

Faculté des bioingénieurs

Ammonia decomposition over praseodymium-doped nickel catalysts

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List of Acronyms

Acronym	Full name
LOHC	Liquid Organic Hydrogen Carriers
NP	Nanoparticle
RDS	Rate-Determining Step
PTI	Programmed Temperature Increase
XRD	X-Ray Diffraction
TPR	Temperature-programmed reduction
BET	Brunnett-Emett-Taylor
BJH	Barrett, Joyner and Halenda
GC	Gas Chromatography
MS	Mass Spectrometry
XPS	X-ray Photoelectron Spectroscopy
FWMH	Full Width at Mid Height
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
GHSV	Gas Hourly Space Velocity

1. Introduction

1.1. Context

In a world growing increasingly aware of climate change and its links to human activities resulting in greenhouse gas emissions, solutions are being worked on to reduce these emissions and mitigate climate change.

Hydrogen can be a part of this solution thanks to its high gravimetric energy density, low molecular weight, and combustion performance ^[7]. Its main strong point is that the combustion of hydrogen only generates heat and water. The gravimetric energy density of hydrogen is 120 MJ/kg compared to 55.60 MJ/kg for methane ^[3].

The prevailing hypothesis suggests that hydrogen will serve as a cornerstone for deep decarbonisation within specific industrial and transport niches that presently lack economically viable transition pathways ^[7]. Ammonia and hydrogen can serve as key energy carriers to defossilise hard-to-electrify sectors.

For example, hydrogen can be used for industrial applications such as steel reduction instead of C-based reductants to greatly reduce CO₂ emissions ^[7]. Hydrogen combustion is useful for applications where electrical furnaces cannot reach the required high temperatures such as glass production.

Regarding using hydrogen to decarbonise mobility, heavy duty trucks or boats would require excessive battery weight to store the energy which they require ^[7]. Hydrogen's high energy density by weight could make it a suitable fit for such applications. Nonetheless, hydrogen's low volumetric energy density makes its use for mobility applications challenging. The highest priority for hydrogen's use as a tool for decarbonisation, is the chemical industry.

The use of hydrogen requires specific safety precautions due to its flammability limits that are larger than conventional fuels ^[2]. Indeed, hydrogen's flammability range is 4.0 % to 75.6 % (hydrogen-to-air volume ratio), whereas, for methane, it's 5.0 % to 15.0 % (methane-to-air volume ratio). Furthermore, the minimum ignition energy for hydrogen in air is 0.017 mJ compared to 0.29 mJ in the case of methane ^[2].

On the other hand, the auto-inflammation temperature, minimal temperature above which the combustion reaction happens spontaneously and completely until a thermodynamic

equilibrium is reached in the burned gases, is similar for hydrogen and methane ^[2]. Indeed, hydrogen's auto-inflammation temperature is 500°C whereas, for methane, it's 537°C.

As of 2022, 95% of the hydrogen supply was produced by fossil fuel-based methods such as steam methane reforming, which emits CO₂ ^[7].

Sustainable production of hydrogen via electrolysis at scale requires abundant and cheap renewable electricity ^[7]. Some regions of the world have more of it than others or have higher potential to develop the infrastructure to do so. Indeed, a crucial factor for a country be able to export large quantities of hydrogen is that it's infrastructure should allow it to be done ^[7].

Once this hydrogen is produced, one way to transport it is by shipping it. There are three main ways to do so; liquid hydrogen, liquid organic hydrogen carriers, and ammonia ^[7].

First, hydrogen can be liquified by using energy-intensive compression and cooling processes ^[4]. Cryo-compressed storage of hydrogen involves cooling the gas into a liquid form at -253°C under 350 bar of pressure. Such methods consume about 30% of the hydrogen's heating value. A large portion of the hydrogen can also be lost due to boil-off. Hydrogen's low molecular size allows it to seep through materials unless specific precautions and materials are used to store it ^[4]. The specialised tanks required to store hydrogen under such conditions make its long-haul transportation unviable given the inherent weight of the tank relative to the weight of hydrogen being transported.

A second option are liquid organic hydrogen carriers (LOHCs) i.e. organic compounds that can absorb and release hydrogen through a chemical reaction ^[7]. LOHCs serve as chemically stable hydrogen carriers that leverage existing petrochemical infrastructure, as they remain in the liquid phase at standard temperature and pressure.

Finally, ammonia can be used as a hydrogen carrier thanks to its 17.8wt% hydrogen content ^[11]. Ammonia can be liquefied at -33.34°C under atmospheric pressure which makes its transportation much easier and the infrastructure for doing so already exists globally. Under such conditions, the volumetric energy density of ammonia is 12.69 MJ/L ^[5]. The volumetric energy density of liquified hydrogen at -253°C under atmospheric pressure is 8.5 MJ/L.

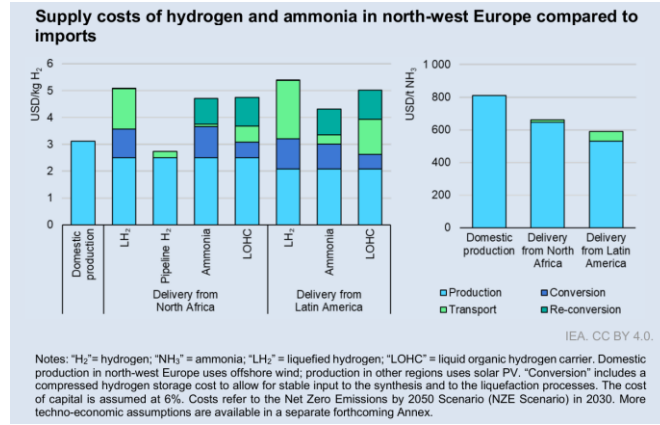


Figure 1: Supply costs of hydrogen and ammonia in north-west Europe compared to imports ^[10]

Such properties make the use of ammonia as a carrier gas for hydrogen the most promising method for long haul transportation of hydrogen via ships ^[10]. Figure 1 confirms this hypothesis. The indicative shipping costs for ammonia is indeed approximately \$100/t compared to \$1500/t in the case of liquified hydrogen ^[7].

Another method is to transport hydrogen via pipelines. A way of doing so is to use current natural gas pipeline infrastructure ^[7]. However, hydrogen being the smallest molecule, it can seep through cracks in the pipeline which results in a leakage. Hydrogen can cause embrittlement of pipelines. Furthermore, such leakages require specialized equipment to be perceived given the invisible and inodorous properties of hydrogen.

Existing natural gas pipeline infrastructure can be repurposed to make it suitable for hydrogen to be carried through. In that case, for large volumes, the cost-effective range can be as high as 8000 km (Figure 2) ^[7].

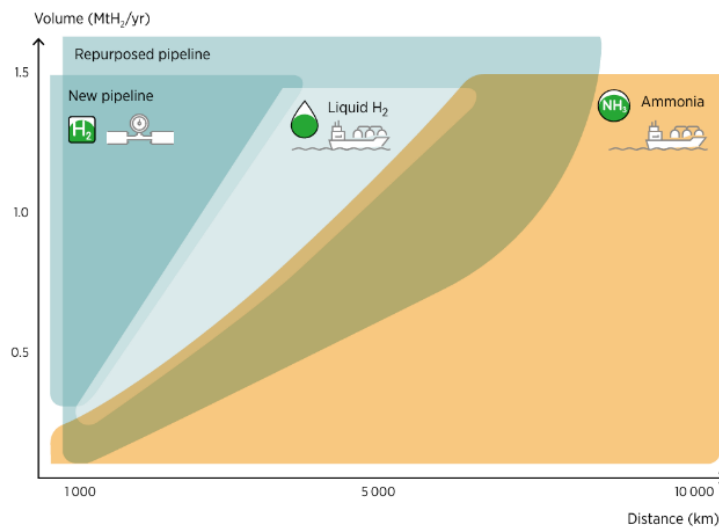


Figure 2: Cost efficiency of transport options when considering volume and distance ^[8]

Ammonia as a carrier gas is not a one size fits all solution. It's a case specific solution that sometimes makes sense for long distance transportation of hydrogen.

