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Use of catalysts for ammonia cracking

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Author(s):

Eino Soini

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Author(s): Eino Soini
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Supervisor(s): M.Sc. Heidi Laitinen, D.Sc. Armin Wehrfritz
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Abstract

Ammonia cracking is recognized as a highly promising hydrogen production method, overcoming the limitations of hydrogen transportation and storage. While a large part of ammonia cracking studies focuses on laboratory-scale catalyst research, recent studies have explored novel solutions by creating highly active catalysts using high entropy alloys (HEAs) and 3D printing the catalyst structures. This enables more efficient heat and mass transfer at the active sites of the catalyst. In this literature review, the recent laboratory research discoveries of highly active catalysts are discussed, including Ru- and Ni-based catalysts and HEAs. In addition, novel 3D-printed TPMS and POCS structures are examined. Finally, Joule heating methods and an integrated reactor configuration are introduced as a pathway to efficient, sustainable, and decentralized on-site hydrogen production.

Tiivistelmä

Termokatalyyttinen ammoniakin hajottaminen on erittäin lupaava vedyn tuotantomenetelmä, jonka avulla vältetään vedyn hankalaan kuljetukseen ja varastointiin liittyvät haasteet. Vaikka suuri osa ammoniakin hajottamiseen liittyvistä tutkimuksista keskittyy laboratoriotason katalyytteihin, viimeaikaiset tutkimukset ovat esitelleet uusia ratkaisuja. Näissä ratkaisuissa korkean entropian metalliseokset (engl. high-entropy alloys, HEAs) ja 3D-tulostetut kantoaineet ovat osoittaneet erinomaista katalyyttistä aktiivisuutta. HEA-katalyytit ja 3D-tulostetut rakenteet tehostavat lämmön- ja aineensiirtoa suoraan katalyytin aktiivisissa kohdissa. Tässä kirjallisuuskatsauksessa käsitellään viimeaikaisia laboratoriotason tutkimuslöytöjä aktiivisimmista katalyyteistä, joihin lukeutuvat Ru- ja Ni-pohjaiset sekä HEA-katalyytit. Lisäksi työssä tarkastellaan

3D-tulostettuja TPMS- ja POCS-rakenteita katalyytin kantoaineina. Lopuksi esitellään teollisen mittakaavan kestävän ammoniakin hajottamiseen tähtääviä Joule-lämmitysmenetelmiä sekä integroitu reaktorikokonaisuus. Tämä mahdollistaa ammoniakin hajottamisen vedyksi uusiutuvalla sähköllä suoraan sen käyttökohteessa, mikä luo pohjan tehokkaalle ja hajautetulle vedyn tuotannolle.

Keywords: Ammonia cracking, Hydrogen economy, Catalysts, Reactor design

Abbreviations:

BCC – body-centered cubic
EIJH – electromagnetically induced Joule heating
GHSV – gas hourly space velocity
HEA – high entropy alloy
LPBF – laser powder bed fusion
NP – nanoparticle
PBR – packed-bed reactor
PEMFC – proton exchange membrane fuel cell
POCS – periodic open cellular structure
TOF – turnover frequency
TPMS – triply periodic minimal surface

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1. Introduction

Hydrogen (H_2) has emerged as a critical green energy carrier with significant prospects to displace fossil fuels in industrial applications and transportation. Fossil fuels have an existing infrastructure and capability to store large amounts of energy, which has been the reason they have maintained their dominance through history. However, the continuous growth of the global population and economy creates an ever-increasing demand for energy, making innovations for sustainable and stable energy production inevitable. [1]

The transition to clean energy sources is also stated as a target to achieve net-zero emissions globally by 2050 [1]. Hydrogen plays a crucial role in this transition as a diverse option, generating only water vapor in the combustion process [1], [2]. The gravimetric energy density of hydrogen fuel is superior compared to gasoline used in internal combustion engines and creates an excellent choice to produce electricity using fuel cells. Although hydrogen is widely studied and solutions to utilize it are already in use, there are still challenges in extracting its maximum potential. [1]

1.1 Challenges in hydrogen economy

Hydrogen is currently produced mainly via catalytic steam reforming of fossil fuels from natural gas, which is a relatively inexpensive method. In addition to H_2 production from non-renewable fossil fuels, difficulties appear in hydrogen's storage and transportation due to its properties. [2] While hydrogen has high energy density by mass (approximately 120 MJ/kg at ambient temperature and pressure) [2], its energy density over volume as a gas is remarkably low, at only 9.8 kJ/L [3]. This volumetric density can be increased to 8.96 GJ/m^3, but it requires liquefying the fuel at -253 °C [2]. The volumetric energy density of hydrogen gas is significantly lower than that of conventional fuels, such as gasoline, in ambient conditions, and therefore H_2 gas is hard to utilize as an energy source [3]. Hydrogen also requires 700 bar pressure at 25 °C to be stored reasonably as compressed gas [2]. In addition to that H_2 is colorless and odorless, it is also flammable [1], and therefore leakages can be hazardous. However, one great solution for hydrogen

storage and transport is to use another compound that contains hydrogen, such as ammonia [2].

