Recent Progress on Ammonia Cracking Technologies for Scalable Hydrogen Production

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Abstract

The global energy transition necessitates the development of technologies enabling cost-effective and scalable conversion of renewable energies into storable and transportable forms. Green ammonia, with its high hydrogen storage capacity, emerges as a promising carbon-free hydrogen carrier. This article reviews recent progress in industrially relevant catalysts and technologies for ammonia cracking, which is a pivotal step in utilizing ammonia as a hydrogen storage material. Catalysts based on Ru, Ni, Fe, Co, and Fe-Co are evaluated, with Co-based catalysts showing exceptional potential for ammonia cracking. Different reactor technologies and their applications are briefly discussed. This review concludes with perspectives on overcoming existing challenges, emphasizing the need for catalyst development, effective reactor design, and sustainable implementation in the context of the energy transition.

Introduction

The energy transition will hinge on technologies that allow cheap and scalable conversion of variable renewable energies into chemical vectors that can be easily stored, transported, and transformed back into energy on demand. Green ammonia is a zero-carbon fuel and hydrogen carrier [1-3], thanks to its high hydrogen storage capacity (17.8 % hydrogen by weight [4]), its simple liquefaction at low pressures (8.6 bar) at 20 °C, or even atmospheric pressure at -33°C [5], and the large infrastructure available for its production, storage, and transportation around the globe. Ammonia catalytic dehydrogenation or cracking, however, has been confined to niche applications in the metallurgical industry [6], production of heavy water [7], and, more recently, backup power generation in fuel cells [8]. In this context, the widespread implementation of ammonia as hydrogen storage material will be limited primarily by the capacity for dehydrogenation at an industrial scale. Several perspectives on hydrogen production and storage [9,10], catalyst design [11-13], and process design [14] for ammonia decomposition were published. Direct utilization of ammonia as hydrogen storage [10,15,16], fertilizer production [17,18], Solid Oxide Fuel Cell (SOFC) technology [19], primary fuel [20], thermal power generation [21], and combustion/spark ignition engines [21,22] were also evaluated. To the best of our knowledge, there are few studies focused on the industrial use of hydrogen produced from the ammonia cracker. This mini review discusses the main advances in industrially relevant catalysts and technologies for ammonia cracking and the future opportunities and challenges in the field.

Ammonia cracking is an endothermic reaction (see Eq. 1) [23] that requires temperatures above 180 °C to be thermodynamically feasible (Figure 1a). The equilibrium conversion of ammonia reaches values above 99% at 400 °C at ambient pressure [24-27] (Figure 1b). Detailed
thermodynamic calculation can be found in Supporting Information. Industrially, it would be desirable to operate at high pressure as this can reduce the reactor footprint. Unfortunately, the reaction is thermodynamically hindered as pressure increases, which forces the utilization of even higher temperatures to achieve sufficiently high single-pass conversion.

\[
\text{NH}_3 \rightleftharpoons \frac{3}{2} \text{H}_2 + \frac{1}{2} \text{N}_2 \quad (\Delta H_{\text{rxn}}^0 = 45.9 \text{ kJ mol}^{-1}) \quad [28] \quad \text{Eq. 1}
\]

Figure 1. (a) Standard Gibbs free energy profile of ammonia cracking, and (b) equilibrium NH\(_3\) conversion at 0.1, 1, 10, and 50 bar.

To conduct this reaction at sufficiently high rates it is essential to employ a catalyst, that is often based on metal nanoparticles supported on high surface area metal oxide. Exceptions include Fe-based catalysts and Fe-Co alloy-based ammonia cracking catalysts, due to the relatively low cost of Fe. These catalysts are typically bulk-based catalysts [29].

