



Catalysts for unlocking H₂ production from NH₃: A process design perspective

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ABSTRACT

NH₃ cracking is gaining attention as a promising route for on-demand, carbon-free H₂ production, particularly in off-grid or distributed energy applications. Nevertheless, its practical implementation hinges on the development of catalysts not only highly active, but also cost-effective and thermally efficient. Starting from the state-of-the-art catalyst for NH₃ decomposition (nickel-based), the most promising catalytic systems (ruthenium-based) are critically reviewed, with a focus on the interplay between catalyst activation energy, thermal duty and operating conditions. In view of discussing whether the implementation of noble-based catalysts can be practical or not, a technical analysis of the cracking furnace with different Ru-based catalytic systems is presented, referring to a decentralized application representative of compact yet industrially relevant units. The trade-off between technical and economic performance is quantified, with the aim of offering design guidelines for developing scalable NH₃ cracking.

1. Introduction

Ammonia cracking has emerged as a critical technology in the transition to a sustainable, hydrogen-based energy economy [1]. However, for NH₃ to be used as a H₂ source, particularly in mobility sector applications requiring high-purity hydrogen [2], it must first be cracked into its elemental gases.

This decomposition reaction is thermodynamically favourable at high temperatures but kinetically slow without a catalyst. Therefore, active catalysts play a pivotal role in enhancing the rate of ammonia cracking at practical temperatures [3]. The choice of catalyst directly influences the efficiency, energy consumption and feasibility of the cracking process.

Catalysts used for ammonia decomposition include noble metals, non-noble metals, bimetallic compounds, nitrides and carbides [4]. Among these, ruthenium (Ru)-based catalysts demonstrate the highest catalytic activity at low temperatures [5]. However, the high cost of Ru significantly restricts its widespread industrial use.

To mitigate this limitation, researchers have explored the development of bimetallic catalysts by combining Ru with more economical transition metals such as nickel (Ni) and iron (Fe). These combinations

leverage synergistic effects to improve catalytic efficiency while reducing overall costs [6]. Nevertheless, due to the inherent complexity of bimetallic catalyst synthesis and surface characteristics, further research is necessary to precisely control their structure and composition to achieve optimal performance.

In contrast to noble metals, non-noble metal catalysts, including Ni, Fe and Co, are more economically viable. Among these, Ni-based catalysts earned considerable interest in industrial ammonia decomposition due to their favourable cost and catalytic performance, which is second only to Ru-based systems. Efforts to enhance the activity and thermal stability of Ni-based catalysts under low-temperature and low-pressure conditions often involve doping with secondary metals to improve dispersion and metal-support interactions, thereby boosting overall catalytic efficiency [7].

As nickel-based catalysts are widely recognized as the state-of-the-art of ammonia cracking, while ruthenium remains the gold standard for it, these two options are deepened in Section 2, while NH₃ cracking mechanism is briefly reviewed in Section 3.

With the aim of offering a valuable framework to guide research efforts toward catalysts design for their viable industrial application, a preliminary techno-economic analysis of NH₃ cracking furnace is

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presented. Considering different Ru-based catalysts, the interplay between activation energy, thermal duty and operating conditions is examined and compared with the Ni benchmark. As a result, performance indicators required for Ru-based catalysts to match or exceed the NH_3 decomposition efficiency of the Ni-based alternative are identified. These performance thresholds, together with highlighting the trade-offs between catalytic activity, energy requirements and cost, can contribute to a deeper understanding of the operating and economic parameters necessary for scaling ammonia cracking technologies, particularly in decentralized H_2 production scenarios.

2. State-of-the-art and future ammonia cracking catalysts

Some of the ammonia cracking catalysts are already available commercially and are mostly Ni-based, as shown in Table 1.

2.1. State-of-the-art of NH_3 cracking: Ni-based catalysts

Nickel is among the most extensively studied non-noble metal catalysts for ammonia decomposition due to its favourable catalytic activity and low cost. As the second most active metal after ruthenium, Ni-based catalysts are already commercial for large-scale and economically viable hydrogen production.

Nevertheless, compared to Ru-based catalysts, Ni-based systems generally require higher reaction temperatures to achieve a comparable NH_3 conversion. This limitation is primarily attributed to the lower intrinsic activity of Ni for the nitrogen desorption step, often identified as the rate-determining step in the reaction mechanism.

To enhance the performance of Ni-based catalysts, researchers have employed several strategies, including the following.

- **Support modification.** The choice of support material plays a critical role in influencing Ni dispersion, particle size, and metal-support interactions. Common supports include Al_2O_3 , MgO , SiO_2 and carbon-based materials. Basic support, such as MgO , can enhance electron density around Ni active sites, facilitating ammonia activation and improving catalytic efficiency. Appropriate support not only ensures uniform dispersion of Ni particles but also enhances their stability and interaction with reactant molecules through its acid-base characteristics. This, in turn, helps prevent sintering and early deactivation, thereby prolonging the catalyst's lifespan and improving the performance of Ni-based catalysts [7].
- **Promoter addition.** Alkali and alkaline earth metals such as K, Cs and Sr are often introduced as promoters. These elements donate electrons to the Ni surface, which facilitates nitrogen desorption by weakening the Ni–N bond. Additionally, promoters can modify the acid-base properties of the support and suppress the formation of inactive Ni species.

- **Bimetallic and alloy formation.** Combining Ni with other transition metals such as Fe, Co, or Cu can induce synergistic effects that improve activity, selectivity, and thermal stability. These combinations can alter the electronic structure of Ni, enhance its resistance to sintering, and improve catalyst longevity under harsh reaction conditions.
- **Nanostructuring and morphological control.** The development of Ni-based catalysts with controlled morphologies (nanowires, nanospheres or core-shell structures) has shown potential for increasing surface area and active site accessibility. These structures also contribute to improved thermal stability and resistance to deactivation.

Despite the quite mature technology, challenges remain in enabling low-temperature operation and long-term stability of Ni-based catalysts. Deactivation due to sintering, nitrogen poisoning and support degradation can significantly reduce catalyst's lifespan.

Table 2 offers a summary of the most recent literature discussing the experimental evaluation of Ni-based catalysts for NH_3 cracking, considering operating conditions, activity and apparent activation energy.

As a general remark, catalysts with lower apparent activation energy exhibit higher reaction rates at a given temperature, thereby demonstrating greater activity. This enhanced activity allows the reaction to proceed at reduced operating temperatures while maintaining high conversion levels. Consequently, the thermal duty required to sustain the process is significantly lowered. This relationship is especially critical in endothermic systems, as the NH_3 cracking case-study. Therefore, the development of highly active catalysts with low activation energy is not only essential for improving reaction kinetics but also for minimizing energy consumption, enabling cost-effective H_2 production from NH_3 . In this respect, to critically analyse the outcomes of the experimental activities of Table 2, Fig. 1 provides an overview of the apparent activation energy of each Ni-based catalyst, depending on the supports analysed, also considering active phase loading.

Overall, the apparent activation energies for these systems ranges from 40 to 100 kJ/mol. Ce-modified Al_2O_3 supports show the lowest value of E_{app} , for a Ni loading of 10 wt%. On the other hand, the highest values are registered for $\text{SrNiO}_{3.8}\text{-600H}_2$ and $\text{La}_{0.2}\text{Sr}_{0.8}\text{NiO}_{3.8}\text{-600H}_2$ supported catalyst, also having the highest amount of active phase dispersed on the support (around 29 wt% and 27 wt%, respectively).

