Radiofrequency Plasma Synthesis of Ammonia over Ni-MOF-74

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Herein, we demonstrate a synergistic approach consisting on radiofrequency plasma to synthesize ammonia in the presence of Ni-MOF-74 as catalyst. The Ni-MOF displayed higher ammonia yields as compared to the pure Ni metal. Specifically, ammonia yields as high as 0.23 g-NH₃ (kWh-g-catalyst)⁻¹ and energy cost of 265 MJ mol⁻¹ over Ni-MOF were observed. The enhanced catalytic activity of the Ni-MOF in the presence of plasma was attributed to the presence of pores that improved mass transfer of guest and product molecules during reaction, the presence of open Ni metal sites, and lower surface hydrogen re-combination. Furthermore, the ammonia energy
yield of our plasma-Ni MOF catalyst is superior to those of the state-of-the-art RF plasma catalytic systems.

INTRODUCTION

Ammonia, a chemical discovered over 100 years ago has found its way into every aspect of human life. At some stage in the food, fertilizer, textile, cosmetic and chemical industry ammonia has been used. Besides such heavy use in various industries, ammonia is found in regular household as a water treatment and cleaning agent. Ammonium nitrate, ammonium phosphate, pigments, urea, industrial solvents and coolants are a few compounds manufactured from ammonia. Recently, ammonia has gained attention as fuel and a safer hydrogen storage alternative due to its high hydrogen density as compared to metal hydrides.1

The Haber-Bosch process is the benchmark technology for ammonia production.2 Typically, this is an energy intensive process which conventionally operates at a pressure of 150-250 bar and temperature of 400-500 °C in the presence of an iron-based catalyst.3 The anticipated 2018 ammonia production is projected to be 186 million metric tonnes.4 A chemical used at such large scale also accounts to a share of more than 1% of global electricity consumption5 as well as 2-3% of total greenhouse gas emissions.6 Most of the energy in the Haber-Bosch process is spent in excitation and breakage of the triple nitrogen bond, the rate limiting step.7 Due to the thermodynamic feasibility of the process, a maximum of 15 % yield can be obtained. A constant recycle of the unreacted product is required to make the process economical.8 In principle, this process can be made less energy intensive by (a) employing a highly active catalyst and/or (b) aiding the process at low temperature.
Plasma, the fourth state of matter where the molecules or atoms exist as excited species and ions can help to dissociate the strong triple nitrogen bond. In the past few decades, non-thermal plasma technology has been used for various gas-phase chemical synthesis such as ozone,\textsuperscript{9} VOC removal,\textsuperscript{10} NO\textsubscript{x} treatment,\textsuperscript{11} among others. Furthermore, various plasmas such as dielectric barrier,\textsuperscript{12-17} cascading arc,\textsuperscript{18} microwave\textsuperscript{19-20} and radiofrequency discharge\textsuperscript{21} have been used for ammonia synthesis. Most of these reports are either non-catalytic or employ a metal loaded on a porous support such as alumina or silica.\textsuperscript{22} The metal acts as the active phase, while the support material is usually a dielectric, not having much effect on the yield of ammonia. In particular, Nickel has been used as an active metal for the synthesis of ammonia. For instance, Mizushima et al. employed a Ni-loaded alumina membrane for ammonia synthesis in a Dielectric Barrier Discharge (DBD) reactor.\textsuperscript{23} In general, the activity of Ni was better than Fe which is a traditional catalyst for ammonia synthesis. In this report, it was proposed that Ni adsorbed the hydrogen which then reacted with nitrogen on the alumina support membrane.\textsuperscript{23} Akay and Zhang employed Ni/SiO\textsubscript{2} filled in BaTiO\textsubscript{3} cavities as catalytic promoters for ammonia synthesis in a DBD reactor. The energy cost was decreased about 20% with this catalyst. However, if the mass of catalyst was increased above 5 wt\% the energy cost increased.\textsuperscript{24} This can be due to decrease in the mass or void volume of dielectric material required to sustain the plasma. A potential way to alleviate this issue is employing high surface area catalysts. In this respect, Metal organic frameworks (MOFs) combine highly desirable properties that make them ideal candidates for diverse catalytic applications,\textsuperscript{25} such as uniform crystallinity, microporosity high surface area,\textsuperscript{26} and high thermal and chemical stability.\textsuperscript{27-28} In principle, the open and unsaturated metal cations or metal-based-clusters can act as the catalytic active species, and the ordered microporous crystalline structure can serve as the pathway for guest and product molecules to effectively diffuse with enhanced
mass transfer.\textsuperscript{29-31} Besides plasma catalysis, electrochemical reduction has also gained attention for the reduction of nitrogen to ammonia at ambient conditions. Liu et al. in their review lists the use of Co and Mo catalysts, which are shown to have high potential for ammonia synthesis.\textsuperscript{32} The catalysts mediate the reaction by breaking the nitrogen triple bond.\textsuperscript{33} These results were also corroborated computationally by Martirez et al.\textsuperscript{33} and experimentally by Tusji et al.\textsuperscript{34} Yan’s group currently working on electrochemical synthesis of ammonia employed nanomaterials such as PdCu nanocluster on Graphene,\textsuperscript{35} ceria-reduced graphene oxide hybrid,\textsuperscript{36} Au nanoclusters on titania\textsuperscript{37} and Au nanorods as catalysts.\textsuperscript{38} Ammonia as well as hydrazine evolved as products. The peak ammonia yield of 21.3 $\mu$g-NH$_3$ h$^{-1}$ mg$_{\text{cat}}$$^{-1}$ was obtained with a Faradaic efficiency of $\sim$10\%.\textsuperscript{37} The alternative pathway to electrocatlaytic reduction was elucidated using DFT while Au nanoclusters were used as catalysts. Interestingly, the pathway changed with the plane orientations of the Au catalysts. Au(310) catalyzed reaction was reported to have lower activation energy as compared to Au(210) catalyzed nitrogen reduction reaction.\textsuperscript{38}

