PLASMA CATALYTIC NH_3 SYNTHESIS: THE ROLE OF THE SUPPORT IN SILVER ENHANCED PLASMA NH_3 SYNTHESIS

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Abstract

Plasma catalysis is a promising but young alternative to conventional ammonia synthesis. Plasma can make chemically stable molecules, such as nitrogen, more reactive, enabling their use in producing valuable and widely demanded chemical compounds like ammonia under milder temperatures and pressure conditions. Combining non-thermal plasma discharges with heterogeneous catalysts enables further enhancement of the desired reaction; however, the mechanisms still need to be understood. In this study, we focused on exploring the impact of support by comparing a single metal (silver) on various substrates made of the same material to address the roles of both the support and the catalyst.

Introduction

Plasma catalysis is a promising method integrating plasma discharges with catalytic processes to enable hard-to-promote reaction pathways. The high electron temperature of the plasma generates radicals, ions, and excited states, leading to reaction pathways that differ from those observed in thermal catalysis. This approach enables high-energy chemistry to occur under mild conditions (atmospheric pressure and ambient temperature), while the low on/off inertia of plasma systems permits operating with intermittent renewable electricity [1]. However, challenges persist, including the understanding of unclear reaction mechanisms that are unique to the plasma environment [2] and the complex interaction of catalyst supports on the discharge [3]. Another significant issue is the lack of standards in the catalyst preparation and reference protocols, which harms reproducibility across different studies [4]. Our recent work [5] work examines how the preparation of support can affect catalytic activity. We use a fully prepared support, excluding metal loading, as a reference to isolate the role of the metal. To generalize our findings, we tested two discharge types (DBD and NRP) and two supports (alumina beads and monoliths) using silver, a thermally inactive metal that shows potential for plasma-assisted ammonia synthesis [6].

Experimental Set-up and Catalyst

The scheme for the two reactors is shown in Figure 1.

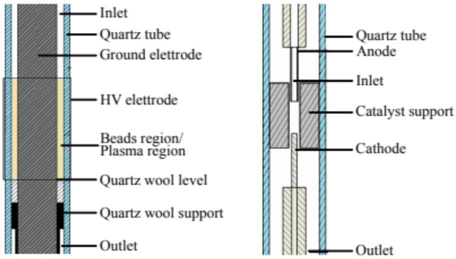

Figure 1. Schematics of the two reactors: **Left** DBD reactor, **Right** NRP reactor.

In the DBD, alumina beads are packed between the inner electrode and the quartz tube. In the NRP, the monolith is held around the electrodes. Both supports undergo drying, $AgNO_3$ impregnation, and calcination at 550 °C, with beads requiring stirring during the impregnation process for better metal distribution.

Results

DBD: Figure 2 (left) illustrates NH_3 production in the DBD reactor: untreated alumina (batch A) outperforms calcined (B) and stirred + calcined (C) supports. Ag-loaded supports (Batch H – K in Figure 2, right) exhibit up to 150% higher NH3 production than the reference, regardless of the silver loading amount.

NRP: Two polyurethane foams (20 and 30 pores per inch) were used to prepare the monoliths (Figure 3). Silver increased NH3 production by an average of 25–30%. All tests utilized γ-alumina monoliths prepared in the same way, with Figure 3 left also showing untreated support, highlighting how incomplete treatment can mask silver's effect.

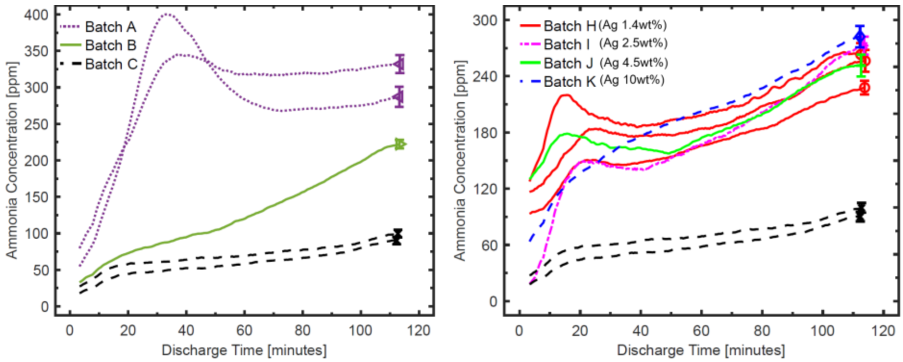

Figure 2. NH3 production in the DBD using beads. **Left:** Comparison between beads treated differently **Right:** Comparison between Ag-loaded and unloaded beads (black line-batch C).

Conclusion

The catalyst support significantly affects experimental outcomes. Treated supports without silver often perform worse than untreated ones, likely due to heat treatment

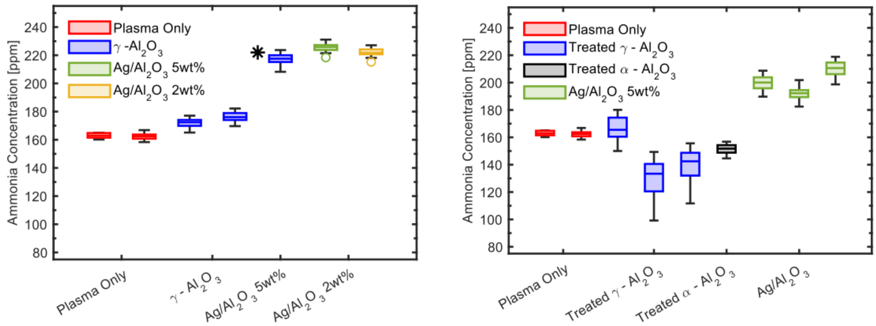

Figure 3. NH3 production using 20 PPI (left) and 30 PPI (right) monoliths as supports. *: untreated (not calcinated) 20 PPI monolith.

activating alumina sites. Proper reference selection is crucial to avoid masking catalytic effects. Silver enhances NH_3 production in both discharges, with an increase of up to +150% with beads in DBD and +30% with monoliths in NRP, regardless of loading amount or catalyst position. Further studies are needed to confirm whether this represents a true catalytic effect or results from plasma–metal–support interactions and to understand the influence of each preparation step on ammonia production. Standardizing catalyst preparation is essential for reproducibility and meaningful comparisons in plasma catalysis research.

Nomenclature

DBD Dielectric Barrier Discharge
NRP Nanosecond Repetitively Pulsed Discharge

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