Ammonia synthesis: On the effect of adding a metal catalyst in a ferroelectric packed-bed plasma reactor

A. Gómez-Ramírez[1,2], P. Navascués[2], J. Garrido-García[2], M. Oliva-Ramírez[1,2], J. Cotrino[1,2], A. R. González-Elipe[2]

[1] *Departamento de Física Atómica, Molecular y Nuclear, Universidad de Sevilla, Avda. Reina Mercedes, E-41012 Seville, Spain*

[2] *Laboratory of Nanotechnology on Surfaces and Plasma. Instituto de Ciencia de Materiales de Sevilla (CSIC-Universidad de Sevilla), Avda. Américo Vespucio 49, E-41092 Seville, Spain*

Abstract: The incorporation of catalysts into packed-bed plasma reactors has been demonstrated to be a useful strategy to increase the performance of different plasma-driven chemical processes. In this work, we analyze the effect of a Ru-catalyst on the plasma-assisted ammonia synthesis, with the aim of determining the role of pure catalytic or plasma interactions during the process, which is a key issue to overcome the current energy efficiency limitations of the plasma-assisted ammonia synthesis.

Keywords: ammonia synthesis, nonthermal plasmas, plasma-catalysis, packed-bed reactors, ferroelectric barrier discharge, ruthenium catalyst.

1. Introduction

Current studies on ammonia synthesis by means of atmospheric pressure plasmas respond to the urgent need of developing less environmentally aggressive processes than the conventional Haber−Bosch catalytic reaction[1-3]. Different atmospheric plasma processes(e.g., gliding arcs or dielectric barrier discharges) and reactor designs[4-6] or the use of different kinds of moderator materials for packed-bed discharges (e.g., ferroelectrics instead of dielectrics)[7-9] have been proposed to overcome energy efficiency limitations. Many authors have tried to select an appropriated catalysts for its incorporation in packed-bed plasma reactors for the synthesis of ammonia. For example, G. Akay and K. Zhang studied the incorporation of a porous Ni-based catalyst into a packed-bed reactor moderated by glass and $BaTiO_3$ pellets, obtaining reaction yield values (i.e., molecular percentage of converted nitrogen) as high as 12%[9]. X. Tu and collaborators have recently studied the effect of incorporating a metal catalyst into $BaTiO_3$ pellets, obtaining energy efficiency values higher than 2 g NH_3/kWh when using nickel particles[10]. M. Carreon and coworkers have reported that porous materials such as zeolites seem to favor the ammonia synthesis into their pores[11-12], and similar results have been obtained by Y. Wang using a Ni catalyst on a mesoporous support[6]. However, there are not yet clear criteria for the choice of the best catalyst, mainly because its function under plasma interaction conditions may be different than its typical activity at high pressures and temperatures. With this purpose, we study the effect of incorporating a ruthenium (Ru) metal catalyst, one of the most widely used metal catalyst for the thermal and plasma-catalytic synthesis of ammonia, into a ferroelectric barrier.

2. Experimental

Herein we study the effect of incorporating a metal catalyst into a ferroelectric PZT barrier (5mm gap, pellet diameter 0.5-2mm), a reactor configuration that provides reaction yield values higher than those obtained with classic dielectrics even without the incorporation of a metal catalyst[7,8,13]. In concrete, the ammonia synthesis reaction has been carried out in a packed-bed reactor using three configurations of the packed bed: i) using pure PZT pellets as discharge moderator (designed as PZT configuration); ii) with these pellets covered by an Al_2O_3 coating (Al_2O_3/PZT configuration), and iii) with this coating containing ruthenium (Ru) nanoparticles (Ru-Al_2O_3/PZT configuration). The coating material were characterized by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Energy Dispersive X-Ray Spectroscopy (EDX), X-ray Photoelectron Spectrometry (XPS), and the nitrogen adsorption BET technique.

A N_2+H_2 mixture has been used as inlet gas. A total effective flow rate of 23 sccm (1:3 N_2:H_2 ratio) was kept constant during all the experiments. All the experiments have been carried out at atmospheric pressure and two different temperatures: ambient temperature and at a nominal temperature of 190ºC -measured at the reactor walls-. At ambient temperature, experiments have been performed in two ways: i) varying the voltage amplitude between 1.75 and 3 kV at a fixed frequency of 5 kHz, and ii) varying the frequency between 1 and 5 kHz at a fixed voltage of 2.5 kV. At 190ºC only mode i) was used applying a fixed voltage amplitude of 2.5 kV, while the frequency was varied between 1 and 3 kHz. The outlet gases were analyzed by mass spectrometry, and the reaction yield and energy efficiency were calculated.

This study has been complemented with the Optical Emission Spectroscopy (OES) analysis of the plasma discharge and Comsol Simulations of the electric field distribution in the packed-bed barrier.

3. Results and conclusions

The results obtained suggest that the incorporation of Ru nanoparticles provokes a negligible enhancement in reaction yield or in energy efficiency as compared to the PZT barrier, even working at 190ºC (this temperature defines a threshold for plasma-catalysis ammonia synthesis using Ru as catalyst). Our results support that, although ruthenium may contribute to ignite more intense plasmas by modifying the electric properties of the discharge it can be also detrimental for the ammonia synthesis through the promotion of undesired reactions, as the ammonia decomposition or hydrogen exchange processes. All these processes seem to hide possible catalytic effects induced by the ruthenium nanoparticles. It is also concluded that the synergy found when incorporating ruthenium to the PZT ferroelectric barrier reactor could be also obtained when using any kind of metal, instead of the high-cost catalyst usually employed for thermal catalysis.

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5. References

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