Herein we demonstrate the use of a Nickel based MOF (Ni-MOF-74) as catalyst for the synthesis of ammonia via non thermal plasma catalysis. In principle, the excited formed plasma species may interact with the Ni open metal sites, and MOF pores may be beneficial for enhanced mass transfer leading to improved ammonia yields.

**EXPERIMENTAL SECTION**

**Synthesis of Ni-MOF-74**

Ni-MOF-74 consists of nickel (II) oxide chains connected by 2,5-dihydroxyterephthalte linkers, displaying one-dimensional parallel hexagonal channels with pore size area of 1.03$\times$0.55 nm$^2$.\textsuperscript{39-42} The nickel oxide chains form a three-dimensional hexagonal packing of helical O5Ni, where 5
oxygen atoms are from the terephthalic and hydroxy group on the ligand and one free-site atom that was originally occupied by a solvent or water molecule, resulting in an activated stable structure with open metal sites providing binding sites for guest gas molecules.$^{40-43}$

The synthesis approach to prepare Ni-MOF-74 was modified from a previous report described elsewhere.$^{39}$ In a typical synthesis, a 1:1:1 (v/v/v) mixture of 10.5 mL dimethylformamide (DMF, Acros, 99.9%), 10.5 mL ethanol (Fisher, 99.99%), and 10.5 mL DI water was placed in one beaker to form the mixed solvent solution. 1.503 g of nickel (II) nitrate hexahydrate (Sigma-Aldrich, ≥97%) and 0.502 g of 2,5-dihydroxyterephthalic acid (H$_4$DHTP, Sigma-Aldrich, 98%) were placed in another beaker. Then the nickel source and the ligand H$_4$DHTP were added to the solvent mixture. The solution was dissolved using a magnetic stirrer until the ligand and the nickel source were completely dissolved. The clear solution was transferred to a 45 mL Teflon lined autoclave (General Acid Digestion Vessel 4744, Parr Instrument). The Ni-MOF-74 crystals synthesis was carried out in a conventional oven at 150 °C for 24 h with heating and cooling rate of 10 °C min$^{-1}$ and 0.1°C min$^{-1}$ respectively. After the autoclave cooled down to room temperature, the clear portion of the solvent was decanted from the solution, replaced by methanol, and centrifuged at 4000 rpm for 5 minutes so that the crystals could be collected. Then the collected crystals were washed with methanol and centrifuged and collected two or three additional times. The resulting crystals were dried under vacuum at 250 °C for 5 h.

