Low-pressure non-thermal plasma assisted heterogeneous catalysis: new insights on the reactor and the processing

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Abstract: this contribution reports on a low pressure, non-thermal plasma reactor designed to investigate the parameters influencing the plasma-assisted heterogeneous catalysis of ammonia. The system was designed in order to operate under different reactor pressure, gas flow, gas flow ratio and temperature. A set of experiments allowed to unveil the role played by the residence time and by the catalytic surface chemistry on the efficiency of the reaction.

Keywords: low-pressure, non-thermal, plasma, heterogeneous, catalysis.

1. Introduction

Low pressure non-thermal plasma assisted heterogeneous catalysis could provide a sustainable and economically viable alternative to a variety of currently adopted non-sustainable and/or highly expensive chemical processes, such as the synthesis of ammonia (NH_3) and the conversion of methane (CH_4) into carbon monoxide (CO) and hydrogen. [1,2] It can be implemented in radiofrequency reactors operated on renewable sources such as photovoltaic, [1] and exploit a set of physical phenomena to overcome the limitation imposed by the otherwise thermally-activated molecular dissociation and/or formation occurring on the catalytic surface in conventional catalytic processes, allowing for low temperature reactions with competitive conversion efficiency. Those physical phenomena include in-flight molecule-electron impact and electron- and ion-catalyst impact. While the former promotes in-flight molecules dissociation and vibronic excitations [3], the latter can promote the dissociation of the catalyst adsorbate by means of a multi-step energy transfer process called Dynamics Induced by Electronic Transition (DIET). [4] However, despite the potentialities of the plasma assisted heterogeneous catalysis have been theoretically predicted and experimentally confirmed, [1,2] more than twenty years of research on the topic have not been sufficient to fully understand the physical mechanisms underlying the process, and nowadays the scientific community is still debating about how the plasma and the catalyst interact with each other to promote the reactions. In particular, different reactor types, catalyst geometry and catalytic materials have been studied for different chemical processes, with promising results that are not easily comparable and thus do not allow a straightforward interpretation of the physical phenomena occurring in the process.

This contribution provides a systematic investigation of the NH_3 synthesis from N_2 and H_2 gases in a low pressure, non-thermal, capacitive plasma reactor with the aim to unveil the effect of the catalyst in the process and ultimately decouple the contribution to the gas conversion coming from the plasma and from the catalyst. The synthesis of NH_3 is currently based on the thermally-activated Haber-Bosch process, which operates at 450-600°C, has an efficiency around 15 % [5] and consumes 1-2 % of the world's energy, a large fraction of which is ascribed to the chemical reactions occurring inside the reactor and in particular to the dissociation of the N_2 molecules.[1] The implementation of an alternative sustainable process would thus significantly reduce the environmental impact that the Haber-Bosch is currently having on the environment. The heterogeneous catalysis in a non-thermal plasma reactor provides all the aforementioned additional physical phenomena that strongly promote the dissociation of the N_2 molecules (in-flight and on the catalytic surface) allowing for decent efficiency of ammonia synthesis (1-5 %) even at room temperature, [6] with reactors that can be operated on renewable energy sources.

2. Experimental

A non-thermal capacitive plasma reactor was designed to operate under different gas conditions, i.e. gases flow and ratios, plasma pressure and power, and temperature. A schematic of the reactor is shown in Fig. 1. It essentially consists of a one inch quartz tube installed inside a tubular furnace and three coaxial electrodes symmetrically arranged along the tube. The two outer electrodes are grounded, while the central one is driven by a 13.56 MHz radiofrequency power supply (Advanced Energy RFX 600A) in series with a T-type matching box (MFJ Versa Tuner V) to minimize the rejected power along the coaxial cables. The furnace (MTI Corporation

