts during an  $\text{NH}_3$  synthesis experiment.

Clearly, the catalyst material, and even how the catalyst is distributed throughout the support, strongly affects the plasma discharge. This change in plasma discharge can have a very significant impact on the gas conversion. The effect, however, is very different for different gas mixtures. Therefore, in order to accurately and reliably compare the performance of various catalysts, the plasma discharge characteristics are indispensable to understand the relevant mechanisms.

#### 4. Conclusion

In this work, Ni and Co catalysts supported on  $\text{Al}_2\text{O}_3$  beads were synthesized in two different ways, one yielding particles throughout the entire support and one where the metal was concentrated at the surface. It was shown that the latter strongly affects the plasma discharge, both for DRM and  $\text{NH}_3$  synthesis. This change in discharge behaviour significantly affected the gas conversion in both cases. However, the effect of the altered discharge on the performance is very different for DRM compared to  $\text{NH}_3$  synthesis. It was shown that the  $\text{NH}_3$  synthesis strongly benefits from the altered plasma discharge, being a more uniform plasma, compared to the more common filamentary discharge, characterized by many microdischarges. The latter discharge type seems to be better for DRM. Overall, it was proven that the catalysts strongly affect the plasma discharge, which is a crucial aspect that requires dedicated analyses in order to reliably compare the performance of various catalysts.

#### 5. References

- [1] A. Bogaerts et al., *Journal of Physics D: Applied Physics* 53 (2020) 443001.
- [2] X. Tu et al., *Journal of Physics D: Applied Physics* 44 (2011) 482003.
- [3] G. Chen et al., *Industrial & Engineering Chemistry Research* 61 (2022) 11436–11443.
- [4] Y. Liu et al., *Plasma Chemistry and Plasma Processing* 42 (2022) 267–282.
- [5] Z. Farshidrokhi et al., *Chemical Engineering & Technology* 44 (2021) 589–599.
- [6] B.S. Patil et al., *Applied Catalysis B: Environmental* 194 (2016) 123–133.
- [7] Y. Gorbanev et al., *Catalysts* 11 (2021).
- [8] F.J.J. Peeters, M.C.M. van de Sanden, *Plasma Sources Science and Technology* 24 (2014) 015016.
- [9] K. van 't Veer et al., *The Journal of Physical Chemistry C* 124 (2020) 22871–22883.
- [10] R. Snoeckx et al., *RSC Advances* 5 (2015) 29799–29808.