**Catalyst Characterization**

Ni-MOF-74 crystals were characterized with X-ray diffraction (PXRD) using a Siemens Kristalloflex 810 diffractometer at 30 kV and 25 mA with Cu Kα1 radiation ($\lambda=1.54059$ Å). A Micromeritics ASAP 2020 automated system was used to measure the sample’s Brunauer–Emmett–Teller surface areas (BET) by N$_2$ physisorption. Scanning electron microscope (SEM,
JEOL JSM-7000F) was used to inspect the morphology of the crystals. The Temperature Programmed Desorption experiments were performed on a Perkin Elmer Pyris I Thermogravimetric Analyzer. The sample was degassed at 150 °C overnight to remove any molecules trapped on the pores. Ammonia was adsorbed on Ni-MOF-74 after degassing. The sample was then heated from 50 °C to 500 °C with a heating ramp of 5 °C/min.

**Plasma Ammonia Synthesis Experiments**

The experiments were performed in an in-house built plasma reactor (Figure S1). The reaction was conducted by introducing nitrogen (Praxair, 99%) and hydrogen (Praxair, 99.99%) at a 1:4 N\textsubscript{2}:H\textsubscript{2} ratio to the reaction chamber using mass flow controllers. The nitrogen and hydrogen flow rates were 4 and 16 sccm, respectively. The plasma was ignited using an RF Power Supply with a Matching Network from Seren IPS, Inc. The vacuum pressure in the chamber is 0.3 torr with N\textsubscript{2} and H\textsubscript{2} flow. Ni-MOF and for comparison Ni metal were used as catalysts. The catalysts were loaded into soda-lime glass pipette plugged with glass wool (Figure S2 and S3). The mass of each catalyst was 0.2 g. The reactor was uniquely designed for ammonia synthesis by adding an on-line Agilent 7820A gas chromatograph (GC), equipped with a gas sampling valve and HP-PlotQ column (30 m x 0.32 mm x 20 µm). The gases were analyzed every 3 minutes for 60 minutes using the GC. The experiments were performed at input powers of 100 W, 150 W, 200 W and 300W. The light emitted from the discharge was lead through an optical system and the emission spectra of the glow region were measured on the loaded catalyst. The measurements were recorded using a dual channel UV-VIS-NIR spectrophotometer in scope mode (Avantes Inc., USB2000 Series). The spectral range was from 200-1100 nm, using a line grating of 600 lines mm\textsuperscript{-1} and resolution of 0.4 nm. A bifurcated fiber optic cable with 400 µm was employed.

**RESULTS AND DISCUSSION**
**Figure 1a** shows the XRD pattern of Ni-MOF-74 collected from the autoclave after synthesis. For comparison, the simulated pattern of this MOF is shown. The XRD pattern of the synthesized crystals match well the simulated XRD pattern$^{39, 44}$, confirming the formation of Ni-MOF-74. **Figure 1b** shows a representative SEM picture of Ni-MOF-74. Elongated $\sim 2 \times 8$-10 micron crystals are observed. Ni-MOF-74 crystals displayed BET surface area of $\sim 723 \, \text{m}^2 \, \text{g}^{-1}$, in well agreement with previous reports.$^{39, 43}$

![XRD pattern and SEM image](image.jpg)

Figure 1. (a) XRD pattern and (b) representative SEM image of synthesized Ni-MOF-74 crystals employed as catalyst in this study (inset – SEM image with higher magnification).
The radiofrequency plasma-catalysis experiments were carried out at constant flow rate and gas ratio at different power. The temperature increased with power. The highest temperature reached was 82.3 °C at 300 W. To understand the catalytic effect of Ni-MOF-74, the catalytic activity was compared with catalytic activity of glass wool bed (no catalyst) and Ni pieces on glass wool bed. The catalytic activity results as a function of plasma power and catalyst are summarized in Figure 2.

Figure 2. Ammonia yield (%) vs. time (min) as a function of plasma power for all studied catalysts, a) 100 W, b) 150 W, c) 200 W and d) 300 W.

Irrespective of the presence or absence of the catalyst, the ammonia yield increased with plasma power. The trend reached almost a steady value in case of glass wool and Ni catalyst after 15 minutes. When Ni-MOF-74 was employed as a catalyst, the ammonia yield follows an
asymmetrical bell type behavior. The ammonia yield reached a maximum between 9 to 15 minutes, then started to decrease steadily. The highest observed ammonia yield achieved was ~10.3% corresponding to the Ni-MOF-74 catalyst at 300 W. The standard deviation was less than 10% in all cases after 20 minutes of reaction time except for recycled Ni-MOF-74 at 300 W.