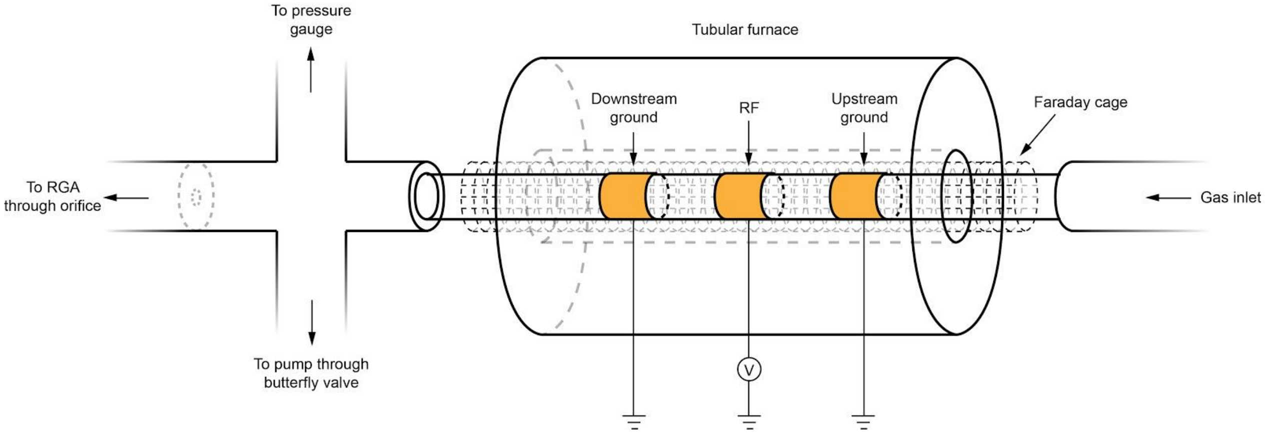

Fig. 1. Schematic of the reactor. The reactor consists of a one inch quartz tube and three electrodes arranged as shown in the figure. The system is assembled inside a tubular furnace, and an RGA is used to sample the gas downstream the reactor.

OTF-1200X) is a key-aspect of the system as it allows to perform temperature dependent studies between room temperature and 500 °C and thus to investigate the activation energy of the catalytic reaction. The catalysts implemented in this work are fine meshes of stainless steel and iron coated stainless steel wrapped in such a way to achieve a conical-like shape and installed in the reactor in the region comprised between the two grounded electrodes. The symmetric configuration of the electrodes allows studying the effect of the relative position between the catalyst and the electrodes, with the ultimate aim to provide insights on the spatial region where the ammonia is effectively produced and/or destroyed within the plasma region. The efficiency of ammonia synthesis is intended to be the efficiency of nitrogen conversion and is calculated according to the formula

$$\eta = \frac{p_{NH_3}}{p_{NH_3} + 2p_{N_2}}$$

where $p_{x<}$ is the partial pressure of the *x*-species. The p_x-s are measured by a Residual Gas Analyzer (RGA) (SRS RGA 300) mounted in a separate chamber that communicates with the reactor by means of a small orifice. The orifice samples the partial pressure downstream the reactor and allows to keep very different pressures between the reactor and the RGA. The partial pressures measured by the RGA are corrected to take into account for the atomic fragments of the various species. The pressure of the reactor is set by using a feed-backed butterfly valve. Upstream mass flows (mks) allow to control the gas flow rate of the injected species in the reactor. In order to assure better accuracy in the gas flow ratio, the latter is calculated by taking the ratio between the partial pressure of the gas sampled by the RGA at room temperature and under condition of no plasma. The set of experiments conducted in the framework of this project includes i) temperature dependent measurement of the efficiency of ammonia synthesis at constant flow rate (residence time), gas ratio, and reactor pressure, ii) power dependent measurement of the efficiency of ammonia synthesis as a function of the flow rate (residence time) at constant gas ratio, reactor pressure and temperature, and iii) surface chemistry dependent measurement of the efficiency of ammonia synthesis at constant flow rate (residence time), gas ratio, reactor pressure and temperature. The latter, in particular, is a study achieved by measuring the efficiency before and after depositing a layer of SiO_2 on the surface of the catalyst without

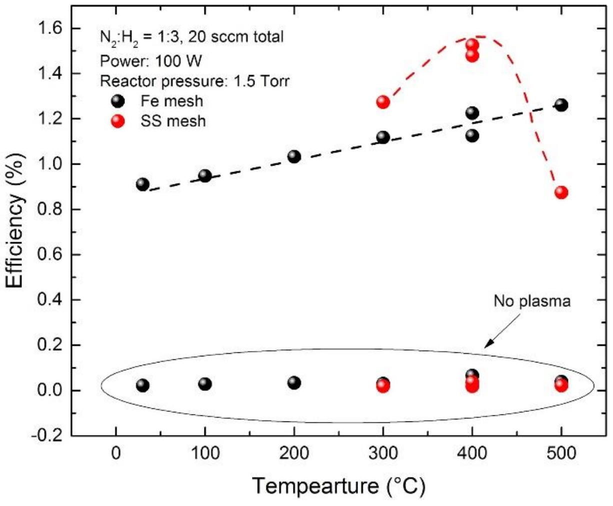

Fig. 2. Example of a temperature dependent measurement of the efficiency ammonia synthesis under condition of 100 W plasma, 1.5 Torr reactor pressure, 20 sccm total flow rate and N2:H2 ratio equal to 1:3.

opening the reactor or moving the catalyst relatively to the electrodes. A procedure to pre-condition the reactor was developed in order to minimize water contaminations that consists of a baking at 550°C under a 100 W argon plasma.

3. Results and discussion

The set of experiments conducted in the framework of this project reveals that the gas residence time, the surface chemistry of the catalyst, its shape and relative position with respect to the electrodes play a relevant role on the efficiency of ammonia synthesis. An example of a typical temperature dependent measurement of the ammonia synthesis efficiency is shown in Fig. 2 for the case of stainless steel and iron catalysts, under condition of 100 W plasma, 1.5 Torr reactor pressure, 20 sccm total flow rate and N_2:H_2 ratio equal to 1:3 (herein these conditions will be called "standard conditions"). The figure clearly shows that the plasma activates the catalytic process and the efficiency is found to depend on the temperature without any significant hysteretic effect, which excludes appreciable further modification (e.g. nanostructuration) of the catalytic surface during the measurements, after the cleaning procedure.