According to the *Global Hydrogen Review 2025*, about 85% of trade-oriented projects for renewable hydrogen production plan to transport it as ammonia ^[8]. The projects planned aim to trade up to 75 Mtpa of ammonia by 2030. The current global production of ammonia is approximately 200 Mtpa and the amount of ammonia traded presently is 20 Mtpa.

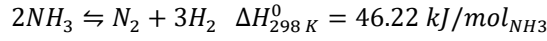
Such a rapid expansion of ammonia trading, in part for ammonia cracking into hydrogen, would require the swift development of large-scale ammonia port facilities, which could be hindered by logistical, legal, and time constraints ^[8]. Furthermore, it requires generating significant new market demand, particularly for technologies like ammonia cracking that are still undergoing commercial testing. Such plants already exist at industrial scale and serve the purpose of optimising ammonia cracking, safety, and catalysis to collect data for future larger-scale plants ^[9].

This master's thesis focuses on developing novel catalysts for the thermocatalytic cracking of ammonia.

1.2. State of the Art

1.2.1. Elemental Steps of Ammonia Decomposition

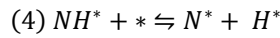
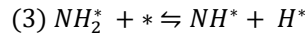
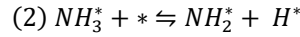
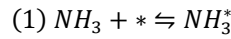
The ammonia cracking, or decomposition, global reaction is the following ^[11]:



The process of ammonia cracking is thermodynamically favoured at high temperatures and low pressures ^[11].

Thermocatalytic cracking of ammonia decreases the activation energy, resulting in a decrease in the required temperature compared to the non-catalytic process ^[11].

The reaction mechanism for the thermocatalytic cracking of ammonia involves 6 steps ^[11]. The * represents an active site of the catalyst.



Step (1) is the adsorption of NH_3 on the active site of the catalyst ^[13]. Steps (2), (3), and (4) correspond to the dehydrogenation of NH_3 one N-H bond at a time. Step (5) is the recombinative desorption of nitrogen atoms (5) and step (6) is the recombinative desorption of H_2

The reaction proceeds through several steps where all intermediates are adsorbed on an active site ^[13]. This heterogeneous dissociative adsorption reaction meets the criteria for a Langmuir-Hinshelwood mechanism. In this model, prior to any species reacting with one another, all species involved in the reaction must adsorb onto the catalyst's active sites ^[13].

1.2.2. Nickel as an Active Site compared to Other Metals

Catalysts for this reaction usually contain a transition metal as active phase ^[11]. The most common active phases for ammonia cracking are Ni or Ru.

Ru- and Ni-based catalyst were found to perform better than all other comparable catalysts with a different metal active phase ^[20]. The turnover frequency (TOF) of ammonia decomposition on a Ni active phase is about 40% lower to a comparable catalyst with a Ru active phase. All other metals considered by Ganley et al., such as Rh, Co, and Fe, were found to be less efficient for ammonia decomposition by several orders of magnitude (Figure 3) ^[20].

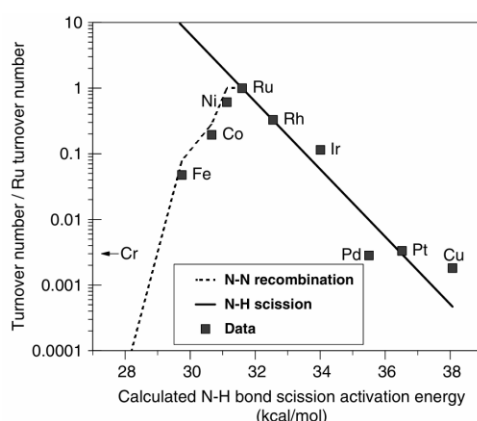


Figure 3: A correlation between the rate of ammonia decomposition on several metals and the relative rate of N–H bond scission, and N–N recombination as estimated from the Blowers–Masel correlation ^[20].

The Langmuir-Hinshelwood mechanism is governed by the Sabatier principle, according to which the interaction between the catalysts and reactants must be optimal ^[19]. Volcano plots illustrate this principle by plotting the catalytic activity against the binding energy of the active site with the reacting species.

If the interaction is too weak, ammonia or its intermediates won't bind effectively to the surface ^[16]. In such cases, adsorption and dehydrogenation steps are unfavourably impacted.

If the interaction is too strong, the products of intermediate reactions bind to the surface in a way that prevents the effective recombination of N ^[16]. In such cases, the catalyst's surface suffers from poisoning, described as a blocking of the active sites which negatively impacts the adsorption of ammonia.

In the Figure 3, the full line corresponds to the rate-determining step (RDS) being caused by a strong binding energy, whereas the dotted line corresponds to the RDS being caused by a weak binding energy ^[20].

The optimum point which leads to peak catalytic activity is one where the species-catalyst bond is strong enough for adsorption and dehydrogenation to occur all whilst, being not too strong, allowing the effective recombination of N ^[16].

Ni or Ru as active metals for the thermocatalytic cracking of ammonia offer a performance optimum where no specific chemical property of the metal acts as a major bottleneck for the reaction ^[20].

There are, however, rate-determining steps (RDS) for ammonia decomposition when using Ni or Ru as active sites. The RDS is different for catalysts with one active phase or the other.

In the case of Ru active sites, the dehydrogenation of H atoms from NH₃ is the RDS ^[20].

In the case of Ni active sites, the recombinative desorption of N atoms is the RDS ^{[20][21]}.

When comparing these active sites for this reaction, the binding of Ni to N contributes more to a decrease in catalytic performance compared to the RDS of dehydrogenation for Ru-based catalyst ^[20].

However, the limited availability and high cost of Ru-based catalysts make their use unfit for scale up of the process to industrial capacity ^[11]. Indeed, as of May 2026, Ru cost \$62.59 per gram while Ni cost \$19.50 per kg ^{[22][24]}. The cost difference is so high that it outweighs the decrease in catalytic performance.

For such reasons, research in that field focuses on finding the best performing catalyst formulation of non-noble metal catalysts ^[11]. Thus, Ni is the ideal active phase.

Ni is a Lewis acid transition metal, Ni⁰ presents empty d-orbitals that can accept electron pairs from the NH₃, a Lewis base ^[21]. The interaction of the d-orbitals with the antibonding orbitals of the N-H bonds is favourable for the adsorption of NH₃ onto the Ni active sites ^[21]. The electron transfer induces an orbital overlap which lowers the N-H bond binding energy ^[21].

There are several potential supports with which Ni can be combined to form a functional catalyst. However, some may be more promising than others.

1.2.3. Support

1.2.3.1. Alumina

Alumina is a potential candidate as support for a catalyst aimed at ammonia cracking ^[12]. It is inexpensive and provides a high thermal stability and mechanical strength required for operating at temperatures as high as 500 °C to 600 °C. The inexpensive nature of this support makes it suitable for industrial scale applications. Its high thermal stability allows alumina to retain its specific surface area and porous structure at high temperatures. The preserved high surface area of the support keeps the Ni nanoparticles well dispersed and, together with metal–support interactions, limits their migration and agglomeration ^[12].