The general trend of catalytic activity was Ni-MOF (Fresh) > Ni-MOF (Recycle) > Ni > Glass Wool except at 300 W. It is evident from these results that the MOF is more active than the pure Ni metal. This can be (at least in part) attributed to the presence of pores that can improve mass transfer of guest and product molecules during reaction. The presence of pores has been demonstrated to be beneficial to increase the catalytic activity in plasma systems. For instance, it has been reported that for several zeolite (microporous crystalline materials) catalysts, when exposed to plasma there is an enhancement on the catalytic activity.\textsuperscript{45-49} It has been postulated that the presence of pores tend to form micro-arc discharges in plasma reactors leading to an improved catalytic activity.\textsuperscript{50-51}

At 100 W, the catalytic activity of Ni-MOF-74 and Ni is comparable but is much better than only glass wool. This can be attributed to the limited excited species available to interact with the catalyst at this low plasma power. Therefore, the catalyst does not have a major impact at this power. At 150 and 200 W, the glass wool and Ni have similar activity but Ni-MOF-74 exhibited and enhanced behavior, almost 1.5 times better. At 300 W, the order of the catalytic activity changes. The fresh Ni-MOF displays the highest ammonia yields at this power but there is steep decrease in the activity of recycled Ni-MOF.

The turnover frequency (TOF) vs. time has been plotted for various powers in Figure S4. The TOF did vary for various powers. The catalyst reaches its peak TOF around 12-15 minutes for all plasma powers and the starts to deactivate. The TOF for fresh and recycled MOFs are quite similar
for low powers (100 W, 150 W and 200 W) while at 300 W there’s a significant difference. As it is seen from Figure 2 that the reaction achieves steady state after 60 minutes we compared the TOF of fresh and recycled catalyst at 100 W, 150 W and 200 W. The catalyst at 300 W is not considered as the recycled MOF loses the crystallinity mid-way of the reaction. The TOF at 60 minutes for pure Ni at 100, 150 and 200 W is 0.07, 0.077 and 0.83 s\(^{-1}\) whereas the TOF for Ni-MOF are 0.2, 0.24 and 0.25 s\(^{-1}\) at 100 W, 150 W and 200 W, respectively. The molar ratio of Ni in Ni:Ni-MOF is 3:1 (approx.). There seems to be deactivation after the average turnover number of 812.92, 1023.79 and 1033.88. The catalysts produced a total of 5.69, 6.92 and 7.55 µmol-NH\(_3\) before deactivating. The percentage deactivation of catalyst (Table S1) for a 60 minute run is 24.5%, 27%, 28.8% and 40.42% for fresh Ni-MOF-74 at plasma powers of 100 W, 150 W, 200 W and 300 W, respectively. The number is bit under-determined at the ammonia absorbed in the MOF is not added to it. As per the TPD experiments (Figure S5), a maximum ammonia loading of 3.14 mmol-NH\(_3\)/g-MOF is obtained on a dry basis which is in accordance with Glover et al.’s reported value of 2.9 mmol-NH\(_3\)/g-MOF.\(^{52}\) A total of 0.624 mmol-NH\(_3\) can be absorbed in the 0.2 g of loaded catalyst. The deactivation can merely be an absorption of the ammonia in the MOF.

The catalyst might be retaining its original activity but the decrease in ammonia signal on the GC can be due to the trapping of ammonia in the pores.

