Experimental strategies to increase ammonia yield in plasma catalysis over LTA and BEA zeolites

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Abstract

Herein we demonstrate the synthesis of ammonia via atmospheric DBD plasma discharge over LTA and BEA zeolites. The presence of the zeolite in the DBD reactor promoted the ammonia formation at low temperature. The zeolites dielectric constant and pore size greatly influenced the ammonia yields. Ammonia yields of 5.31% for zeolite beta and 5.22% for zeolite 5A were observed, which are at least 4 times higher than the yield obtained in the absence of the zeolites.

1. Introduction

Ammonia is the second largest produced chemical at industrial scale. Currently, the Haber-Bosch process is used to produce this chemical at large scale. The Haber-Bosch process considered one of the ground-breaking top 10 inventions of the modern chemistry, has helped to bridge the gap between food supply and its demand making a positive impact in the food market.

The ammonia industry consumes more than 2% of the global electricity and accounts for 1%–2% of the total greenhouse gas emissions [1]. The use of ammonia goes beyond is application as source for fertilizers. A major use of ammonia is its direct application in fuels and as hydrogen storage. The hydrogen storage capacity of ammonia is 40% greater than methanol. In direct fuel application, ammonia has an octane rating of 120 whereas for gasoline it is 86–93 though the energy density is almost half. As a result, vehicles running on pure ammonia [1], as well as gasoline-ammonia mixture [2], are being conceptualized and prototyped. Using pure ammonia has the advantage of reducing the use of fossil fuels, which take time to replenish, whereas ammonia can be manufactured synthetically.

Currently, non-thermal plasma catalytic synthesis of ammonia is emerging as a promising sustainable route to produce this chemical [3]. This is due to the presence of high energy electrons that are generated in this type of plasmas, which can excite ground state gas molecules that can react in the surface of selected materials at lower temperatures and pressures as compared to thermal catalysis. Moreover, plasma reactors have potential to be powered by renewable electricity sources, such as solar and wind. This is due to the intermittent nature of these sources that can be adapted successfully to plasma reactors, which can be easily switched on/off [4]. Several catalysts have been paired with DBD for ammonia production (table S1 is available online at stacks.iop.org/IOPSN/1/024801/mmedia).

Microporous crystalline aluminosilicate molecular sieves (zeolites) displaying unimodal micropores are appealing materials to be used as catalysts in ammonia synthesis plasma due to their remarkable stability [5]. Furthermore, the local electronegativity differences at the surface of zeolites may lead to electrostatic interactions with diverse gas molecules [6]. These interactions coupled with plasma may lead to distinctive catalytic performance.
Herein, we report experimental strategies to increase the ammonia production (yields) during the plasma catalytic synthesis of ammonia when employing three commercially available zeolites: 5A, and 4A (Sigma Aldrich), and beta (ACS Material LLC). Zeolite 5A, and 4A displaying LTA topology have unimodal pore apertures of \( \sim 0.5 \) nm, and 0.4 nm respectively. Zeolite beta with BEA topology consists of large pores of \( \sim 0.76 \) nm, and limiting pores of \( \sim 0.55 \) nm.

2. Experimental section

Figure S1 shows the experimental set-up employed for this study. Details of this set-up and the rational to select the total flow rate to the reactor as 25 sscm are given in the supporting information. The experiments were first carried out without any catalyst. The reactions repeated twice were run at \( \sim 94^\circ \text{C} \) (with fan) and atmospheric pressure. To understand the catalytic effect of the selected zeolites and differentiate it from the only plasma effect, reactions were run at different flow ratios with no catalyst loaded. The flow rates were varied from nitrogen-rich to hydrogen-rich content. The ammonia yield (%) and ammonia synthesis rate are shown in figure 1. The ammonia yield (%) and synthesis rate increased with decreasing nitrogen content. The feed composition that resulted in the highest ammonia yield (%) was the 1:6 nitrogen to hydrogen (\( \text{N}_2: \text{H}_2 \)) with a yield of \( \sim 1.22\% \), and synthesis rate of \( 0.54 \text{ μmol min}^{-1} \).

2.1. Plasma-catalytic ammonia synthesis: the zeolite effect

To evaluate the effect of the zeolites in the reaction, initially we carried out the plasma ammonia synthesis using two different zeolites: 5A and beta. We employed a constant catalyst weight of 0.1 g. The results from these experiments are shown in figure 2. The highest ammonia yields for both zeolites were observed at 1:2 (\( \text{N}_2: \text{H}_2 \)) ratio. These yields were 5.31\% for zeolite beta and 5.22\% for zeolite 5A. The similarity in % yield for zeolite 5A and beta can be partially attributed to the dielectric constants for these two zeolites. A material is classified as dielectric if it has the ability to store energy when an external electric field is applied. The complex electrical properties of zeolites have been the subject of intense studies over decades. However, their dielectric properties and their correlation with their catalytic activity remains unknown, especially for plasma processes.

