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Abstract: Ammonia, primarily made with Haber–Bosch process developed in 1909 and winning two Nobel prizes, is a promising noncarbon fuel for preventing global warming of 1.5 °C above pre-industrial levels. However, the undesired characteristics of the process, including high carbon footprint, necessitate alternative ammonia synthesis methods, and among them is chemical looping ammonia production (CLAP) that uses nitrogen carrier materials and operates at atmospheric pressure with high product selectivity and energy efficiency. To date, neither a systematic review nor a perspective in nitrogen carriers and CLAP has been reported in the critical area. Thus, this work not only assesses the previous results of CLAP but also provides perspectives towards the future of CLAP. It classifies, characterizes, and holistically analyzes the fundamentally different CLAP pathways and discusses the ways of further improving the CLAP performance with the assistance of plasma technology and artificial intelligence (AI).

Keywords: Ammonia synthesis, Chemical looping, Nitrogen carrier, Renewable fuels, Energy carrier

1. Introduction

Nitrogen is an essential element for living organisms. Although nitrogen gas is abundant in the atmosphere, it must be converted into other chemical forms to facilitate use by biological organisms. Nitrogen fixation, a process in which nitrogen in the air is converted to bio-available nitrogenous compounds, can occur naturally through biological nitrogen fixation and other processes like lightning [1, 2] or it can be performed industrially. Currently, the Haber-Bosch process ($3H_2 + N_2 \rightarrow 2NH_3$), developed in the early 20th century, is the basis for most industrial NH_3 production. About 170 million metric tons of ammonia were produced worldwide in 2018, of which about 80% was used for artificial fertilizer production, which has fundamentally changed the way food is produced, facilitating how crops are grown to support a global population of seven billion [3]. Ammonia also can be used for nitric acid (HNO_3) and explosive production. Recently, NH_3 has also been considered as a potential renewable and carbon-free energy carrier due to its high energy density, relatively easy liquefaction and transportation, and zero-carbon emissions [4-7]. However, the centralized and large scale Haber-Bosch process requires severe process conditions (about 100–200 bar pressures (1 bar = 10^5 Pa), 400–500°C reaction temperatures, and high feed purities of H_2 and N_2), which results in intensive energy consumption (3%–5% of global natural gas output and 1%–2% of the world's energy consumption) [8-10]. The high-pressure compression required for the Haber-Bosch process can contribute up to 50% of the total capital cost [11]. In addition, the NH_3 production process has a considerable carbon footprint, producing 1.9 tons (using efficient natural gas derived H_2) to 16.7 tons (using coal-derived H_2) of CO_2 per ton of NH_3, leading to more than 1% of total human-caused CO_2 emissions [12, 13] with the associated environmental impacts [14]. Therefore, developing alternatives for sustainable NH_3 production with good techno-economic viability is societally essential.

Numerous studies have been conducted to develop alternative NH_3 production methods, such as organometallic catalysis [15-18], photocatalysis [19-21], electrochemical methods [22-26], wind-coupled catalysis [27], and chemical looping processes [13, 28-30]. Photocatalytic NH_3 synthesis is a sustainable technology, utilizing solar energy and photocatalyst to produce NH_3 from N_2 and H_2O. Unfortunately, there is still a long way to go before practical photocatalytic NH_3 production [20]. Recently, nitrogen chemical looping processes, consisting of N_2 fixation and NH_3 generation steps at ambient pressure, have gained increased attention. Chemical looping processes split a reaction into multiple spatially separated sub-reactions to generate chemicals or energy via continuous reaction and regeneration of chemical intermediates [31-33]. Chemical looping has been employed for different applications, such as combustion, gasification, reforming, and air separation for oxygen supply. [34-36]. In a typical chemical looping combustion cycle, a solid oxygen carrier donates its lattice oxygen to provide the oxygen for combustion in a fuel reactor; then, the reduced oxygen carrier is transferred to an air reactor for oxidation [37]; finally, the re-oxidized oxygen carrier is sent back to the fuel reactor to complete the cycle. Chemical looping ammonia synthesis (CLAP) processes can be separated into two or three steps, including (1) N activation by forming a bulk metal nitride or metal imide as the nitrogen carrier, (2) ammonia production by reaction of nitrogen carrier materials with water or hydrogen, and (3) regeneration of intermediate(s) for re-use in step (1) [38]. Compared to the

Haber-Bosch process, CLAP can be performed at atmospheric pressure, which circumvents severe process conditions, simplifies ammonia production plants, increases energy efficiency, and decreases the carbon footprint of ammonia production. Suitable thermodynamic and kinetic properties and good stabilities are needed to make CLAP processes feasible for high-yield and high-selectivity NH_3 production. Solar-driven CLAP utilizes concentrated sunlight to provide the energy and therefore has the potential to produce NH_3 sustainably without fossil CO_2 emissions [13, 39, 40].

To the best of our knowledge, there is no comprehensive review or perspective of the CLAP process and its associated nitrogen carrier materials, which should not be the case for such an important emerging noncarbon-based energy source. Accordingly, this work aims to informatively review the recent advancements in CLAP and summatively provide a perspective for the future of CLAP. In this review, we first discuss the paths for sustainable CLAP and the utilization of ammonia. Then state-of-the-art CLAP is systematically classified into four categories (Type I–IV), and defined according to the reactants and intermediate steps. Type I–IV CLAP categories are Type I CLAP with metal nitrides as carriers and H_2 as the hydrogen source, Type II CLAP with metal nitrides as carriers and H_2O as the hydrogen source, Type III with metal nitrides as carriers, H_2O as the hydrogen source, and metal reduction by electrolysis, and Type IV with metal imides as carriers and H_2 as the hydrogen source. Also, recent developments and the required thermodynamic properties of the nitrogen carrier for each type of CLAP are comprehensively reviewed. Finally, the development direction of CLAP technology is envisioned.

2. Chemical looping processes for ammonia production

2.1. Pathways for CLAP

Fig. 1 shows possible paths for sustainable CLAP and the utilization of ammonia as a noncarbon fuel, chemical intermediate, and fertilizer. The hydrogen needed in CLAP is provided via sustainable sources, such as thermochemical water splitting using concentrated solar energy, water electrolysis using electricity from green energy resources, pyrolysis and reforming of biomass, or directly from the reactants used in one of the CLAP loops (e.g., water). Biochar from biomass also can be used as a reductant for nitrogen carrier regeneration in some CLAP processes. In addition, the required energy for CLAP processes can be provided by solar heat or electricity from renewable sources [13]. Ammonia produced via sustainable CLAP pathways can not only be used as a noncarbon fuel for engines, gas turbines, fuel cells, etc., but also for agricultural fertilizer production. In the subsequent discussion, CLAP processes are divided into four types, according to the nitrogen carrier and the hydrogen source.

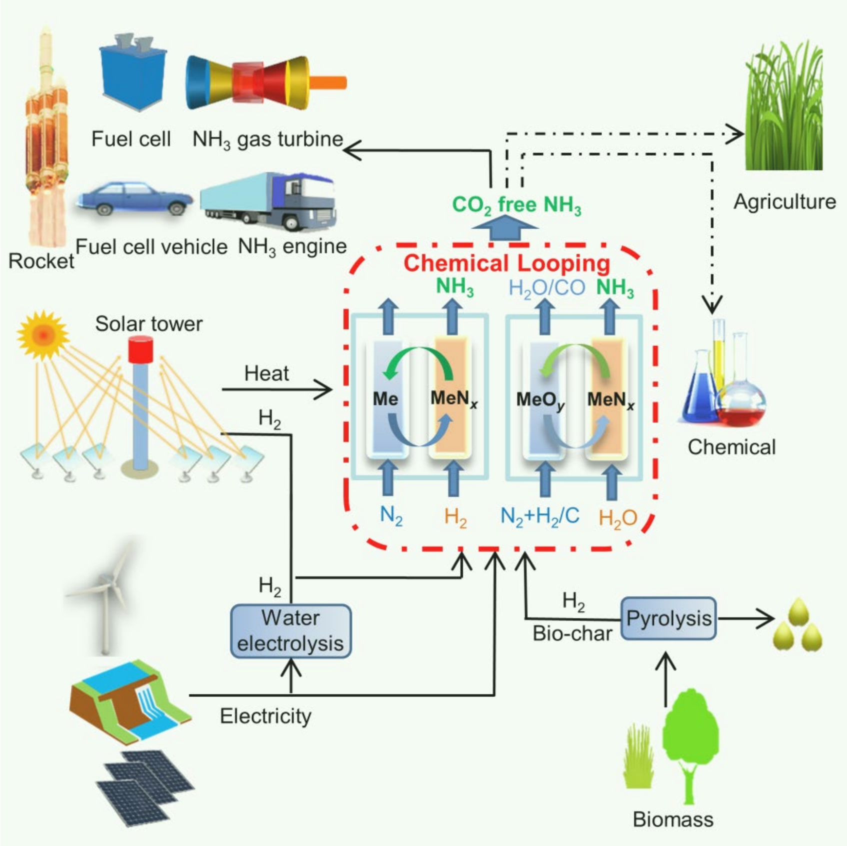

Fig. 1. Pathways for sustainable CLAP and the utilization of ammonia. (Color online)

2.2. Type I CLAP: with metal nitrides as carriers and H_2 as the hydrogen source

As shown in Fig. 2a, Type I CLAP consists of two steps: (1) metal nitridation or metal nitride regeneration with N_2 and (2) metal nitride denitridation with H_2 to produce NH_3. Type I CLAP only uses N_2 and H_2 as reactants and metal nitrides as nitrogen transfer reagents or nitrogen carriers. The precondition of NH_3 generation with Type I CLAP is that both reaction steps proceed under exergonic conditions [13]. As shown in Fig. 2b, Li_3N/HLi systems exhibit the above-mentioned characteristic, since both HLi nitridation and Li_3N denitridation or Li_3N hydrogenation to yield NH_3 are exergonic at relatively high and low temperatures, respectively

[13]. However, the hydrogenation of nitrogen carriers like AlN is not thermodynamically favorable at temperatures below 800 °C at atmospheric pressure.