The simplest description that one could use to model reaction kinetics would be a power-law equation, which offers high accuracy for predicting the catalyst performance within the operational window explored for regressing the kinetic constants and reaction orders (see Eq. 1) [11]. In this reaction, the ammonia cracking rate (\(\dot{r}_{\text{NH}_3}\)) is enhanced by the concentration of ammonia ([\(\text{NH}_3\)]), while nitrogen ([\(\text{N}_2\)]) and hydrogen ([\(\text{H}_2\)]) concentrations hinder the rate. Here, the kinetic constant (\(k\)) and the reaction orders (\(a\), \(b\), and \(c\)) are determined by regression using experimental data. While these models are simple to derive, there is no mechanistic information that can be derived from the regressed orders of reaction and kinetic constants. For this reason, their application is restricted to the operational window in which the data has been collected. In contrast, Langmuir-Hinshelwood kinetics and micro-kinetic models are better suited to extract mechanistic information that can guide catalyst development.

\[
\dot{r}_{\text{NH}_3} = k \times \frac{[\text{NH}_3]^a}{[\text{H}_2]^b[\text{N}_2]^c} \quad \text{Eq. (1)}
\]

Hydrogen production from ammonia cracking occurs via sequential dehydrogenation and nitrogen coupling reactions [30], step (1)-(6) below. Here, the reaction proceeds by the adsorption of ammonia on the active sites, followed by a successive N–H bond scission, and then recombination to \(\text{H}_2\) and \(\text{N}_2\). The reaction rate is dependent on the adsorption strength of ammonia on metal active sites (referred to as M–N). Broadly speaking, strong M–N interaction promotes the N–H activation. However, if the interaction is too strong, then product
desorption from the catalyst surface becomes the limiting step. Weaker M–N interaction could accelerate product desorption but hinder the N–H activation step [31]. In this sequence, there are two steps proposed to possibly be the rate-determining step (RDS), including (i) the first N–H bond scission (step (2)) or (ii) the N* recombination (step 6). The degree of rate control of each one of these steps will depend on the binding strength of the N adatoms to the catalyst surface (step (2)) [32-35]. It has been discovered that the RDS of ammonia decomposition changes with operating temperature [36,37]. At low temperatures (300-500 °C), the RDS is N* recombination, while at higher temperatures the RDS switches to the first N–H cleavage. At these conditions, the surface coverage decreases, due to ammonia desorption, which eventually offsets the enhancements in the N–H bond dissociation rate [38].

(1) Ammonia adsorption: \[ \text{NH}_3 (g) + * \rightleftharpoons \text{NH}_3^* (ads) \]
(2) 1\text{nd} N–H cleavage: \[ \text{NH}_3^* (ads) + * \rightarrow \text{NH}_2^* (ads) + \text{H}^* (ads) \]
(3) 2\text{nd} N–H cleavage: \[ \text{NH}_2^* (ads) + * \rightarrow \text{NH}^* (ads) + \text{H}^* (ads) \]
(4) 3\text{rd} N–H cleavage: \[ \text{NH}^* (ads) + * \rightarrow \text{N}^* (ads) + \text{H}^* (ads) \]
(5) H$_2$ recombination: \[ 2\text{H}^* (ads) \rightarrow \text{H}_2 (g) + 2^* \]
(6) N$_2$ recombination: \[ 2\text{N}^* (ads) \rightarrow \text{N}_2 (g) + 2^* \]

where * is the active surface site.

In industrial applications, ammonia cracking is operated at nearly complete conversion at elevated temperatures and moderate pressures, increasing the contribution of the reverse reaction (i.e. ammonia synthesis) in the kinetics. To account for these effects, Sayas et al. proposed a kinetic model derived from the power-law model [39] (Eq. 2) in which the decomposition rate is hindered by the reverse reaction [40-42].

\[
r_{\text{NH}_3} = k \times \frac{P_{\text{NH}_3}^a P_{\text{H}_2}^b}{(1 - \frac{1}{k_{eq} \frac{P_{\text{N}_2} P_{\text{H}_2}^2}{P_{\text{NH}_3}^2}})} \quad \text{Eq. 2}
\]

In this scenario, one could operate the reactor at even higher pressures to maximize the hydrogen productivity per active site. However, the resulting lower conversion per pass [39] will require a larger recycle stream and ammonia recovery systems, increasing operational and capital expenditures [43].