1.2 Ammonia as a hydrogen carrier

Ammonia (NH_3) is mainly used as a feedstock for fertilizers and fuel, and as a refrigerant and working fluid, having a well-established infrastructure globally [4]. NH_3 has a high content of hydrogen, 17.8 wt%, and a volumetric density of 121 kg H_2 m^{-3} at 10 bars. It requires only 8.6 bar pressure at ambient temperature to liquefy, making it feasible for storage and transport, and therefore functions excellently as a hydrogen carrier. [2]

Different NH_3 properties and phases are feasible for different storage and transportation applications. Liquid ammonia is applicable for maritime transportation because of its higher density over unit volume compared to gaseous ammonia. Refrigerated ammonia is commonly used in storage functions. Ammonia transportation is mainly operated by e.g. railroads, ships and pipelines, and the transportation infrastructure of ammonia is advanced, especially compared with hydrogen. [5]

Although ammonia acts as a storage and transport carrier for hydrogen, it still requires a separation process of hydrogen and nitrogen. Predominantly, ammonia decomposition for hydrogen is done with electrocatalytic or non-electrocatalytic processes. Non-electrocatalytic process, such as thermo-catalytic ammonia cracking, is the reverse reaction of ammonia synthesis and the Haber-Bosch process. However, to achieve an equilibrium conversion of >99 %, the ammonia decomposition reaction requires temperatures over 400 °C. Thus, catalysts are used to increase the reaction activity and preferably lower the reaction temperatures. [5]

1.3 Structure of the thesis

This work covers the state of the art of literature on ammonia cracking and reviews different catalysts that have been proven to have high catalytic activity and high ammonia conversion at low temperatures. Different reactor configurations are also reviewed, as additive manufacturing has given the opportunity to manufacture complex catalyst structures that enhance heat and mass transfer through the reactor, increasing catalytic activity. Finally, direct Joule heating methods are discussed, including their

potential to be utilized in large-scale hydrogen production with integrated ammonia cracking reactor configurations.

AI-powered language tools Gemini and Grammarly were used in the preparation of this thesis to assist with English language editing, including grammar checking, proofreading, rephrasing, and translation of specific terms to improve the readability and clarity of the text. These tools were used according to the guidelines of the University of Turku. The author takes full responsibility for the content of the thesis.

2 Thermo-catalytic ammonia cracking

Ammonia cracking or ammonia decomposition reaction decomposes ammonia into hydrogen and nitrogen in a ratio of 3:1 and total reaction enthalpy of ΔH=46.22 kJ · mol^{-1}, as presented in Equation 1 [6]:

$$2NH_3 \rightleftharpoons N_2 + 3H_2, \Delta H = 46.22\ kJ \cdot mol^{-1} \quad (1)$$

The reaction is endothermic and theoretically reaches equilibrium conversion of > 99 % at 400 °C in atmospheric pressure. Above 500 °C, the conversion is almost complete. In the actual decomposition of ammonia, the conversion is not necessarily that high because a high activation energy is required, and slow reaction kinetics occur. By using catalysts, decomposition can be achieved at lower temperatures, and therefore with less energy supply. This method is called thermo-catalytic ammonia cracking. [6]

The industrial use of ammonia decomposition reaction has been mostly utilized in metal annealing and galvanizing processes, but the research nowadays aims to find suitable and cost-effective ways to use the reaction in ammonia-to-power applications. In ammonia-to-power solutions where the decomposition product H_2 is fed to fuel cells like proton exchange membrane fuel cells (PEMFC), the purity of the H_2 plays a crucial role since PEMFCs deteriorate rapidly by even trace amounts of ammonia. Thus, the high conversion of ammonia in the cracking process is a prerequisite for efficient power generation. [2]

The focus of current research on ammonia cracking is based mainly on thermo-catalysis. The reaction kinetics of thermo-catalytic ammonia decomposition process include adsorption of ammonia molecules on the active sites of the catalyst (indicated with *), decomposition of ammonia into N and H atoms, formation of N_2 and H_2 molecules from N and H atoms (Figure 1). This process is described in Equations 2-7 [7]:

$$NH_3 + * \rightarrow NH_3 * \quad (2)$$

$$NH_3 * + * \rightarrow NH_2 * + H * \quad (3)$$

$$NH_2 * + * \rightarrow NH * + H * \quad (4)$$

$$NH* + * \rightarrow N* + H* \quad (5)$$

$$2N* \rightarrow N_2 + 2* \quad (6)$$

$$2H* \rightarrow H_2 + 2* \quad (7)$$

As the reaction is highly dependent on temperature, solutions for lowering the heat input are largely studied. Catalysts' properties and ammonia's capability to interact with them have a significant impact for the reaction kinetics, and by using the right reaction promoters and supports in addition to catalysts, decomposition temperatures can be lowered [3]. A significant amount of comparative literature is available from different catalysts and their promoters and supports used in thermo-catalytic ammonia cracking to find solutions to lower the reaction temperatures and increase NH_3 conversion.