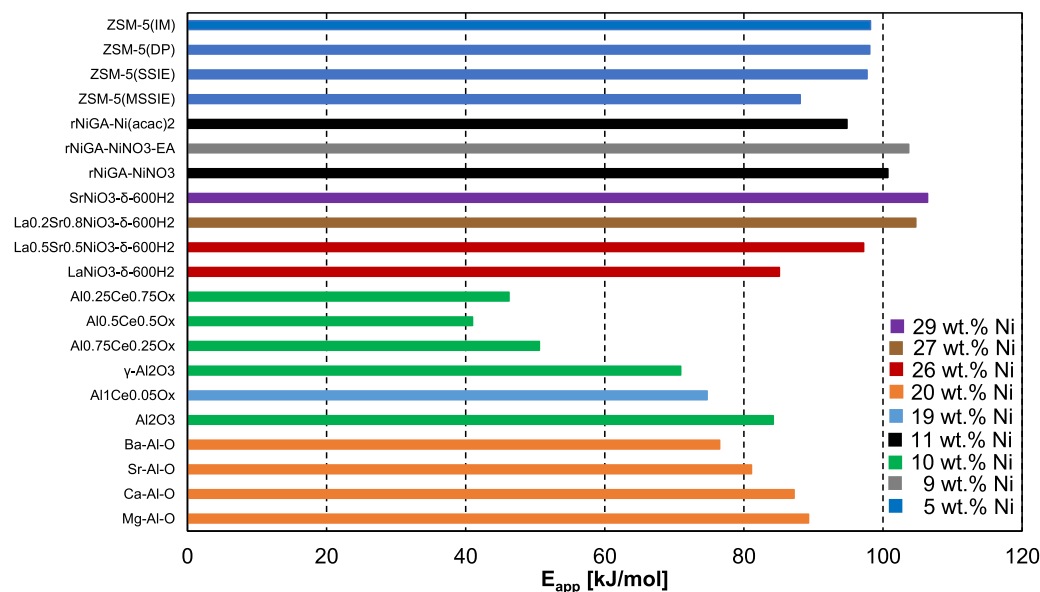
In addition, Fig. 2 provides NH_3 conversion (χ) both as a function of temperature and active phase loading. The different catalytic activities experienced at same temperatures and same loadings confirm the structure-sensitive nature of the NH_3 cracking reaction. Ce-modified Al_2O_3 supported catalysts, if compared with H-ZSM-5 zeolite catalysts, present lower NH_3 conversion despite the doubled Ni loading. This evidence can be due to the appropriate interaction between Ni particles and ZSM-5 support [5].

Table 1
Summary of commercially available NH_3 cracking catalysts.

Supplier	Catalyst name	Active phase	T [°C]	Applications
BASF [8]	SYNSPIRE™ ARC series 2	ruthenium	280–580	not reported
	SYNSPIRE™ ARC series 6	nickel	420–640	
	SYNSPIRE™ ARC series 8	nickel	620–800	
Johnson Matthey [9]	KATALCO™ 27–2	nickel	700–950	large-scale H_2 production for industrial application (>1000 MTPD NH_3) decentralized H_2 generation (>100 kg/h NH_3)
	KATALCO™ 27–612	Platinum Group Metals (PGM)	400–500	
Clariant [10]	HyProGen™ 820 DCARB	nickel	400–650	adiabatic reactors
	HyProGen™ 830 DCARB	nickel	550–750	reformer-type fired tubular reactors
	HyProGen™ 850 DCARB	ruthenium	370–550	small-scale, decentralized applications
Topsoe [11]	DNK–2R	iron-cobalt		100–3400 MTPD NH_3 single-line capacity range
	DNK–20	nickel		
	DNK–30	nickel		

Table 2Summary of most recent literature on experimental evaluation of Ni-based catalyst for NH₃ cracking.

Name	Support	Loading [wt%]	T [°C]	P [bar]	GHSV [mL h ⁻¹ g _{cat} ⁻¹]	NH ₃ conversion [%]	H ₂ production rate [mmol min ⁻¹ g _{cat} ⁻¹]	E _{app} [kJ mol ⁻¹]	Reference
Al-oxides	Mg-Al-O	20	450	1	6000	6.7		89.3	Im et al.
	Ca-Al-O	20	450	1	6000	11.5		87.2	[12]
	Sr-Al-O	20	450	1	6000	16.5		81.1	
	Ba-Al-O	20	450	1	6000	24.8		76.5	
Ce-modified Al ₂ O ₃	Al ₂ O ₃	9.6	500	1	6000	43	2.9	84.2	Do et al.
	Al ₁ Ce _{0.05} O _x	9.6	500	1	6000	76	5.1	74.7	[13]
	Al ₁ Ce _{0.05} O _x	19.3	500	1	6000	84.9	5.7	—	
	γ-Al ₂ O ₃	10	650		30,000	30	9.73	70.9	Yu et al.
	Al _{0.75} Ce _{0.25} O _x	10	650		30,000	55	18.31	50.58	[14]
	Al _{0.5} Ce _{0.5} O _x	10	650		30,000	65	21.79	40.98	
La ₂ O ₃	Al _{0.25} Ce _{0.75} O _x	10	650		30,000	52	17.48	46.23	
	LaNiO _{3-δ} -600H ₂	25.5	550	1	30,000	48.7	16.3	85.1	Guo et al.
	La _{0.5} Sr _{0.5} NiO _{3-δ} -600H ₂	25.6	550	1	30,000	87.7	29.4	97.2	[15]
	La _{0.2} Sr _{0.8} NiO _{3-δ} -600H ₂	26.8	550	1	30,000	66.5	22.3	104.7	
	SrNiO _{3-δ} -600H ₂	28.6	550	1	30,000	48.9	16.4	106.4	
Graphene aerogel	rNiGA-NiNO ₃	11.4	600	1	30,000	55.4	17	100.7	Kocer et al.
	rNiGA-NiNO ₃ -EA	9.3	600	1	30,000	63.3	19.4	103.7	[16]
	rNiGA-Ni(acac) ₂	11.1	600	1	30,000	70.2	21.6	94.8	
H-ZSM-5 zeolite	ZSM-5(MSSIE)	5	650		30,000	97.6	32.7	88.1	Hu et al.
	ZSM-5(SSIE)	5	650		30,000	92.9	31.1	97.7	[17]
	ZSM-5(DP)	5	650		30,000	81.3	27.2	98.1	
	ZSM-5(IM)	5	650		30,000	50.1	16.8	98.2	

**Fig. 1.** Apparent activation energy (E_{app}) of Ni-based catalysts of Table 2.

2.2. Future of NH₃ cracking: Ru-based catalysts

Ruthenium is widely recognized as the most active metal for ammonia decomposition, exhibiting superior catalytic performance even at moderate temperatures (400–500°C) compared to other transition metals. Its exceptional activity, particularly at lower temperatures, is primarily attributed to its optimal balance of adsorption energies for ammonia and its decomposition intermediates, as well as its high intrinsic activity for nitrogen desorption, *i.e.*, the rate-limiting step in the reaction mechanism.

However, ruthenium is one of the rarest metals, typically found in platinum ores and recovered as a byproduct of nickel and platinum refining. While demand is increasing, supply remains constrained, creating a structural mismatch between industrial needs and scalable availability. As recognition of its strategic importance grows, securing future supply will require stronger recycling systems and diversified recovery pathways in view of its reliable industrial application.

Significant research efforts have been devoted to improving the atom efficiency and catalytic performance of Ru while minimizing its loading.

To address these limitations, ongoing research is focused on optimizing support–metal interactions, developing low-Ru or Ru-free alternatives with comparable activity, and exploring regeneration strategies to prolong catalyst's lifetime.

Table 3 summarizes the most recent experimental studies on Ru-based catalysts available in literature.

With the aim of an overall review of the experimental results, Fig. 3 shows the apparent activation energy of Ru-based catalysts of Table 3, considering Al₂O₃ supported, MgO supported, rare earth supported and other tested catalytic systems.

Also in this case, high variability is experienced depending on the support, with the apparent activation energy ranging from 65 to around 200 kJ/kmol, this very high value achieved for the MgO supported catalyst. For Mg-based supports, the apparent activation energy ranges from 70 to 210 kJ/mol, with the lowest value shown for the K-promoted

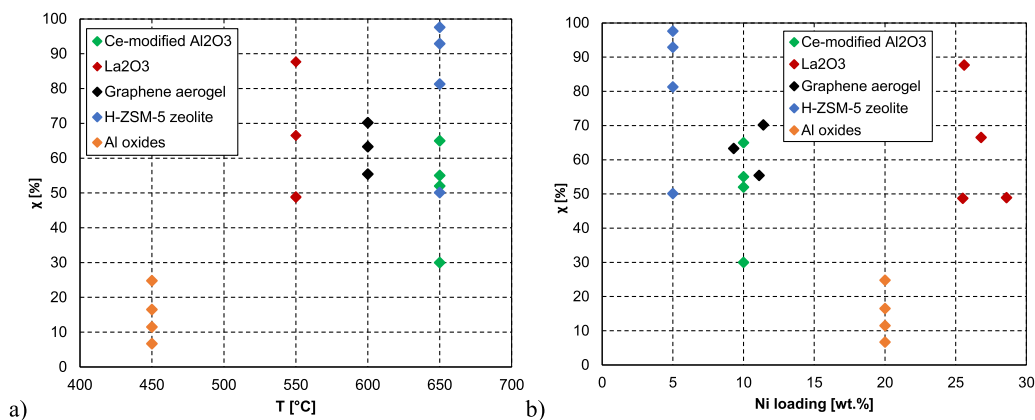


Fig. 2. NH₃ conversion (χ) for some of the Ni-based catalysts of Table 2 explored in literature, as a function of: a) temperature (T) and b) Ni loading. $GHSV$ is fixed at 30000 mL h⁻¹ g_{cat}⁻¹.