Figure 3a-d shows representative SEM images of the recycled catalysts. These images suggest that the shape and size of Ni-MOF-74 are preserved after plasma treatment, irrespective of the plasma power. However, XRD patterns of the recycled MOF samples (Figure 3e) indicate that there is a slight XRD peak displacement as a function of plasma power that may be related to small changes in the unit cell volume of the framework. Specifically, there is a displacement to higher 2 theta angles indicating a decrease in the interplanar spacing. This decrease in interplanar spacing
suggests framework contraction, and therefore a higher degree of structural local disorder within the porous framework. The degree of structural local disorder increased with plasma power. This is supported by the fact that for low plasma powers (100, 150, and 200 W), two well defined sharp XRD peaks are evident. For higher plasma powers (300 W) only one broad peak is observed. The XRD peak displacement may be caused by internal stress within the porous framework developed by plasma irradiation. The presence of one broader peak for the 300 W sample suggests onset of framework amorphization. Therefore, the limited stability of the Ni-MOF catalysts at 300 W (Figure 2d) may be related to higher degree of structural local disorder, and amorphization. The local structural distortion in the Ni-MOF may occur due to the partial damage occurring from plasma species such as excited electrons and non-reactive species. As the energy from the species is transferred to a bond or atom in the structure due to collision, the molecular structure undergo minor transformation forming defects as reported in other common catalysts.\textsuperscript{53-54}

![Figure 3](image.png)

Figure 3. SEM images of spent catalyst at various plasma powers a) 100 W, b) 150 W, c) 200 W and d) 300 W, e) XRD pattern of spent catalyst.

For all studied plasma powers, Ni-MOF catalysts displayed a decrease in ammonia yield as a function of time. This behavior can be explained by the high ammonia sorption capacity over Ni
based MOFs. Recently, Dinca’s group studied the ammonia sorption on several MOFs containing triazolate linker. The Ni based MOFs displayed the highest ammonia sorption capacity without disrupting the structure. A pore filling behavior of ammonia was also established and a high ammonia sorption capacity of 35 mmol/g was achieved.\(^{55}\) In our study, as the reaction proceeded, the ammonia molecules start to fill the pores of the MOF which likely reduced the ammonia detection in the exhaust gases greatly. The ammonia sorption is a quasi-reversible process between 25-100 °C which makes release of ammonia trapping easier by physical treatment such as thermal heating.\(^{55}\) Yaghi’s group confirmed the retention of ammonia in Ni-MOF-74.\(^{52,56}\) We run a TPD study of ammonia (Figure S5) which showed that ammonia started releasing at 60 °C and stopped at 210 °C while catalyst decomposition is seen at 300 °C. The total ammonia loading was found to be 3.14 mmol/g-MOF whereas the Glover et al. reports a value of 2.9 mmol/g-MOF.\(^{52}\) The slight reduction in the catalytic activity after overnight thermal treatment at 100 °C confirms the finding. To achieve the complete activation, the catalyst should be heated at 200 °C for 2 hours. The decrease in activity can be a direct result of ammonia adsorption in the MOF. We found that the peak and average energy yield for ammonia formation was 0.26 g-NH\(_3\) (g-catalyst*kWh\(^{-1}\)) and 0.23 g-NH\(_3\) (g-catalyst*kWh\(^{-1}\)) at 50 W when Ni-MOF-74 was used as a catalyst. The energy yields decreased with increase in plasma power. Table 1 compares the catalytic performance of existing Ni based catalysts in the presence of plasma for ammonia synthesis. The Ni-MOF catalysts displayed the highest reported energy yields, and ammonia synthesis rate which is comparable to previous reported Ni based catalysts. Furthermore, the energy cost associated for the Ni-MOF catalyst is lower than most of the Ni-plasma catalytic systems. Plasma-catalytic ammonia energy yields range from 0.025-4.45 g-NH\(_3\) kWh\(^{-1}\) and energy costs range from 32-850 MJ/mol.\(^{12-13,16-17,23-24,57-60}\) Finally, it is important to highlight that our radiofrequency plasma Ni-MOF system
displays energy yields which are one order of magnitude higher than the only previous reported work on the synthesis of ammonia using RF plasma-catalyst system. Specifically the energy yield for our system was as high as 0.23 g-NH₃ kWh⁻¹, as compared to the state of the art literature for RF plasma-Fe catalyst of 0.012 g-NH₃ kWh⁻¹.

Table 1. Ammonia yield (%) vs. time (min) as a function of plasma power for all studied catalysts, a) 100 W, b) 150 W, c) 200 W and d) 300 W.