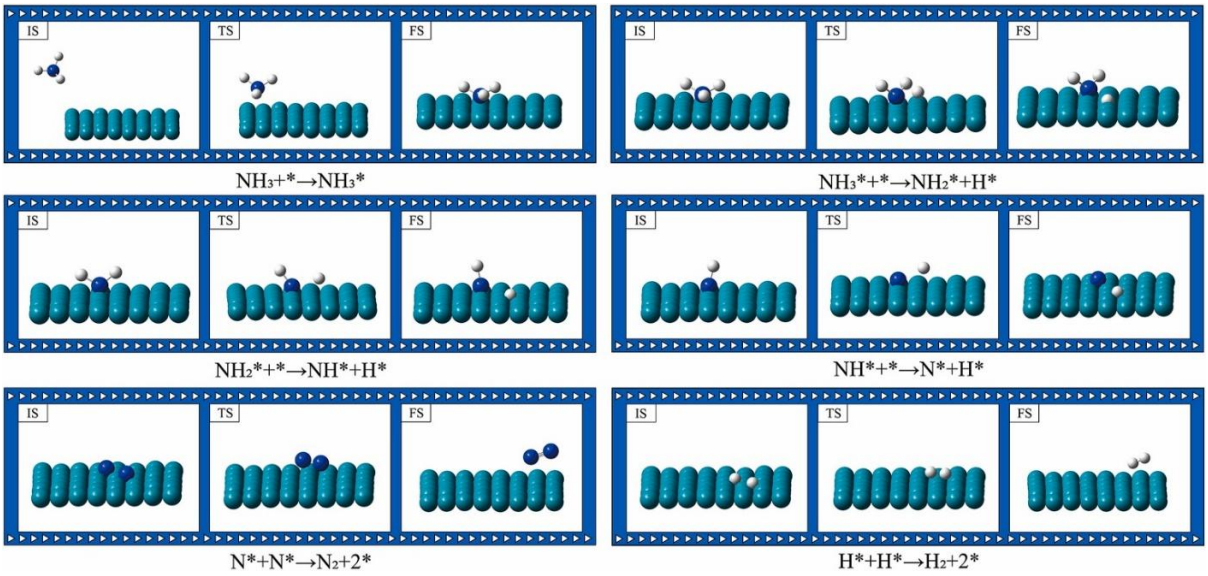

Figure 1. Illustration of the initial, transitional, and final stages of hydrogen production from NH_3 decomposition on the catalyst bed surface, corresponding to Equations 2-7. Reproduced with permission from [8].

3 Catalysts

3.1 Ruthenium and Nickel catalysts

Ruthenium is widely recognized as the most efficient catalyst for ammonia cracking among noble and non-noble metals. The key to its high activity lies in its ideal Ru-N binding strength, which facilitates efficient adsorption and desorption processes. With this efficiency decomposition reaction approaches equilibrium at temperatures as low as 375 °C. Even though Ru is an ideal catalyst material, it is expensive, and there have been significant efforts to create cost-effective alternatives to Ru-based catalysts. Nickel has also taken its place in industrial ammonia cracking as a cost-effective and active non-noble metal catalyst. [8]

The catalytic process depends, in addition to the active metal, also on the support and promoters used to improve the performance of the reaction. Proper support enhances catalytic activity by revealing the active sites of the metal particles while maintaining their structural integrity. Studies have shown that high-surface-area supports combined with metal nanoparticles (NPs), and promoters that tend to donate electrons significantly improve catalytic activity. Furthermore, the addition of promoter metals boosts catalytic performance through several key mechanisms. They not only optimize the shape and dispersion of active NPs, but they also increase the basicity of the support, which is crucial for promoting efficient ammonia dehydrogenation and the subsequent release of nitrogen gas. [9]

Various studies of Ru-based catalysts have demonstrated increased NH_3 conversion when utilizing advanced supports such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), and metal oxides like Al_2O_3, often combined with electron-donating promoters like potassium (K) and cesium (Cs). These specific support materials and promoters are highly favored because they provide excellent surface area for Ru dispersion. [2] In their study, Hu et al. demonstrated improved results in low temperature NH_3 decomposition using Ru particles supported with 1D ceramic nanorods (NRs) of ceria (CeO_2), alumina (Al_2O_3), and titanite nanotubes (Ti-NT) and CNTs. Ru/ CeO_2 NR had the best catalytic activity among the catalysts studied with > 99% NH_3 conversion at a temperature as low as 450 °C. They also added sodium (Na) promoter to the previously mentioned catalysts

with improved activity among CNT, Al_2O_3, and Ti-NT and resulting in even lower temperatures. The best catalytic results of the study are displayed in Table 1. [10]

Nickel-based catalysts are more applicable for large scale industrial use as they are cheap compared to noble metal catalysts such as Ru. The size of Ni particles plays a crucial role in reaction activity in the decomposition of NH_3, usually achieving higher catalytic activity with smaller than 5 nm particles. To achieve optimal performance in NH_3 decomposition, Ni-based catalysts rely on the properties of their metal oxide supports. A combination of well-dispersed Ni NPs, robust metal-support interactions, and the presence of surface oxygen vacancies work synergistically and boost catalytic activity. This not only increases the availability of Ni active sites but also facilitates smoother NH_3 activation and cracking process. [9]

Usman et al. studied NH_3 decomposition on Ni/Al_2O_3 promoted with rare earth metals (La, Ce, Nd, and Sm) and achieved significant results of 90% NH_3 conversion at 500 °C with a $5\%La/Ni/Al_2O_3$ catalyst and a catalyst loading of 100 mg. $5\%Ce/Ni/Al_2O_3$ showed the second-best results with the same conversion at 525 °C. Foregoing, also showed great over 65 h stability. Other promoters studied, containing 5% Nd and Sm, also indicated the same conversion at temperatures below 550 °C. These results are displayed in Table 1. [11]

Table 1. Catalytic performance of different Ni- and Ru-based catalysts in NH_3 decomposition. GHSV is gas hourly space velocity and NH_3 is NH_3 in He (vol%).

Catalysts	Ni, Ru (wt%)	Temperature (°C)	NH_3 (vol%)	GHSV (mL g_{cat}^{-1} h^{-1})	Conversion (%)	Ref.
Ru-Na/CNT	7.0	390	29.4	6000	99.7	[10]
Ru-Na/CeO_2 NR	7.0	410	29.4	6000	96.0	[10]
Ru/CeO_2 NR	7.0	425	29.4	6000	97.4	[10]
Ru/Al_2O_3 NR	7.0	475	29.4	6000	95.5	[10]
Ru/CNT	7.0	500	29.4	6000	99.0	[10]
$5\%La/Ni/Al_2O_3$	51.4	510	10	20 400	90.0	[11]
$5\%Ce/Ni/Al_2O_3$	43.4	525	10	20 400	90.0	[11]
$5\%Sm/Ni/Al_2O_3$	47.9	530	10	20 400	90.0	[11]
$5\%Nd/Ni/Al_2O_3$	57	540	10	20 400	90.0	[11]