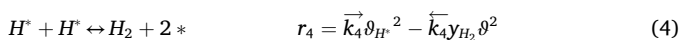
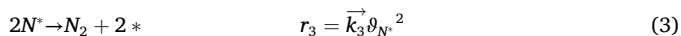
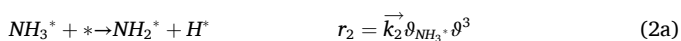
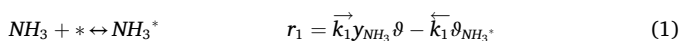
MgO supported catalyst proposed by Sayas et al. [23]. Indeed, the alkaline promoter is beneficial for improving the catalytic performance of NH₃ cracking. Nevertheless, research on the promoting mechanism is still not mature enough and results are controversial.

On the other hand, trivalent rare earth oxides (RE₂O₃) exhibit excellent performance in ammonia decomposition reaction even at low operating temperatures ($T = 450$ °C), as also shown in Fig. 4.

Xu et al. [19] suggested that the RE₂O₃ with intrinsic surface O_v promoted the adsorption and activation of the catalyst on Lewis basic reactant molecules and enhanced the interaction between the active metals and the rare earth oxide supports, raising the d band of Ru and increase the energy of surface adsorbed NH₂. As a result, these catalytic species offer moderate adsorption of NH₃, maintaining active species in metallic state and forming unique RE-N-H-Ru configurations for the N-H bond breaking.

2.3. Kinetics of NH₃ decomposition

NH₃ decomposition involves adsorption, stepwise dehydrogenation and recombination, as in Eq. (1) to (4) (* stands for the catalyst active site) [34].



The rate-determining step (RDS) for ammonia decomposition differs slightly between Ru and Ni catalysts due to differences in their surface binding energies. For Ru-based systems, the RDS is widely supposed to be nitrogen recombination. Ru strongly binds nitrogen atoms (N*), but the recombination and desorption of N₂ gas is energetically demanding. First-principles and experimental studies consistently identify this as the slowest step [5].

For Ni-based catalysts, the RDS can be either nitrogen recombination or one of the earlier NH_x dehydrogenation steps, depending on temperature and hydrogen partial pressure.

Ni binds hydrogen more strongly than Ru, so surface H* coverage can be high. This evidence can lead to hydrogen poisoning of the catalyst surface, which may slow dehydrogenation steps. Under hydrogen-rich

conditions, the dehydrogenation from NH₂* to NH* can become rate-limiting [35].

One of the first attempts to derive a detailed kinetic model of NH₃ decomposition on Ru and Ni catalysts was made by Takahashi and Fujitani [34]. They found that kinetic constants for NH₃ dehydrogenation over Ru-based catalyst was about 1 order of magnitude higher than over Ni catalyst. In contrast, the kinetic constant for recombinative N₂ desorption for Ru catalyst was 1/2 that over Ni catalyst. These results suggested that N₂ recombination step is faster on Ni catalysts, while reactions on the surface involving H₂ are assumed to proceed more readily on the Ru catalysts.

Since then, few references have been published in literature trying to draw conclusions on kinetics, as a follow up of the experimental testing. Rate expressions are mostly empirical and usually follow the Temkin–Pyzhev kinetics. Table 4 provides an overview of kinetic modelling proposed in literature for Ni- and Ru-based catalysts of Table 2 and Table 3. Usually, the reaction order for N₂ is assumed to be zero for all the catalysts, meaning that N₂ adsorption is extremely weak at such low total pressures, typical of NH₃ cracking. On the other hand, the reaction order for NH₃ partial pressure was a positive value at the reaction conditions for all the catalysts but for Ru/TiO₂-500N-6h. According to Yan et al. [32], this negative α -value manifests that the dissociation of N–H bonds is inhibited because of the nitridation of TiO_x species, considered unfavourable for the dissociation of N–H bonds.

In contrast, the reaction order for H₂ partial pressure was negative for all the catalysts. Hydrogen exhibits the inhibitory effect on NH₃ decomposition as adsorbed H₂ occupies the active sites. Im et al. [12] suggested that the strong basic property of the catalysts can alleviate this H₂ inhibitory effect, as proved by the increasing H₂ reaction order with increased basic strength. In addition, Qiu et al. [24] showed that first order on NH₃ kinetic dependences and -1.5 on H₂ are in line with the assumption

that the rate determining step is the NH₃ dehydrogenation, excluding the hypothesis of associative desorption of N₂, which would imply a quadratic dependence on NH₃ and the negative order -3 with respect to H₂.

To analyse the predictions of the rate expressions of Table 4 consistently, a pseudo-homogeneous 1-D isothermal packed bed reactor has been simulated, at variable temperature and with different Ni- and Ru-based catalyst particles. The space velocity is fixed at 6 m³/h/kg_{cat}, pure NH₃ is assumed as the feed stream, while the catalyst mass is 300 kg for all the case-studies. Where parameters of the Temkin–Pyzhev kinetics were not provided by the references considered (typically, the pre-exponential factor, k_0), they were regressed against available experimental data. Details about experimental data fitting are provided in section S1.

Fig. 5 offers an overview of the NH₃ conversion (χ) for Ni- and Ru-

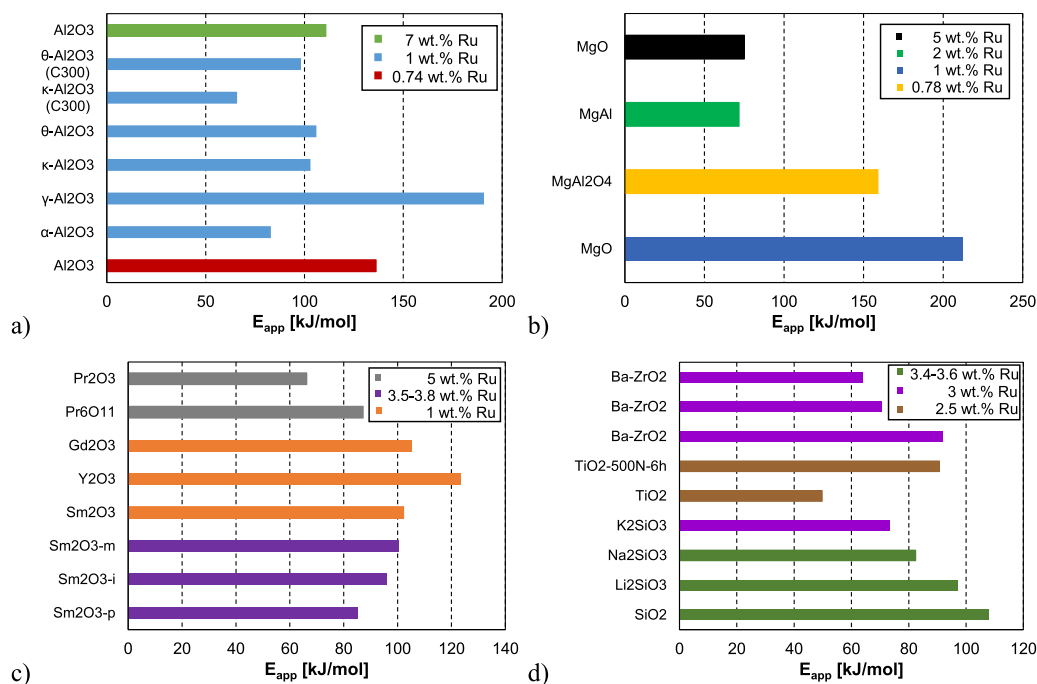
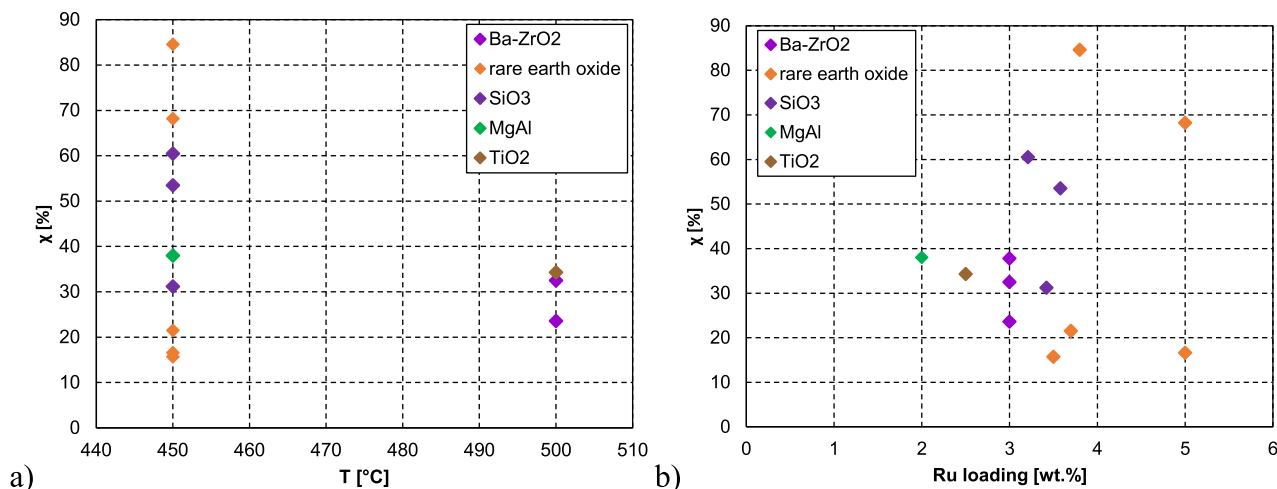
Table 3Summary of most recent literature on experimental evaluation of Ru-based catalyst for NH₃ cracking.