To activate this reaction, one can resort to supported transition metals, metal alloys, and metal compounds such as metal oxides hydrides, carbides, nitrides, amides, or imides [11,31,44]. Among those, transition metals such as Ru, Ni, Fe, and Co have been widely studied as catalytic centers for ammonia decomposition [45]. Ru-based materials provide the highest reactivity, especially at low pressures [46]. Here, it has been proposed that B5-type surface sites on Ru control the observed activity [47], which is linked to nitrogen recombination as a rate-determining step [48]. These sites are present in larger concentrations on Ru nanoparticles of ca. 2 nm [49]. The density of B5 sites can be further increased by tailoring the shape of the nanoparticles. For instance, Karim et al. [50] reported that hemispherical Ru with an average size of ca. 2.4 nm has the highest activity due to the larger concentration of B5 sites. Similar results were reported by Zheng et al. [51] on Ru nanoparticles of ca. 2.2 nm. Unfortunately, Ru-based catalysts are expensive and prone to H$_2$ inhibition due to the low dissociation barrier of hydrogen. It was found that the coverage of H$_2^*$ and H* species increases with the partial pressure of H$_2$, together with the decrease in vacant sites [52]. The dissociation of H$_2^*$ to H* is typically rapid on Ru surfaces which suppresses the NH$_3$ dehydrogenation and, thus, ammonia
decomposition rate, leading to lower catalyst utilization at high conversion levels and at elevated pressures [53]. Thus, finding alternatives to Ru is key for large-scale implementation of ammonia cracking.

Nickel is a promising candidate for ammonia dehydrogenation due to its abundance, acceptable activity, and high resistance to the 0.2–0.5 wt.% H\textsubscript{2}O in commercial-grade anhydrous ammonia. For reference, Fe- and Fe-Co alloy-based catalysts suffer from H\textsubscript{2}O inhibition [54], preventing their use based on commercial-grade anhydrous ammonia. Nickel has a lower cost than cobalt and is currently used for steam methane reforming (a similar catalyst formulation). The small amount of water contamination could possibly be present due to its hydroscopic character, which leads to water adsorption during storage, transportation or transfer[55]. Nevertheless, the presence of small water content (~0.5%) in ammonia significantly reduces its corrosiveness [55], in which copper, brass, and zinc-alloys are highly reactive towards ammonia [56]. Therefore, these materials must be avoided for the ammonia cracking system, while aluminum, cast iron, carpenter 20, and stainless steel (304 or 316) are recommended due to their higher stability.

N-containing compounds, such as metal imides or amides, were found to be effective materials for ammonia cracking. They can also be used as a support to promote the activity of non-noble metal catalysts [57–62]. However, they are very sensitive to water. In this case, oxynitrides, which are stable in water, would be more promising. Previous studies reported that the N-containing materials that can form N-vacancies are likely to be active for ammonia decomposition [63]. Hence, perovskite-type oxynitrides were developed for ammonia cracking.