3.2 HEA catalysts

High entropy alloy (HEA) catalysts are promising alternatives to conventional single-element catalysts such as Ru and Ni catalysts. The defining feature of HEAs is the random mixing of multiple base metals within a shared crystal lattice, generating a complex atomic neighborhood. This structural and electronic diversity is highly beneficial for catalysis, as it allows for precise tuning of adsorption and desorption energies. Such tailor-made properties are crucial for stabilizing essential intermediates while effectively preventing unwanted side reactions. Another major advantage of using HEAs as catalysts is their cost-effectiveness and availability, as they usually consist of low-cost metal elements, especially when compared to ruthenium. [12]

Xie et al. used a carbothermal shock technique to synthesize HEA nanoparticles consisting of five metals in a single solid-solution phase. In their study on NH_3 decomposition, they investigated CoMoFeNiCu HEA NPs and the effect of Co:Mo elemental ratio, comparing their performance against Co-Mo bimetallic and Ru monometallic catalysts. Table 2 shows that CoMoFeNiCu HEA with a ratio of $Co_{55}Mo_{15}$ had the best performance of the studied HEAs with different elemental ratios. HEA-$Co_{55}Mo_{15}$ had also a significant improvement compared to Co-Mo bimetallic and Ru catalysts. [13]

Yao et al. studied homogenous and ultrafine multi-elemental HEA nanoparticles (3-5 nm) as catalysts in the NH_3 decomposition reaction. They achieved superior results by designing and testing RuRhCoNi and RuRhCoNiIr HEA NPs and their catalytic activity. RuRhCoNi HEA NPs reached 100% NH_3 conversion at a temperature of approximately 470 °C, while RuRhCoNiIr HEA achieved the same conversion at 500 °C. These results are also presented in Table 2. RuRhCoNi also showed a major increase in catalytic performance compared to Ru and RhCoNi catalysts in the same conditions. These multi-elemental HEA NPs also showed high thermal stability after the catalytic reaction, as the nanoparticles remained evenly distributed and preserved their alloy structure. [14]

Table 2. Catalytic performance of different HEA catalysts in NH_3 Decomposition.

GHSV is gas hourly space velocity, NH_3 is NH_3 in He (vol%) and TOF is turnover frequency.

Catalysts	Metals (wt%)	Temperature (°C)	NH_3 (vol%)	GHSV (mL g_{cat}^{-1} h^{-1})	Conversion (%)	TOF (h^{-1})	Ref.
HEA-$Co_{25}Mo_{45}$	7.8	500	5	36 000	84	1571	[13]
HEA-$Co_{35}Mo_{35}$	8.3	500	5	36 000	67	1128	[13]
HEA-$Co_{45}Mo_{25}$	8.8	500	100	36 000	64.5	19 633	[13]
HEA-$Co_{55}Mo_{15}$	9.3	500	100	36 000	100	25 209	[13]
RuRhCoNi HEA	(50 mg total)	470	5	36 000	100	-	[14]
RuRhCoNiIr HEA	(50 mg total)	500	5	36 000	100	-	[14]

4 Ammonia cracking reactors

The research work for achieving high-performance catalysts alone is not enough to enable efficient ammonia cracking. Reactor and catalysts design, as well as optimizing input parameters for the reaction, plays significant role in efficient ammonia decomposition and high purity H_2 production, especially when moving to industrial scale. One of the most common reactor types is packed-bed reactors, but recently additive manufacturing, i.e. 3D printing, has also gained attention in reactor and catalysts design as it enables manufacturing complex structures that are not possible or simple to make with traditional manufacturing processes.

4.1 Packed-bed reactor

In a recent larger-scale experimental study, Jin et al. designed ammonia cracking packed-bed reactors (PBRs) using non-uniform heat input to determine optimal parameters for reactor designs, such as reactor volume, weight hourly space velocity (WHSV), heat input, and shape. They used four well recognized Ru- and Ni-based catalysts supported with Al_2O_3 and La-Al_2O_3 in their study to optimize catalytic activity in their designs. Their objective was to achieve 90% NH_3 conversion as the excess NH_3 was used as an energy source in the reaction. They achieved ~90% conversion with their four catalysts using PBR 1.73 m in diameter and 0.8019 m in length with the parameters shown in Table 3. [15]

Table 3. Optimal parameters for four Ru- and Ni-based catalysts in a PBR reactor with a 1.73 (m) diameter and a 0.8019 (m) length. [15]

Catalysts	Metal loading (kg_{cat})	WHSV ($mL(NH_3)/g_{cat}/h$)	Conversion (%)	Heat input (kW)
2Ru/Al_2O_3	1.9000	30 000	90.06	228.41
0.5Ru/Al_2O_3	3.1008	15 000	89.98	228.74
40Ni/ Al_2O_3	3.1910	6000	90.02	228.65
2Ru/La-Al_2O_3	1.5981	30 000	90.05	228.44

4.2 Monolith reactor

Lucentini et al. studied 3D-printed CeO_2 monolith structures and their geometries to achieve higher catalytic activity in ammonia decomposition. They tested impregnating the monolith structures with three different loading ratios of Ni:Ru active metal, of which 0.5Ni0.1Ru (Figure 2) was chosen as the optimal composition for further testing. Various simulations of CeO_2 structures with different wall thicknesses, channel widths, and quantities, as well as volumetric surface areas of the unit cells, were conducted to optimize ammonia cracking targeting 90% NH_3 conversion. The monolith diameter was kept constant (14.5 mm). The ultimately optimized 3D structure (6 mm in length, 76 channels, 0.78 mm channel width, and 0.46 mm wall thickness) exhibited excellent and stable performance, showing only a 0.02% h^{-1} decrease in NH_3 conversion over a 100-hour stability test. Furthermore, this geometry enhanced the hydrogen production rate by approximately 20% per unit weight and 13% per unit volume compared to the baseline structure. [16]