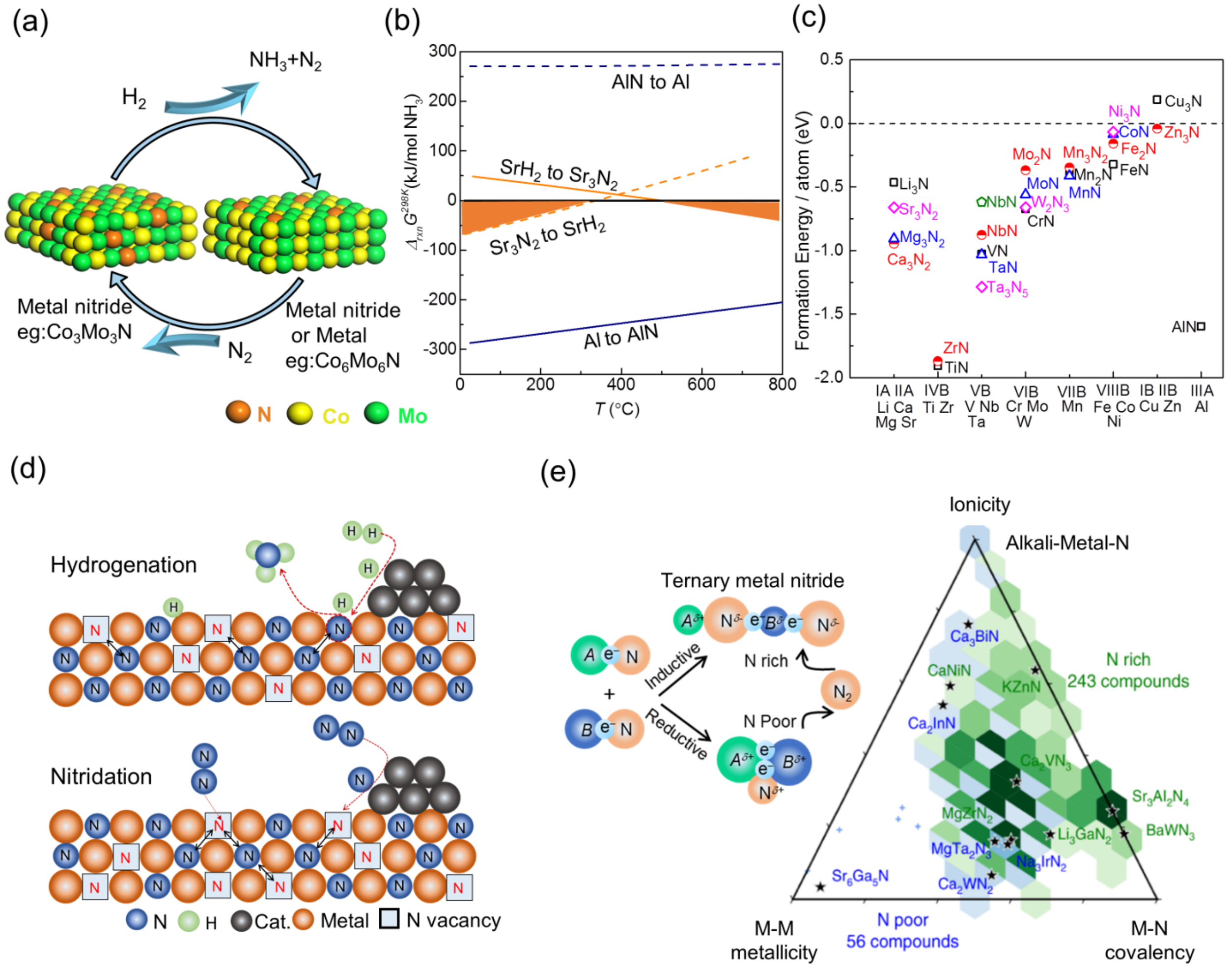

Fig. 1. Scheme and thermodynamic analysis Type I CLAP. (a) NH_3 production via Type I CLAP using metal nitrides as carriers and H_2 as the hydrogen source. (b) Thermodynamic analysis of ammonia synthesis via denitridation of metal nitrides (Sr_3N_2 and AlN) by H_2 and N_2 reduction by Al or SrH_2 at 1 bar and up to 800 °C (thermodynamic data from National Institute of Standards and Technology (NIST) Standard Reference Database Number 69). (c) Formation energies of metal nitrides (data from the Materials Project database). (d) Models representing catalytic hydrogenation of metal nitrides to produce NH_3 and catalytic regeneration of the metal nitride. (e) Metallicity, ionicity, and covalency of stable alkali-metal based ternary nitrides, with color

intensities corresponding to the number density in each hexagon. Reproduced with permission from Ref. [41], copyright © 2019 Springer Nature. (Color online)

The efficiency of CLAP rests on the properties of the nitrogen carriers. Various binary (i.e., M_xN_z) and ternary (i.e., $M1_xM2_yN_z$) transition metal nitrides have been investigated as nitrogen carriers for ammonia synthesis [13, 42-47]. The formation of transition metal nitrides is generally considered to occur by incorporating nitrogen into the interstitial sites of the metal structures [48, 49]. Transition metal nitrides are characterized by face-centered cubic, simple hexagonal, and hexagonal-closed packed structures [50]. The nitrogen content in each transition metal nitride can drastically affect its structure and properties. For example, Mn_4N, Mn_2N, Mn_3N_2, and MnN respectively possess cubic, hexagonal, tetragonal, and tetragonal structures [43, 51] and different formation energies. These nitrides are usually prepared by reduction of the transition metal oxide precursor in flowing gaseous NH_3 or N_2/H_2 mixtures [52]. However, the chemical looping process must use N_2 as the nitriding agent.

Binary metal nitrides, such as Ni_3N, Cu_3N, Zn_3N_2, Ta_3N_5, Mn_2N, Mg_3N_2, Ca_3N_2, Sr_2N, Mo_2N, and Co_3Mo_3N, etc., have been investigated for Type I CLAP [13, 42-47, 53]. The binary early transition metal nitrides, such as Ta_3N_5 [42, 44], $Mn_6N_{2.58}$ [13], Mn_3N_2 [43], and β-$Mo_2N_{0.78}$ [45], are relatively stable (Fig. 2c), and thus require denitridation temperatures up to 700 °C (Table 1). The yield of ammonia based on the percentage of available lattice nitrogen converted to ammonia is an important parameter for evaluating the efficiency of nitrogen transfer materials. The reported ammonia yields for binary early transition metal nitrides are typically <25% (e.g., ~8 mol% for $Mn_6N_{2.58}$ and 13 mol% for Ta_3N_5 via denitridation at temperatures up to 700 °C) [13, 44]. Although reaction kinetics are expected to increase with temperature, undesirable N_2 formation via decomposition is also favored at higher temperatures (e.g., MnN_4 thermally decomposes to Mn and N_2 at 1000 °C) [13].

Table 1 Some nitrogen carrier systems for CLAP.

Carrier system	Process	Condition	Efficiency$^{a)}$	Ref.
Ca_2N/Ca_2NH	Type I	700 °C denitridation	12% yield	[13]
Li-Mn_3N/Mn	Type I	500 °C denitridation	5% yield 5 h	[43]
$Ta_{2.5}Co_{0.5}N_{5-y}$	Type I	500 °C denitridation	25% yield 24 h	[44]

$Mo_2N_{0.78}/Mo$	Type I	750 °C denitridation and regeneration	13% yield	[45]
Co_3Mo_3N/Co_6Mo_6N	Type I	700 °C denitridation and regeneration	20% yield 5 h	[47]
$Mn_6N_{2.58}/Mn_4N$	Type I	700 °C denitridation	8% yield 1 h	[58]
AlN/Al_2O_3	Type II	1000 °C hydrolysis, >1500 °C regeneration	88% yield	[28]
$CrN/Cr_2O_3/Cr$	Type II	1000 °C denitridation, >1000 °C regeneration	0.15% yield 1 h	[38]
Mn_5N_2-NaOH/MnO	Type II	500 °C denitridation, 1150 °C reduction	54% yield 2 h	[59]
$Li_3N/LiOH/Li$	Type III	100 °C nitridation, ≤450 °C electrolysis, 4 V	~100% yield, 88.5% Faradaic efficiency (FE)	[75]
$Li_3N/Li^+/Li$	Type III	220 °C nitridation, 6.2–6.8 V	52.3% FE	[78]
$Li_3N/Li^+/Li$	Type III	180 °C nitridation, 5.3 V	57.2% FE	[79]
Ni-BaNH/BaH_2	Type IV	300 °C nitridation and denitridation	~95% yield, 3,125 μmol g^{-1} h^{-1}	[83]
Ni–Li_2NH/LiH	Type IV	300 °C nitridation and denitridation	1530 μmol g^{-1} h^{-1}	[83]

[a] Yield is defined as the percentage of lattice nitrogen converted to ammonia

As one moves from the early to the late transition metals, increasing effective nuclear charge reduces the chemical reactivity due to the downshift of the metallic electronic bands. As a result, Group 8 to 12 transition metal-based nitrides are relatively unstable (Fig. 2c) and decompose readily back to the corresponding elements. As shown in Fig. 2d, the mechanisms for denitridation of metal nitrides by H_2 and nitridation of partially reduced metal nitrides are analogous to Mars-van Krevelen reaction mechanism involving lattice oxygen, indicating that the diffusion of lattice nitrogen plays an important role in these two reactions [43]. Since metal nitrides with less negative formation energies have weaker bonding between the metal and lattice nitrogens, group 8 to 12 transition metals-based nitrides have high mobility of lattice nitrogen. Thermally unstable Cu_3N and Ni_3N can be totally denitrided at a relatively low reaction temperature of 250 °C, with up to 30% NH_3 yield [42]. Zn_3N_2 is partially denitrided at 400 °C with a low NH_3 yield of 15% [42]. One of the challenges of using late transition metal nitrides for CLAP is they are too unstable to be regenerated with N_2 at atmospheric pressure [42]. This challenge can be overcome by using low-temperature synthesis methods for these relatively unstable nitrides. For example, the partially nitrided iron nitride (Fe_xN) can be prepared via a mechano-chemical method at 45 °C [54].

Ternary transition metal nitrides also have been reported as nitrogen carriers for Type I CLAP. The reduction of Co_3Mo_3N can convert lattice nitrogen into ammonia [46, 47, 55]. In the experiment, Co_3Mo_3N was reduced to Co_6Mo_6N by a H_2 and Ar mixture at temperatures up to 700 °C, followed by regeneration of Co_3Mo_3N via nitridation of Co_6Mo_6N with N_2 at 700 °C. This process converted about 20% of the removed lattice nitrogen into NH_3 [55]. Tuning the reactivity of ternary metal nitrides is possible by controlling the variation of the metal composition. For instance, anti-perovskite nitrides (Co_3ZnN, Ni_3ZnN, Co_3InN, and Ni_3InN) showed very different reactivities. Co_3InN displayed an ammonia yield of only 8% at 400 °C, while that of Co_3ZnN was 81% under the same conditions [56]. According to high-throughput computational studies, there are hundreds of potential ternary metal nitrides with promising ionicity, metallicity, and covalence properties (Fig. 2e). The findings enhance the possibilities of finding suitable ternary metal nitrides for CLAP [41]. As mentioned previously, ammonolysis is generally used for the preparation of ternary metal nitrides in the literature [42, 46, 52, 56]. Therefore, additional studies on material synthesis methods need to be conducted to confirm the feasibility of using N_2 as the nitrogen source for the preparation and regeneration of ternary transition metal nitrides in CLAP processes.

Besides transition metal nitrides, alkali-earth metal nitrides also have been tested for CLAP. All of the alkaline-earth metals can form nitrides and these nitrides can be considered as ionic nitrides, consisting of metal cations and N_3^- anions. Alkali-earth metal nitrides are relatively active and readily react with hydrogen or water to produce NH_3. Mg_3N_2, Ca_3N_2, and Sr_3N_2 have been reported as nitrogen carriers for CLAP. Mg-based nitrides are good candidates for CLAP because Mg has a higher potential to reduce N_2 to N^{3-} and Mg_3N_2 is relatively stable compared to Ba_3N_2. NH_3 formation via the reduction of Ca_3N_2 and Sr_2N with H_2 has also been reported [13]. Both Ca_3N_2 and Sr_2N produced NH_3 with faster rates and significantly larger quantities in comparison to transition metal nitrides [13]. Substitution of lattice nitrogen by hydrogen is possible in Li_3N, Ca_3N_2, and Sr_2N, which facilitates the denitridation of these metal nitrides to yield NH_3 at low temperatures and N_2 reduction with the metal hydrides at elevated temperatures. Electronic structure calculations have been performed to investigate how the intercalation of hydrogen and NH_3 production are controlled by nitrogen vacancies in the metal nitride. According to a computational study, the activity of lattice nitrogen is proposed to control the formation and denitridation reactions of adsorbed nitrogen and the formation of lattice hydrogen

[13]. One challenge of using alkali-earth metal nitrides for Type I CALP is that it involves the use of metallic Mg, Ca, Sr under very reducing condition. Since Mg, Ca, Sr are reactive towards air and water, the safety of the alkali-earth metal nitride based CLAP should be further investigated.

Doping of another metal is a promising approach that can improve the reactivity of nitride materials by modifying the nitrogen transfer properties of the parent metal nitride and impacting strongly its reactivity. A computational study has predicted that Fe or Ni dopants in the sublayer of Mn_4N could facilitate N diffusion by reducing the diffusional energy barrier [57]. Experimental results also have confirmed that adding dopants may improve the reactivity of metal nitrides. For example, in the reduction of tantalum nitride using H_2, cobalt-doped $Ta_{2.5}Co_{0.5}N_{5-y}$ increased the 5 h NH_3 yield from 49 μmol for the undoped Ta_3N_5 to 380 μmol due to enhanced nitrogen transfer [44]. Similarly, Li-doped Mn_3N_2 significantly improved the NH_3 yield [43]. However, dopants can also cause negative effects [43, 45], such as accelerating lattice nitrogen depletion as N_2 instead of NH_3 formation, which significantly reduces NH_3 yield. Also, the addition of dopants, such as Li, may limit the ability to regenerate the reduced metal nitride with N_2 as the nitrogen source [43].