Name	Support	Loading [wt%]	T [°C]	P [bar]	GHSV [mL h ⁻¹ g _{cat} ⁻¹]	NH ₃ conversion [%]	H ₂ production rate [mmol min ⁻¹ g _{cat} ⁻¹]	E _{app} [kJ/mol]	References
rare earth oxide	Sm ₂ O ₃ -p	3.8	450	1	30,000	84.6	25.9	85.1	Zhang et al.
	Sm ₂ O ₃ -i	3.7	450	1	30,000	21.5	6.6	96	[18]
	Sm ₂ O ₃ -m	3.5	450	1	30,000	15.7	4.9	100.2	
	Sm ₂ O ₃	1.03	450		30,000	72	24	102.2	Xu et al.
	Sm ₂ O ₃	1.03	450		300,000		138.2		[19]
	Y ₂ O ₃	1.06	450		300,000		124.9		
	Y ₂ O ₃	1.06	450		30,000		20.4	123.5	
	Gd ₂ O ₃	0.82	450		300,000		103.4		
	Gd ₂ O ₃	0.82	450		30,000		21.4	105.1	
	Pr ₆ O ₁₁	4.7	450	1	30,000	16.6	5.1	87.2	Zhang et al.
La-Ce-based	Pr ₂ O ₃	4.8	450	1	30,000	68.2	20.9	66.3	[20]
	Ce ₁	1.8	400	1	6000		5.1	91	Le et al.
	La _{0.09} Ce _{0.91}	1.9	400	1	6000	79	5.1		[21]
	La _{0.2} Ce _{0.8}	1.9	400	1	6000	82	5.6		
	La _{0.33} Ce _{0.67}	1.8	400	1	6000	91.9	6.2	80	
	La _{0.5} Ce _{0.5}	1.8	400	1	6000	90	5.9		
	La ₁	1.8	400	1	6000	43.9	2.9	139	
	La ₂ O ₃	4.8	450	1	18,000	58.2	11.7	41.55	Huang et al.
	La ₂ O ₃ -K	4.8	450	1	18,000	72.8	14.6	34.71	[22]
	MWCNT	5Ru, 10 K	400	1	9000	30.8	2.66		Sayas et al.
Al ₂ O ₃	CNT	7	400		6000	12.6		103.8	[23]
	Al ₂ O ₃	0.74	450		30,000		4.3	136.2	Hu et al. [27]
	Al ₂ O ₃	0.74	450		300,000		41.6		Xu et al.
	γ-Al ₂ O ₃	1.1	380	1	20,000	65		190.8	[19]
	α-Al ₂ O ₃	1.3	400	1	60,000	22	5.07	83	Qiu et al.
	κ-Al ₂ O ₃	1	400	1	60,000	15	2.3	103	Kim et al.
	θ-Al ₂ O ₃	1	400	1	60,000	10	1.5	106	[25]
	κ-Al ₂ O ₃ (C300)	1	400	1	60,000	40	7	65.9	
	θ-Al ₂ O ₃ (C300)	1	400	1	60,000	40	6.9	98.2	
	Al ₂ O ₃	1.1	350	1	22,000		0.83		Hu et al.
CeO ₂	Al ₂ O ₃	7	400		6000	23		110.8	[26]
	CeO ₂	7	400	1	6000	85.5		82.5	Hu et al.
	CeO ₂	1	450	1	228,000		99.24		[27]
	CeO ₂	1	450	1	124,000		83.03	150.7	Hu et al.
	CeO ₂	1	340	1	110,000		16.18	150.7	[26]
	CeO ₂	1	350	1	22,000	32	8.14	150.7	
	CeO ₂	1	300	1	22,000	9	2.03	150.7	
	CeO ₂	5.1	400	1	2000	90		167	Furusawa et al.
	CeO ₂	1	450		30,000		1.446		[28]
	CeO ₂ -I	1	400	1	22,000		0.91		Xu et al.
Mg-based	CeO ₂	1	450		300,000		1.266		[19]
	MgO	1	380	1	20,000	68		212.1288	Hu et al.
	MgO	1	350	1	22,000		2.54		[24]
	MgO	1	450	1	22,000	75	18.57		Qiu et al.
	MgOa	3.5	450	1	36,000		11.25		[26]
	MgAl ₂ O ₄	0.78	350	1	20,000	65		158.992	
	MgAl	2	450	1	30,000	38	12	71.7	Shin et al.
	MgO	5Ru, 10 K	400	1	9000	39.4	3.36		[29]
									Sayas et al.
									[23]
carbon xerogels	CX	1.35	350	1	2000			102.6	Mazzone et al.
	ACX 1 h	1.32	350	1	2000			82.3	[30]
	ACX 5 h	1.37	350	1	2000			93.3	
	UCX	1.36	350	1	2000			81.9	
	Na-CX	1.38	350	1	2000			88.2	
	Na-ACX 1 h	1.42	350	1	2000			76.1	
	Na-ACX 5 h	1.32	350	1	2000			90.9	
	Na-UCX	1.34	350	1	2000			80.2	
others	NS	5Ru, 10 K	400	1	9000	46.6	3.91		Sayas et al.
	CaO	5Ru, 10 K	400	1	9000	53.7	4.74		[23]

(continued on next page)

Table 3 (continued)

Name	Support	Loading [wt%]	T [°C]	P [bar]	GHSV [mL h ⁻¹ g _{cat} ⁻¹]	NH ₃ conversion [%]	H ₂ production rate [mmol min ⁻¹ g _{cat} ⁻¹]	E _{app} [kJ/mol]	References
SiO ₂		3.64	450	1	30,000		5.9	108	Zhinqiang et al.
Li ₂ SiO ₃		3.42	450	1	30,000	31.2	10.4	97.1	[31]
Na ₂ SiO ₃		3.58	450	1	30,000	53.5	17.8	92.4	
K ₂ SiO ₃		3.21	450	1	30,000	60.5	20.3	73.3	
TiO ₂		2.5	500		30,000	34.3	11.5	49.8	Yan et al.
TiO ₂ -500N-6h		2.5	500		30,000	17.8	6	90.7	[32]
Ba-ZrO ₂	3		500		30,000	23.6	7.9	92.1	Wang et al.
Ba-ZrO ₂		3	500		30,000	32.5	10.9	70.7	[33]
Ba-ZrO ₂		3	500		30,000	37.8	12.7	64.2	