Alumina, synthesised via the sol-gel process, presents a high specific surface area in several of its phases, allowing for a high dispersion of active metal nanoparticles ^[12]. Alumina has great mechanical strength, but its surface is slightly acidic. This acidity is a disadvantage for ammonia decomposition over Ni. The RDS of the reaction is the recombinative desorption of N₂, if the Ni-N binding energy is too strong, the N accumulates and poisons the surface. Basic sites donate electron density to Ni, which favours the weakening of the Ni-N bond and facilitates N₂ desorption. An acidic surface such as alumina, in contrast, does not provide this electronic promotion. The high specific surface area of alumina, facilitating a high dispersion of Ni, has the potential to compensate this lack of basicity by increasing the number of accessible active metals ^[12].

A study, reported by Aika and Kobayashi, assessed ammonia conversion at 550°C as a function of specific surface area of supports for 10 wt% Ni catalysts supported on various oxides (Figure 4) ^[12]. Alumina appears very promising thanks to its high specific surface area. Indeed, the Ni/Al₂O₃ catalyst presents a specific surface area nearing 200 m²/g and a conversion of 70% under a 100% NH₃ concentration and a gas hourly space velocity (GHSV) of 6000 kg/h*L. This performance is better than comparable catalysts with other supports.

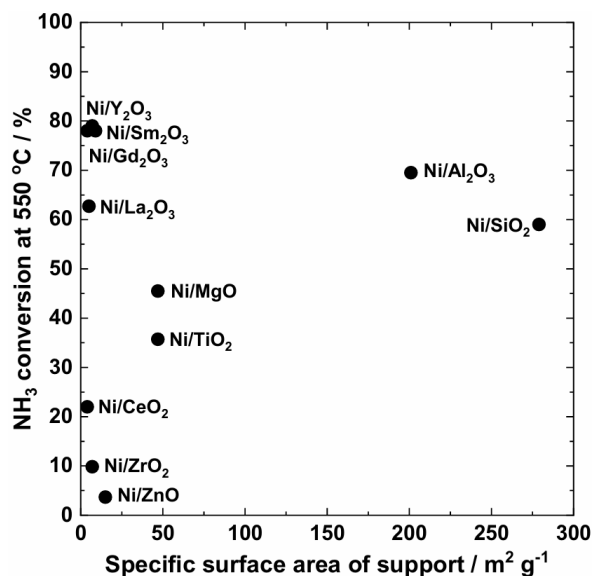


Figure 4: Ammonia conversion at 550 °C as a function of specific surface area of supports for 10 wt% Ni catalysts supported on various oxides. Reaction conditions; 100% NH₃, Space velocity (S. V.): 6000 l kg⁻¹ h⁻¹ [12].

According to Li et al., Al₂O₃ showed higher Ni dispersion compared to Ni/CeO₂, Ni/ZrO₂, and Ni/Y₂O₃ [47]. That is due to the large specific surface area and stability under high temperature conditions of Al₂O₃.

In Ni/Al₂O₃, the strong metal support-interaction resulted in the effective prevention of the aggregation of Ni nanoparticles [47]. However, this same interaction can lead to the formation of a spinel which could be unfavourable to the catalytic performance.

The acidity of Al₂O₃ makes this support efficient at adsorbing NH₃, which is basic [16]. This ammonia reservoir effect results in a steady supply of NH₃ to the Ni active sites [30]. However, this acidity of Al₂O₃ was confirmed by Kowalczyk et al. to have adverse effects on N₂ desorption kinetics due to strong Ni-N bonding [16].

The recombination of N bound to Ni on the surface of the catalyst requires the diffusion of N on the surface [16]. This diffusion requires that the atoms surmount a substantially high activation-energy barrier. The lower this energy barrier, the faster the overall reaction will be, so long as N₂ recombination and desorption is the RDS.

The crystalline phase regulation serves as a way of regulating the interaction between the support and the metal nanoparticle of the active phase [31].

Several phases of alumina exist [14]. The phase is determined by the calcination temperature during the support synthesis. Three phases of alumina were compared in the project; pseudoboehmite, γ-alumina, and δ-alumina.

Pseudoboehmite is the precursor to γ -alumina of which the formula is $\text{Al}(\text{OH})_3$. It is obtained at calcination temperatures near 400 °C and is in the shape of needle-like particles with pores between these needles ^[14]. It is rarely used as a catalyst support without further transformation given its instability as temperatures increase.

At calcination temperatures nearing 550°C, pseudoboehmite changes into the γ - Al_2O_3 phase ^[14]. The shape of its particles is now purely spherical, and its specific surface area is in the 200 m²/g range. It results in a high dispersion of Ni nanoparticles.

The drawbacks of γ -alumina include the tendency to endure strong hydrogen inhibition ^[28]. Indeed, NH_3 and H_2 can compete for active sites on an acidic support which hinders the ammonia decomposition reaction. Furthermore, γ -alumina is prone the formation of stable NiAl_2O_4 spinel phase ^[17]. This spinel is only reducible at temperatures above 800°C-1000°C to generate metallic Ni. However, this leads to sintering and thus, a decrease of specific surface area ^[29].

δ -alumina is formed at higher temperatures than γ -alumina (800°C-1000°C) ^[31]. The higher calcination temperature leads to δ -alumina presenting a slightly lower specific surface area than γ -alumina due to the formation of slightly larger nanoparticles. However, δ -alumina is more resistant to sintering than γ -alumina, which contributes to improved catalytic properties under high temperature conditions ^[31]. Furthermore, δ -alumina provides an electronic environment that is different from γ -alumina. This can result in differences in the reducibility and metal dispersion of Ni during synthesis ^[31].

The sol-gel process can be used to synthesise Al_2O_3 supports.

1.2.3.2. Sol-gel process

The sol-gel process for the synthesis of the support of a catalyst can improve its specific surface area.

The sol-gel process is a chemical synthesis technique used to produce high-purity, homogeneous nanomaterials such as metal oxides ^[38]. Indeed, it allows for the uniform, molecular-level mixing of precursors. This versatile and cost-effective process involves the conversion of a liquid system in the form of a colloidal suspension of solid particles, named a “sol”, into a solid “gel” phase ^[39].

The fundamental stages of the sol-gel process are precursor dissolution and sol formation, gelation, drying and xerogel formation, hydrothermal synthesis, and lastly, calcination.

At first, precursor dissolution is the process of dissolving metal precursors in a solvent, such as distilled water or alcohols ^[41]. Metal precursors are commonly alkoxides or inorganic salts. Hydrolysis describes the phenomena of the precursors being broken down by water to form a sol.

Gelation occurs next, through continuous stirring and controlled heating of the sol ^[40]. During this ageing step, the particles undergo condensation, resulting in a three-dimensional polymeric network appearing as a uniform gel.

The next step is hydrothermal synthesis. It involves placing the gel in an autoclave to undergo a high pressure and temperature which promotes nucleation and crystal growth as well as improved porosity and stability. The powder is then calcined to remove all impurities so that only the oxide form remains. The phase of the oxide can be changed depending on the calcination temperature.

Hydrothermal synthesis is a high temperature and pressure process which provides a control over the structure and morphology of the material ^[43]. Such a method leads to the production of high-purity polycrystalline materials and controlled particles sizes.

The sol-gel process provides control over the structure and morphology of the catalyst ^[40]. When integrating the active phase into the support using this method, the metal-support interactions are greatly enhanced.

The preparation method is a significant factor regarding the textural properties of the synthesized catalysts. Sol-gel synthesis of a support can lead to an increased specific surface area which can provide more opportunities for the dispersion of the active phase like Ni nanoparticles ^[44].

This method is effective at generating oxygen vacancies ^[40]. These vacancies improve basicity since the oxygen vacancies act as electron-rich sites. The lacking oxygen leaves an unsaturated metal site which can attract electrons, thus acting as a strong Lewis basic site that can donate electrons to the Ni active metal ^[40].