Type I CLAP is relatively simple, only involving gas-solid reactions between H_2, N_2, and nitrogen carriers. The required temperatures for the two spatially isolated steps of the process are usually less than 800 °C, which is second highest among the four types of CLAP. Although various metal nitrides have been investigated as nitrogen carriers for this process, only some of the reduced metal nitrides could be successfully regenerated by N_2. Currently, most of the reported nitrogen carriers show low NH_3 selectivity and yield, even with catalysts and promoters. Type I CLAP shows the lowest NH_3 yield among the four types of CLAP. The development of efficient nitrogen transfer reagents, which can reversibly liberate fixed lattice nitrogen as NH_3 and react with N_2 to restore lattice nitrogen at low temperatures, is key to this process. The development of effective catalysts and promoters is a possible approach to improve nitrogen transfer properties and enhance NH_3 formation from the reduced metal nitrides [43, 44].

2.3. Type II CLAP: with metal nitrides as carriers and H_2O as the hydrogen source

As shown in Fig. 3a, Type II CLAP processes can be divided into three steps: (1) N activation of a metal to form a bulk metal nitride, (2) ammonia production through hydrolysis of the metal nitride, and (3) reduction of the metal oxide to metal. In some cases, the reduction of the metal oxide and formation of the metal nitride may occur in one reaction, for example, carbothermal reduction of Al_2O_3 to AlN [28]. Unlike Type I CLAP, H_2O (instead of H_2) provides the hydrogen for NH_3 formation and a metal oxide (instead of a metal) is produced after fully denitridation in Type II CLAP. Hydrogen, methane, biochar, and active carbon have been reported as reductants of the metal oxide to metal. The use of a solid reducing agent complicates the CLAP process compared to gaseous reducing agents, like H_2 or CH_4. Interestingly, solar energy has been proposed to produce H_2 or provide the energy needed for this reduction process, which would make the whole process more sustainable [13, 30, 58]. AlN, Mn_5N_2, Cr_2N, Mo_2N, Mg_3N_2, etc. have been evaluated as nitrogen transfer reagents for this process [28-30, 38, 58-65].

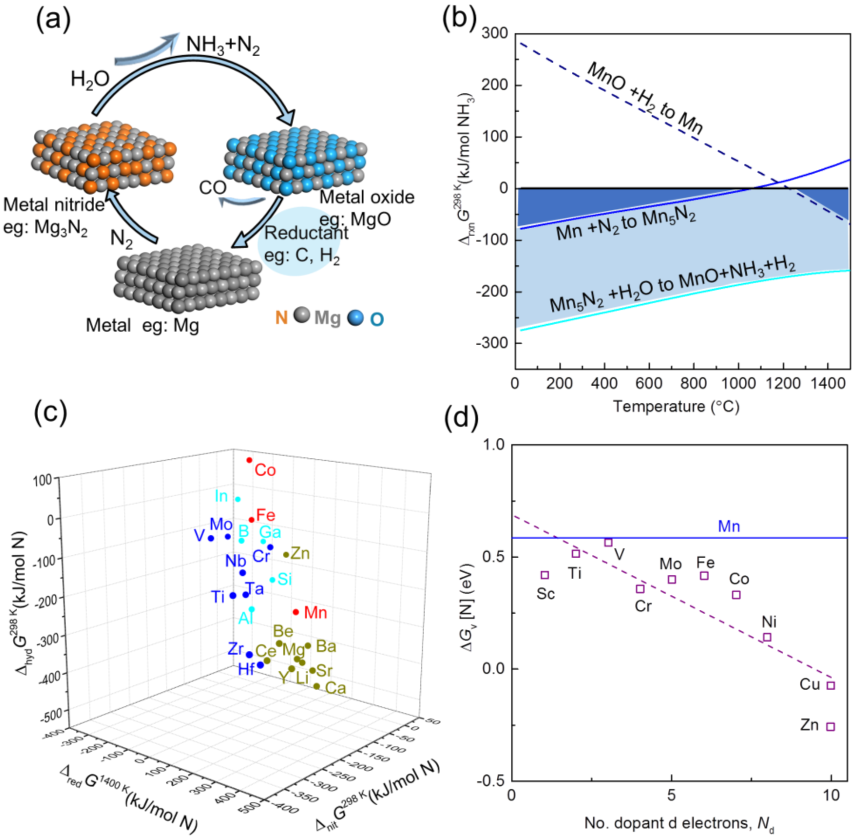

Fig. 2. Scheme and thermodynamic analysis of Type II CLAP. (a) Scheme for Type II CLAP with metal nitrides as carriers and H_2O as the hydrogen source. (b) Thermodynamic analysis of ammonia synthesis via manganese nitride based Type II CLAP. Reproduced with permission from Ref. [39], Copyright © 2015 the Royal Society. (c) Feasibility of various elements for reactive NH_3 synthesis at atmospheric pressure: $\Delta_{rxn}G$ of carbothermal metal oxide reduction (x

axis) vs. $\Delta_{rxn}G$ of metal nitridation (y axis) vs. $\Delta_{rxn}G$ of metal nitride hydrolysis (z axis). Adapted with permission from Ref. [60], Copyright © 2011 American Institute of Chemical Engineers (AIChE). (d) Free energy of nitrogen-vacancy formation in doped $D_{0.25}Mn_{1.75}N$ metal nitrides versus the number of dopant d electrons. Reproduced with permission from Ref. [39], Copyright © 2015 the Royal Society. (Color online)

Thermodynamic analysis of CLAP is a useful approach to screen potential nitrogen carriers. Fig. 3b shows the temperature dependences of the changes in the Gibbs free energy of reaction steps in a typical CLAP process. The nitridation of the metal to produce the metal nitride and the hydrolysis of the metal nitride to yield NH_3 are exergonic at low temperatures, while the reduction of the metal oxide to the metal is exergonic at elevated temperatures. One of the challenges for Type II CLAP is the high temperature required for the reduction of metal oxide. The analysis of Gibbs free energy ($\Delta_{rxn}G$) of metal nitridation, carbothermal metal oxide reduction, and hydrolysis of metal nitrides as candidate nitrogen carriers is useful to guide the metal choice. Fig. 3c presents some initial thermodynamic analyses of 35 candidate nitride/oxide systems for Type II CLAP [60]; those with negative Gibbs free energies of the individual reaction steps under the chosen reaction conditions (Fig. 3c) [60] are of interest. Unfortunately, only a few of the evaluated nitrogen carriers are thermodynamically favored for all three reaction steps at the chosen conditions. In addition, promising nitrogen carriers must balance competing requirements, such as good kinetics for N_2 activation and NH_3 yield, reduction of the oxidized nitrogen carrier at reasonable temperatures, good efficiency of reducing agent per mole of ammonia formation, good energy conversion efficiency. For example, although Mn_4N/MnO meets the thermochemical requirements, the high consumption of chemical reducing agents (4 mol C for per mol NH_3) impedes it from working as a promising nitrogen carrier [66].

The first proposed Type II CLAP processes used AlN as the nitrogen carrier [67]. The reactions involved in this process are

$$3\mathrm{C} + \mathrm{N_2} + \mathrm{Al_2O_3} \rightarrow 2\mathrm{AlN} + 3\mathrm{CO} \qquad (1)$$

$$2\mathrm{AlN} + 3\mathrm{H_2O} \rightarrow \mathrm{Al_2O_3} + 2\mathrm{NH_3} \qquad (2)$$

The endothermic carbothermal reduction of Al_2O_3 in a N_2 atmosphere (2) requires high temperatures, above 1500 °C [67-69]. Due to its poor reaction kinetics, the steam-hydrolysis of AlN also requires a high reaction temperature of up to 1000 °C. One advantage of using AlN as a nitrogen carrier is that it displays a high NH_3 yield up to 88% after steam hydrolysis at 1000 °C [67].

Transition metal nitrides such as CrN, Mo_2N, and Mn_5N_2 also have been reported as nitrogen carriers for Type II CLAP. CrN based CLAP includes three steps: (1) nitridation of Cr with N_2 at 1000 °C to produce Cr_2N and CrN, (2) hydrolysis of the nitride at 1000 °C to produce NH_3, and (3) reduction of Cr_2O_3 at 1200–1600 °C with CO and H_2 [38]. Cr can readily fix N_2 as chromium nitride at ~1000 °C, but the CrN liberates NH_3 slowly and has a low NH_3 yield of 0.15 mol% of the lattice nitrogen, while 99 mol% of the liberated N forms undesired N_2 [38]. Mo_2N is one of the promising nitrogen carrier candidates for Type II CLAP due to its favorable thermodynamic properties. The reduction of MoO_2 is favored thermodynamically above 1155 °C [58]. In addition, Mo_2N liberates NH_3 much faster than other stable transition metal nitrides, such as CrN, Mn_4N, or AlN, and has an NH_3 yield of 14 mol% at a relatively low denitridation temperature (500 °C) [66]. Similarly, a Mn_5N_2 based Type II CLAP process was achieved by MnO reduction at 1150 °C under 4 vol% CH_4, nitridation at 800 °C, and steam hydrolysis of the nitride at 500 °C [59]. However, the Mn-nitride showed low NH_3 yield without the use of a promoter.

For alkali-earth metal nitrides, although ionic Mg_3N_2, Ca_3N_2, and Ba_3N_2 form NH_3 readily through hydrolysis, only Mg-based materials allow each reaction step of CLAP to be thermodynamically favorable at temperatures below 1600 °C. Typical Mg_3N_2-based CLAP is performed by reducing MgO with CH_4, C, or H_2 to produce metallic Mg at high temperatures, nitriding Mg to form Mg_3N_2 at decreased temperatures, and hydrolyzing Mg_3N_2 to yield NH_3 [30, 66]. Hydrolysis of Mg_3N_2 at low temperature (500 °C) can totally liberate the lattice nitrogen to obtain an NH_3 yield of 70 mol% [66]. The apparent activation energies of NH_3 formation via the hydrolysis of highly ionic Mg_3N_2 and Ca_3N_2 are low (<15 kJ/mol), indicating that NH_3 liberation from Mg_3N_2 is gas-phase diffusion-limited [66].

Several strategies have been applied to assist Type II CLAP. The first is to add a catalyst or promoter to improve the reaction kinetics. The use of Fe_2O_3 as a catalyst can significantly decrease the apparent activation energy of AlN steam-hydrolysis [29]. Also, catalysts such as

TiO_2 can cause dissociative adsorption of H_2O on their surface to provide hydroxyl groups for further N-desorption reactions, resulting in a higher NH_3 yield [70]. This mechanism agrees with a computation study showing hydroxyl-mediated proton diffusion as the predominant mechanism for AlN hydrolysis [50]. The addition of suitable promoters or dopants can also increase the yield of NH_3 by modifying the lattice nitrogen's bonding strength. For instance, the addition of NaOH to Mn_5N_2 weakened the Mn–N bonds, resulting in more nitrogen liberation as NH_3, and thus significantly improving the NH_3 yield from 4 mol% to 54 mol% [59]. Computational results also show that transition metal dopants can decrease the stability of lattice nitrogen (Fig. 3d). The second strategy is to design nitrogen carrier systems with desirable kinetic and thermodynamic properties. Designing ternary metal nitrides with different desired properties compared to the parent metal nitrides is one approach. For example, the reduction temperature for the bimetallic oxides of a ternary metal nitride system may be significantly lower than that for either of the parent metal oxides [60]. In addition, the bimetallic nitrogen carrier can combine the desired properties of one parent metal nitride for N_2 reduction with those of another single parent metal nitride for NH_3 liberation, resulting in better performance in both N_2 fixation and NH_3 formation [71]. Another approach is to prepare porous metal nitrides or to load the metal nitride on a high-surface support to provide more reactive sites. The use of high-surface SiO_2 increased NH_3 yield for Cr nitride hydrolysis under the same reaction conditions [38]. Also, integration of the chemical looping process with other processes is a strategy to improve overall sustainability and energy efficiency. As mentioned previously, solar water splitting and concentrated solar energy have been proposed to produce H_2 or to provide energy for CLAP [13, 39, 40]. A 69.3% energy efficiency was achieved by an integrated system of nitrogen separation, CLAP, and electrical power generation [72].

