



Green Hydrogen Production via Low Thermal NH_3 Splitting Over Non-Metallic Biochar Catalysts

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Abstract. Hydrogen fuel is one of the most ecological. However, its storage and transport still pose a challenge to the modern industry. This paper presents the use of ammonia as a liquid hydrogen carrier. It has been proven that it is possible to obtain green hydrogen in the splitting process conducted in non-thermal plasma conditions on carbon catalysts. Additionally, it has been shown that the process is almost 100% efficient and has very high selectivity. Another advantage of the method is the lack of need to use environmentally toxic metals.

Keywords: ammonia splitting, carbon catalyst, green hydrogen.

1 Introduction

The use of hydrogen, the only fuel that does not destroy the atmosphere, is key to decarbonizing the energy sector in the future. Due to the difficulties in storage and transport, significant attention has been paid to liquid hydrogen carriers, both organic and inorganic. Ammonia is one of the most important energy stores due to its ability to easily transport and decompose into nitrogen and hydrogen at the destination. [1] Additionally, ammonia is already transported worldwide because of its use in the chemical and fertilizer industries. Surpluses could then be used to produce hydrogen fuel.[2]

A commonly known and used method is the thermal decomposition of ammonia. This is an endothermic reaction, the reverse of the Haber-Bosch synthesis with an enthalpy of 92 kJ/mol,[3] which requires the use of a catalyst to be carried out efficiently and cost-effectively. The most commonly used catalysts are iron, ruthenium, and cobalt. [4-6] Unfortunately, metals are expensive, especially noble ones, and easily accumulate in the environment, causing its degradation. They are also the cause of many diseases in humans.[7] Therefore, thermal decomposition is very unfavorable from an ecological and economic point of view, especially due to the huge energy consumption during the process. A better method is decomposing ammonia under non-thermal plasma (NTP) conditions, which is innovative and much more efficient. Energy consumption is much lower than in the case of using high temperatures. An important advantage of plasma is the ability to turn the process on and off easily.[8]

Combination of using NTP with catalysis allows to achieve much better results; there are many examples describing the application of metals and their oxides as catalysts in ammonia splitting. Nevertheless, molecules adsorbed on metal active sites often block them, causing catalyst deactivation. This problem is not observed in the case of using

carbons, and our previous work proved the possibility of obtaining green hydrogen by using carbon catalysts. It is also possible to achieve almost 100% conversion of NH₃ by using carbon catalysts. [9]

This study was conducted using biochar derived from waste biomass. This approach ensures the secondary use of waste and, consequently, reduces raw materials consumption. The research focused on testing the influence of pressure, biochar origin, and plasma power on conversion efficiency and selectivity. Another important parameter was also the resistance of catalysts to process conditions.

2 Materials and methods

2.1 Materials characterization

Biochars used in the research come from the carbonization of waste biomass of the following origins: oat (O-1), sunflower (SF-1), and pine (P-1). Carbons were characterized with Raman spectroscopy. The spectra were measured with the Senterra micro-Raman (Bruker Optiks, Billerica, MA, USA) spectrometers. The spectral parameters were as follows: laser power, 2 mW at 532 nm; an objective 20× was used. The presence of acidic and basic functional groups on the surface of biochars was determined using the Boehm method.

2.2 Plasma-Assisted Catalytic NH₃ Conversion Investigations

The IR spectroscopic studies were carried out in a vacuum cell described previously [9], and plugged into the vacuum line. The composition of the gas phase in contact with the catalysts was also monitored by Mattson Genesis II FTIR spectrophotometer.

3 Results and discussion

Carbon labeled O-1 has the highest concentration of acidic groups on its surface. In turn the most basic is P-1. SF-1 carbon has a large amount of both acidic and basic functional groups.(Tab.1) They are really important in this process because they constitute the adsorption active sites. Ammonia is alkaline and therefore adsorbs well on acidic centers. However, these basic sites are also needed because they are the place where dissociated hydrogen is adsorbed and then recombined.[10]

Table 1. Surface acid-base characteristics of tested biochars.