1.2.4. Praseodymium as a Doping Agent

Doping agents, also called promoters, are substances added in small quantities that improve catalytic activity, selectivity, and stability [36]. They do not consist in the primary active phase of the catalyst, but they modify this active phase or the support in several ways. Either rare earth or non-rare earth elements can play this role, but the two families behave very differently. The advantage of rare earths such as Pr or Ce is that they possess multiple valence states [35]. This property makes rare earth dopants more effective than non-rare earth dopants at improving the redox performance of catalysts. In fact, some non-rare earth dopants such as W and Nb inhibit the redox behaviour of a support, leading to an increase in the starting reduction temperature [37]. Rare earth dopants can greatly increase the density and strength of surface basic sites, whereas W and Nb provide acidic sites [35][37]. The Ni/Al₂O₃ catalyst requires basic sites to improve the kinetics of the recombinative desorption of N₂, which is the RDS of the ammonia decomposition reaction [47][37]. Rare earth elements are thus more suitable dopants for this reaction.

The performance of rare earths as dopants on Ni/Al₂O₃ was assessed for the ammonia decomposition reaction (Figure 5) [46]. Amongst rare earths such as Y, La, Ce, Pr, Nb, Sm, Eu, and Gd, La is the ideal promoter for maximal catalytic performance of the ammonia decomposition reaction. A 12 % weight loading of La as a dopant on 9%Ni/Al₂O₃ catalyst results in a NH₃ conversion of 92 % at a GHSV of 6000 cm³/(g.h) at 550 °C, against only 60 % for the undoped catalyst. Under identical conditions, Pr- and Nd-doped catalysts result in a conversion nearing 90 % [46].

Pr thus delivers near-optimal performance yet, unlike the extensively studied La system, remains comparatively little investigated for ammonia decomposition, which leaves a clear research gap. Further research is required to better understand the properties of Pr-doped Ni/Al₂O₃, for the ammonia decomposition reaction.

Furthermore, as of May 2026, Pr cost \$0.25 per g, much less than Ru at \$62.60 per gram [23][22]. Combined with Ni, at a cost of \$0.02 per g, a Pr-promoted Ni catalyst on Al₂O₃ support is explored here as a noble-metal-free alternative at a fraction of the cost of Ru-based systems [24].

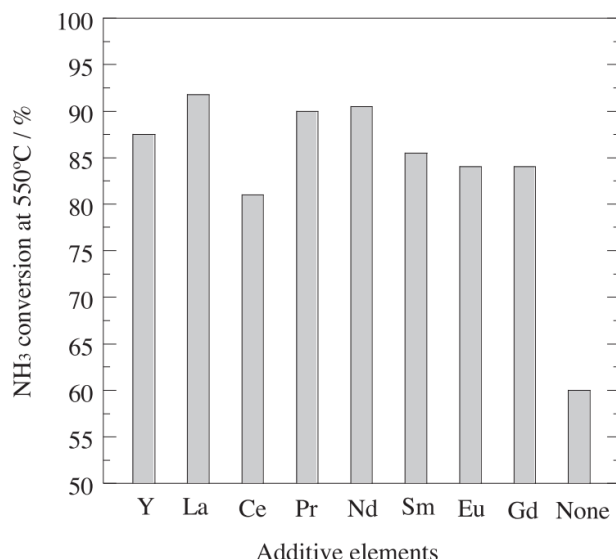


Figure 5: Ammonia conversion at 550 °C for ammonia decomposition over M-modified Ni/Al₂O₃ after calcination at 500 °C [46].

The promotional impact of Pr is mainly linked to its electronic and acid-base properties. PrO_x donates electrons to the active phase by undergoing valence state transitions from Pr³⁺ to Pr⁴⁺, behaving as an electron reservoir [12] [33]. This redox cycling generates oxygen vacancies which are themselves electron-donating, although oxygen itself does not take part in the ammonia decomposition reaction [33]. As a result, the electron density of Ni increases, which weakens the Ni-N bond and thus facilitates the recombinative desorption of N₂. In parallel, the basic character of PrO_x leads to a rise in the overall basicity of the catalyst, as confirmed by TPD-CO₂ for the Pr promotion of a Co/mesoporous-alumina catalyst [32] [35]. This basicity promotes the recombinative desorption of N₂ and suppresses hydrogen inhibition [12].

PrO_x also impacts the structure and reducibility of the catalyst. When dispersed on a Al₂O₃ support of high specific surface area, it strengthens the metal–support interaction, improves metal dispersion (integrating onto Al₂O₃ at the nanoscale [47]), and limits sintering of the active phase at high temperature, with lanthanide-based mixed oxides being more resistant to sintering than the pure lanthanides [32]. Correspondingly, Pr promotion of a Co/mesoporous-alumina catalyst reduced the Co₃O₄ crystallite size from 16.8 to 7.8 nm [35]. Furthermore, the reducibility of Ni is improved in the presence of a Pr dopant. In H₂-TPR of Ni/Al₂O₃, NiO is reduced at 379 °C (forming a small peak), and the NiAl₂O₄ spinel, formed by the strong Ni-Al interaction, reduces above 700 °C (forming a broad peak) [33]. PrO_x alone reduces at 492 °C, and Ni/PrO_x shows a sharp reduction peak at 444 °C (onset ~290 °C) assigned to the combined reduction of Ni and Pr [33]. The strong interaction between the oxygen of PrO_x and

that of NiO weakens the Ni–O bond and, together with the oxygen vacancies from $\text{Pr}^{3+}/\text{Pr}^{4+}$ cycling, markedly improves the reduction of Ni^{2+} to the catalytically active Ni^0 [33].

Such observations describe Pr as the bulk support itself (Ni/PrO_x) or as a dopant added to a $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst. In this work, Pr is used in the second form, as a PrO_x promoter co-supported with Ni on Al_2O_3 at low loading. Al_2O_3 is kept as the support for its high specific surface area, its dispersing ability, and its low cost, none of which a bulk PrO_x support would match. Pr is added to bring, on this Al_2O_3 support, the benefits identified above: additional basic sites, increased Ni electron density and oxygen-vacancy concentration, improved dispersion and sintering resistance, and better Ni reducibility through partial disruption of the NiAl_2O_4 spinel.

In short, Pr is selected as the dopant for the $\text{Ni}/\text{Al}_2\text{O}_3$ ammonia decomposition catalyst because it combines near-La catalytic performance with a still-open research gap, a cost far below that of Ru, and a coherent set of promotional effects. These effects, which act directly on the rate-limiting steps of the reaction, include electron donation to Ni, enhanced basicity, oxygen-vacancy formation, and improved Ni reducibility.

2.Objectives

This work investigated nickel-based catalysts for the conversion of ammonia into hydrogen at low temperature, together with the role of praseodymium as a promoter. The study was organised around three objectives.

The first objective was to identify the optimal sol-gel synthesis conditions for a Ni/Al₂O₃ catalyst, taking the ammonia conversion measured at 550 °C as the performance benchmark to be maximised.

The second objective was to assess the effect of praseodymium as a dopant on this catalyst, by varying both the Pr loading and the order in which it was introduced during synthesis, to establish whether, and to what extent, its reported promotional effects translated into improved ammonia decomposition.

The third and principal objective was to determine whether Pr improved catalytic performance relative to the corresponding undoped Ni/Al₂O₃ catalyst to an extent significant enough to justify further investigation.

3.Strategy

For this research project, mesoporous alumina was synthesised via a sol-gel process based on a protocol from Chen et al. [41]. Al_2O_3 was synthesised via this process according to varying hydrothermal synthesis and calcination parameters to determine the optimal settings for the ammonia decomposition reaction.