Fig. 4 presents a combined frontier orbital-density of states analysis of catalyst-assisted chemical looping ammonia synthesis. At the initial stage of nitridation, the dissociation of N_2 on the metal surface is of vital importance. However, the activation of N_2 is extremely difficult because the triple bond of N_2, consisting of 1 σ-bond and 2 π-bonds, is very stable. The complete triple bond dissociation requires 945 kJ/mol [73], while the first (σ bond) cleavage takes 410 kJ/mol [74]. The activation of N_2 only by interaction with the main-group metals (M) or s/p-band metals is illustrated in Fig. 4a. The N_2 orbitals are shifted downwards to broadened resonance when coupling with the s/p-band. Only if the metals have an s/p-band centered at an appropriate energy level is the lowest unoccupied molecular orbital (LUMO) of N_2 partially filled by electrons that shift from the metal to weaken the N_2 internal bonds. N_2 is negligibly activated by main-group metals because this filling of the antibonding orbital does not occur. At the stage of denitridation, reductants are used to extract nitrogen out of metal nitrides. Water, for instance, must first dissociate on the MN_x surface and then the generated protons can weaken the M–N bond, form N–H bonds, and produce ammonia. However, the activation of H_2O on the MN_x surface is ineffective, as shown in Fig. 4b, because no electron density is transferred to the LUMO, while the highest occupied molecular orbital (HOMO) of H_2O remains filled by interaction with the broad s/p-band of MN_x. Accordingly, the uncatalyzed nitridation and denitridation by main group metals are both kinetically unfavorable.

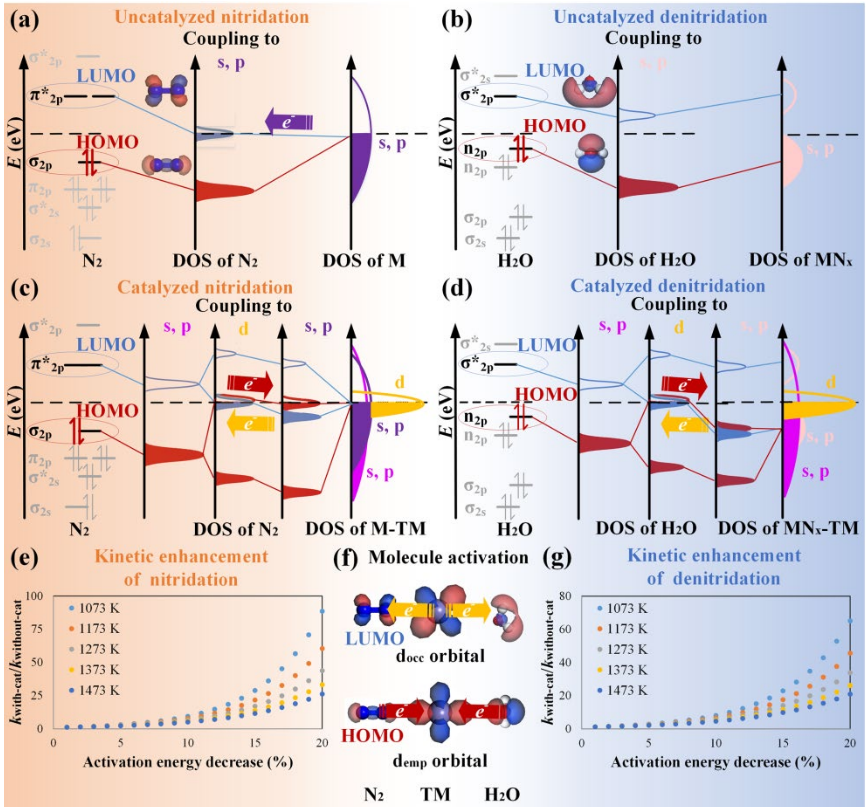

Fig. 4. A combined frontier orbital-density of states analysis of catalyst-assisted chemical looping ammonia synthesis. (a) Uncatalyzed nitridation by N_2 of main group metals (M). (b) Uncatalyzed denitridation by H_2O of main group metal nitrides (MN_x). (c) Nitridation of M by N_2 catalyzed by transition metals (TM). (d) Denitridation of MN_x by H_2O catalyzed by TM. (e) Normalized rate constant of nitridation as a function of decreasing activation energy due to catalysis. (f) Molecular orbital schematic diagram showing the effect of TM catalysts. (g)

Normalized rate constant of denitridation as a function of decreasing activation energy due to catalysis. (Color online)

Conversely, N_2 can be highly or even fully activated with transition metals (TMs or d-band metals). As shown in Fig. 4c, the complex interaction among N_2, TMs, and main-group metals are divided into three sequential steps: (1) coupling to the s/p-band of TMs, (2) coupling to the d-band of TMs, and (3) coupling to the s/p-band of main-group metals. Since the s/p-band of TMs are all partially filled and have a broad width, a broadened resonance is first formed when N_2 couples to the s/p-band of TMs. Due to the narrow, but strong, density of d states, the resonance band splits in succession when coupling to the d-band of TMs. As displayed in Fig. 4c, both the original LUMO and HOMO of N_2 split into bonding and antibonding states. In detail, the bonding level of the N_2 LUMO is filled mainly by d-electron donation from TMs, while the antibonding level of the N_2 HOMO is depopulated mainly by electrons accepted into empty d orbitals of TMs. Upon coupling to the s/p-band of main-group metals, the resonance is further downshifted, giving rise to more electrons filling the N_2 LUMO bonding states and the N_2 HOMO antibonding states. Similarly, the scission of H–O bonds in H_2O is promoted when TMs are involved. The promotion mechanism is the same as that for N_2 activation. As shown in Fig. 4d, the non-bonding lone pairs (HOMO of H_2O) rehybridize with the d-band of TMs, splitting into anti-bonding and bonding states. Meanwhile, the σ^* antibonding orbital (LUMO of H_2O) is separated into two resonances as well. Some d-electrons from TMs occupy the LUMO levels of H_2O and some electrons in the HOMO levels of H_2O shift into the empty d-band of the TMs. As a result, H_2O dissociation is favored and the subsequent denitridation is kinetically more reactive as well. In consideration of the charge transfer processes in the previous analysis, TMs act as an electron donor-acceptor, facilitating the activation of dinitrogen and water, as displayed in Fig. 4f. Fig. 4e and g illustrate how the kinetics (rate constants) of nitridation and denitridation can be enhanced by decreasing the corresponding activation energies. The activation energies of nitridation and denitridation without catalysts are 200.0 kJ/mol and 186.3 kJ/mol, respectively, based on reported values [67]. If a catalyst induces a 20% reduction in these activation energies, the nitridation reaction rate constant increases 26.2 to 88.5 times, while the denitridation rate constant improves 21.0 to 65.1 times, depending on the reaction temperature.

Type II CLAP using carbon compounds as reductants for the metal oxide involves gas-solid or solid-solid reactions. However, the reduction of the metal oxide required for nitride regeneration requires a relatively high temperature, even up to 1600 °C. Some nitrogen carriers show high NH_3 yields in Type II CLAP, but the required temperature for steam-hydrolysis of some stable metal nitrides can be up to 1000 °C due to the poor kinetics. The Type II CLAP requires the highest reaction temperature among the four types of CLAP. Although some catalysts and promoters have been reported for this process, the required temperature is still relatively high, particularly for the synthesis of metal nitride from metal oxide. Therefore, discovering efficient nitrogen carrier systems with low chemical looping temperatures is vital for the implementation of Type II CLAP. In addition, since some Type II CLAP processes also involve the use of active metal under very reducing conditions, safety considerations of such a process should be further evaluated.

2.4. Type III CLAP: with metal nitrides as carriers, H_2O as the hydrogen source, and metal reduction by electrolysis

Type III CLAP processes consist of metal nitridation with N_2 to form the metal nitride, followed by hydrolysis to produce ammonia. Electrolysis of the resulting metal hydroxide or metal ion is used to regenerate the metal (Fig. 5a and b), which is unusual in chemical looping. The unique feature of this process is the use of electrolysis for metal reduction instead of a thermal chemical reaction. The process uses only water and nitrogen as reagents, with electricity, to produce ammonia at atmospheric pressure and low temperatures [75]. Again in this process, electrical energy from renewable energy sources can be used to produce NH_3 sustainably without the use of fossil resources or CO_2 production.

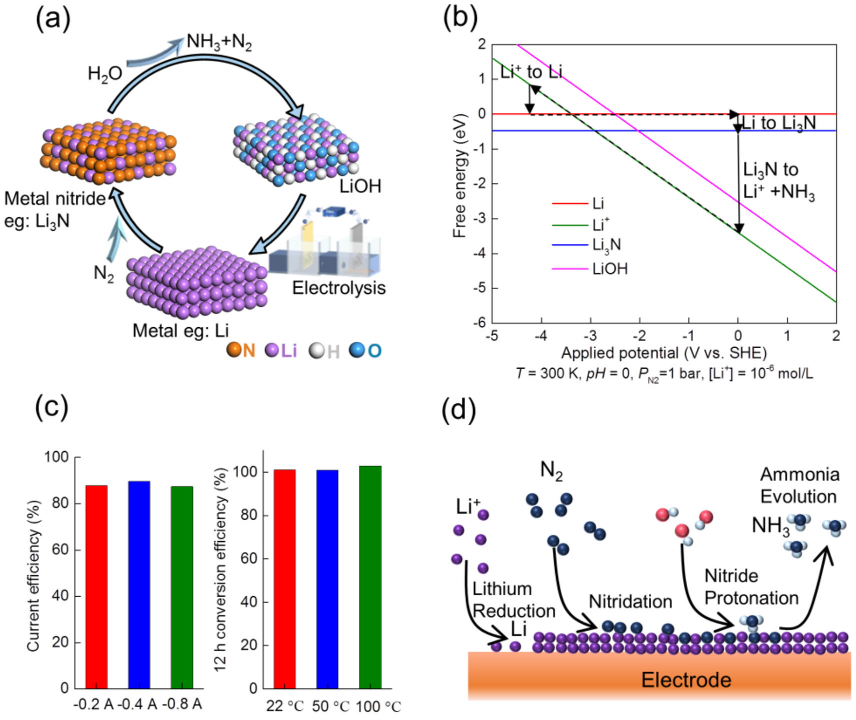

Fig. 5. Scheme, thermodynamic analysis, and performances data of Type III CLAP. (a) Scheme for NH_3 production using Li_3N as the N carrier and electrolysis for metal reduction. (b) Thermodynamic behavior of Li–N–O–H species with Li cycle steps. (c) LiOH electrolysis with corresponding current efficiencies toward lithium yield. Adapted with permission from Ref. [75], Copyright © 2017 the Royal Society of Chemistry. (d) Schematic of lithium-mediated nitrogen reduction on the surface of an electrode. Adapted with permission from Ref. [76], Copyright © 2019 Elsevier. (Color online)

Lithium is the only alkali metal that has been reported to form a stable ionic nitride and studied for CLAP so far. Density functional theory (DFT) calculations indicate that Li can form a strong bond with atomic N with a low N_2 dissociation barrier [75]. Moreover, Li has a relatively low applied potential and good lattice structure flexibility, which are beneficial for facile nitridation. The first reported Type III CLAP process involves (1) molten salt electrolysis of LiOH to produce Li, (2) nitridation of Li with N_2 to form Li_3N, and (3) Li_3N hydrolysis to produce ammonia [75, 77]. A minimum total cell potential of ~3.0 V is required for molten salt electrolysis of LiOH at 450 °C, which is much lower than the reduction temperature usually used in Type II CLAP. The three advancements of this process include highly efficient LiOH electrolysis, easy Li nitridation, and exceptional NH_3 selectivity. As shown in Fig. 5c, an average current efficiency of 88.5% was observed for molten salt electrolysis of LiOH. Remarkably, the lattice nitrogen in Li_3N could be completely converted, resulting in an approximate 100% yield of NH_3 after Li_3N hydrolysis at room temperature.

Besides molten-salt electrolytic cells, Li-ion conducting glass ceramic material (LISICON) electrolytic cells have been reported for Li deposition in Type III CLAP, which can reduce the operating temperature and thus avoid potential complexity of separating liquid Li from the molten salt [78]. In the LISICON electrolytic cell, an organic electrolyte is used on the metallic Li side and an aqueous electrolyte is used on the O_2/air side. Washing the deposited metallic Li with 2-methyltetrahydrofuran before nitridation inhibits side reactions between Li and the solvent. This process showed a high Faradaic efficiency (FE) of 52.3%. However, LISICON is expensive and exhibits questionable long-term chemical stability.