Biochar	Acidic groups [mmol/g]	Basic groups [mmol/g]
O-1	0.98	0.5
SF-1	0.31	0.72
P-1	0.18	1.12

Figure 1 shows the gas-phase FTIR spectra before and after the ammonia conversion process under NTP conditions at 500 mBa pressure over the tested biochars. A significant decrease in the intensity of the bands at 900 cm^{-1} and 1624 cm^{-1} indicates the loss of ammonia. The conversion efficiency increases with increasing plasma power, which is clearly visible in the right panel of Figure 1. Differences between the efficiency of the processes catalyzed by individual biochars were also observed. They are most visible at the low plasma power range. The reason for the differences is most likely the differences in the nature and type of functional groups on the surface of the materials. The best results were observed in the case of the SF-1 sample, which has a large number of acidic active sites on which ammonia is adsorbed. Additionally, the surface is also rich in basic sites, which enable the adsorption and recombination of hydrogen dissociated from the NH_3 molecule.^[10] The results below show that it is possible to achieve almost 100% ammonia conversion using undoped carbon as a catalyst. This eliminates the need for toxic and/or expensive metals.

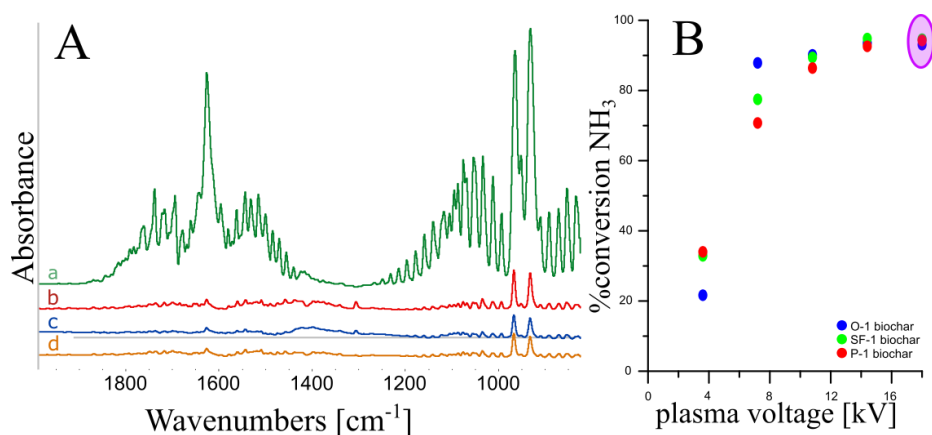


Fig. 1. . A: FTIR spectra of the gas phase (a) before and (b-d) after the NH_3 splitting process under pressure of 500mBa, over tested carbons: (b) O-1 (c) SF-1, (d) P-1. B: quantitative results of catalytic conversion of tested systems.

The next step of the research was testing how pressure influences the NH_3 conversion. The same process was conducted using four different pressure conditions. SF-1 carbon was used as the catalyst because it showed the best catalytic activity in previous tests. The biggest differences in conversion efficiency were observed at low plasma voltage, it is clearly visible that higher pressure allows better conversion. Nevertheless, using high-power plasma, the process occurs with almost 100% conversion regardless of pressure.

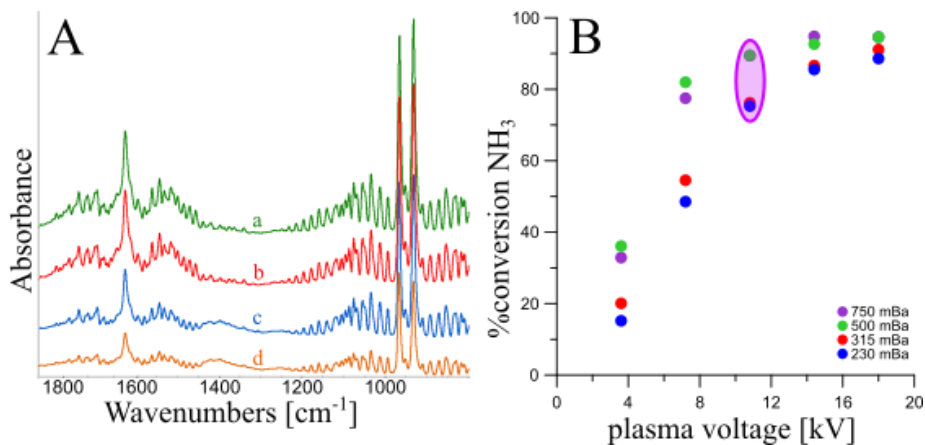


Fig. 2. . A: FTIR spectra of the gas phase after the NH₃ splitting process under: (a) 750 mBa, (b) 500 mBa, (c) 315 mBa, and (d) 230 mBa, over SF-1; B: catalytic conversion of tested systems.