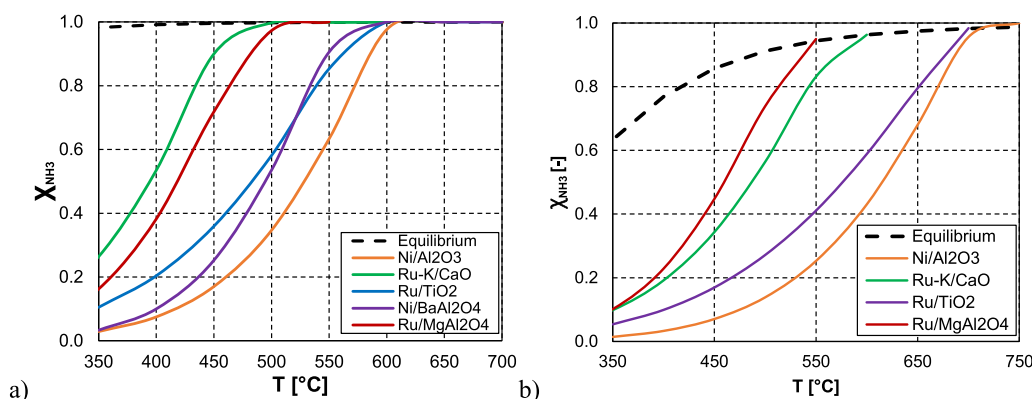
Fig. 3. Apparent activation energy (E_{app}) of: a) Al₂O₃ supported; b) Mg supported; c) rare earth supported d) others Ru-based catalysts of Table 3.Fig. 4. NH₃ conversion (χ) for some of the Ru-based catalysts of Table 3 explored in literature, as a function of: a) temperature (T) and b) Ru-loading. GHSV is fixed at 30,000 mL h⁻¹ g_{cat}⁻¹.

based catalysts as a function of temperature (T) and considering two pressure levels: atmospheric and 40 bar. A benchmark Ni/Al₂O₃ catalyst is also included for the sake of comparison.

As illustrated in Fig. 5, the benchmark Ni/Al₂O₃ catalyst exhibits significantly lower catalytic activity in NH₃ decomposition compared to all other evaluated systems. In contrast, the Ni/BaAl₂O₃ catalyst

Table 4Rate expressions of NH₃ cracking for Ni- and Ru-based catalysts of, respectively, Tables 2 and 3.

Active phase	Support	Rate expression	Parameters			Reference
			E_{att} [kJ/mol]	α	β	
Ni	Mg-Al-O	$r = k_0 e^{-\frac{E_a}{RT}} P_{NH_3}^\alpha P_{H_2}^\beta$	89.3	0.39	-0.62	Im et al. [12]
	Ca-Al-O		87.2	0.7	-0.47	
	Sr-Al-O		81.1	0.58	-0.38	
	Ba-Al-O		76.5	0.47	-0.37	
Ru	CaO (3 %Ru)	$r = k_0 e^{-\frac{E_a}{RT}} P_{NH_3}^\alpha P_{H_2}^\beta \left(1 - \frac{1}{K_{eq}} \left(\frac{P_{N_2} P_{H_2}^3}{P_{NH_3}^2}\right)\right)$	96	0.8	-1.9	Sayas et al. [23]
	CaO (3 %Ru10 %K)		75	0.5	-1.2	
	TiO ₂	$r = k_0 e^{-\frac{E_a}{RT}} P_{NH_3}^\alpha P_{H_2}^\beta$	49.8	0.32	-0.71	Yan et al. [32]
	TiO ₂ -500N-6h		90.7	-0.16	-0.19	
	Al ₂ O ₃	$r = k_0 e^{-\frac{E_a}{RT}} P_{NH_3}^\alpha P_{H_2}^\beta$	190.8	1	-1.5	Qiu et al. [24]
	MgO		212.1	1	-1.5	
	MgAl ₂ O ₄		159.0	1	-1.5	

**Fig. 5.** NH₃ conversion (χ) for Ni- and Ru-based catalysts as a function of temperature (T) at: a) atmospheric pressure and b) 40 bar, considering the rate expressions of Table 4 and a Ni/Al₂O₃ benchmark cracking catalyst.

demonstrates markedly improved performance in comparison with the benchmark, confirming that the enhanced basicity of the BaAl₂O₃ support contributes positively to NH₃ cracking activity, as it facilitates the catalytic cleavage of the N-H bonds. The positive effect of basic promoters is also evident in the case of Ru-K/CaO, which achieves high NH₃ conversion efficiencies even at relatively low reaction temperatures ($T = 450$ °C): the synergy between the Ru active phase and the highly basic CaO support, further promoted by potassium, effectively enhances the reaction kinetics.

At elevated pressures the NH₃ decomposition reaction becomes less favourable both thermodynamically and kinetically. Despite these constraints, the Ru-K/CaO catalyst maintains superior NH₃ conversion performance even at 40 bar (see Fig. 5b).

It should be noted that the Ni/BaAl₂O₃ catalyst is not represented in Fig. 5b, as the proposed kinetic model fails to accurately predict NH₃ conversion under pressures above atmospheric conditions.

For the development of economically viable NH₃ cracking, the maximum acceptable catalyst cost plays a crucial role. In this respect, a preliminary techno-economic analysis can provide a critical framework for identifying performance trade-offs in catalyst selection. Ru-based catalysts can be a promising choice for NH₃ cracking, particularly when high purity H₂ is needed for downstream mobility applications. Nevertheless, the high cost of ruthenium as a raw material must be weighed against its superior ammonia conversion at lower energy expenses with respect to the commercially available nickel-based alternative. Defining an acceptable cost threshold for catalysts helps benchmark commercial viability and directs research toward materials that satisfy both performance and economic targets. To support this, the

following section provides a technical assessment of NH₃ cracking.

2.4. Technical assessment of NH₃ cracking for decentralized H₂ application

In this section, a technical assessment of NH₃ cracking technologies is presented, focusing on the analysis of different Ru-based and Ni-based catalysts.

For the sake of comparison, the basis of design must first be established. According to the NH₃ value chain depicted in Fig. 6, ammonia produced from renewable energy or natural gas in combination with carbon capture and storage, referred to as green and blue ammonia, respectively, is assumed to be transported to multiple cracking plants located near end-use sites, such as hydrogen refuelling stations and steel industries. Given the distributed nature of hydrogen utilization, these cracking plants are characterized by a small scale.

A typical ammonia cracking process includes the following process steps: ammonia vaporization, cracking, heat recovery and hydrogen separation/purification. To facilitate downstream H₂ purification and reduce associated volumes and costs, it is preferable to operate the cracking reactor under pressure, even though this negatively affects reaction kinetics (see Fig. 5). Since ammonia is typically stored and transported as a liquid, at the cracking plant it is pumped to the desired pressure before vaporization, avoiding the need for costly gas compression. Industrially available crackers are reported to operate at pressures between 20 and 40 bar [10].

For this case-study, a plant fed with 15 ton/d of NH₃ is considered, representative of a small-scale facility for decentralized hydrogen

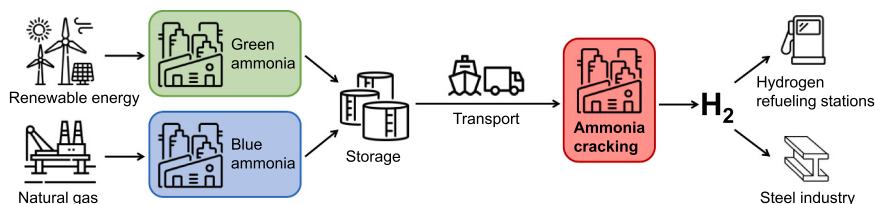
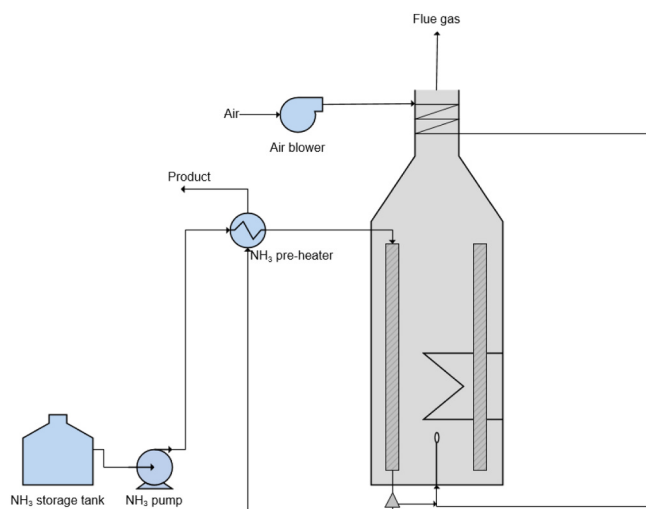


Fig. 6. Ammonia value chain.