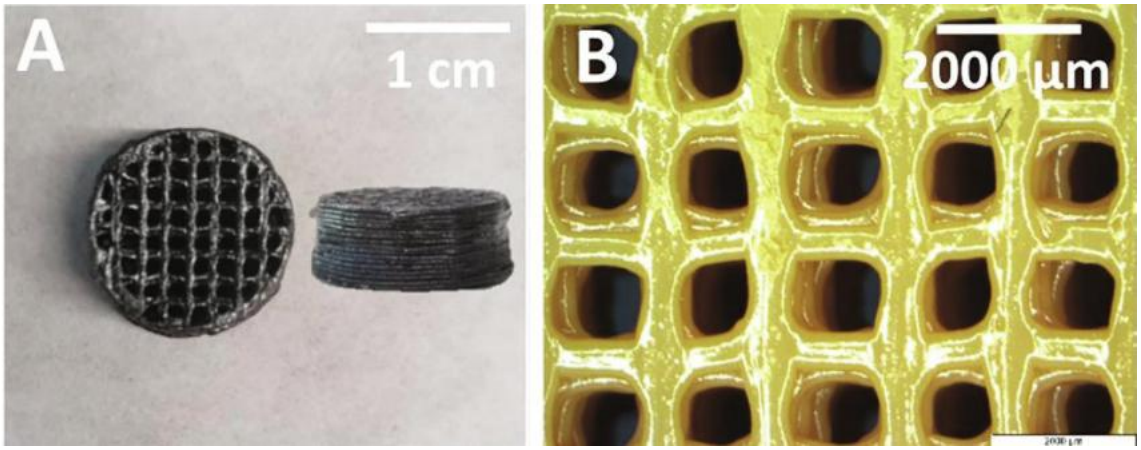

Figure 2. **(a)** Photograph of 0.5Ni0.1Ru-CeO_2 3D-printed monolith and **(b)** stereomicroscope image of the CeO_2 monolith channels. Adapted with permission from [16].

4.3 POCS and TPMS structured reactors

To explore advanced support geometries, Italiano et al. recently investigated the performance of 3D-printed Ni-alloy supports with a Ru/Al_2O_3 catalyst coating. These were produced using laser powder bed fusion (LPBF) with Ni-alloy powder, enabling complex structures like periodic open cellular structures (POCS) and triply periodic

minimal surface (TPMS) structures. They designed and studied three different catalyst supports with cell types including body-centered cubic (BCC) and Kelvin POCS, as well as a Gyroid TPMS (Figure 3) in the NH_3 decomposition reaction. [17]

The Gyroid (5 mm cell and 0.34 mm strut) performed the best among the studied structures in the temperature range of 400-500 °C with higher ammonia conversion. Its intricate structure promotes efficient mass transfer and demonstrates better low-temperature catalytic activity, allowing reactants to contact the active sites more effectively. Furthermore, the Gyroid catalysts showed higher H_2 production per unit volume and per unit weight. The POCS also performed well and represent promising structures for future studies. [17]

Overall, these researchers provided important findings for future geometric catalyst design by evaluating pivotal aspects like strut and cell sizes, specific surface area, and the thickness of the catalyst coating. They observed that pressure drops across the supports increased with larger solid volumes, thicker struts, and smaller cell sizes, whereas higher porosity caused decreasing pressure losses. These insights are crucial for future catalysts and reactor design to achieve better catalytic activity and space-saving reactors. [17]

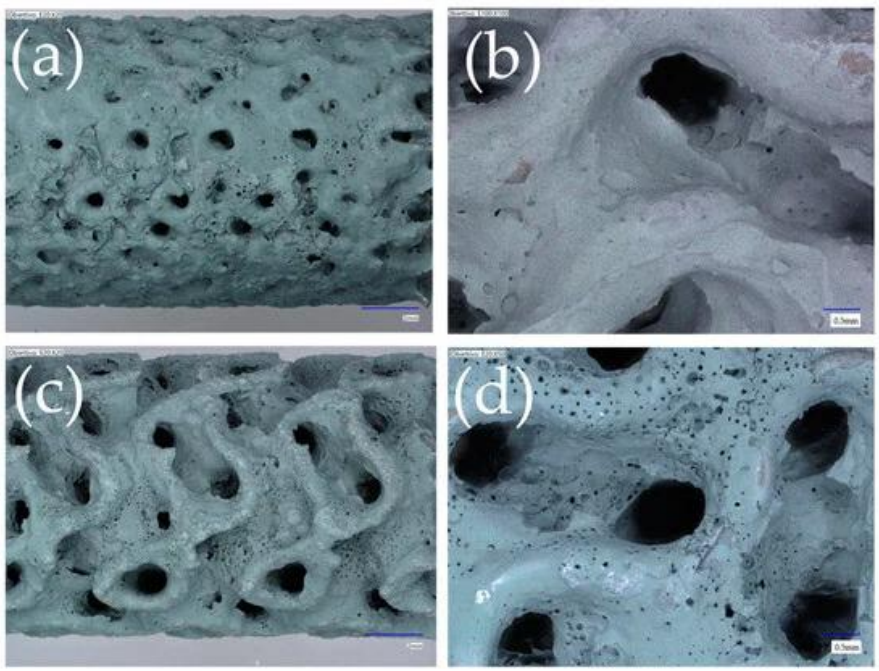

Figure 3. 5 wt% Ru/Al_2O_3-coated Gyroid nickel-alloy support. **(a, b)** Cell size: 3 mm, strut size: 0.4 mm, catalyst loading: ~0.21 g/cm^3. **(c, d**) Cell size: 5 mm, strut size: 0.34 mm, catalyst loading: ~0.19 g/cm^3. Reproduced with permission from [17]. Licensed under CC BY.