A membrane-free electrochemical cell for lithium electro-deposition might overcome these disadvantages of LISICON electrolytic cells [79]. In the membraneless electrochemical cell, a biphasic system of aqueous $LiClO_4$ solution and $LiClO_4$ in propylene carbonate reinforced with poly(methyl methacrylate) is used as the electrolyte system. The biphasic interface of the immiscible aqueous/organic electrolytes can serve as a Li-ion conductor and a physical barrier at the same time. Type III CLAP using membrane-free electrochemical cells for lithium deposition also have a high FE (57%) [79]. Similarly, the lithium-mediated nitrogen reduction cycle has been shown to operate continuously in a non-aqueous electrochemical cell system with tetrahydrofuran as solvent and ethanol as proton source [76]. Li deposition, Li nitridation, and nitride protonation occur continuously and simultaneously on the electrode of the electrochemical cell (Fig. 5d), but the electrochemical cell method shows a much lower FE (18.5% ± 2.9%) than the Li-based Type III CLAP [76].

Besides Li, iron-based nitrogen carriers can be used for electro-thermo-CLAP. Unlike the Li-based process, Fe-based Type III CLAP consists only of two reaction steps: (1) molten salt electrolysis of iron oxide to Fe and (2) formation of NH_3 by the reaction of Fe with H_2O and N_2 [80]. Both of these steps can proceed at 250 °C, which is fairly low compared to the operating temperatures in Type II CLAP. Fe-based Type III CLAP can achieve a high FE (79.8%) and a high NH_3 formation rate (1.34×10^{-8} mol/(s cm^2) at 1.75 V) [80], but the cycling stability needs further improvement. Other metals, such as Co, Ni, Cu, and Zn, may be able to replace Fe as the chemical intermediate in similar Type III CLAP processes.

In general, the use of electrolysis for the metal reduction in Type III CLAP avoids the high reaction temperatures required for thermal chemical reduction of the metal oxide/metal hydroxide. The regeneration of the metal can be achieved at ambient temperature for an electrolytic cell with aqueous/organic electrolytes or at about 200–450 °C for molten salt electrolysis. This process displays high FE, high conversion rate, and good NH_3 formation selectivity. However, the use of electrolysis also increases the complexity of the whole looping system. Integration of the electrolysis process with the thermal chemical reaction process for large-scale ammonia production is not trivial and must be further investigated in the future. In addition, Type III CLAP involving the use of metal Li, which is extremely reactive towards air and water, needs special safety precautions.

2.5. Type IV CLAP: with metal imides as carriers and H_2 as the hydrogen source

Besides metal nitrides, metal imides are a suitable nitrogen carrier candidates for CLAP and the literature contains reports of metal imide denitridation to produce NH_3 [81-84]. As shown in Fig. 6a, a typical Type IV CLAP process consists of two steps: (1) nitridation of alkali or alkaline earth metal hydrides with N_2 to form imides and (2) denitridation of imides with H_2 to regenerate the metal hydrides and produce NH_3 simultaneously [83]. Like Type I CLAP, only H_2 and N_2 are used as feedstock for NH_3 synthesis in this process. The negative hydride ion in metal hydrides is highly active for N_2 reduction, making the nitridation of metal hydrides possible at relatively low temperatures.

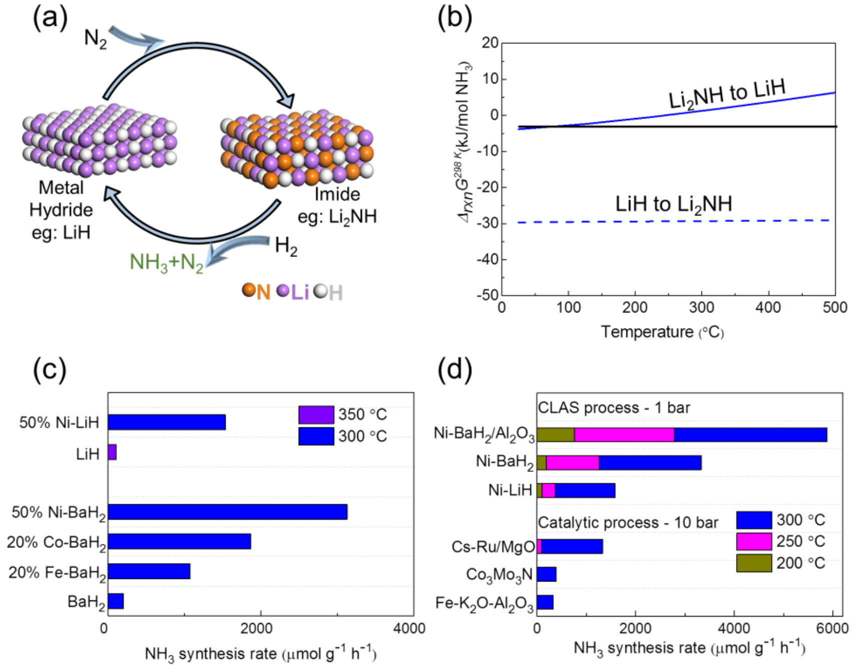

Fig. 6. Scheme, thermodynamic analysis, and performances data of Type IV CLAP. (a) Scheme for NH_3 production using metal imides as carriers. (b) Thermodynamic analysis of reaction steps in Li_2NH based Type IV CLAP with P_{NH3} fixed at 1.0×10^{-3} atm (1 atm = 101325 Pa, thermodynamic data from NIST Standard Reference Database Number 69 and the Ref. [83]). (c) NH_3 production rates of metal imides-based chemical looping with and without catalysts. (d) Comparison of NH_3 production rates of Ni-catalyzed CLAP (1 bar) and the conventional thermo-catalytic process (10 bar). Reproduced with permission from Ref. [83], Copyright © 2019 Springer Nature. (Color online)

Imides such as BaNH, Li_2NH, and CaNH are promising nitrogen carriers for Type IV CLAP [83]. Thermodynamic feasibility of evaluated nitrogen carrier systems in Type IV CLAP is in the order of $LiH/Li_2NH \approx BaH_2/BaNH > CaH_2/CaNH > MgH_2/MgNH$ (Mg_3N_2) [83]. Late 3d transition metal catalysts, such as Ni, Co, and Fe, are reported to significantly accelerate the reaction rates of both nitridation and denitridation steps and thus the NH_3 synthesis rate by significantly reducing the temperature required for nitridation by more than 100 °C and decreasing the apparent activation energy of both reactions [83]. Ni addition produced the highest activity, with nitrided 50%Ni-BaH_2 producing up to 3120 $\mu mol_{NH_3} g_{BaH_2}^{-1} h^{-1}$ at 300 °C (Fig.

6c). As shown in Fig. 6d, metal imide-based CLAP displays a markedly higher NH_3 synthesis rate at 1 bar than the thermo-catalytic process operated under the same temperature and 10 bar pressure [83]. The presence of noble metal Pd in a Pd-LiH composite also promotes N_2 fixation by LiH and denitridation of Li_2NH to NH_3 [85]. Interestingly, synergistic effects of binary nitride–imide composite nitrogen carriers may enhance CLAP performance. A Mn nitride-BaH_2 imide composite nitrogen carrier showed a significantly improved CLAP performance compared to neat Mn nitride or BaH_2 [86]. The Mn nitride in this Mn_4N/Mn_2N composite nitrogen carrier not only functions as a catalyst to promote the N_2 fixation and denitridation reactions of BaH_2/BaNH, but also directly performs these reactions, working as a second nitrogen carrier pair.

Although the Type IV CLAP process using metal imides as the nitrogen carrier is relatively new, it has shown some promising results. Since metal hydrides and imides are very active, this process can display high activity and NH_3 formation selectivity under mild conditions (300 °C, 1 bar). The development of new composite alkali/alkaline earth metal mixtures, promoters, and catalysts should further increase the feasibility of this process. Since the active metal hydrides and metal imides can react with the H_2O and O_2 impurities to form metal oxides and cause deactivation of the nitrogen carriers, the long-term stability and recyclability of these nitrogen carriers, particularly in the presence of H_2O and O_2 impurities, should be further studied. Moreover, processes involving alkali and alkaline earth metal hydrides also require special safety precautions.

3. Thermodynamic analysis

The thermodynamic properties of the nitrogen carriers dictate their suitability for chemical looping reactions. Thermodynamic analysis of CLAP has been used to evaluate the thermodynamic viability of reaction steps and to screen potential nitrogen carriers. Ideally, each reaction in CLAP processes should be thermodynamically favorable at reasonable temperatures [40, 58, 87, 88].

For Type I CLAP, the standard state Gibbs free energy of the nitridation reaction (Fig. 3c) is negative for most of the investigated metals, besides metals like Fe, Zn, and Co [60]. The metal nitride formation reaction is generally thermodynamically preferred at low temperature, resulting in fewer metal nitrides possessing negative standard Gibbs free energies of formation (ΔG_f°) with increasing temperature [40]. One challenge is that the reaction may not proceed at an appreciable reaction rate unless at an elevated temperature due to kinetic limitations, despite the thermodynamics of the nitridation reaction being more favorable at low temperatures [40]. Since $\Delta G_f°$ of metal nitrides are less than $\Delta G_f°$ of NH_3 (-16.4 kJ/mol), the standard state Gibbs free energy of the denitridation reaction of metal nitrides with hydrogen is positive [61], indicating the reaction temperature needs to be increased. However, high denitridation temperatures decrease NH_3 selectivity [13]. Further, the reported temperatures for denitridation of metal nitrides with hydrogen are usually in the range of 500–800 °C, but this reaction for some metal nitrides, including CrN, TaN, and NbN, is not thermodynamically favorable (i.e., is endergonic) below 800 °C.

Type II CLAP reactions generally have negative standard state Gibbs free energy changes for both nitridation of the metal and hydrolysis of the metal nitrides (Fig. 3c). Metal oxides usually have much more negative ΔG_f values than their corresponding metal nitrides under standard state conditions, and thus the free energy differences between nitride and their corresponding oxides usually exceed the free energy differences between H_2O and NH_3 [40]. The hydrolysis reactions of covalent, intermediate, and interstitial nitrides are generally kinetically limited and require elevated temperatures to achieve appreciable reaction rates. The challenge again is that the high hydrolysis temperature decreases the NH_3 selectivity. The reduction of the metal oxide also usually requires high temperatures to be thermodynamically viable. As shown in Fig. 3c, only a few metal oxides have negative Gibbs free energies for carbothermal reduction even at 1400 K and 0.1 MPa. The number of potential nitrogen carriers is further restricted when the thermodynamics of each step is considered.

For Type III CLAP, Li nitridation and Li_3N hydrolysis are both thermodynamically favored at low temperatures. At a suitable applied electric potential, the Gibbs free energy for lithium ion formation is larger than that for Li metal, making the reduction of Li^+ to Li metal thermodynamically favored. Li^+ ions can be reduced to Li metal at electric potentials < -3.3 V vs. the standard hydrogen electrode under theoretical aqueous conditions [75].

Similar to the nitridation of metals to their corresponding nitrides, the nitridation reaction of alkali and alkaline earth metal hydrides with N_2 to metal imides or amides (Type IV CLAP) has a negative Gibbs free energy at low temperatures. Like the denitridation step in Type I CLAP, the denitridation in Type IV CLAP requires elevated reaction temperatures. Since the Gibbs free energy difference of a metal hydride/metal imide pair is smaller than its corresponding metal/metal nitride pair, denitridation of metal imides to metal hydrides requires a lower temperature. The experimental results discussed previously show that both steps of Type IV CLAP can be thermodynamically favored at atmospheric pressure and 100–350 °C.

4. Outlook

Although encouraging progress has been achieved, efficient NH_3 synthesis via CLAP is still very challenging. To overcome these challenges, which include prohibitively high reaction temperatures, low activity of lattice nitrogen in nitrogen carriers, poor NH_3 selectivity, low NH_3 yield, and low long-term nitrogen carrier stability, further research efforts into the different aspects of this field are demanded. The development of efficient nitrogen carrier systems, novel CLAP processes, and process integration of CLAP with other processes are three major future research directions to achieve commercially viable efficiencies.