Fig. 7. NH₃ cracking furnace simplified process flow diagram.

applications. The cracking process is assumed to occur in a fired tubular reactor, operating at 40 bar and achieving an ammonia conversion of 90 %. The downstream hydrogen purification section is not included in this study, as it does not impact on the performance comparison of the different ammonia cracking technologies.

Fig. 7 shows the process flow diagram of the analysed ammonia cracking furnace. A simulation of the furnace reactor has been developed using Aspen Plus® V14, with the PC-SAFT Equation of State selected to model the system under the high-pressure, high-temperature conditions within the furnace. Ammonia from the storage tank, available at 25 °C and 15 bar, is first pressurized to 40 bar and preheated before entering the furnace, which has a cylindrical shape and is equipped with 65 vertical tubes. Each tube is a 1-D pseudo-homogeneous packed bed reactor, with an internal diameter of 0.04 m and a length of 5 m. Different catalyst particles are packed in the tubes, with specifications provided in Table 5. Bed voidage of 0.4 was fixed for all case studies. Further details about the furnace geometry are available in section S2. Pressure drops along the tube are accounted through the Ergun equation, considering a spherical catalyst particle of 0.1 m diameter.

The catalyst-packed tubes are located in the radiant section of the cracking furnace. Radiant and convective heat sources provide the energy required to drive the endothermic cracking reaction, converting most of NH₃ into H₂ and N₂. A portion of this cracked gas is directed to

the burner, where it is mixed with preheated combustion air and ignited to supply heat to the furnace. The flow rate of the cracked gas directed to the burner is adjusted to achieve an outlet ammonia conversion of 90 %. Combustion air, available at ambient temperature and pressure, flows through tubes in the convective section at the top of the furnace, exchanging heat with the flue gases. The stack temperature of the flue gases is set at 120 °C. The excess air ratio is controlled to manage the flame temperature, which must remain below 1400 °C to prevent damage to the stainless-steel tubes. The majority of the product gas is routed to the ammonia preheater to enable energy recovery, cooling down significantly before entering downstream separation units for H₂ and N₂. The approach temperature difference in this heat exchanger is set at 10 °C.

3. Results and discussions

Referring to the system described in Section 4, Table 6 provides an overview of the results obtained, considering product mass flow, required duty for the cracking reaction to occur and fraction of the cracked product to burner in order to sustain the reaction. The fraction to burner was modified to enable the operating temperature of the system to increase in order to reach 90 % NH₃ conversion at the reactor outlet. As a consequence of the fixed NH₃ conversion, outlet cracked gas had a composition of 10 wt% NH₃, 15.99 wt% H₂, 74.02 wt% N₂. As the inlet ammonia flow rate is fixed as well as the ammonia conversion, the required duty of Table 6 is a direct indication of the catalytic species performance. K-promoted Ru/CaO shows very similar performance to Ru/MgAl₂O₄, the latter with about 1/3 of Ru active phase loading than the former.

In addition, Fig. 8 displays the tube side temperature profiles for all the case-studies. As shown, for the Ni/Al₂O₃ case-study, the highest temperature of 700 °C was experienced at the reactor outlet, while, for the Ru/MgAl₂O₄, the lowest value of about 580 °C was registered.

To enable a meaningful comparison between the case studies in terms of catalyst's economics and performance, a parameter, ξ , is introduced, to account for both capital and operating expenditures. By assuming identical reaction furnace across all simulations (any cost difference due to lower operating temperatures is assumed to be negligible), the primary variation in capital expenses is attributed to the cost of the catalyst. For the Ni-based benchmark, a capital cost of 46 \$/kg_{cat} [37] is assumed, while the expected lifetime is fixed at five years [38]. This cost also includes the metal recovery values and fees.

Regarding the operating expenses, a portion of the unconverted NH₃-H₂-N₂ mixture is utilized as fuel to supply the thermal energy required for the ammonia cracking reaction. Consequently, operating costs are inherently embedded in the net H₂ output, thereby simplifying the analysis. On this basis, Eq. (5) is employed to calculate the ξ parameter, which results 0.0158 \$/kgH₂ for the Ni/Al₂O₃ benchmark.

$$\xi = \frac{\text{CAPEX}_{\text{catalyst}}}{H_{2,\text{out}}} \quad (5)$$

The ruthenium-based catalyst can emerge as a potentially effective alternative to the nickel-based benchmark if its ξ , indication of process economics, is lower or, at most, meets ξ of the latter (see Eq. (6)). To assess this, a breakeven analysis is conducted for each scenario,

Table 5
Specifications of NH₃ decomposition catalysts assumed in process simulation.

Catalyst	Support density [kg/m ³]	Catalyst mass [kg]
2.8 %Ru9.6 %K/CaO [23]	3340	822
2.5 %Ru/TiO ₂ [32]	4260	1072
0.78 %Ru/MgAl ₂ O ₄ [24]	3600	892
10 %Ni/Al ₂ O ₃ [36]	3970	1094

Table 6
Results for the case-studies analysed.

case-study	2.8 %Ru9.6 %K/CaO	2.5 %Ru/TiO ₂	0.78 %Ru/MgAl ₂ O ₄	Ni/Al ₂ O ₃
Product mass flow [kg/h]	506.4	506.2	506.4	505.3
Q [kW]	700.88	705.01	699.85	714.75
fraction to burner [-]	0.1897	0.1901	0.1897	0.1916

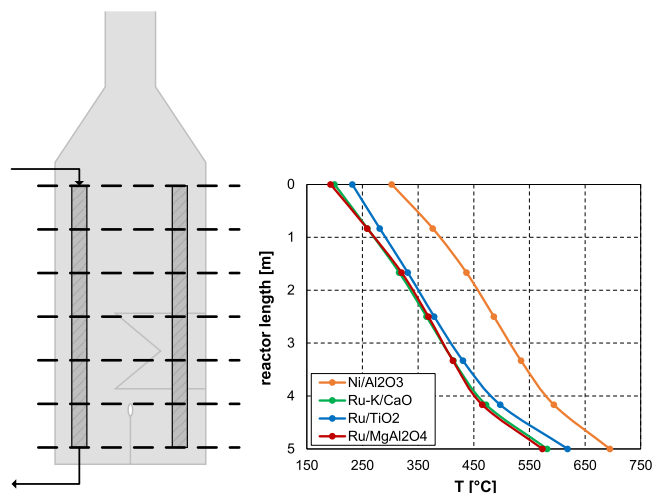


Fig. 8. Tube side temperature profiles within the cracking furnace.

considering the hydrogen production flow rate of Table 6. By determining the breakeven point, the analysis offers insight into the feasibility of adopting ruthenium-based catalysts in practical applications, particularly within decentralized hydrogen production systems where performance and cost efficiency must be carefully balanced. Eq. (7) is applied for accounting for the breakeven point and resulting values are reported in Table 7.

$$(\xi)_{Ru-cat} \leq (\xi)_{Ni-cat} \quad (6)$$

$$\left(\frac{CAPEX}{catalystlife} \right)_{Ru-cat} \leq (H_{2,out})_{Ru-cat} \cdot (\xi)_{Ni-cat} \quad (7)$$

To further explore these results, the methodology proposed by Super and mentioned by the National Renewable Energy Laboratory is applied [37,39].

According to this methodology, the Precious Metal Loop is applied to identify catalyst cost, which includes 4 steps: buy the catalyst, make the product, ship spent catalyst to a refiner and receive the Platinum Group Metal (PGM) settlement [40]. For identification of the expenses, assumptions of Table 8 are introduced. Accountability stands for the recovery percentage of the noble metal upon refining. The amount of noble metal not recovered must be reintroduced and this is regarded as a cost in retrieving the overall catalyst expense. The PGM to be reintroduced is credited to the pool account.