In another study of TPMS structures, Zhu et al. used LPBF to fabricate FeCoNiCuAl HEA catalysts and dealloyed them in hydrochloric acid (HCl) to generate pores on the catalyst surface. The macroporous TPMS structure optimized internal fluid flows, and the nanoporous structure created through dealloying provided a higher availability of active sites on the 3D HEA catalyst. They tested different HCl concentrations of 3, 6, and 12% for 0, 12, 24, 36, and 48 h, observing that with higher concentrations and longer dealloying times, the pores expanded and merged more effectively. However, they observed that prolonged dealloying led to a decrease in catalytic activity as the specific surface area decreased. This experimental study provided valuable insights into how porosity and HEA materials in 3D-printed TPMS structures increase catalytic activity. [18] Therefore, this method should also be studied for NH_3 cracking.

In a recent study on optimizing reactor design, Franchi et al. studied an aluminum alloy POCS structured reactor (Figure 4) filled with Ru/Al_2O_3 spherical pellet catalysts (1 mm in diameter) to derive an optimized kinetic expression for NH_3 cracking reactors comparable to industrial ones. The purpose of the thermally highly conductive POCS was to limit temperature gradients that bias the evaluation of the reaction rate and to achieve near-isothermal reactor conditions. These temperature profiles were measured with two K-type thermocouples, one along the center and another along the outer wall of the reactor. The packed POCS reactor was tested with different operating parameters such as varying GHSV, pressure, and argon (Ar), H_2, and N_2 co-feeds. [19]

It was observed that with higher GHSVs, the flow rate was too high for the reactor oven to heat the reactor, causing the reactor temperature to drop below the oven temperature. They also proved that with increasing pressure, ammonia conversion was lower. Another observation was that with a 50% Ar or N_2 co-feed, in addition to NH_3 at the inlet, the conversion increased significantly. Furthermore, there was almost no difference in NH_3 conversion with N_2 co-feed compared to Ar co-feed, indicating that the reaction has no kinetic dependence on N_2 partial pressure. [19] The increased

conversion occurs because of the Le Chatelier's principle, as the diluting reduces the partial pressures of the gas mixture, which shifts the equilibrium forward [15], [19].

In contrast, a 50% H_2 co-feed led to a major decrease in ammonia conversion. This decrease is due to H_2 inhibitive adsorption on the active sites of the Ru/Al_2O_3. Ultimately, they were able to develop a kinetic model for NH_3 conversion in the range of 1.5-99.7%, providing a highly valuable tool for designing future industrial reactor configurations. [19]

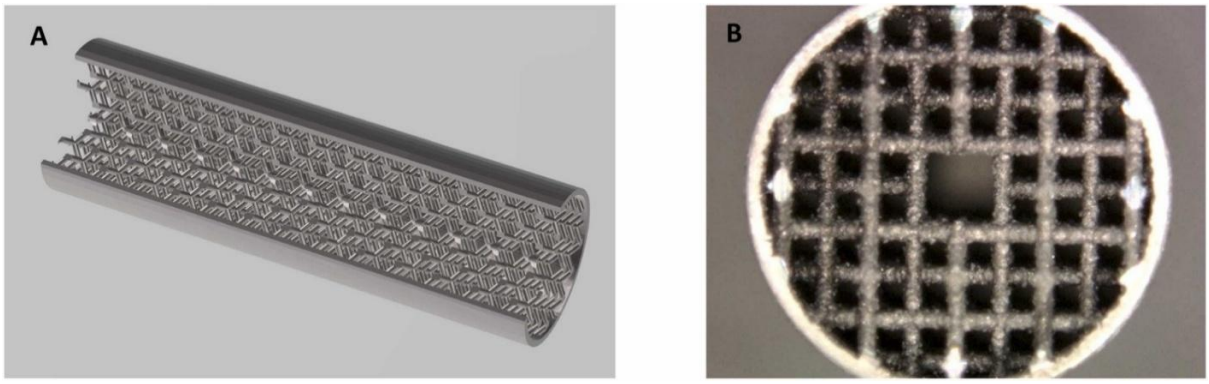

Figure 4. **(a)** 3D printed aluminum alloy POCS. **(b)** The cross-section of the POCS. Reproduced with permission from [19]. Licensed under CC BY.

5 Industrial scalability and future outlook

Literature on ammonia cracking and catalyst research is primarily concentrated on laboratory-scale studies. However, to achieve the goals of future sustainable and reliable energy production, more research and development for large-scale, industrial energy production from ammonia is required. The laboratory research work on NH_3 cracking solutions is still necessary to analyze the behavior and performance of different materials, reaction parameters, and geometrical aspects of the reactors. This fundamental research forms the baseline for reaching larger-scale green hydrogen production from ammonia in the future. Another challenge in this transition is creating a reliable infrastructure for the distribution and storage of the final products of the process, as well as an effective on-site H_2 separation process from N_2 and unreacted NH_3 for H_2 use in fuel cells and pipeline distribution [20], [21].