Different trends are observed for the case of the iron coated stainless steel mesh and the pristine stainless steel mesh. In Fig. 3 the efficiency of ammonia synthesis is plotted as a function of the power delivered to the plasma and of the flow rate (residence time) at constant reactor pressure and temperature. The figure reveals that some ammonia is produced in the plasma phase even without the necessity of a catalyst (the plasma itself acts as a catalyst for the reaction). However the efficiency is pretty low (approximately 0.5 % in standard conditions). On the other hand, when a catalyst is installed in the reactor, the efficiency of conversion increases significantly (up to approximately 2.5 % in standard conditions).

The figure clearly shows that the stainless steel and the iron coated stainless steel meshes do not provide appreciable differences in the conversion efficiency. The figure also shows that the lower is the residence time (the higher the flow rate), the higher is the efficiency of conversion, and that there is a power value at which the production of ammonia is maximized. Interestingly, the power that maximizes the efficiency on conversion shifts towards higher values when increasing the flow rate (decreasing the residence time). This evidence goes in the direction that the ammonia molecules are destroyed within the plasma. The phenomenon is observed both with and without a catalyst. The normalized efficiency of ammonia synthesis as a function of power and catalytic surface chemistry is shown in Fig. 4 for the case of the iron coated stainless steel mesh. The efficiency largely drops after passivating the catalytic surface with a film of SiO_2 deposited by chemical vapor deposition. This result

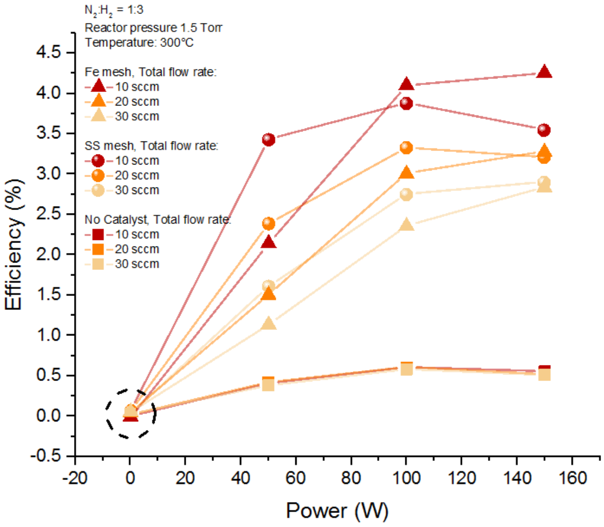

Fig. 3. Efficiency of ammonia synthesis as a function of power delivered to the plasma, total flow rate and catalytic surface.

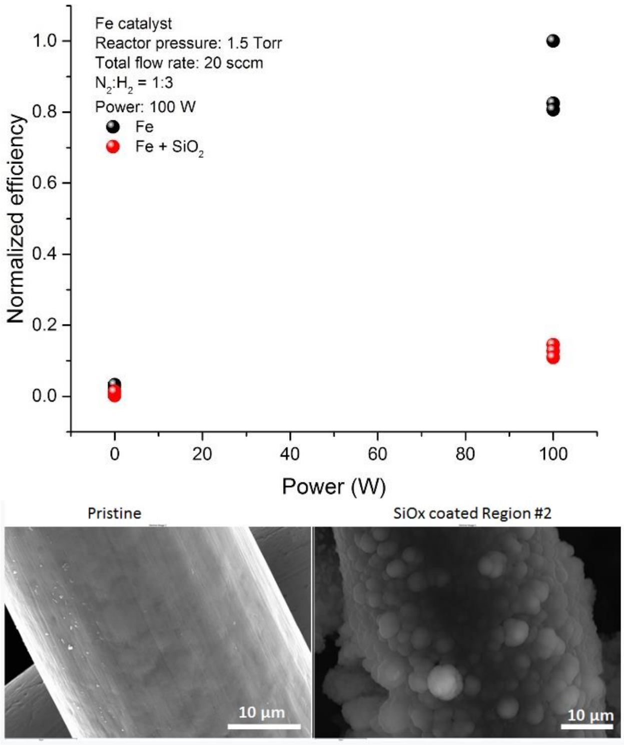

Fig. 4. Efficiency of ammonia synthesis as a function of the power delivered to the plasma and of the catalytic surface chemistry (top). Scanning electron microscopy images of the pristine and coated catalytic surface (bottom).

confirms the fundamental role played by the catalytic surface in the reaction.

The investigation has succeeded in developing a protocol to isolate the different phenomena contributing to the activity of plasma-catalytic reactor, i.e. gas-phase plasma chemistry vs. plasma-activated surface chemistry. Future studies will build on these results to investigate other relevant chemistries, such as plasma-activated hydrocarbon reforming.

3. References

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