# Exploring Regimes of Plasma Synthesis of Ammonia with Porous Silica Catalysts

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**Abstract:** Plasma catalytic ammonia synthesis promises decentralized production with a reduced CO2 footprint, but depends on intelligent catalyst design. Our experiments show that porous silica with and without metal can exhibit two regimes, a pore size dominated regime at higher power and an active metal site regime at mild conditions. To understand the mechanisms, we design two reactors that reproduce the packed bed plasma conditions, for in-situ operando access to gas composition, and for in-situ study of catalyst surface.

Keywords: plasma catalysis, ammonia synthesis, porous silica, packed bed reactor

#### 1. Introduction

Plasma catalytic synthesis of ammonia, coupled with the use of renewable energy sources, can enable decentralized production of ammonia with a reduced  $CO_2$ footprint [1] compared to the current industrial production. However, plasma synthesis has very high energy cost and high separation and output recycling costs due to low concentrations of NH<sub>3</sub> and unreacted H<sub>2</sub>, N<sub>2</sub>. To become viable plasma catalytic system needs specially designed catalysts combined with efficient reactors and carefully chosen plasma conditions that are based on thorough understanding of plasma catalyst interactions, an understanding that so far remains insufficient.

Oxides, such as SiO<sub>2</sub>, are low cost abundant materials that offer design flexibility for a wide range of catalysis applications [2]. Recent experimental results and DFT calculations [3] lead to the hypothesis that an optimal catalyst for plasma catalytic synthesis of ammonia synthesis delays the recombination of adsorbed hydrogen radicals into molecular hydrogen allowing them to bind instead to adsorbed nitrogen plasma generated species to form NH $\cdot$ . Solid oxides can facilitate hydrogen dissolution [4]. In addition, porous silica (ex., mesoporous SBA-15) offers high surface area for the surface reactions, has weak bonding with nitrogen [5], improves discharge stability, has high thermal and chemical stability, and offers a wide range of possible wall compositions.

#### 2. Results

To study plasma-assisted ammonia synthesis with porous silica catalyst we have employed optical emission spectroscopy (OES), Fourier transform infrared absorption spectroscopy (FTIR-AS), and electrical measurements to characterize selected plasma-catalytic packed bed dielectric barrier reactors (PB) [6, 7]. One type of packing tested was only mesoporous silica SBA-15 (7 nm pores) and another SBA-15 enriched with 10% wt. Ag, both operating in a 1:1 N<sub>2</sub> and H<sub>2</sub> gas mixture. At lower operating power, ~10 W, SBA-15-Ag had a ~20% higher yield of NH<sub>3</sub> suggesting that the presence of a metal catalyst improves NH<sub>3</sub> production under these plasma conditions. These results suggest that SBA-15 PB reactor operates in a plasma/surface dominated regime while SBA-15-Ag operated in a metal dominated regime. Further OES analysis showed a 10% lower rotational temperature, a higher vibrational excitation temperature and a higher electron density in SBA-15 PB reactor as compared to SBA-15-Ag at the same conditions. SBA-15 reactor also showed the presence of H\* and NH\*. The differences in plasma parameters for the two reactors at the same conditions also support the effect of surface composition on plasma conditions which in turn can influence the catalytic pathways. Therefore, we propose the possibility of two different regimes, one where the metal catalyst plays an important role, and one dominated by the mesoporous oxide. In practical terms, elimination of a metal catalyst may reduce the cost of plasma reactors. In fundamental terms, these results indicate deficiencies in the understanding of plasma-catalyst interaction.



Fig. 1. Cylindrical packed bed reactor with in-situ access to gas composition measurements. The optical path for FTIR-AS measurements is along the axis of the reactor. The inset shows the cross section of the reactor.

One of the obstacles to advance the understanding of plasma-catalyst interaction is the difficulties in diagnostics of the catalytic surface and plasma properties in situ and operando that are essential for possible detection of reaction intermediates and dynamic changes of the catalytic surface properties [8, 9]. This is particularly difficult in the case of a packed bed reactor where the discharge gap of <1 mm is packed with powder. Changing the discharge gap and/or the particle shape or size changes the discharge conditions and although such reactors can provide valuable insight into the basic mechanisms, the information obtained may not be transferrable to the commonly used PB reactors.

In this work we present new reactor designs that preserve the discharge parameters, so that plasma is ignited and sustained at the same voltage and operated at the same discharge power density as the reactor used for the results described above [6, 7]. The reactor has cylindrical geometry (Figure 1) with an optical path axially through the center of the reactor for the detection of the gas products in operando using FTIR-AS. The packed bed reactor region is an annular with a perforated center electrode so the gas products penetrate the center region. The reactor is suitable for scanning plasma conditions as seen for example from the changes in concentration recorded within one data collection time (approximately 2 minutes). The reactor also allows for simultaneous plasma OES and imaging. The reactor was tested for ammonia synthesis using porous silica of various porosities and morphologies. The main drawback of this system is relative inaccessibility to diagnostics of the catalyst surfaces. This has motivated us to design another version of this reactor specifically for the purposes of investigating the surface changes in the catalyst in situ and in operando.

The new reactors allow access to in situ and operando diagnostics of plasma assisted catalysis for packed bed reactors necessary to advance mechanistic understanding of plasma catalysis.

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