<table>
<thead>
<tr>
<th>Plasma</th>
<th>Catalyst</th>
<th>Ammonia Synthesis Rate (µmol min⁻¹)</th>
<th>Energy Yield (g-NH₃ kWh⁻¹)</th>
<th>Energy Cost (MJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBD²³-²⁴</td>
<td>Ni/Alumina Membrane</td>
<td>27</td>
<td>0.178</td>
<td>344</td>
</tr>
<tr>
<td></td>
<td>4.5 wt% Catalyst (Ni/SiO2) + 94.5 wt% BaTiO₃</td>
<td>-</td>
<td>-</td>
<td>81</td>
</tr>
<tr>
<td>Non-thermal Atmospheric Pressure Plasma¹⁷</td>
<td>Ni Mesh</td>
<td>32</td>
<td>0.018</td>
<td>400</td>
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<tr>
<td>RF Plasma (This Study)</td>
<td>Ni</td>
<td>16.67</td>
<td>0.17</td>
<td>359</td>
</tr>
<tr>
<td></td>
<td>Ni-MOF-74</td>
<td>21.17</td>
<td>0.23</td>
<td>265</td>
</tr>
</tbody>
</table>

To learn about the effect of the formed plasma species on the ammonia yield and plasma-catalytic interaction, we collected the emission spectra of the plasmas as a function of time through operando UV-Vis. Not only the ammonia interaction with the Ni-MOF but the plasma species and catalyst interactions affect the ammonia yield. The emission spectra revealed the presence of seven different species. The nitrogen derived species detected were N₂ second positive system($C^3Π_u \rightarrow$...
$B^3Π_g$, N2+ first negative system ($B^3Π_u^+ \rightarrow X^2Σ_g^+$), N2 first positive system ($B^3Π_g \rightarrow A^3Σ_u^+$) and atomic N($2p^23p \rightarrow 2p^23s$) with characteristic peaks at 337.1 nm, 391.4 nm, 662.3 nm and 746.8 nm, respectively. The hydrogen species present were Hα (656.3 nm) and Hβ (486.1 nm). The NH peak comes up as a pre-shoulder at 336 nm to N2 SPS characteristic peak. The Hβ peak was observed only at higher powers. Figure S6 shows the emission spectra at plasma-catalyst interface as a function of plasma power. When comparing the spectrums for Ni versus Ni-MOF-74 it is clear that the Hα peak intensity is much higher in the metal than in the Ni-MOF. For several metals including Ni, the peak intensity is directly attributed to the hydrogen recombination. Therefore, higher intensity of Hα peak increases the probability of surface hydrogen recombination with the gas phase atomic hydrogen in turn reducing the total surface hydrogen available to react and lead to ammonia. In addition, the surface hydrogen plays a major role in formation of NH₃ rather than the gas phase radicals and gas phase reactions. This may explains in part the higher ammonia yields obtained when using the Ni-MOF-74 as compared to Ni metal.

Conclusions

In summary, we demonstrate a radiofrequency plasma-catalyst approach to synthesize ammonia. Specifically, a Ni based metal organic framework was employed as catalyst. As compared to pure Ni, the Ni-MOF displayed higher ammonia yields. The structural stability of the Ni-MOF catalyst depended on the plasma power. The Ni-MOF catalyst was stable at low to moderate plasma powers (100-200 W). High plasma powers (300 W) caused internal stress within the porous framework leading to amorphization, and therefore compromising the catalyst performance. Ammonia yields as high as 0.23 g-NH₃ (kWh-g-catalyst)⁻¹ and energy cost of 265 MJ mol⁻¹ over Ni-MOF were observed. The enhanced catalytic activity of the Ni-MOF in the presence of radiofrequency plasma was attributed to the porous structure which improved mass transfer of guest and product
molecules during reaction, the presence of unsaturated Ni metal sites, and lower surface hydrogen recombination.

ASSOCIATED CONTENT

Supporting Information.
The following files are available free of charge.
Emission Spectra at different powers and catalyst, Schematic of Experimental Setup, Pictures of Catalyst loading, formula for calculating energy cost and energy yield, details of GC calibration.

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Author Contributions

The manuscript was written through contributions of all authors

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REFERENCES


BRIEFS. Alternate routes for ammonia synthesis have gained attention due to the energy intensive process, the letter describes the use of a molecular sieve for catalysis which opens a whole new class of material that can used for catalysis as well as ammonia storage in one-pot synthesis.

SYNOPSIS. A novel framework, Ni-MOF-74 for the synthesis of ammonia via plasma catalysis. The MOF exhibits a better catalytic activity than pure metal as well as goes through structural changes.