On commercial catalysts, Ni clusters are supported on γ-Al\textsubscript{2}O\textsubscript{3}, CaAl\textsubscript{2}O\textsubscript{4}, or MgAl\textsubscript{2}O\textsubscript{4}, providing excellent heat and mechanical stability during reactions at high temperatures [1]. More recently, Co-based catalysts have been shown to achieve surprisingly high activities that surpassed those observed on conventional Ni and Ru catalysts. To illustrate the evolution of the catalyst developments over the last decade, we have summarized in Figure 2, the activity of the catalysts based on Ru [39,64-81], Ni [63,65,82-101], Fe [93,102-104], Co [88,93,104-113], bimetallic [114-116] and compound [117,118] as a function of the year of publication. Detailed operating conditions and conversion levels can be found in Table S2 in the Supporting Information. One could use this analysis to identify the most promising candidates for ammonia dehydrogenation at a large scale. In this line, one can see in Figure 2a that Ru- (entries 2 and 8, T\textsubscript{rxn} = 400–500 °C) and Ni-based (entries 32, 37, 43, and 45, T\textsubscript{rxn} = 600–650 °C) catalysts have shown high hydrogen productivities with values c.a. 100 ton\textsubscript{H\textsubscript{2}} ton\textsuperscript{-1}\textsubscript{cat} day\textsuperscript{-1}, until 2012 when Co-based catalysts (entry 72, T\textsubscript{rxn} = 600 °C) were reported by the group of Kaykac et al. [105]. These cobalt catalysts have shown excellent hydrogen productivity with values of c.a. 300 ton\textsubscript{H\textsubscript{2}} ton\textsuperscript{-1}\textsubscript{cat} day\textsuperscript{-1}. This three-fold increase in productivity has positioned these materials as one of the frontrunners for large-scale ammonia cracking. Interestingly, hydrogen productivity obtained by ammonia cracking has surpassed that of the steam reforming of methane (c.a. 65ton\textsubscript{H\textsubscript{2}} ton\textsuperscript{-1}\textsubscript{cat} day\textsuperscript{-1}) [119,120]. In the past two years (Figure 2b), Ni-based catalysts (entries 46–58, T\textsubscript{rxn} = 500–600 °C) have become more attractive in catalyst development for ammonia cracking. A 10% Ni/Co\textsubscript{2} (entry 52) provided the highest H\textsubscript{2} productivity at 115.5 ton\textsubscript{H\textsubscript{2}} ton\textsuperscript{-1}\textsubscript{cat} day\textsuperscript{-1} at 550 °C. Nevertheless, Co-based catalysts are still more active. For instance, K-promoted Co loaded on MgO-Co\textsubscript{2}–SrO (entry 76) exhibited 166.2 ton\textsubscript{H\textsubscript{2}} ton\textsuperscript{-1}\textsubscript{cat} day\textsuperscript{-1} H\textsubscript{2} production at 500 °C. In addition, bimetallic, such as Ni-Co (entry 84), and perovskite La\textsubscript{0.5}Sr\textsubscript{0.5}NiO\textsubscript{3–δ} (entry 92) catalysts have also shown a promising H\textsubscript{2} productivity of 93.5 and 84.7 ton\textsubscript{H\textsubscript{2}} ton\textsuperscript{-1}\textsubscript{cat} day\textsuperscript{-1} at 650 °C and 550 °C, respectively.
Figure 2. Summarized H₂ productivity over Ru, Ni, Fe, and Co active sites from (a) 2010 to 2021 and (b) 2022 to 2024 (including bimetallic and compound catalysts) at ambient pressure. The numbers shown in the Figure are the entries of the references presented in supplementary Table S2. The detailed table can also be found in Table S2 in the Supporting Information.

Ammonia cracking technology

The successful implementation of ammonia cracking will require careful selection of the catalyst formulation and reactor technology. The elevated temperatures, moderate pressures, and endothermicity restrict the available options for conducting this process to multi-tubular reactors with hydrogen and/or ammonia burners or electrical heaters, and, more recently, membrane reactors. The schematic diagram of a typical ammonia cracking process is shown in Figure 3.

Figure 3. Schematic diagram of ammonia cracking process [121].

In the following section, we briefly discuss the main challenges and opportunities of these strategies.

Multi-tubular reactor with hydrogen and ammonia burners

The reactor setup is similar to that of a steam methane reformer. The feedstock is replaced by ammonia, and the reactor is equipped with external burners where ammonia and part of produced hydrogen are used as fuels [122]. The reactor is loaded with Ni-, Fe-Co-, or Ru-based catalysts, allowing the ammonia to crack inside the tubular reactor. Heat integration with the
downstream H₂ purification unit is also possible [122,123], and the pilot plant is planned to be operational in 2024 [124]. Furthermore, energy losses to the environment are quite substantial, leading to specific energy inputs (SEI) of ca. 10.1 kWh kg⁻¹H₂ [125-127]. The high temperatures inside the furnace lead to substantial NOx and N₂O emissions (global warming potential, GWP, of -10 to 542 for NOx [128] and nearly 300-fold for N₂O [129], compared to that of CO₂), which further increase the environmental impact of the technology. This technology is currently used for producing heavy water on a large scale as will be discussed later [130], reaching more than 1000 tonNH₃ day⁻¹, albeit with natural gas burners and Fe-Co alloy-based catalysts. Therefore, several companies have been developing ammonia burners with reduced heat losses and low nitrogen oxide emissions [131,132]. Also, DeNOx technology such as selective catalytic reduction (SCR) can be utilized to reduce nitrogen oxide emissions [133].