The dielectric constants for both zeolites are very similar. The dielectric constant for 5A is \( \sim 22 \) [7], while the dielectric constant for zeolite beta is \( \sim 23 \) [8]. It is well known that the dielectric constant influences the electric field, which affects the conversion. However, due to the complexity of the plasma-catalysis synergism, the dielectric constant may be only one of the parameters affecting the catalytic performance. In figure 2, we have compared the catalytic performance (yields) of two common catalytic supports: SiO\(_2\) and Al\(_2\)O\(_3\). The yields for these two supports are considerably lower than those of the zeolites. The difference in % yield for SiO\(_2\) and Al\(_2\)O\(_3\) can be also partially attributed to the difference in the dielectric constants for these two packing materials. The dielectric constant for alumina is 9.1 whereas the dielectric constant for silica is 3.9 [9]. Despite these
observations, it should be noted that there is still no agreement among the plasma scientific community about the dielectric constant effect. For instance, the C2F6 plasma decomposition has been reported to be independent of the material dielectric constant \[10\]. However, the benzene removal efficiency in plasma increases up to a dielectric constant of 1100 \[11\], suggesting that the effect of the dielectric constant might vary with the gas composition. It has been recently reported that supports with lower acidity favour the ammonia production \[12–14\]. This is in agreement with our results, since alumina gives always higher percentage ammonia yields that silica which is considered an inert support \[15\].

The specific surface areas from the Chemical providers are ∼500, ∼560, and ∼570 m² g⁻¹ for zeolite beta, 4A, and 5A respectively. Zeolite 4A and 5A having very similar surface areas show different ammonia yields (figure 4(b)) suggesting that surface area does not have an effect in ammonia yield. In the case of zeolite 5A and beta, they have different surface areas, and both show similar ammonia yield, again suggesting that surface area does not have a significant effect in ammonia yield. Pore size and dielectric constant are the key parameters affecting ammonia yields. Moreover, previous reports have described that surface area and porosity do not seem to be crucial for plasma formation citing α-Al₂O₃ and γ-Al₂O₃ (with similar surface properties, but differing levels of acidity) demonstrated almost identical ammonia formation despite an almost 100-fold different surface area \[12\].

### 2.2. Emission spectroscopy analysis

Optical emission spectra of the DBD N₂ and H₂ species were measured to get a better understanding on the role of the gas phase species in the plasma synthesis of ammonia. The collected emission spectra for the feed ratio 1:2 N₂:H₂ when using fan is shown in figure 3 for only plasma reaction, 5A, beta and 4A zeolites. Zeolite 4A is analogous to zeolite 5A, with the difference that it has an average pore size of ∼0.4 nm. This latest was added to this analysis since to better understand the effect of pore size. Interestingly, the identification of N atomic species \((2p^23p \rightarrow 2p^23s)\) and Hα Balmer atomic species suggest the dissociation of N₂ and H₂ by electron impact. This has been reported previously for ammonia synthesis in a DBD reactor \[13\]. Interestingly, in all the collected emission spectrum zeolite 5A and zeolite beta showed higher intensity peaks as compared to only plasma and zeolite 4A. The higher intensity of the peaks suggests plasma-catalyst synergism. Moreover, the intensity of the peaks for the zeolites with high values of ammonia yield is also higher compared to the lower yield zeolite (4A). This observation points out to a correlation of the plasma excited species in the gas phase to the ammonia yield.