Two Ni addition methods were evaluated. Direct reduction of Ni onto Al_2O_3 , using NaBH_4 as a reducing agent, was compared to the incorporation of Ni into the bulk of Al_2O_3 by simultaneous synthesis.

The potential of Pr as dopant was initially assessed by testing three different ways of including it in the catalyst preparation. In all three cases, Ni or Pr were added by direct reduction, using NaBH_4 . One way was to add Ni onto Al_2O_3 by direct reduction followed by filtering, drying, and grinding before adding Pr onto Ni/ Al_2O_3 in the same way. Another method started by adding Pr onto Al_2O_3 by direct reduction followed by filtering, drying, and grinding before adding Ni onto Pr/ Al_2O_3 in the same way. Lastly, the addition of Ni and Pr simultaneously onto Al_2O_3 was also performed by adding the precursors of both elements onto the support at once before filtering, drying, and grinding.

Further research was done on the best performing Pr-containing catalyst to determine the optimal Pr loading.

For every step of the research, extensive characterisations were performed on fresh and spent catalysts to assess the textural, structural, and chemical properties of each sample, and their influence on the catalytic performance for the ammonia decomposition reaction.

The details of each catalyst preparation, characterisation techniques, and catalytic test parameters are given in the experimental section.

4. Experimental

4.1. Catalyst Preparation

4.1.1. Al_2O_3 Synthesis

In practice, 12.27 g of ethanol (VWR; Purity = 99.95 %) and 12.03 g of isopropanol (TCI; Purity > 99.5 %) were poured into a covered round-bottom flask. The temperature was raised to 50 °C before adding 6.947 g of aluminium isopropoxide (Aldrich; Purity $\geq$ 98 %) followed by 1.2 g of distilled water into the flask.

The solution was stirred at 250 rpm at room temperature for 9h before raising the temperature to 70 °C for an additional 24h under continuous stirring resulting in the formation of a gel. Finally, the gel temperature was raised to 100 °C for 2h before being set from the flask to a stainless-steel PTFE lined autoclave reactor for hydrothermal synthesis. The temperature of the sealed autoclave was raised to 120 °C or 150 °C in an oven for 12h. Catalysts or supports having undergone hydrothermal synthesis at 120 °C had “H120” included in their name. In the case of hydrothermal synthesis at 150 °C, “H150” was included in their name.

The obtained powder was dried overnight at room temperature. The powder was then calcined at 550 °C or 800 °C in a Vecstar furnace for 2h at the target temperature. In the case of calcination at 550 °C, a Programmed Temperature Increase (PTI) of 5 °C/min was performed. Catalysts or supports having undergone calcination at 550 °C had “C550” included in their name.

In the case of hydrothermal synthesis at 800 °C, the temperature was raised without at PTI until reaching the set temperature which was maintained for 2h. “C800” was included in the name of such catalysts.

The resulting powder was grounded with a mortar and pestle before being sieved until the diameter of a grain of catalyst was smaller than 200 μm .

In some cases, it was explicitly mentioned that a certain kind of support was used to make the catalyst, however, “H120” and “C800” were not specified in the name of the final catalyst.

4.1.2. Ni/Al₂O₃ Simultaneous Synthesis

In this case, the active site Ni was included into the bulk and “Sim” was added at the end of the catalyst’s name to indicate this.

In practise, 12.27 g of ethanol (VWR; Purity = 99.95 %) and 12.03 g of isopropanol (TCI; Purity > 99.5 %) were poured into a covered round-bottom flask. The temperature was raised to 50 °C before adding 6.95 g of aluminium isopropoxide (Aldrich; Purity >= 98 %) into the flask.

In a separate beaker, 2.45 g of nickel nitrate hexahydrate (Roth; Purity > 99 %) was added to 1.2 g of distilled water. The solution was stirred until full dissolution of the compound. The Ni-containing solution was then added into the flask containing the Al precursor.

The solution in the flask was stirred at room temperature for 9h before raising the temperature to 70 °C for an additional 24h under continuous stirring resulting in the formation of a gel. Finally, the gel temperature was raised to 100 °C for 2h before being set from the flask to a stainless-steel PTFE lined autoclave reactor for hydrothermal synthesis. The temperature of the sealed autoclave was raised to 120 °C or 150 °C in an oven for 12h.

The obtained powder was dried overnight at room temperature. The powder was then calcined at 550 °C or 800 °C in a Vecstar furnace for 2h at the target temperature. In the case of calcination at 550 °C, a Programmed Temperature Increase (PTI) of 5 °C/min was performed. Catalysts having undergone calcination at 550 °C had “C550” included in their name.

In the case of hydrothermal synthesis at 800 °C, the temperature was raised without PTI until reaching the set temperature which was maintained for 2h. “C800” was included in the name of such catalysts.

The resulting powder was grounded with a mortar and pestle before being sieved until the diameter of a grain of catalyst was smaller than 200 µm.

4.1.3. Pr Direct Reduction

Praseodymium nitrate pentahydrate (Acros Organics; Purity = 99.90 %) was set in a 200 mL beaker containing 50 mL of distilled water under continuous stirring at room temperature. After 15 minutes of stirring, once the compound was fully dissolved, 0.5 g of alumina synthesised using the Al₂O₃ synthesis protocol was added to the beaker.

Sodium borohydride (Sigma-Aldrich) (NaBH_4) was set in another beaker containing 50 mL of distilled water for 2 minutes continuous stirring at room temperature. The solution must be prepared just before use because sodium borohydride degrades rapidly. The NaBH_4 solution was added dropwise to the alumina-containing solution to promote the direct reduction of Pr onto the alumina support.

The loading of Pr on Al_2O_3 or $\text{Ni}/\text{Al}_2\text{O}_3$ was always expressed in weight fraction of Pr relative to the mass of Al_2O_3 according to the following formula:

$$\frac{m_{Pr}}{m_{Pr} + m_{\text{Al}_2\text{O}_3}} * 100 = x [\%]$$

The details of each required mass value for different Pr loadings were expressed in Table 1.

NaBH_4 was added to be in a large excess to make sure that all Pr elements are firmly on the support and do not leach during the filtration step. The required number of moles of NaBH_4 was determined as a multiple of the number of moles n of Pr in the solution according to the following ratio:

$$\frac{n_{\text{NaBH}_4}}{n_{Pr}} = 15 \left[\frac{\text{mol}_{\text{NaBH}_4}}{\text{mol}_{Pr}} \right]$$

3 sealed 50 mL containers were filled with distilled water are heated to 100 °C in an oven. After 1h of stirring the mixture at room temperature, a vacuum filtration system was set up on a Büchner using an Isopore 0.2 µm PC membrane (hydrophilic). Once the solution had gone through the filter and only the cake remained, one 50 mL container of water was added. This step was repeated 3 times with breaking of the cake after each time water was added. The cake was then set in a beaker and dried at 120 °C in an oven overnight.

The resulting powder was grounded with a mortar and pestle before being sieved until the diameter of a grain of catalyst was smaller than 200 µm.

Table 1: Masses for direct reduction of Pr

Catalyst	Mass of support [mg]	Mass of $\text{Pr}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ [mg]	Mass of NaBH_4 [mg]
5%Pr20%Ni/ Al_2O_3	400	46.75	63.6
1%Pr/ Al_2O_3	500	14.94	20.3
3%Pr/ Al_2O_3	500	45.76	62.2
5%Pr/ Al_2O_3	500	77.87	105.9
7%Pr/ Al_2O_3	500	111.4	150.1

4.1.4. Ni Direct Reduction

Nickel chloride (Alfa Aesar; Purity > 98%) was set in a 200 mL beaker containing 50 mL of distilled water under continuous stirring at room temperature. After 15 minutes of stirring, once the compound was fully dissolved, alumina synthesised using the Al₂O₃ synthesis protocol was added to the beaker.