**Multi-tubular reactor with electric heater**

The electrical heating reactor has been commercially operated in small-scale applications (1500 kgH₂ day⁻¹) [134], such as metallurgy and stationary power generation. The major difference is that the reactor is electrified to provide heat instead of gas-firing. The benefits of electric heating are faster on/off responses, uniform heating, and pollutant-free [135], as compared to the gas-firing one, allowing it to follow fluctuating renewable electricity or fluctuating demand. AFC has disclosed the first modular ammonia cracker that is purely electrically operated [136,137]. The cracker could be fully operated within 10 minutes from room temperature and achieved 9.5 kWh electrical power consumption per kilogram of produced hydrogen. A drawback of the electrical heater is that heat integration between the reactor and H₂ purification is not feasible, limiting the energy efficiency of the process, if pure H₂ is required. Moreover, there will be a limitation of the electrically heated reactor. For instance, in the Siemens reactor, silicon rods are used and heated by passing the direct current through the rods [138]. The temperature at the center of the rod must be below its melting temperature, in this case 1687 K is the maximum value that can be reached before structural failure [139]. Thus, electrically heated reactors are industrially scalable even for high-temperature applications.

**Membrane reactor**

Ammonia cracking via membrane technology has been operated to generate highly purified hydrogen for a proton-exchange membrane (PEM) fuel cell. The reactor allows for H₂ purification through permeation by a Pd membrane concurrently with an ammonia cracking reaction at 500-600 °C [53,140]. However, pure Pd membranes normally encounter H₂ embrittlement at temperatures and pressures lower than 300 °C and 2 MPa, respectively [141]. Moreover, defects can be formed at temperatures higher than 550 °C, suppressing the permeation selectivity. Therefore, precise temperature control is required for the pure Pd membrane system. The process is applicable to small-scale hydrogen production only due to the high cost of the palladium membrane. Furthermore, long-term testing and minimization of the Pd loading should be achieved to enable commercial implementation. For instance, microporous ceramic membranes are more cost-effective [142]. However, their porous structure frequently leads to H₂ with insufficient purity [143-147]. In this case, dense ceramic membranes (such as perovskites, pyrochlores, and tungstates) could be more suitable [148]. These types usually require elevated temperatures (> 400 °C) [149] for better H₂ conductivity, which is also favorable for ammonia cracking. The major drawback of the dense ceramic membranes is its poor H₂ flux. Distinct techniques, such as doping trivalent ions to perovskites [150-152], dispersing metal (e.g., Pd) to the ceramic matrix (so called cermet) [153-155], or blending two ceramic membranes (namely cercer) [156-159], can be applied for higher H₂ flux. Alternatively, Pd-coated on V membrane shows the ability to permeate H₂ without inhibition
Commercial applications of ammonia cracking

Metallurgy industry

There is a current commercial application of an ammonia cracker unit in the metallurgy industry for welding, brazing, and nitriding [6]. Ammonia is preheated and fed through the reactor loaded with Ni-based catalyst. The process is generally operated at high temperatures of 850-1000 °C to ensure full conversion. Small units are heated electrically, while large units use a gas-burning heater. The hydrogen productivity of these crackers is in the range of 1-1500 kgH₂ day⁻¹, with a typical energy efficiency of 30-60% [134]. The energy efficiency is defined by the energy content of hydrogen at the outlet divided by the energy of the inlet stream:

\[
\text{Energy efficiency} = \frac{m_{H_2,\text{out}} \times LHV_{H_2}}{(m_{NH_3,\text{in}} \times LHV_{NH_3}) + E_{\text{fuels}} + E_{\text{electricity}}}
\]

Where \(m_{H_2,\text{out}}\) is the mass of hydrogen at the outlet, \(m_{NH_3,\text{in}}\) is the mass of ammonia at the inlet, \(E_{\text{fuels}}\) and \(E_{\text{electricity}}\) are the energy input from other fuels and electricity, respectively, and LHV is the lower heating value, in which the LHVs for H₂ and NH₃ are 120 MJ kg⁻¹ H₂ and 18.646 MJ kg⁻¹ NH₃, respectively.