5.1 Industrial operating conditions and scale-up

Laboratory-scale research operates at low pressures, usually near atmospheric pressure, as NH_3 conversion is higher at low pressures. However, in the industrial decomposition of ammonia, higher pressures are needed for reasonable H_2 gas distribution to pipelines. Due to the high cost of hydrogen compression required for pipelines, the energy industry currently focuses on higher NH_3 cracking pressures, near 50 barg, which is around pipeline-grade H_2 pressure. Another crucial factor that must be considered in new H_2 production systems is the purity of the H_2 (>98 mol% H_2, 2 mol% inerts) required for pipelines. [20]

Liang et al. conducted an experimental study testing different high pressures in NH_3 cracking with a commercial catalyst, providing a basis for scale-up in future industrial ammonia decomposition systems and further studies. Based on their test setups, they concluded that at temperatures exceeding 650 °C at high pressures, the effect of pressure does not limit the NH_3 conversion that much anymore, as kinetic rates increase significantly. At these high temperatures, conversion rates stay high, and expensive hydrogen compression facilities are not needed. [20] Additionally, high-pressure ammonia decomposition is a relevant solution to applications that do not

need high-purity hydrogen, like in mixed combustion fuels. NH_3 itself is not a very efficient fuel for internal combustion engines or gas turbines, as it has low flammability and high NO_x emissions. Therefore, a mixture of NH_3 and H_2 or partially cracked NH_3 can be applied, since H_2 has better flammability. [21]

The choice of catalyst material for large-scale hydrogen production is highly dependent on cost-effectiveness. Ruthenium generally has the best catalytic activity, but as a noble metal, it is very expensive for industrial use [8]. Whereas Nickel is a preferable option for larger-scale use but requires usually much higher temperatures than Ru in effective NH_3 decomposition [8], [9]. Typically used gas-fired furnaces in industrial applications usually provide non-uniform temperature inside the reactor and can generate unwanted side reactions or decrease the efficiency of the reactor [22], and they produce considerably large carbon emissions [23]. Joule heating and electromagnetically induced Joule heating (EIJH) are prominent alternatives for conventional furnace heaters, as they can be utilized by renewable electricity [23].

The advantage of conductive Joule heating in NH_3 cracking is that the heat is conducted directly to the catalyst and the active sites, providing a more uniform temperature in the reactor, lowering the heat loss. It also enables rapid and precise temperature control. In their work, Smith et al. studied a 3D-printed carbon-metal oxide nanocomposite, applying the structure as a Joule heater in NH_3 decomposition. They observed that their structure required low activation energy and low power consumption via Joule heating, which is a significant step for better NH_3 decomposition efficiency and decarbonization of the process. [22]

The EIJH method utilizes contactless heating of a conductive material by induced eddy currents, created with an alternating magnetic field. In a recent study of EIJH, Li et al. performed a comparison between EIJH and common resistance furnace heating, using EIJH with an inductive iron tube packed with iron wires in NH_3 decomposition (Figure 5). The results showed decreased electricity consumption with respect to H_2 production, high catalytic activity with low activation energy, and enhanced heat and mass transfer. In addition, EIJH provides rapid heat input still remaining as an energy efficient method

in NH_3 cracking, but requires improvement for insulation since there is much heat loss to the surroundings, especially when utilizing in larger-scale. [23]

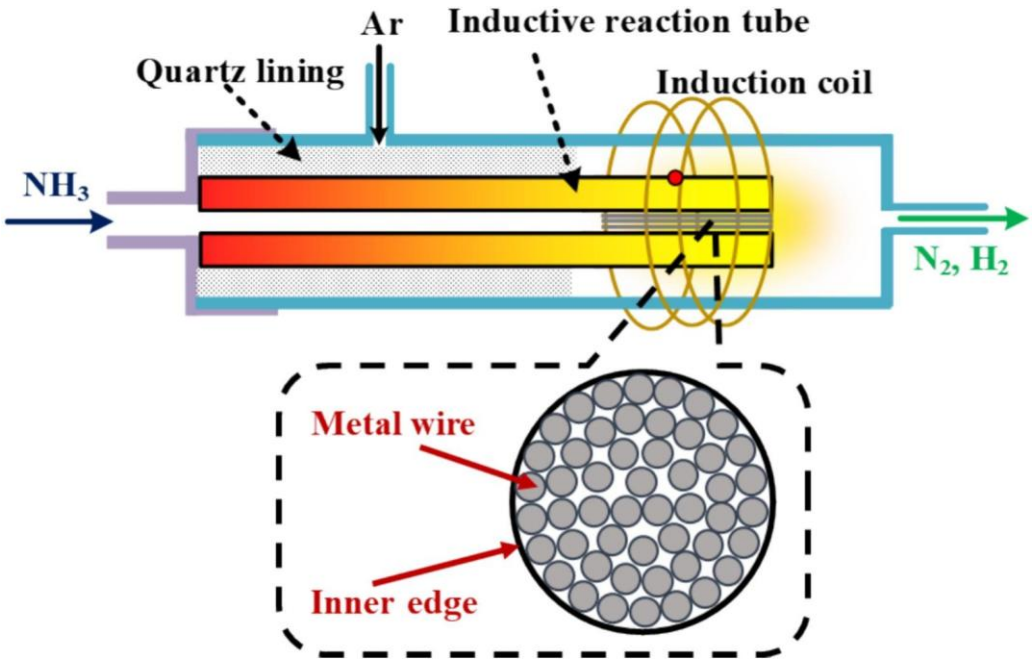

Figure 5. Schematic of NH_3 decomposition using EIJH inductive heating with iron tube filled with iron wire. Reproduced with permission from [23].

5.2 Future outlook and system integration

Fully electrified NH_3 cracking provides a unique opportunity to integrate various advanced catalyst materials, structures, and reactor configurations into one compact and high-performance unit. By combining 3D-printed HEA structures, such as TPMS or POCS, with direct Joule heating, the reactor can simultaneously act as the catalyst, the structural support, and the internal heating element. With multi-metal HEA structures, discussed in *Chapter 3.2*, it is possible to achieve an electronically conductive catalyst structure with high catalytic activity, and relatively inexpensive materials [12], [13], [14]. When these HEA catalysts are manufactured by 3D printing into TPMS or POCS structures, they also offer the necessary surface area for the reaction and enable efficient mass transfer [17], [18]. This integrated structure could then be utilized with direct Joule heating or EIJH powered by renewable electricity, leading to extremely efficient, quick, and sustainable NH_3 cracking [22], [23].