As a result, referring to the total catalyst expense to the catalyst mass of Table 8, the catalyst cost [\$/kg] can be retrieved. When compared to the nickel-based (Ni-based) system, these costs are significantly higher for the ruthenium-based (Ru-based) alternatives. For the Ru-based alternatives to be economically viable, i.e., to meet the $\frac{CAPEX}{catalystlife}$ ratio of the

Ni-benchmark provided in Table 7, their catalyst lifetime must be substantially extended. Specifically, the lifetimes must be increased by factors of 3.4, 2.8 and 1.8 times than Ni-based catalyst for 2.8 %Ru9.6 %K/CaO, 2.5 %Ru/TiO₂ and 0.78 %Ru/MgAl₂O₄, respectively. Among these options, the Ru/CaO catalyst emerges as the least viable route for practical NH₃ cracking, due to its disproportionately high cost-performance ratio, despite its higher NH₃ conversion activity. The MgAl₂O₄-supported catalyst, which contains the lowest concentration of active metal, presents itself as the most promising candidate from both technical and economic perspectives. The 0.78 %Ru/MgAl₂O₄ system stands out as a compelling starting point for future investigations into catalyst design aimed at optimizing performance and reducing overall cost.

4. Conclusions

NH₃ cracking is garnering increasing attention as a promising route for on-demand, carbon-free hydrogen (H₂) production. However, the commercial viability of this process is heavily dependent on the development of highly active, stable, and economically feasible catalytic systems. Among the most extensively studied catalysts are those based on nickel (Ni) and ruthenium (Ru), each offering distinct advantages and limitations.

Ru-based catalysts exhibit outstanding catalytic activity due to favourable Ru–N interactions, which facilitate efficient NH₃ decomposition. Nevertheless, the high cost associated with Ru significantly impedes their large-scale deployment. To mitigate this, efforts have focused on reducing Ru content through various strategies, including support engineering, alkali metal doping, and the use of activity-enhancing promoters such as K, Na, and Cs. These approaches aim to maximize catalytic efficiency while minimizing precious metal usage.

Ni-based catalysts, on the other hand, offer a more cost-effective alternative but are generally hindered by lower intrinsic activity and limited long-term stability. Enhancement strategies for Ni systems include transition metal doping, utilization of advanced support materials such as layered double hydroxides and perovskites, and incorporation of rare-earth promoters like Ce, La, and Sr. While these measures have led to noticeable performance improvements, Ni catalysts still lag behind Ru systems in terms of overall efficiency.

To systematically assess the interplay between catalyst performance and economic viability, a techno-economic analysis of NH₃ cracking using various catalytic formulations (2.8 %Ru9.6 %K/CaO, 2.5 %Ru/TiO₂ and 0.78 %Ru/MgAl₂O₄) was conducted. As expected, for Ru-based systems to be competitive with Ni-based benchmark, significantly extended catalyst lifetimes and/or NH₃ conversion performance are required. Specifically, the Ru/CaO catalyst necessitates an impractically long lifetime, rendering it unrealistic for commercial application.

Of these, the MgAl₂O₄-supported catalyst, characterized by the lowest noble metal loading, emerges as a particularly viable candidate for further development. Its balance of reduced cost and satisfactory

Table 7
Process and cost performance indicators for the case studies analysed.

Case-study	2.8 %Ru9.6 %K/CaO	2.5 %Ru/TiO ₂	0.78 %Ru/MgAl ₂ O ₄	Ni/Al ₂ O ₃
$\frac{CAPEX}{catalystlife}$ [\$/y]	5.2025	5.1998	5.2023	5.1903

Table 8

Estimation of capital expenses for PGM-based catalysts.

Assumptions		Output			
Description	Value	Description	2.8 %Ru9.6 %K/CaO	2.5 %Ru/TiO ₂	0.78 %Ru/MgAl ₂ O ₄
Ru cost [\$/Toz]	675 [41]	loading [wt%]	2.8	2.5 ^a	0.78
Toz/kg	32	dry cat [kg]	822	1072	892
Recovery of PGM [%]	90 [39]	catalyst purchase ex PGM [\$]	46,980	39,690	36,990
cost of fabrication and support [\$/kg]	45 [37]	PGM make-up [\$]	17,089	12,890	3748
kg _{dry cat} /kg _{spent cat}	8 [39]				
Refining					
PGM lease [\$]	13,160				
	[39]				
shipping to refine [\$]	2500				
	[39]				
handling charges [\$/kg _{spent cat}]	2.5 [39]	total refining cost [\$]	173,182	27,142	20,976
refining fee [\$/Toz _{recovered}]	11 [39]	replenish pool account [\$]	80,380	60,631	17,630
Accountability [%]	97 [39]				
		total capital expense [\$]	173,182	140,623	88,756
		catalyst cost [\$/kg]	170	156	106

^anominal noble metal loading. The actual Ru content is not provided by reference [32].

activity highlights the critical role of support selection and active phase dispersion in achieving both technical efficiency and economic sustainability.

These results emphasize the necessity of tailoring catalyst design not only for reactivity but also for cost-effectiveness, particularly in applications targeting decentralized or scalable hydrogen production. Future research should prioritize enhancing catalyst durability, further reducing Ru content and exploring alternative supports and promoters.

CRediT authorship contribution statement

Pellegrini Laura Annamaria: Writing – review & editing, Supervision, Methodology, Conceptualization. **Giorgia De Guido:** Writing – review & editing, Supervision. **Stefania Moiola:** Writing – review & editing, Supervision. **Elvira Spatolisano:** Writing – original draft, Methodology, Investigation, Conceptualization. **Federica Restelli:** Writing – review & editing, Software, Methodology.

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.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcata.2025.120670](https://doi.org/10.1016/j.apcata.2025.120670).

Data availability

Data will be made available on request.