Heavy water production

The production of heavy water by cracking ammonia has been operated since the 1960s, with current facilities operational in Thal Vaishet (India) and Arroyito (Argentina). The deuterated ammonia is produced via the H/D exchange reaction with HD and liquid NH₃ at low temperature (15 K) [163] or the reaction of deuterium gas (D₂) with nitrogen at elevated temperature (400-600 °C) and pressure (10-30 MPa) [164]. In this way, deuterium is enriched in deuterated ammonia (NH₃-Dₓ, where \(x = 1\) or \(2\)) [7]. The cracking unit with a Co-Fe bimetallic catalyst is fed deuterated ammonia at high pressure (120-150 bar) to produce a mixture of deuterium gas (D₂), hydrogen-deuterium gas (HD), and N₂ [165,166]. The productivity of hydrogen from this ammonia cracker is 30000-425000 kgH₂ day⁻¹. The heavy water is obtained by combusting the gas mixture produced from the ammonia cracker.

Stationary power (low-temperature fuel cell)

Ammonia is used as a carbon-free hydrogen storage/carrier for off-grid fuel cells operation [167,168]. Ammonia crackers are currently commercially available for stationary power generation in low-temperature alkaline fuel cells [169]. Vaporized ammonia is passed through an electrically heated ammonia cracker at temperatures below 700 °C [170]. The outlet mixture (approximately 75% H₂ and 25% N₂ with trace amounts of residual NH₃ and water) can be directly fed to the fuel cell without purification. Moreover, a portion of the electricity produced by the fuel cell is allocated to power the electric heating system for the ammonia cracker. The present ammonia cracking technology with alkaline fuel cells yields a power output ranging from 5-600 kW [171,172], corresponding to a hydrogen production capacity spanning from 12-1410 kgH₂ day⁻¹ at 35% efficiency. However, capturing and utilizing the heat waste from the hot product stream remains challenging [173].

Pipeline-grade H₂

Gaseous ammonia is fed through a heat exchanger prior to entering the cracking unit, which is generally operated at 600-900 °C and 10-80 bar. The ammonia cracker comprises of a multi-
tubular reactor with burners loaded with supported Ni catalysts. The downstream hydrogen will be purified using a pressure swing adsorption (PSA) technique. The cracking unit has been aimed to produce pipeline-grade hydrogen in 2026 in Port of Rotterdam [174]. The productivity of hydrogen is approximately 10000-500000 kg \( \text{H}_2 \) day\(^{-1} \) with an energy efficiency of 85-90%.

Conclusions and perspectives

Catalytic dehydrogenation of ammonia can be readily accomplished on a variety of metal-supported catalysts with sufficient activity for large-scale deployment. While Ru-based catalysts have served as the benchmark for hydrogen productivity, their high cost induces limited industrial application. Despite their lower activity, Ni-based materials have become the standard formulation for industrial ammonia cracking thanks to their robust performance and lower costs. Additionally, the advent of Co-based materials has changed this picture. These materials have shown excellent performance at industrially relevant operating conditions, making them an excellent candidate for large-scale ammonia cracking. Coupling the correct catalyst and reactor technologies is essential to ensure stable operation of the process at large scale. While gas-fired crackers have been demonstrated at large scale for ammonia dehydrogenation, their low efficiency, large carbon footprint, and NO\(_x\)/N\(_2\)O emission will complicate adoption in the framework of the energy transition. Electrical heating offers a unique opportunity to decarbonize heat generation and to improve the flexibility of ammonia crackers, which is mostly applicable to processes that do not require purified hydrogen. Finally, membrane-based reactors offer a unique opportunity to conduct reaction and separation, producing high-purity hydrogen in a single step. However, the use of expensive palladium membranes and complex operations hinders the scalability of this technology.

In this context, the utilization of highly active catalysts with electrically heated crackers will be key to ensuring fast commercial uptake of the ammonia dehydrogenation technology at a large scale. This will require additional research to develop catalysts with improved tolerance to hydrogen poisoning, water resistance, and high activity to enable operation at high pressures and low temperatures. Next to this, regarding carbon and NO\(_x\)/N\(_2\)O emissions from the gas-fired ammonia crackers, developing electrified fixed bed reactors with high energy efficiency will enable substantial reductions in the polluted gas of the process.

Credit authorship contribution statement

Korawich Trangwachirachai: Literature review, data processing, and writing of the original draft. Kevin H.R. Rouwenhorst: formal analysis, writing review, and editing, and visualization. Jimmy Faria Albanese: Conceptualization of the scope, supervision, project administration, editing and review of the manuscript, and funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supporting Information.

Supplementary data Supplementary material related to this article can be found in the online version.
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Declaration of interests

☐ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☒ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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