More effort should be devoted to the rational design of nitrogen carrier systems to significantly improve the activity of lattice nitrogen and selectivity of NH_3 formation. The nitrogen carrier is vital for the implementation of the chemical looping ammonia synthesis, since the efficiency of CLAP depends on the nitrogen carrier properties. As shown in Fig. 7, the development of a suitable nitrogen carrier system including catalysts and promotors involves numerous aspects of materials science and technology, including structural considerations, composition, synthesis techniques, reactivity and mechanical properties, reaction mechanism, etc. The shape, size, elemental composition, porosity, etc., of the nitrogen carrier system, can be cleverly designed to modify nitrogen vacancy density, lattice nitrogen transfer properties, and kinetics, and thus reduce the reaction temperatures to promote NH_3 formation (Fig. 7a). Smaller particle size and higher porosity enhances surface area to expose lattice nitrogen and catalytic active site. Also, the thermodynamic and kinetic properties may be tuned via control of the elemental composition of the nitrogen carrier system. For example, the reactivity of lattice nitrogen in Co_3Mo_3N and Ni_2Mo_3N should be very different compared to Co_2N and Mo_2N. Since the bimetallic catalyst may show an enhanced catalytic performance for CLAP than its corresponding single metal catalyst, more studies on bimetallic catalyst for CLAP are needed in the future.

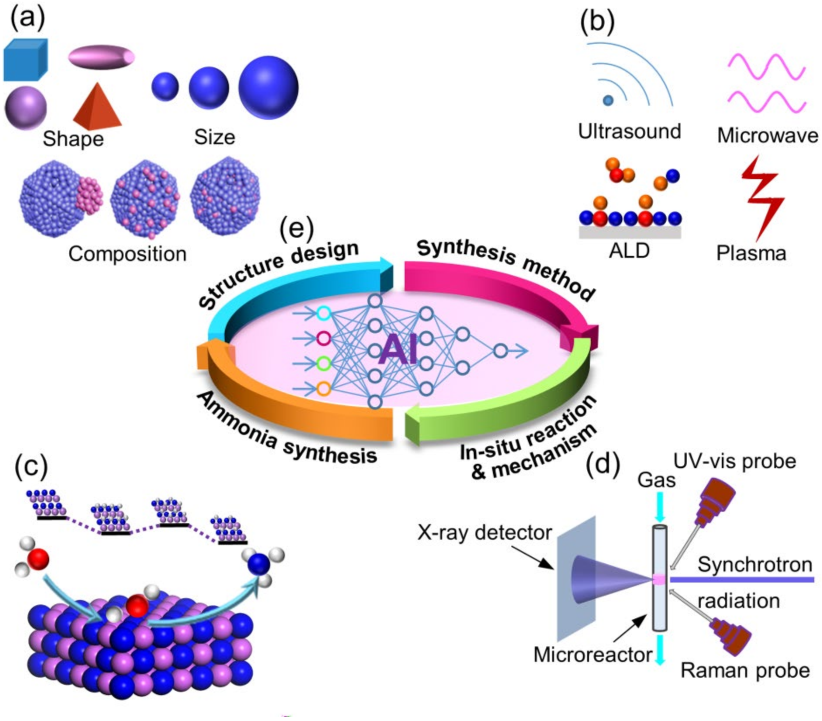

Fig. 7. Schemes of proposed strategies for the development of nitrogen carrier systems for CLAP. (a) Designing materials with special structures. (b) Applying new material synthesis technologies for nitrogen carrier synthesis. (c) Using *in-situ* characterization techniques to investigate reactions. (d) Investigating mechanisms via computational study and experiment. (e) AI assisted nitrogen carrier development. (Color online)

New material synthesis and modification techniques, such as ultrasound, microwave, atomic layer deposition (ALD), plasma treatments, can be applied to the synthesis of novel nitrogen carrier systems (Fig. 7b). The extraordinary conditions with extreme hot spots provided by cavitation-induced sonochemistry may allow for the synthesis of nitrogen carriers with special structures and properties [89]. Also, microwave-assisted synthesis methods can be used for the preparation of metal nitride systems with uniform structure and high phase purity in a short reaction time [90]. ALD is another powerful technique that should be useful for the synthesis of nitrogen carrier systems due to its capabilities in depositing material with atomic-level precision, tuning material composition, realizing different crystallinities, manipulating novel nanostructures, and so on. The catalyst, dopant, and promotor can be precisely deposited to synthesize complexly doped and mixed nitrogen carrier systems with specific spatial arrangements using the ALD technique.

Further understanding of fundamental bonding characteristics (covalent versus ionic nitride), reaction mechanisms, catalytic mechanisms, and structure-reactivity relationships is essential for designing suitable nitrogen carrier systems for CLAP (Fig. 7c and d). Currently, studies on the effect of lattice nitrogen diffusion and nitrogen-vacancy formation on the activity of nitrogen carriers are lacking. The combination of theoretical calculations, experimental data, and advanced characterizations would be a useful approach to provide deeper insights into the reaction mechanisms. *In-situ* characterization methods may provide information on reaction pathways, structure, and phase change, intermediates of reaction steps, and structure-reactivity relationships in the looping process. Unfortunately, experimental studies on nitrogen vacancies in nitrogen carriers are difficult to perform due to limitations of spectroscopic techniques, especially those under *in-situ* or operando conditions. However, computational simulations allow this kind of mechanistic study, which help to interpret experimental results and accelerate the discovery of reaction mechanisms. Detailed understanding of the reaction mechanism will eventually guide the design of nitrogen carrier systems.

Artificial intelligence (AI) could be a powerful tool for the development of CLAP. As shown in Fig. 7e, AI can be applied to important stages of CLAP research, such as nitrogen carrier system design, nitrogen carrier system synthesis, mechanistic studies, and ammonia synthesis process optimization. First, AI can facilitate the discovery and design of promoters, catalysts, and nitrogen carriers with superior properties for CLAP. The AI approach can use measurements and simulation data to establish quantitative relationships for material property predictions and new materials discovery, facilitating the screening of promising nitrogen carrier system candidates [91]. For example, the application of AI can use models to screen various combinations of components and structures to find nitrogen carriers with the desired properties from a candidate set. Second, AI can be used to speed up the synthesis of nitrogen carrier systems by suggesting which synthesis method, reagents, and experimental conditions to use. In the future, AI should be able to find optimal synthesis conditions by machine learning from failed attempts and even to predict synthesis conditions for new nitrogen carrier synthesis from historical data about other nitrogen carriers [92]. Third, AI can accelerate the discovery of CLAP reaction mechanisms and provide insight into novel nitrogen carrier system design. Besides assisting mechanism studies by addressing the reaction network complexity, AI approaches accelerate calculations to find transition states and minimum energy paths [93]. In addition, AI can be employed to optimize the reaction conditions and thus improve the reaction outcome of the overall CLAP process [94]. Although AI for material science and chemical engineering is still in a primitive stage, we expect that AI can offer many promising future applications in CLAP.

Developing innovative CLAP processes is another important approach to overcome the challenges in traditional CLAP and thus advance the field. One strategy for developing new CLAP processes is to combine preexisting CLAP with novel technologies and processes. For example, the microware technology can be applied for CLAP [95]. A new plasma-based CLAP process could be developed by using plasma technology for ammonia synthesis via the looping process. The applied electrical energy in a plasma reactor can selectively generate highly energetic electrons which subsequently collide with gas molecules to cause excitation, ionization, and dissociation, which allows otherwise thermodynamically unfavorable reactions to proceed; additionally, this process can be green by using renewable electricity [96]. Using plasma to activate stable molecules is appealing. Although plasmas have been used in the catalytic formation of ammonia and preparation of metal nitrides, it has not been applied for CLAP to date. In plasma-based CLAP, the plasma can be used for both nitrogen activation and NH_3 production steps (Fig. 8) [96, 97]. As shown in Fig. 8, the plasma discharge is able to break the stable triple $N\equiv N$ bond (9.8 eV) and create reactive atomic nitrogen. The excited N atoms can actively bind with metal atoms, resulting in the formation of the metal nitride phase (M_xN_y), with significantly enhanced kinetics. In addition, the high energy of nitrogen species in plasmas can cause significant heating of the metal surface and thus increase the surface temperature to much above the reaction zone temperature, resulting in high nitrogen diffusion rates and rapid nitridation of the metal. Similarly, in the NH_3 production step, the plasma can be used to directly dissociate H_2 to form active $H_{(g)}$ atoms, which will further react with M_xN_y to produce ammonia. Compared to conventional CLAP, plasma-based CLAP is able to operate at lower temperatures (25–450 °C) to efficiently produce NH_3 with rapid kinetics. For example, Ni–Mo nitride could be prepared via N_2 plasma treatment with a shorter reaction time (~10 min) at 450 °C compared to conventional high-temperature nitriding that requires several hours of reaction time at 700 °C [98]. Furthermore, the plasma is able to rapidly synthesize unstable metal nitrides that are too unstable to be produced with metal and N_2 at atmospheric pressure. Therefore, plasma-based CLAP can use relatively unstable and active metal nitrides, like Ni_3N and CoN, as nitrogen carriers.

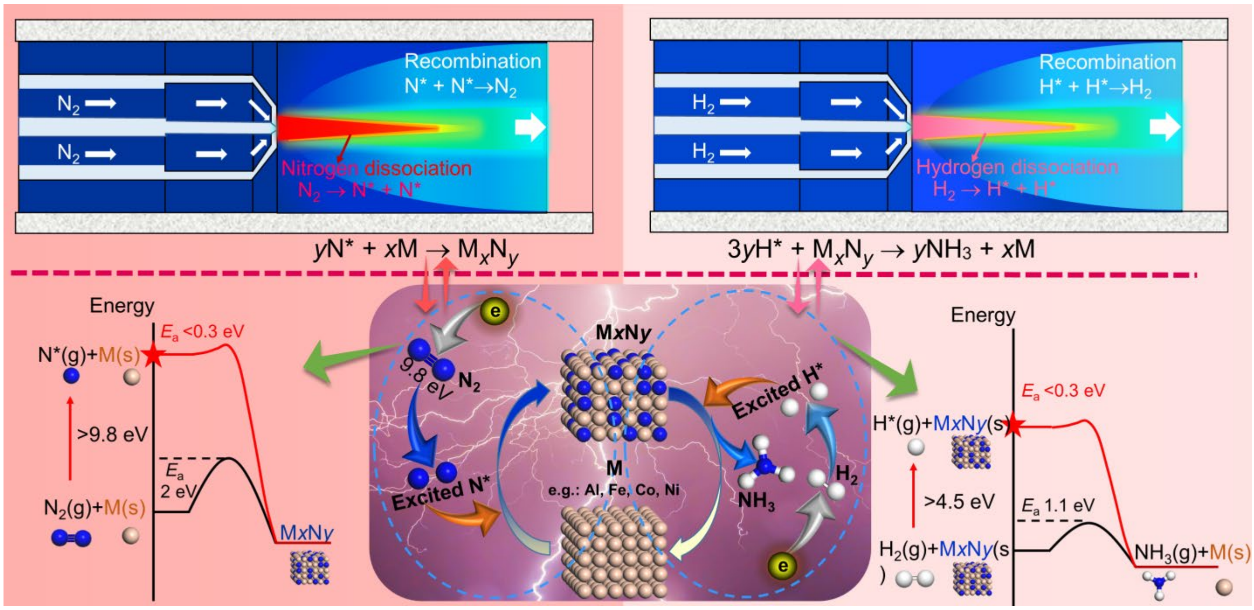

Fig. 8. Plasma-based chemical looping ammonia synthesis. (Color online)

Radiofrequency discharge, dielectric barrier discharge, microwave discharge, etc. can be used as sources to generate the plasma for CLAP. The particle balance (Eq. (1)) and power balance (Eq. (2)) for single-component electropositive plasma show that different parameters can affect the ion bombardment energies and thus the energies of the plasma species [99, 100]. Hence, the essential parameters (e.g., reactor type, input power, frequency) of plasmas for CLAP can be promptly controlled to effectively generate electrons with certain energies for the activation of N_2 and H_2. For the nitrogen activation step, the parameters can be controlled to set the reduced electric field (*E*/*N*, defined as the electric field strength (*E*) divided by the total gas number density (*N*)) above 200 Townsend (*Td*), to make N_2 dissociation the dominant N_2 electron impact process in the plasma regime [96]. Since H_2 has much lower bond dissociation energy than N_2, the dissociation of H_2 can become important at much lower *E*/*N* values. Therefore, for the ammonia production step, an *E*/*N* above 10 *Td* can be controlled to make hydrogen dissociation the important H_2 electron impact process in the plasma regime. In addition, the reactor geometry parameters (e.g., radius, length, and active species density profiles as a function of pressure in the axial and radial directions) and plasma operation parameters (e.g., *E/N*, electron temperature, and plasma power) can be further tailored to enhance the plasma efficiency.