The loading of Ni on Pr/Al₂O₃ or Al₂O₃ was always expressed in weight fraction of Ni relative to the mass of Al₂O₃ according to the following formula:

$$\frac{m_{Ni}}{m_{Ni} + m_{Al_2O_3}} * 100 = x [\%]$$

The details of each required mass value were expressed in Table 2. The Pr content of the support was excluded from the denominator so that the Ni loading remains independent of the Pr loading. Had Pr been included, reaching the same nominal value would have required a higher Ni mass, making the catalyst no longer comparable to the corresponding Ni/Al₂O₃ reference.

Sodium borohydride (Sigma-Aldrich) (NaBH₄) was set in another beaker containing 50 mL of distilled water for 2 minutes continuous stirring at room temperature. The solution must be prepared just before use because sodium borohydride degrades rapidly. The NaBH₄ solution was added dropwise to the alumina-containing solution to promote the direct reduction of Ni onto the alumina support.

NaBH₄ was added to be in a large excess to make sure that all Ni elements are firmly on the support and do not leach during the filtering step. The required number of moles of NaBH₄ was determined as a multiple of the number of moles n of Ni in the solution according to the following ratio:

$$\frac{n_{NaBH_4}}{n_{Ni}} = 15 \left[\frac{mol_{NaBH_4}}{mol_{Ni}} \right]$$

3 sealed 50 mL containers were filled with distilled water are heated to 100 °C in an oven. After 1h of stirring the mixture at room temperature, a vacuum filtration system was set up on a Büchner using an Isopore 0.2 µm PC membrane (hydrophilic). Once the solution had gone through the filter and only the cake remained, one 50 mL container of water was added. This step was repeated 3 times with breaking of the cake after each time water was added. The cake was then set in a beaker and dried at 120 °C in an oven overnight.

The resulting powder was grounded with a mortar and pestle before being sieved until the diameter of a grain of catalyst was smaller than 200 μm .

Table 2: Masses for Ni direct reduction

Catalyst	Mass of support [mg]	Mass of NiCl_2 [mg]	Mass of NaBH_4 [mg]
20%Ni/ Al_2O_3	500	276.0	1209
20%Ni1%Pr/ Al_2O_3 Final	440	240.4	1052
20%Ni3%Pr/ Al_2O_3 Final	430	230.3	1008
20%Ni5%Pr/ Al_2O_3 Final	430	225.5	987
20%Ni7%Pr/ Al_2O_3 Final	450	231.0	1011

Masses for the simultaneous addition of Ni and Pr onto Al_2O_3 are: 276.0 mg (NiCl_2), 77.9 mg ($\text{Pr}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), 500.0 mg (Al_2O_3), 1314.0 mg (NaBH_4). This catalyst was named 5%Pr20%Ni Sim/ Al_2O_3 .

4.2. Characterisation Techniques

4.2.1. N_2 Physisorption

N_2 physisorption is a characterisation technique that provides information on the textural properties of catalysts, mainly specific surface area, pore volume, and average pore size ^[51].

Brunauer, Emmet and Teller have developed a method named BET ^[51]. It is an equation for the determination of the specific surface area of a solid based on non-specific physisorption of a gas onto a solid at a temperature nearing the condensation point of the adsorbing gas.

The Barrett, Joyner, and Halenda (BJH) method provides an estimate of the pore size distribution and pore volume ^[51].

N_2 physisorption of powders was performed on a TriStar 3000 surface area and porosity analyser from Micromeritics. One physisorption round could characterise 3 sample tubes at a once.

About 60 mg of powder was weighed then introduced into a physisorption tube. The tube and its cap were weighed before and after adding the sample. The sample was then degassed at 150°C for 6 h (time to reach a pressure of 50 to 100 mTorr) using a Vacprep 061 degasser from Micromeritics. The tube containing the sample was weighed after degassing to know the mass of the degassed sample. An isothermal jacket was added to the tube before being set in a liquid N_2 bath to reach -196 °C within the TriStar 3000 analyser.

The quantity of adsorbed N₂ (cm³ g⁻¹ STP) was measured stepwise over for relative pressures ranging from 0.01 to 0.99 p/p^o with a volumetric analyser, yielding the full adsorption and desorption branches.

The BJH method was applied to adsorption branch for relative pressures ranging from 0.42 to 0.98 P/P₀ to obtain pore size and pore diameter values. The adsorption branch was used because several samples exhibited hysteresis loops closing close to the nitrogen cavitation floor (~0.42 p/p^o), so the desorption branch would have been distorted by pore-blocking and cavitation-induced evaporation through narrow necks (ink-bottle behaviour), yielding artefactually small apparent pore sizes.

4.2.2. X-Ray Diffraction (XRD)

XRD is a characterisation technique used to determine the crystalline phase of solids such as heterogeneous catalysts. This technique relies on the constructive interferences between incident x-rays and x-rays reflected on various crystalline layers within the sample.

The diffractograms appear as counts relative to a 2θ angle. Elements and molecules, if present in a crystalline form, appear on the diffractogram as peaks at specific 2θ angles. The diffraction peaks were indexed by comparison with reference patterns, using the expected elemental composition of the sample to restrict the candidate crystalline phases.

To perform XRD, a polished Si single crystal sample holder was covered with a thin layer of petrolatum cream (Vaseline®) as a fixing agent. The sample was then added onto this layer of fixing agent before being placed in a Bruker D8 Advance diffractometer (Bragg-Brentano geometry) to record XRD patterns. The XRD diffractograms were the result of the Kα emission line of Cu as the x-ray source (λ = 0.15418 nm) operated at 1200 W (30 mA, 40 kV) and a Lynxeye XE-T Bruker detector. The operating parameters were a 2θ range of 5°-80° with a step size of 0.01488° (2θ) and steps lasting 0.15 seconds each.

The crystallite sizes were determined thanks to the Scherrer equation:

$$Crystallite\ size = \frac{K * \lambda}{FWMH * \cos(\theta)} [nm]$$

K as the Scherrer constant (0.94 for spherical crystals in cubic symmetry), λ (nm) as the wavelength of the x-ray source, θ (°) as the peak diffraction angle, and FWHM (rad) as the full width at mid height of the peak. The 44.5° peak was used to determine the Ni crystallite size of spent catalysts.

4.2.3. H₂ Pulsed Chemisorption

The dispersion of the metallic Ni on a catalyst was determined by comparing the total number of Ni atoms in the sample to the number of accessible metallic Ni atoms on the surface, based on the amount of H₂ that was chemisorbed onto the surface.

Ni dispersion on the Al₂O₃ or Pr/Al₂O₃ supports was measured by H₂ chemisorption in a Microtrac BELCAT II catalyst analyser. To do so, around 30 mg of catalyst was reduced for 3h under 5% H₂/Ar (Air Liquide; Purity > 99.999 %) at 550°C before cooling and flushing under a He flux.

The measurements of H₂ chemisorption on Ni were performed by pulse injection at 35 °C under 2.5% H₂/Ar. Known volumes of H₂ go over the sample at each pulse injection. The excess hydrogen was measured by a TCD detector, and the volume difference was calculated to determine the volume of H₂ which was chemisorbed onto Ni.

The following equation was used to determine the Ni dispersion:

$$Dispersion [\%] = \frac{V_{adsorbed\ H_2} * 2 * M_{Ni}}{22.4 * m_{catalyst} * loading} * 100 \left[\frac{L_{H_2} * \frac{mol_{H_2}}{mol_{Ni}} * \frac{g_{Ni}}{mol_{Ni}}}{\frac{L}{mol} * g_{catalyst} * \frac{g_{Ni}}{g_{catalyst}}} * \% \right]$$

4.2.4. H₂ Temperature-Programmed Reduction (H₂-TPR)

The reduction temperature of a catalyst was determined by measuring the amount of H₂ that was consumed to reduce it at gradually increasing temperatures.