References

- [1] E. Spatolisano, L.A. Pellegrini, A.R. de Angelis, S. Cattaneo, E. Roccaro, Ammonia as a carbon-free energy carrier: NH₃ cracking to H₂, *Ind. Eng. Chem. Res.* 62 (2023) 10813–10827.
- [2] E. Spatolisano, F. Restelli, L.A. Pellegrini, S. Cattaneo, A.R. de Angelis, A. Lainati, E. Roccaro, Liquefied hydrogen, ammonia and liquid organic hydrogen carriers for harbour-to-harbour hydrogen transport: a sensitivity study, *Int. J. Hydrog. Energy* 80 (2024) 1424–1431.
- [3] Z. Su, J. Guan, Y. Liu, D. Shi, Q. Wu, K. Chen, Y. Zhang, H. Li, Research progress of ruthenium-based catalysts for hydrogen production from ammonia decomposition, *Int. J. Hydrog. Energy* 51 (2024) 1019–1043.
- [4] I. Lucentini, X. Garcia, X. Vendrell, J. Llorca, Review of the decomposition of ammonia to generate hydrogen, *Ind. Eng. Chem. Res.* 60 (2021) 18560–18611.
- [5] T. Su, B. Guan, J. Zhou, C. Zheng, J. Guo, J. Chen, Y. Zhang, Y. Yuan, W. Xie, N. Zhou, Review on Ru-based and Ni-based catalysts for ammonia decomposition: research status, reaction mechanism, and perspectives, *Energy Fuels* 37 (2023) 8099–8127.
- [6] N. Li, C. Zhang, D. Li, W. Jiang, F. Zhou, Review of reactor systems for hydrogen production via ammonia decomposition, *Chem. Eng. J.* 495 (2024) 153125.
- [7] N. Zhu, F. Yang, Y. Hong, J. Liang, Hydrogen production from ammonia decomposition: Advances in Ru- and Ni-based catalysts, *Int. J. Hydrog. Energy* 98 (2025) 1243–1261.
- [8] BASF, SYNSPiRE™ ARC – Ammonia reforming catalysts, 2025.
- [9] T. Davison, J. Ashcroft, Making and breaking NH₃ – Ammonia and its place in the low carbon economy. Nitrogen + Syngas Conference, Johnson Matthey, Berlin, Germany, 2022.
- [10] Clariant, Catalysts to tackle the challenges of ammonia cracking, Nitrogen+Syngas 384(www.nitrogenandsyngas.com), 2023.
- [11] P. Brito, H2Retake™Ammonia Cracking –TOPSOE's innovative technology. Building on industrial experience., AEA Conference -Ammonia Cracking Session, 2024.
- [12] Y. Im, H. Muroyama, T. Matsui, K. Eguchi, Ammonia decomposition over nickel catalysts supported on alkaline earth metal aluminate for H₂ production, *Int. J. Hydrog. Energy* 45 (2020) 26979–26988.
- [13] Q.C. Do, Y. Kim, T.A. Le, G.J. Kim, J.-R. Kim, T.-W. Kim, Y.-J. Lee, H.-J. Chae, Facile one-pot synthesis of Ni-based catalysts by cation-anion double hydrolysis method as highly active Ru-free catalysts for green H₂ production via NH₃ decomposition, *Appl. Catal. B Environ. Energy* 307 (2022) 121167.
- [14] M. Yu, R. Sun, G. Luo, L. Wang, X. Li, H. Yao, Ammonia partial cracking over low-cost Ni catalysts for enhancing combustion, *Fuel* 367 (2024) 131306.
- [15] X.-Y. Guo, J.-H. Wang, Q. Zhang, T.-Z. Li, H. Dong, C.-J. Jia, C. Li, Y.-W. Zhang, Alkaline Earth metal promoted hydrogen production from ammonia decomposition over Ni/La₂O₃-based catalysts, *Appl. Catal. B Environ. Energy* 348 (2024) 123844.
- [16] T. Kocer, F.E. Saraç-Öztuna, S.F. Kurtoglu-Öztulum, U. Unal, A. Uzun, Effect of Nickel precursor on the catalytic performance of graphene aerogel-supported nickel nanoparticles for the production of CO_x-free hydrogen by ammonia decomposition, *Energy Technol.* 10 (2022) 2100794.
- [17] Z.-P. Hu, C.-C. Weng, C. Chen, Z.-Y. Yuan, Catalytic decomposition of ammonia to CO_x-free hydrogen over Ni/ZSM-5 catalysts: A comparative study of the preparation methods, *Appl. Catal. A Gen.* 562 (2018) 49–57.
- [18] X. Zhang, L. Liu, J. Feng, X. Ju, J. Wang, T. He, P. Chen, Metal-support interaction-modulated catalytic activity of Ru nanoparticles on Sm₂O₃ for efficient ammonia decomposition, *Catal. Sci. Technol.* 11 (2021) 2915–2923.
- [19] K. Xu, J.-C. Liu, W.-W. Wang, L.-L. Zhou, C. Ma, X. Guan, F.R. Wang, J. Li, C.-J. Jia, C.-H. Yan, Catalytic properties of trivalent rare-earth oxides with intrinsic surface oxygen vacancy, *Nat. Commun.* 15 (2024) 5751.
- [20] X. Zhang, L. Liu, J. Feng, X. Ju, J. Wang, T. He, P. Chen, Ru nanoparticles on Pr₂O₃ as an efficient catalyst for hydrogen production from ammonia decomposition, *Catal. Lett.* 152 (2022) 1170–1181.
- [21] T.A. Le, Y. Kim, H.W. Kim, S.-U. Lee, J.-R. Kim, T.-W. Kim, Y.-J. Lee, H.-J. Chae, Ru-supported lanthania-ceria composite as an efficient catalyst for CO_x-free H₂ production from ammonia decomposition, *Appl. Catal. B Environ.* 285 (2021) 119831.
- [22] C. Huang, Y. Yu, J. Yang, Y. Yan, D. Wang, F. Hu, X. Wang, R. Zhang, G. Feng, Ru/La₂O₃ catalyst for ammonia decomposition to hydrogen, *Appl. Surf. Sci.* 476 (2019) 928–936.
- [23] S. Sayas, N. Morlanés, S.P. Katikaneni, A. Harale, B. Solami, J. Gascon, High pressure ammonia decomposition on Ru-K/CaO catalysts, *Catal. Sci. Technol.* 10 (2020) 5027–5035.
- [24] Y. Qiu, F.S. Franchi, N. Usberti, A. Beretta, Kinetic Investigation of NH₃ Decomposition Over Ru-Based Catalysts: The Limiting Role of H* Surface Coverage Demonstrated by Experiments and Modelling, Available at SSRN 4923910.
- [25] H.B. Kim, E.D. Park, Ammonia decomposition over Ru catalysts supported on alumina with different crystalline phases, *Catal. Today* 411 (2023) 113817.

- [26] X.-C. Hu, X.-P. Fu, W.-W. Wang, X. Wang, K. Wu, R. Si, C. Ma, C.-J. Jia, C.-H. Yan, Ceria-supported ruthenium clusters transforming from isolated single atoms for hydrogen production via decomposition of ammonia, *Appl. Catal. B Environ.* 268 (2020) 118424.
- [27] Z. Hu, J. Mahin, S. Datta, T.E. Bell, L. Torrente-Murciano, Ru-based catalysts for H₂ production from ammonia: effect of 1D support, *Top. Catal.* 62 (2019) 1169–1177.
- [28] T. Furusawa, H. Kuribara, K. Kimura, T. Sato, N. Itoh, Development of a Cs-Ru/CeO₂ spherical catalyst prepared by impregnation and washing processes for low-temperature decomposition of NH₃: characterization and kinetic analysis results, *Ind. Eng. Chem. Res.* 59 (2020) 18460–18470.
- [29] J. Shin, U. Jung, J. Kim, K.D. Kim, D. Song, Y. Park, B.-S. An, K.Y. Koo, Elucidating the effect of Ce with abundant surface oxygen vacancies on MgAl₂O₄-supported Ru-based catalysts for ammonia decomposition, *Appl. Catal. B Environ.* 340 (2024) 123234.
- [30] S. Mazzone, T. Goklany, G. Zhang, J. Tan, E.I. Papaioannou, F.R. García-García, Ruthenium-based catalysts supported on carbon xerogels for hydrogen production via ammonia decomposition, *Appl. Catal. A Gen.* 632 (2022) 118484.
- [31] F. Zhiqiang, W. Ziqing, L. Dexing, L. Jianxin, Y. Lingzhi, W. Qin, W. Zhong, Catalytic ammonia decomposition to CO_x-free hydrogen over ruthenium catalyst supported on alkali silicates, *Fuel* 326 (2022) 125094.
- [32] W. Yan, W. Wang, Q. Gu, B. Zhang, G. Bi, H. Zhuo, X. Shang, G. Xu, F. Wang, T. Zhang, Interfacial evolution of Ru/TiO₂ catalysts in NH₃ decomposition, *J. Energy Chem.* (2025).
- [33] Z. Wang, Y. Qu, X. Shen, Z. Cai, Ruthenium catalyst supported on Ba modified ZrO₂ for ammonia decomposition to CO_x-free hydrogen, *Int. J. Hydrog. Energy* 44 (2019) 7300–7307.
- [34] A. Takahashi, T. Fujitani, Kinetic analysis of decomposition of ammonia over Nickel and Ruthenium catalysts, *J. Chem. Eng. Jpn.* 49 (2016) 22–28.
- [35] S. Sun, Q. Jiang, D. Zhao, T. Cao, H. Sha, C. Zhang, H. Song, Z. Da, Ammonia as hydrogen carrier: Advances in ammonia decomposition catalysts for promising hydrogen production, *Renew. Sustain. Energy Rev.* 169 (2022) 112918.
- [36] K. Okura, T. Okanishi, H. Muroyama, T. Matsui, K. Eguchi, Ammonia decomposition over Nickel catalysts supported on rare-earth oxides for the on-site generation of hydrogen, *ChemCatChem* 8 (2016) 2988–2995.
- [37] F.G. Baddour, L. Snowden-Swan, J.D. Super, K.M. Van Allsburg, Estimating precommercial heterogeneous catalyst price: a simple step-based method, *Org. Process Res. Dev.* 22 (2018) 1599–1605.
- [38] S. Richard, A. Ramirez Santos, P. Olivier, F. Gallucci, Techno-economic analysis of ammonia cracking for large scale power generation, *Int. J. Hydrog. Energy* 71 (2024) 571–587.
- [39] J.D. Super, The precious metal loop, costs from an operating company perspective, *Top. Catal.* 53 (2010) 1138–1141.
- [40] L. Cline, Precious Met. Recovery Precious Met. 'Loop' (2017) 71–80.
- [41] J. Matthey, PGM management, 2025.