We employed the emission spectra data to find a possible correlation between the plasma activated species and the ammonia yield. Figure 4 shows the relative intensity of the Hα, N₂(SPS), N₂⁺(FNS), and N⁺(S) atomic peaks, which is defined as the ratio of the Hα, N₂(SPS), N₂⁺(FNS), and N⁺(S) peaks intensity in the presence and absence of the catalyst at 1:2 N₂:H₂ ratio. In other words, the relative intensity is an indication of the relative gas-
phase concentration of these species when a catalyst is used to promote the reaction. For the case of hydrogen, it is expected to be primarily reduced by atomic H adsorption on the catalyst surface and dissolution in the bulk. Interestingly, the H$_\alpha$ concentration directly correlates with ammonia yield (figure 4(a)). It should be noted that when using a rich hydrogen environment i.e., 1:6 N$_2$:H$_2$ ratio the yields are lower compared to 1:2 N$_2$:H$_2$ ratio, suggesting there is an ideal hydrogen content threshold. Moreover, there must be a considerable hydrogen coverage in the surface and dissolution in the bulk. This can saturate the potential sites available for nitrogen species that can react to produce ammonia, explaining the lower yield for rich hydrogen environment. On the other hand, figure 4(b) shows the importance of the nitrogen species in the ammonia % yield. It can be observed that the Natomic, N$_2^+$ (FNS), N$_2$(SPS) species directly correlate with the ammonia % yield. However, there are the plasma activated nitrogen species N$_2^+$ (FNS) and N$_2$(SPS) in the gas phase that play a main role.

Figure 3. Emission spectra collected during plasma catalytic ammonia synthesis at 1:2 N$_2$:H$_2$ ratio when employing (a)–(e) only plasma, zeolite 5A, zeolite 4A and zeolite beta, and (f) summary of important plasma species.
While the applied voltage was maintained constant for all the reactions (30 kV), it should be noted that the discharge power for the different catalysts despite not being the same it was found to be in the range between 8–12 W. In addition, we have conducted the electrical characterization multiple times (4 times per catalyst per condition) in order to verify the correct discharge power at particular N₂ & H₂ feed ratio. While it should be recognized that the comparison of spectral intensity can be debatable, it can serve to shed some light to the underlying process, and it has been employed by other researchers in plasma catalytic ammonia synthesis[13] when using a DBD. Finally it should be noted that the discharge power for the different feed ratios of N₂ & H₂ constantly observed a linear increase with respect to the N₂* (337 nm) peak, followed by a peak nitrogen concentration observed at (3:1) (N₂:H₂) and a decline at (1:6) (N₂:H₂).

2.3. The temperature and the pore size effect

Figure 5 shows the effect of catalyst pore size on ammonia yield at different N₂:H₂ ratios. From this figure two main observations can be made: First, at the same N₂:H₂ ratios, and same temperatures, the ammonia yields were similar for zeolites 5A and beta. As mentioned previously, the similar dielectric constants for these two zeolites may be (in part) responsible for this behavior. Interestingly, while both zeolites have different large pore apertures, they have similar diffusing pore apertures, or limiting pore apertures of ~0.5 nm (5A) and ~0.55 nm (beta). This also contributes to the similar observed ammonia yields. To test this hypothesis, we evaluated another zeolite with smaller pore aperture (zeolite 4A, pore size ~0.4 nm). This zeolite shows consistently lower ammonia yields. Second, at the same flow rate, the ammonia yields increased as temperature decreased. This can be possibly explained from two different perspectives. The first one, may be due to the possible ammonia decomposition which can occur most likely at high temperature (figure S4). From another perspective, one can compare the non-thermal plasma pathway versus the thermal catalytic pathway in terms of the nitrogen activation pathways (recalling nitrogen species play a main role).

In thermal heterogeneous catalysis the dissociative adsorption step on the catalyst surface can be described as:

\[
N_2 + 2^* \leftrightarrow 2N^*
\]

where " is the active site and N" is the nitrogen adsorbed on the active site.

In non-thermal plasma catalysis, it is the electron collision that produces ‘plasma activated’ nitrogen species that subsequently dissociate on the catalysts surface. Being the role of plasma to lower the activation energy for this step. This effect has been observed in other plasma mediated processes [16].

\[
N_2 + e^- \rightarrow N^+(\text{plasma activated}) + e^-
\]

If the rate of the thermal dissociative adsorption on the catalyst surface is faster that the rate of production of ‘plasma activated’ nitrogen species, then the use of plasma is not advantageous. And it is at high average bulk temperatures that the thermal dissociative adsorption of nitrogen is favored on most of the catalytic surfaces. On the other hand, at lower temperatures the production of ‘plasma activated’ nitrogen species can be favored as observed also in our UV–vis spectra collected leading to high ammonia yields.
3. Conclusion

In summary, we demonstrate the synergism between plasma and LTA and BEA zeolites for ammonia synthesis in an atmospheric DBD plasma discharge. The presence of the zeolites in the DBD reactor results in an enhancement of the ammonia yield at low average bulk temperature. At lower temperature the production of ‘plasma activated’ nitrogen species is favored leading to higher ammonia yields.

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All data that support the findings of this study are included within the article (and any supplementary information files).

Data availability statement

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