H₂-TPR was performed in a Microtrac BELCAT II catalyst analyser. To do so, around 30 mg of catalyst was reduced under 5% H₂/Ar at temperatures that gradually rose from 100 °C up to 800 °C before cooling down.

Known volumes of H₂ go over the sample at each temperature setpoint. The excess hydrogen was measured by a TCD detector, and the volume difference was calculated to determine the volume of H₂ which was consumed to reduce the catalyst.

4.2.5. X-ray Photoelectron Spectroscopy (XPS)

XPS allows for quantification of the elemental composition of solid samples at the surface layer, over a depth of around 10 nm. It also detects characteristic shifts in the binding energy of core-level photoelectrons, the chemical shifts, that reflect the local bonding environment of each atom. Thanks to that information, XPS provides information on the chemical environment and oxidative state of elements near the surface. The binding energy of an electron is specific to each orbital within a single element.

XPS is based on the interaction between a photon and a core electron at the surface of a material resulting in the release of the photoelectron at a given kinetic energy. The binding energy E_b can be determined as the difference between the energy of the source $h\nu$, with h as the Planck constant and ν as the frequency of the monochromatic x-ray source, and the kinetic energy of the released photoelectron E_k .

$$E_b = h\nu - E_k$$

Measurements were taken using an SSX 100/206 spectrometer (Surface Science Instruments) with a monochromatic Al K α micro-focused source. The analysis chamber maintained a pressure of approximately 10^{-6} Pa, with a 55° analysis angle and 150 eV pass energy. Data was processed via CasaXPS and calibrated using the adventitious C 1s at 284.8 eV.

Each photoelectron peak was linked to a binding energy corresponding to the specific core orbital of an element. The elemental composition of the surface layer of each sample was quantified from the integrated area of each element-specific peak, after Shirley background subtraction, with the peak areas normalised by their respective relative sensitivity factors.

This was done for all detected elements at the surface on the sample, including the signals corresponding to the presence of adventitious CO₂ at the surface. The C 1s region was deconvoluted into its hydrocarbon and carbonate components, and the carbon counts attributable to these contamination peaks. The atomic concentration of each element was then corrected by subtracting the adventitious CO₂ from the total to recover a composition representative of the catalyst surface alone.

Where relevant, elemental content ratios were computed for Pr/Al, Ni/Al, and Pr/Ni were used in preference to absolute atomic percentages to cancel systematic artefacts. It provided a more reliable cross-sample comparison than the individual atomic percentages would.

4.2.6. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

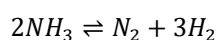
ICP-OES, which reaches a limit of detection (LOD) in the order of the ppb, is based on the ionisation of samples in a plasma of Ar at temperatures ranging from 6000 to 10 000 °C ^[50]. As the samples return from the excited state to the ground state, energy is released in the form of photons. Each element releases photons of a specific wavelength. The spectrometer coupled to the ICP separates the different wavelengths. Once calibrations curves have been established using a standard for each of the targeted elements, photons of a specific wavelength can be measured to quantify the concentration of a given element in the sample.

An ICP-OES Perkin Elmer, Avio 220 Perkin Elmer S23 Auto-Sampler was used to perform analyses on solid samples to determine the elemental concentrations of Pr, Ni, and Al in the bulk.

To perform this analysis, the samples were previously dissolved by a strong acid solvent ^[50]. Indeed, each solid catalyst sample weighing around 0.011 g was digested in 3 mL of HCl/HNO₃ 3/1 for 1h before raising the volume to 50 mL with a HNO₃ solution at 2% concentration.

4.3. Catalytic Tests

A catalyst sample was introduced into a gas phase continuous fixed bed reactor where NH₃ underwent thermocatalytic cracking into H₂ and N₂.



To perform catalytic tests, quartz wool was inserted into a fixed bed reactor tube before the addition of 40 mg of catalyst (Diameter < 200 µm), previously mixed with 250 mg of quartz beads (Diameter = 200 – 500 µm). The quartz beads increased the gas flow uniformity and the dispersion of the catalyst in the reactor. A metallic ring was placed between the reactor tube and a thermocouple to hermetically seal the reactor. This sealed reactor tube was then set in a Micromeritics FR 100 flow reactor connected to a Scion instruments 8500 GC Gas Chromatograph (GC).

The GC contained two separate columns (Hayesep Q, 80/100 Mesh, inert steel from Scion, carrier gas: He) which both ended with a TCD-DEFC-14 detector. Column 1 separated NH₃ from the gas mixture. Column 2 was a combination of two columns in series. The first one was identical to the Column 1 and separated slow molecules from the gaseous mixture to protect the second one. The second column in the Column 2 system (Molsieve 5A, 60/80 mesh, inert

steel column from Scion, carrier gas: Ar) separated fast molecules such as H₂ and N₂. A backflush of the first column took place 6 minutes after each injection.

For this project, a H₂ reduction pre-treatment was performed before initiating catalytic reactions following a stepwise temperature ramp. More specifically, the temperature was raised to 550 °C under a 30 mL/min H₂ (Air Liquide; Purity > 99.999 %) flow for 2h. The H₂ flow was then stopped and a 50 mL/min N₂ flow was initiated to cool the reactor down to 25 °C. As the 5% NH₃/Ar (Air Liquide; Purity > 99.999 %) flow was initiated, the GC was activated on Analyzer Both Channels mode to prepare the device for the detection of NH₃ and H₂. The GC analysis was launched after the 5% NH₃/Ar flow had been stable at 80 mL/min for 2 minutes.

The reactor followed a stepwise temperature ramp starting at 25 °C to get a baseline NH₃ signal when none is reacted. After that, the temperature was raised straight to 300 °C and reached up to 550 °C by 50 °C increments. The GHSV was set at 6000 mL_{NH3}/g_{catalyst}*min. At temperatures in the 25-350 °C range, 5 GC injections took place at each setpoint; whilst at temperatures in the 400 °C and above range, 9 GC injections took place at each setpoint.

The GC analysis method consisted of 6 minutes of injection time performed repeatedly during each temperature setpoint. The injections stopped during each increase in temperature before stabilising at the new temperature setpoint.

In the case of stability tests of catalytic performance. The reactor operated at 550 °C for 3 days to assess the long run performance of the catalyst. GC injections of 6 minutes were performed at 1h intervals.

Based on the GC data, the average integrated area under a NH₃ signal at 25 °C for the gas exiting the reactor was compared to that value for a given higher temperature to determine the NH₃ conversion yield.

$$NH_{3\text{conversion}} = \frac{Area_{NH_3}(25\text{ }^{\circ}C) - Area_{NH_3}(T^{\circ})}{Area_{NH_3}(25\text{ }^{\circ}C)} * 100 [\%]$$

5. Results and discussion

5.1. Support Synthesis Optimisation

5.1.1. Results

5.1.1.1. N₂ Physisorption

Nitrogen physisorption was carried out on all Al₂O₃ supports and 20%Ni/Al₂O₃ catalysts to determine their specific surface area, pore volume, and pore diameter. The complete dataset is presented in Table 3, followed by a systematic analysis of the effects of hydrothermal temperature, calcination temperature, and Ni deposition.

Table 3: Specific surface area, pore volume, and pore diameter of Al₂O₃ and Ni/Al₂O₃ with different synthesis parameters.