Ultimately, to introduce these integrated reactors for power generation and on-site refueling in transportation, a robust infrastructure for the distribution of ammonia and hydrogen is needed. Figure 6 [21] illustrates both centralized and decentralized H_2 production systems. In a centralized system, H_2 is produced in a large-scale ammonia decomposition plant and then delivered to gas stations for PEMFC vehicle refueling. Contrarily, in a decentralized system, NH_3 is transported directly to the gas station for on-site hydrogen production via ammonia cracking. Additionally, stationary power generation utilizing fuel cells is illustrated. [21]

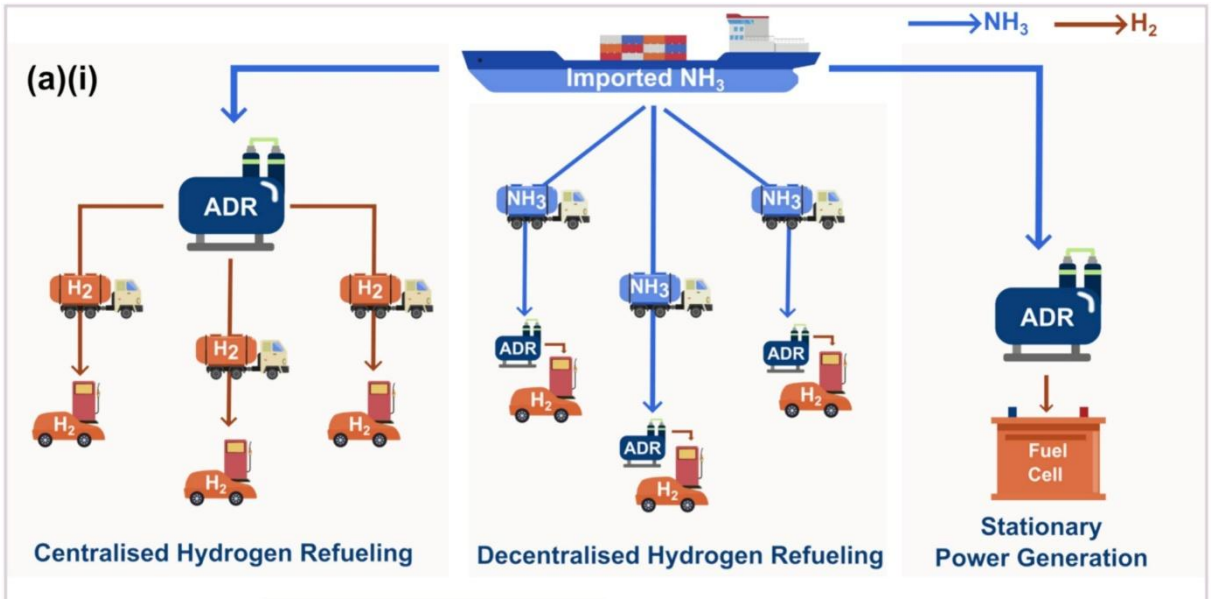

Figure 6. Utilizing ammonia decomposition reactors (ADR) for centralized and decentralized hydrogen refueling in transportation, and for stationary power generation. Adapted with permission from [21].

A decentralized hydrogen refueling solution would be highly preferable for the integrated Joule-heated reactors discussed in this work, as they offer a compact and efficient on-site hydrogen production method. By producing hydrogen on-site directly at the end-use location, challenging and expensive H_2 gas distribution can be avoided, and the energy transition would be significantly more economically viable and sustainable. Therefore, continuous development and research of electrified reactor technologies are crucial for the large-scale commercialization of green hydrogen.

6 Conclusions

The transition to global hydrogen economy relies heavily on solutions for rational transportation and storage of hydrogen gas, making ammonia highly viable, high-density energy carrier. However, to produce hydrogen, ammonia has to be decomposed, for example via thermo-catalytic ammonia cracking that usually requires high energy input and active catalysts. While ruthenium shows high catalytic activity, its high cost and scarcity limit its use in industrial applications. Consequently, non-noble nickel is favored in industrial scale despite the higher operating temperatures required in NH_3 cracking. To overcome these limitations on the conventional catalysts, high entropy alloy (HEA) catalysts provide tunable and multi-metallic alternatives. With high catalytic activity and stable reaction performance, they are also relatively inexpensive and form a strong material foundation for future NH_3 cracking technologies.

Besides advanced catalyst materials, optimization of reactor design and reaction parameters is crucial for industrial-scale NH_3 cracking, where non-uniform heat input and pressure drops limit the efficiency of conventional packed-bed reactors. Additive manufacturing of complex catalyst frames, such as periodic open cellular structures (POCS) and triply periodic minimal surfaces (TPMS), brings out solutions for the reactor heat and mass transfer limitations. These geometrically optimized structures significantly improve catalytic activity in NH_3 decomposition.

Furthermore, by using electrically conductive 3D-structures, such as multi-metal HEAs, the heat input for the reaction can be provided rapidly via Joule heating or electromagnetically induced Joule heating. This integrated approach ensures a uniform temperature profile at the active sites of the catalyst, minimizing energy losses of the process. Development of these compact reactors can be seen as a solution to decentralized, on-site hydrogen production by bypassing the bottlenecks of hydrogen transportation. This promotes the transition to economically viable and large-scale green hydrogen commercialization.

7 References

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