The selectivity of hydrogen production is very high, but there are two intermediate products— methane and ethyne. Their formation is easily controlled by modifying the process parameters. As one can see in Figure 3, it depends on the pressure and plasma voltage, and selectivity decreases with the increase in these parameters. It can also be seen that increasing voltage has a much stronger effect than increasing pressure. Only a small amount of acetylene is present when the process is carried out at low power. No other carbon by-products are observed. When the voltage is increased, methane and ethyne are observed, which are responsible for the bands at positions 3000 and 720 cm⁻¹.

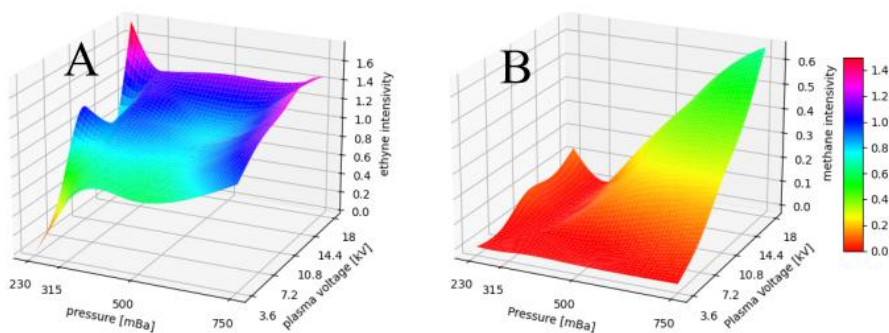


Fig. 3. The influence of pressure and plasma voltage on the ethyne (A) and methane (B) formation.

To prove that these materials are resistant to NTP conditions, a series of spectroscopic analyses were performed. The catalysts were tested before and after use. The Raman spectra (Fig. 4) show typical features of graphitized carbon. The G band at 1593 cm^{-1} has a high intensity compared to the D bands at 1544 , 1369 and 1219 cm^{-1} . After the catalytic process, the mode positions do not change, but a slight increase in the intensity of the D bands is visible. Before the trial, the I_G to I_D ratio was 1.50, while after it decreased to 1.26. This means an increase in amorphousness, indicating a subtle degradation of the sample. It is also worth mentioning that the RS spectra are very similar for all tested samples.

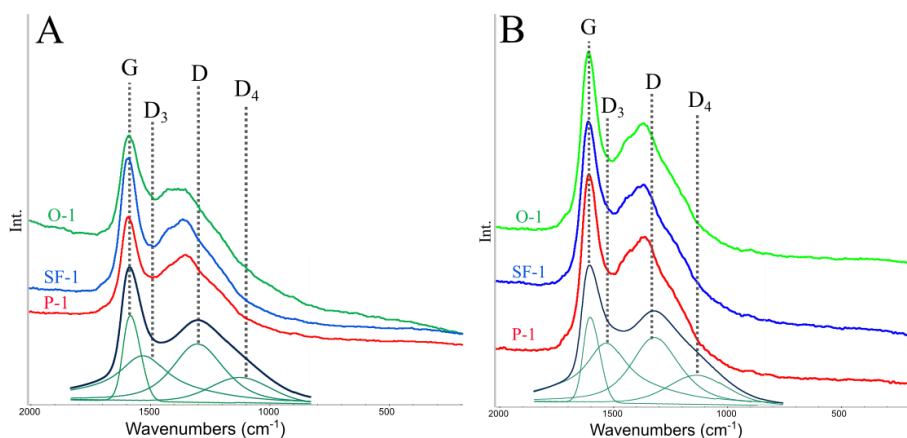


Fig. 4. A: Raman spectra of biochars before the ammonia splitting process. B: Raman spectra of biochars after the ammonia splitting process.

4 Conclusions

The results presented in this work proved the possibility of efficient NH_3 splitting under NTP conditions without using metals. The use of biochar made it possible to achieve almost 100% conversion. Additionally, it turned out that the hydrogen obtained was green.

It has also been proven that the catalysts are stable and undergo little change under process conditions. Their resistance to NTP conditions allows for longer use of the material and, consequently, lower consumption of raw materials.

Non-thermal plasma is the medium supporting the process, and easy controllability and appropriate manipulation of pressure conditions and applied voltage allow for obtaining optimal conditions and the best possible efficiency and selectivity.

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