The particle balance equation for the determination of electron temperature is given in Eq. (1):

$$k_{\mathrm{iz}} n_{\mathrm{n}} n_{\mathrm{i}} \pi R^2 L = n_{\mathrm{i}} U_{\mathrm{B}} (2\pi R^2 h_{\mathrm{L}} + 2\pi R L h_{\mathrm{R}}) \tag{1}$$

where k_{iz} is the ionization rate coefficient for different N or H ions in nitrogen or hydrogen plasmas; n_{n} is the neutral background gas density; $\mathrm{n_i}$ is the N or H ion density; U_{B} is the Bohm velocity, $\sim(\mathrm{e}T_{\mathrm{e}}/\mathrm{m_i})^{1/2}$; R and L are the radius and length of the cylindrical source; h_{L} and h_{R} are the variations in the density profile with pressure in the axial and radial directions. The unit for the electron temperature, T_{e}, is eV and $\mathrm{m_i}$ is the mass of N or H species.

The power balance equation is shown in Eq. (2):

$$P_f = \sum_i \left(\frac{\mathrm{n_i e}}{A}\right) \left[\epsilon_{\mathrm{T,i}} U_{\mathrm{B,i}} (2\pi R^2 h_L + 2\pi R L h_{\mathrm{R}}) + \frac{\epsilon_{\mathrm{L,i}} \pi R^2 L}{\tau_{\mathrm{rec}}}\right] \tag{2}$$

where P_{f} is the input power density; n_{i} are positive N or H ions in nitrogen or hydrogen plasmas; e is the electron charge; A is the surface area of the chamber; $\varepsilon_{\mathrm{T,i}}$ is the total energy loss per electron-ion pair created for each N or H species, $\varepsilon_{\mathrm{L,i}}$ is the collisional electron energy loss per electron-ion pair created in the plasma; and τ_{rec} is the recombination time constant.

Finally, process integration, optimization, and techno-economic analysis of CLAP processes are necessary for their practical industrial application. Integration of energy flows, mass flows, and even other processes like nitrogen production and power generation may result in economic benefits and efficiency optimization of the overall system. The integration of CLAP and sustainable processes like wind and solar energy also results in improving the sustainability of CLAP. For example, the CLAP can integrate with sustainable processes photocatalytic and electrocatalytic processes, which provide green H_2 feedstock for CLAP. In addition, techno-economic studies on CLAP are limited so far. Therefore, there is a need to perform both techno-economic and environmental evaluations of CLAP processes to provide useful information on the additional value provided by integration, economic feasibility, and environmental impacts of the process. If the possible energy, economic, and environmental benefits of new CLAP processes are positively supported by this kind of investigation, additional effort will be attracted to this field.

In summary, significant progress in CLAP has shown the potential of using this process for ammonia production. Although there are grand challenges to overcome, we believe that progress in the combination of theoretical and experimental studies, design of carrier systems, characterization techniques, and process integration will further push the development of this field in the near future.

Conflict of interest

The authors declare that they have no conflict of interest.

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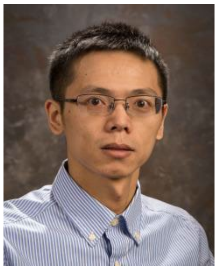
Author contributions

Maohong Fan, Jian Liu, and Qinghua Lai conceived the work. Jian Liu and Maohong Fan supervised the work. Qinghua Lai led the writing of the manuscript, Ruiping Ye and Tianyi Cai as well as Ye Wu co-wrote the manuscript. Qinghua Lai, Tianyi Cai, and Xia chen contributed to the visualization. Qinghua Lai, Shik Chi Edman Tsang, Xia Chen, Zhenghe Xu, Morris D. Argyle, Dong Ding, Yongmei Chen, Jianji Wang, Armistead G. Russell, Jian Liu, and Maohong Fan designed the structure of the manuscript. Shik Chi Edman Tsang, Zhenghe Xu, Morris D. Argyle, Dong Ding, Yongmei Chen, Jianji Wang, Armistead G. Russell, Jian Liu, and Maohong reviewed and edited the manuscript.

Biography



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References

[1] Vance CP. Symbiotic nitrogen fixation and phosphorus acquisition. Plant nutrition in a world of declining renewable resources. Plant Physiol, 2001, 127: 390-397

[2] Hill RD, Rinker RG, Wilson HD. Atmospheric nitrogen rixation by lightning. J Atmos Sci, 1980, 37: 179-192

[3] Erisman JW, Sutton MA, Galloway J, et al. How a century of ammonia synthesis changed the world. Nat Geosci, 2008, 1: 636

[4] Rees NV, Compton RG. Carbon-free energy: a review of ammonia- and hydrazine-based electrochemical fuel cells. Energy Environ Sci, 2011, 4: 1255-1260

[5] Zamfirescu C, Dincer I. Ammonia as a green fuel and hydrogen source for vehicular applications. Fuel Process Technol, 2009, 90: 729-737

[6] Schüth F, Palkovits R, Schlögl R, et al. Ammonia as a possible element in an energy infrastructure: catalysts for ammonia decomposition. Energy Environ Sci, 2012, 5: 6278-6289

[7] Kobayashi H, Hayakawa A, Somarathne KDKunkuma A, et al. Science and technology of ammonia combustion. Proc Combust Inst, 2019, 37: 109-133

[8] Chen JG, Crooks RM, Seefeldt LC, et al. Beyond fossil fuel–driven nitrogen transformations. Science, 2018, 360: eaar6611

[9] Ye T-N, Park S-W, Lu Y, et al. Vacancy-enabled N_2 activation for ammonia synthesis on an Ni-loaded catalyst. Nature, 2020, 583: 391-395

[10] Iriawan H, Andersen SZ, Zhang X, et al. Methods for nitrogen activation by reduction and oxidation. Nat Rev Methods Primers, 2021, 1: 56

[11] Wang L, Xia M, Wang H, et al. Greening ammonia toward the solar ammonia refinery. Joule, 2018, 2: 1055-1074

[12] Rafiqul I, Weber C, Lehmann B, et al. Energy efficiency improvements in ammonia production - Perspectives and uncertainties. Energy, 2005, 30: 2487-2504

[13] Michalsky R, Avram AM, Peterson BA, et al. Chemical looping of metal nitride catalysts: low-pressure ammonia synthesis for energy storage. Chem Sci, 2015, 6: 3965-3974

[14] Lai Q, Toan S, Assiri MA, et al. Catalyst-$TiO(OH)_2$ could drastically reduce the energy consumption of CO_2 capture. Nat Commun, 2018, 9: 2672

[15] Tanabe Y, Nishibayashi Y. Developing more sustainable processes for ammonia synthesis. Coord Chem Rev, 2013, 257: 2551-2564

[16] Anderson JS, Rittle J, Peters JC. Catalytic conversion of nitrogen to ammonia by an iron model complex. Nature, 2013, 501: 84-87

[17] Arashiba K, Miyake Y, Nishibayashi Y. A molybdenum complex bearing PNP-type pincer ligands leads to the catalytic reduction of dinitrogen into ammonia. Nat Chem, 2010, 3: 120

[18] Tanaka H, Nishibayashi Y, Yoshizawa K. Interplay between theory and experiment for ammonia synthesis catalyzed by transition metal complexes. Acc Chem Res, 2016, 49: 987-995

[19] Chen XZ, Li N, Kong ZZ, et al. Photocatalytic fixation of nitrogen to ammonia: state-of-the-art advancements and future prospects. Mater Horiz, 2018, 5: 9-27

[20] Zhang S, Zhao Y, Shi R, et al. Photocatalytic ammonia synthesis: Recent progress and future. EnergyChem, 2019, 1: 100013

[21] Gao X, An L, Qu D, et al. Enhanced photocatalytic N2 fixation by promoting N2 adsorption with a co-catalyst. Sci Bull, 2019, 64: 918-925

[22] Tong Y, Guo H, Liu D, et al. Vacancy engineering of iron-doped $W_{18}O_{49}$ nanoreactors for low-barrier electrochemical nitrogen reduction. Angew Chem Int Ed, 2020, 59: 7356-7361

[23] Qiao L, Duan G, Zhang S, et al. Electrochemical ammonia synthesis catalyzed with a CoFe layered double hydroxide – A new initiative in clean fuel synthesis. J Clean Prod, 2020, 250: 119525

[24] Martín AJ, Shinagawa T, Pérez-Ramírez J. Electrocatalytic reduction of nitrogen: From Haber-Bosch to ammonia artificial leaf. Chem, 2019, 5: 263-283

[25] Andersen SZ, Čolić V, Yang S, et al. A rigorous electrochemical ammonia synthesis protocol with quantitative isotope measurements. Nature, 2019, 570: 504-508

[26] Wang P, Ji Y, Shao Q, et al. Core@shell structured Au@SnO_2 nanoparticles with improved N_2 adsorption/activation and electrical conductivity for efficient N_2 fixation. Sci Bull, 2020, 65: 350-358

[27] Zheng J, Liao F, Wu S, et al. Efficient Non-dissociative activation of dinitrogen to ammonia over lithium-promoted ruthenium nanoparticles at low pressure. Angew Chem Int Ed, 2019, 58: 17335-17341

[28] Gálvez ME, Halmann M, Steinfeld A. Ammonia production via a two-step Al_2O_3/AlN thermochemical cycle. 1. Thermodynamic, environmental, and economic analyses. Ind Eng Chem Res, 2007, 46: 2042-2046

[29] Wu Y, Jiang G, Zhang H, et al. Fe_2O_3, a cost effective and environmentally friendly catalyst for the generation of NH_3 – a future fuel – using a new Al_2O_3-looping based technology. Chem Commun, 2017, 53: 10664-10667

[30] Swearer DF, Knowles NR, Everitt HO, et al. Light-driven chemical looping for ammonia synthesis. ACS Energy Lett, 2019, 4: 1505-1512

[31] Tong A, Bayham S, Kathe MV, et al. Iron-based syngas chemical looping process and coal-direct chemical looping process development at Ohio State University. Appl Energy, 2014, 113: 1836-1845

[32] Fan L-S, Zeng L, Wang W, et al. Chemical looping processes for CO_2 capture and carbonaceous fuel conversion – prospect and opportunity. Energy Environ Sci, 2012, 5: 7254-7280

[33] Zeng L, Cheng Z, Fan JA, et al. Metal oxide redox chemistry for chemical looping processes. Nat Rev Chem, 2018, 2: 349-364

[34] Wang Q, Guo J, Chen P. Recent progress towards mild-condition ammonia synthesis. J Energy Chem, 2019, 36: 25-36

[35] Adanez J, Abad A, Garcia-Labiano F, et al. Progress in chemical-looping combustion and reforming technologies. Prog Energy Combust Sci, 2012, 38: 215-282

[36] Adánez J, Abad A, Mendiara T, et al. Chemical looping combustion of solid fuels. Prog Energy Combust Sci, 2018, 65: 6-66

[37] Zhu X, Imtiaz Q, Donat F, et al. Chemical looping beyond combustion – a perspective. Energy Environ Sci, 2020, 13: 772-804

[38] Michalsky R, Pfromm PH. Chromium as reactant for solar thermochemical synthesis of ammonia from steam, nitrogen, and biomass at atmospheric pressure. Solar Energy, 2011, 85: 2642-2654

[39] Michalsky R, Pfromm PH, Steinfeld A. Rational design of metal nitride redox materials for solar-driven ammonia synthesis. Interface Focus, 2015, 5:

[40] Bartel CJ, Rumptz JR, Weimer AW, et al. High-throughput equilibrium analysis of active materials for solar thermochemical ammonia synthesis. ACS Appl Mater Interfaces, 2019, 11: 24850-24858

[41] Sun W, Bartel CJ, Arca E, et al. A map of the inorganic ternary metal nitrides. Nat Mater, 2019, 18: 732-739

[42] Alexander A-M, Hargreaves JSJ, Mitchell C. The reduction of various nitrides under hydrogen: Ni_3N, Cu_3N, Zn_3N_2 and Ta_3N_5. Top Catal, 2012, 55: 1046-1053

[43] Laassiri S, Zeinalipour-Yazdi CD, Catlow CRA, et al. The potential of manganese nitride based materials as nitrogen transfer reagents for nitrogen chemical looping. Appl Catal B: Environ, 2018, 223: 60-66

[44] Laassiri S, Zeinalipour-Yazdi CD, Catlow CRA, et al. Nitrogen transfer properties in tantalum nitride based materials. Catal Today, 2017, 286: 147-154

[45] Cairns AG, Gallagher JG, Hargreaves JSJ, et al. The effect of low levels of dopants upon the formation and properties of beta-phase molybdenum nitride. J Solid State Chem, 2010, 183: 613-619

[46] Hunter SM, McKay D, Smith RI, et al. Topotactic nitrogen transfer: Structural transformation in cobalt molybdenum nitrides. Chem Mater, 2010, 22: 2898-2907

[47] Gregory DH, Hargreaves JSJ, Hunter SM. On the regeneration of Co_3Mo_3N from Co_6Mo_6N with N_2. Catal Lett, 2011, 141: 22-26

[48] Peng X, Pi C, Zhang X, et al. Recent progress of transition metal nitrides for efficient electrocatalytic water splitting. Sustain Energy Fuels, 2019, 3: 366-381

[49] Dong S, Chen X, Zhang X, et al. Nanostructured transition metal nitrides for energy storage and fuel cells. Coord Chem Rev, 2013, 257: 1946-1956

[50] Bartel CJ, Muhich CL, Weimer AW, et al. Aluminum nitride hydrolysis enabled by hydroxyl-mediated surface proton hopping. ACS Appl Mater Interfaces, 2016, 8: 18550-18559

[51] Yu R, Chong X, Jiang Y, et al. The stability, electronic structure, elastic and metallic properties of manganese nitrides. RSC Adv, 2015, 5: 1620-1627

[52] Rasaki SA, Zhang B, Anbalgam K, et al. Synthesis and application of nano-structured metal nitrides and carbides: A review. Prog Solid State Chem, 2018, 50: 1-15

[53] Yang S, Zhang T, Yang Y, et al. Molybdenum-based nitrogen carrier for ammonia production via a chemical looping route. Appl Catal B: Environ, 2022, 312: 121404

[54] Han G-F, Li F, Chen Z-W, et al. Mechanochemistry for ammonia synthesis under mild conditions. Nat Nanotechnol, 2021, 16: 325-330

[55] McKay D, Gregory DH, Hargreaves JSJ, et al. Towards nitrogen transfer catalysis: reactive lattice nitrogen in cobalt molybdenum nitride. Chem Commun, 2007, 3051-3053

[56] Goto Y, Daisley A, Hargreaves JSJ. Towards anti-perovskite nitrides as potential nitrogen storage materials for chemical looping ammonia production: Reduction of Co_3ZnN, Ni_3ZnN, Co_3InN and Ni_3InN under hydrogen. Catal Today, 2021, 364: 196-201

[57] Shan N, Chikan V, Pfromm P, et al. Fe and Ni dopants facilitating ammonia synthesis on Mn_4N and mechanistic insights from first-principles methods. J Phys Chem C, 2018, 122: 6109-6116

[58] Michalsky R, Parman BJ, Amanor-Boadu V, et al. Solar thermochemical production of ammonia from water, air and sunlight: Thermodynamic and economic analyses. Energy, 2012, 42: 251-260

[59] Heidlage MG, Kezar EA, Snow KC, et al. Thermochemical synthesis of ammonia and syngas from natural gas at atmospheric pressure. Ind Eng Chem Res, 2017, 56: 14014-14024

[60] Michalsky R, Pfromm PH. Thermodynamics of metal reactants for ammonia synthesis from steam, nitrogen and biomass at atmospheric pressure. AlChE J, 2012, 58: 3203-3213

[61] Wu Y, Gao Y, Zhang Q, et al. Promising zirconia-mixed Al-based nitrogen carriers for chemical looping of NH_3: Reduced NH_3 decomposition and improved NH_3 yield. Fuel, 2020, 264: 116821

[62] Fu M, Jin J, Ma H, et al. Thermodynamic analysis of novel vanadium redox materials for solar thermochemical ammonia synthesis from N_2 and CH_4. Int J Hydrog Energy, 2020, 45: 2569-2577

[63] Zhang Q, Wu Y, Gao Y, et al. High-performance mesoporous (AlN/Al_2O_3) for enhanced NH_3 yield during chemical looping ammonia generation technology. Int J Hydrog Energy, 2020, 45: 9903-9913

[64] Fang J, Xiong C, Feng M, et al. Utilization of carbon-based energy as raw material instead of fuel with low CO_2 emissions: Energy analyses and process integration of chemical looping ammonia generation. Appl Energy, 2022, 312: 118809

[65] Xiong C, Wu Y, Feng M, et al. High thermal stability Si-Al based N-carrier for efficient and stable chemical looping ammonia generation. Appl Energy, 2022, 323: 119519

[66] Michalsky R, Pfromm PH. An Ionicity rationale to design solid phase metal nitride reactants for solar ammonia production. J Phys Chem C, 2012, 116: 23243-23251

[67] Gálvez ME, Frei A, Halmann M, et al. Ammonia production via a two-step Al_2O_3/AlN thermochemical cycle. 2. Kinetic analysis. Ind Eng Chem Res, 2007, 46: 2047-2053

[68] Selvaduray G, Sheet L. Aluminium nitride: review of synthesis methods. Mater Sci Technol, 1993, 9: 463-473

[69] Wang Q, Cao W, Kuang J, et al. Spherical AlN particles synthesized by the carbothermal method: Effects of reaction parameters and growth mechanism. Ceram Int, 2018, 44: 4829-4834

[70] Gao Y, Wu Y, Zhang Q, et al. N-desorption or NH_3 generation of TiO_2-loaded Al-based nitrogen carrier during chemical looping ammonia generation technology. Int J Hydrog Energy, 2018, 43: 16589-16597

[71] Wang B, Guo H, Yin X, et al. N-Sorption capability of Al_2O_3-supported Mn-/Fe-based nitrogen carriers during chemical looping ammonia synthesis technology. Energy Fuels, 2020, 34: 10247-10255

[72] Juangsa FB, Aziz M. Integrated system of thermochemical cycle of ammonia, nitrogen production, and power generation. Int J Hydrog Energy, 2019, 44: 17525-17534

[73] Geng C, Li J, Weiske T, et al. Complete cleavage of the N≡N triple bond by Ta_2N^+ via degenerate ligand exchange at ambient temperature: A perfect catalytic cycle. PNAS, 2019, 116: 21416-21420

[74] Shi L, Yin Y, Wang S, et al. Rational catalyst design for N_2 reduction under ambient conditions: Strategies toward enhanced conversion efficiency. ACS Catal, 2020, 10: 6870-6899

[75] McEnaney JM, Singh AR, Schwalbe JA, et al. Ammonia synthesis from N_2 and H_2O using a lithium cycling electrification strategy at atmospheric pressure. Energy Environ Sci, 2017, 10: 1621-1630

[76] Lazouski N, Schiffer ZJ, Williams K, et al. Understanding continuous lithium-mediated electrochemical nitrogen reduction. Joule, 2019, 3: 1127-1139

[77] Jain A, Miyaoka H, Kumar S, et al. A new synthesis route of ammonia production through hydrolysis of metal – Nitrides. Int J Hydrog Energy, 2017, 42: 24897-24903

[78] Kim K, Lee SJ, Kim D-Y, et al. Electrochemical synthesis of ammonia from water and nitrogen: A lithium-mediated approach using lithium-ion conducting glass ceramics. ChemSusChem, 2018, 11: 120-124

[79] Kim K, Chen Y, Han J-I, et al. Lithium-mediated ammonia synthesis from water and nitrogen: a membrane-free approach enabled by an immiscible aqueous/organic hybrid electrolyte system. Green Chem, 2019, 21: 3839-3845

[80] Cui B, Yu Z, Liu S, et al. Highly selective and efficient ammonia synthesis from N_2 and H_2O via an iron-based electrolytic-chemical cycle. Int J Hydrog Energy, 2020, 45: 94-102

[81] Gao W, Wang P, Guo J, et al. Barium hydride-mediated nitrogen transfer and hydrogenation for ammonia synthesis: A case study of cobalt. ACS Catal, 2017, 7: 3654-3661

[82] Wang Q-R, Guan Y-Q, Gao W-B, et al. Thermodynamic properties of ammonia production from hydrogenation of alkali and alkaline earth metal amides. ChemPhysChem, 2019, 20: 1376-1381

[83] Gao W, Guo J, Wang P, et al. Production of ammonia via a chemical looping process based on metal imides as nitrogen carriers. Nat Energy, 2018, 3: 1067-1075

[84] Tagawa K, Gi H, Shinzato K, et al. Improvement of kinetics of ammonia synthesis at ambient pressure by the chemical looping process of lithium hydride. J Phys Chem C, 2022, 126: 2403-2409

[85] Yan H, Gao W, Wang Q, et al. Lithium palladium hydride promotes chemical looping ammonia synthesis mediated by lithiumimide and hydride. J Phys Chem C, 2021, 125: 6716-6722
[86] Feng S, Gao W, Wang Q, et al. A multi-functional composite nitrogen carrier for ammonia production via a chemical looping route. J Mater Chem A, 2021, 9: 1039-1047
[87] Michalsky R, Steinfeld A. Computational screening of perovskite redox materials for solar thermochemical ammonia synthesis from N_2 and H_2O. Catal Today, 2017, 286: 124-130
[88] Sarafraz MM, Tran NN, Pourali N, et al. Thermodynamic potential of a novel plasma-assisted sustainable process for co-production of ammonia and hydrogen with liquid metals. Energy Convers Manage, 2020, 210: 112709
[89] Bang JH, Suslick KS. Applications of ultrasound to the synthesis of nanostructured materials. Adv Mater, 2010, 22: 1039-1059
[90] Houmes JD, zur Loye H-C. Microwave Synthesis of Ternary Nitride Materials. J Solid State Chem, 1997, 130: 266-271
[91] Butler KT, Davies DW, Cartwright H, et al. Machine learning for molecular and materials science. Nature, 2018, 559: 547-555
[92] Raccuglia P, Elbert KC, Adler PDF, et al. Machine-learning-assisted materials discovery using failed experiments. Nature, 2016, 533: 73-76
[93] Goldsmith BR, Esterhuizen J, Liu J-X, et al. Machine learning for heterogeneous catalyst design and discovery. AlChE J, 2018, 64: 2311-2323
[94] Zhou Z, Li X, Zare RN. Optimizing chemical reactions with deep reinforcement learning. ACS Cent Sci, 2017, 3: 1337-1344
[95] Brown SW, Robinson B, Wang Y, et al. Microwave heated chemical looping ammonia synthesis over Fe and CoMo particles. J Mater Chem A, 2022, 10: 15497-15507
[96] Rouwenhorst KHR, Engelmann Y, van 't Veer K, et al. Plasma-driven catalysis: green ammonia synthesis with intermittent electricity. Green Chem, 2020, 22: 6258-6287
[97] Bogaerts A, Neyts EC. Plasma technology: an emerging technology for energy storage. ACS Energy Lett, 2018, 3: 1013-1027
[98] Zhang Y, Ouyang B, Xu J, et al. 3D porous hierarchical nickel–molybdenum nitrides synthesized by RF plasma as highly active and stable hydrogen-evolution-reaction electrocatalysts. Adv Energy Mater, 2016, 6: 1600221
[99] Sun X, Bao J, Li K, et al. Advance in using plasma technology for modification or fabrication of carbon-based materials and their applications in environmental, material, and energy fields. Adv Funct Mater, 2021, 31: 2006287
[100] Lee C, Graves DB, Lieberman MA, et al. Global model of plasma chemistry in a high density oxygen discharge. J Electrochem Soc, 1994, 141: 1546-1555