Catalyst	Specific surface area [m ² /g]	Pore volume [cm ³ /g]	Pore width [nm]
Al ₂ O ₃ – H120	490	1.29	9.5
Al ₂ O ₃ – H120 – C550	400	1.68	15.1
Al ₂ O ₃ – H120 – C800	230	1.20	18.4
Al ₂ O ₃ – H150	550	1.96	12.1
Al ₂ O ₃ – H150 – C550	390	1.90	17.6
20%Ni/Al ₂ O ₃ – H120	220	0.12	4.8
20%Ni/Al ₂ O ₃ – H120 – C550	350	0.70	11.6
20%Ni/Al ₂ O ₃ – H120 – C800	140	0.38	13.4
20%Ni/Al ₂ O ₃ – H150 – C550	300	0.63	11.7
20%Ni/Al ₂ O ₃ – H150 – C800	210	0.57	14.0

A pore size diameter of 2 nm to 20 nm is described as mesoporous. A pore size diameter greater than 20 nm is described as macroporous.

Effect of Calcination on Al₂O₃ Textural Properties

Non-calcined supports consistently exhibited higher specific surface areas than their calcined counterparts, reflecting the densification that accompanies thermal treatment. For hydrothermal synthesis at 120 °C:

- Calcination at 550 °C reduced the specific surface area by 18 % while increasing the pore diameter by 59 % and the pore volume by 30 %.
- Calcination at 800 °C reduced the specific surface area by 53 %, increased the pore diameter by 94 %, and slightly decreased the pore volume by 7 %.

For hydrothermal synthesis at 150 °C, calcination at 550 °C led to a 29 % decrease in specific surface area and a 45 % increase in pore diameter, while the pore volume remained

approximately constant at $\sim 1.9 \text{ cm}^3/\text{g}$. Across both synthesis temperatures, calcination at 550°C consistently produced higher specific surface areas and pore volumes than calcination at 800°C — by a factor of 43–150 % and correspondingly larger pore volumes — though the average pore diameter was systematically $\sim 18\%$ larger after 800°C calcination.

Effect of Ni Deposition on Textural Properties

Direct reduction of Ni onto Al_2O_3 substantially modified the textural properties of all supports. The nature and magnitude of the modifications in textural properties due to direct reduction of Ni varied with the synthesis parameters of the Al_2O_3 support. The Ni loading (20 wt%) inherently reduces the specific surface area by a dilution effect ($\sim 20\%$), but the total drops observed significantly exceeded this contribution, indicating that pore blocking was the dominant mechanism.

For uncalcined $\text{Al}_2\text{O}_3\text{-H120}$, Ni deposition caused a 55 % decrease in specific surface area, reduced the pore volume by about a factor 10, and halved the pore diameter. For calcined supports synthesised at 120°C , the losses were less severe: the sample calcined at 550°C lost 13 % of specific surface area, while the sample calcined at 800°C lost 39 %. In both cases, pore volume decreased by about a factor 3 and pore diameter decreased by $\sim 25\%$. For the 150°C series, the calcined sample (C550) lost 23 % of specific surface area, 67 % of pore volume, and 34 % of pore diameter.

A notable reordering occurred after Ni deposition: the uncalcined Al_2O_3 , which initially exhibited the highest specific surface area, fell to the lowest value after Ni direct reduction. This behaviour is attributed to the metastable nature of pseudoboehmite, whose fragile platelet structure is vulnerable to the strongly alkaline, H_2 -evolving, and exothermic conditions generated during NaBH_4 reduction.

Isotherm Analysis and Pore Structure

Uncalcined supports (and Ni catalysts derived from them) exhibited Type II adsorption isotherms, and calcined supports (and their Ni-loaded counterparts) exhibited Type IV(a), all accompanied by H3-type hysteresis loops, the signature of mesoporous adsorbents whose porosity arises from interparticle voids between non-rigid plate-like aggregates^[56]. Hysteresis loops were confined to high relative pressures with no saturation plateau, indicating that the porosity extended continuously into the large mesopore–macropore boundary range without a defined upper opening width.

Al₂O₃ supports (H120 series — Figures 6 and 8)

The adsorption and desorption branches were consistent with slit-like pores interparticle voids between plate-like crystallites ^[51]. For the uncalcined sample, the gradual, stepless rise of the adsorption branch and the H3-type hysteresis are both characteristic of this geometry, with no capillary condensation step expected. The calcined samples showed a more clearly defined high-pressure rise. The isotherm shape moved toward Type IV(a) with a partial H1 character in the loop body sitting on the persistent H3 saturation tail, consistent with a narrower distribution of wider interparticle openings. The series differed in the width and uniformity of the interparticle openings:

- Uncalcined Al₂O₃ (pseudoboehmite): hysteresis closure at $p/p^\circ \approx 0.5$, with a broad distribution of slit-like pores between packed needle- and plate-like crystallites, lean H3 character with a broad pore size distribution.
- C550 Al₂O₃: transition from pseudoboehmite to Al₂O₃, by calcination-induced dehydration, widened and somewhat better defined the interparticle openings. The H3 hysteresis shifted to higher relative pressures (closure near $p/p^\circ \approx 0.7$) and the high-pressure rise became more pronounced, reflecting a more uniform distribution of wider slit/wedge widths inherited topotactically from the parent boehmite platelets.
- C800 Al₂O₃: sintering and coalescence further widened and shifted the hysteresis loop to higher relative pressures, with a narrowing (though still non-uniform) pore size distribution and the clearest Type IV character of the series, reflecting a coarsening of plate-like aggregates.

Al₂O₃ supports (H150 series — Figures 10-12)

Samples synthesised at 150 °C exhibited larger pore volumes and wider interparticle openings than their 120 °C counterparts while behaving similarly at low relative pressures. This is consistent with a coarsening of pseudoboehmite into larger platelets and wider interparticle voids ^[51]. The uncalcined sample gave a Type II-shaped adsorption isotherm and the calcined samples a Type IV(a)-shaped one, both with H3 hysteresis loops closing in the $p/p^\circ \approx 0.6$ – 0.7 range. The closure pressure sat well above the nitrogen cavitation floor at $p/p^\circ \approx 0.42$, below which the trapped meniscus is mechanically unstable and evaporates by spontaneous cavitation regardless of pore geometry. Because the closure pressure was higher than this threshold, the desorption was governed by Kelvin-equilibrium evaporation through real, accessible openings rather than by cavitation through narrow (<4–5 nm) constrictions, with no significant bottleneck population ^[56].

20%Ni/Al₂O₃ catalysts (Figures 7, 8, 9, 11 and 13)

Calcined supports (C550, C800) retained their Type IV(a) + H3 character after Ni deposition. Their remaining mesopores were essentially unchanged in character, suggesting that Ni settled preferentially into the interplatelet slit-like gaps without fundamentally altering pore geometry. The uncalcined support underwent a more dramatic transformation. Its isotherm flattened into a plateau from $p/p^\circ \approx 0.1$ to 0.9, sliding into the featureless Type II profile of low-porosity solids. The desorption branch dropped steeply at $p/p^\circ \approx 0.42$ — precisely the cavitation floor imposed by the physical instability of the nitrogen meniscus — indicating the formation of ink-bottle pores whose necks (~ 4.8 nm) trap condensates until spontaneous cavitation^[56]. This textural collapse is attributed to the combined chemical attack (strongly alkaline medium) and mechanical disruption (vigorous H₂ evolution) during NaBH₄ reduction acting on the fragile pseudoboehmite framework.

Taken together, the N₂ physisorption results demonstrate that (i) calcination stabilises the Al₂O₃ texture against the harsh conditions of direct Ni reduction, and (ii) the Ni-bearing phase deposited by NaBH₄ direct reduction partially offset the specific surface area loss caused by its occupation of the support's interparticle voids, by contributing its own accessible surface from the deposited nanoparticles themselves.

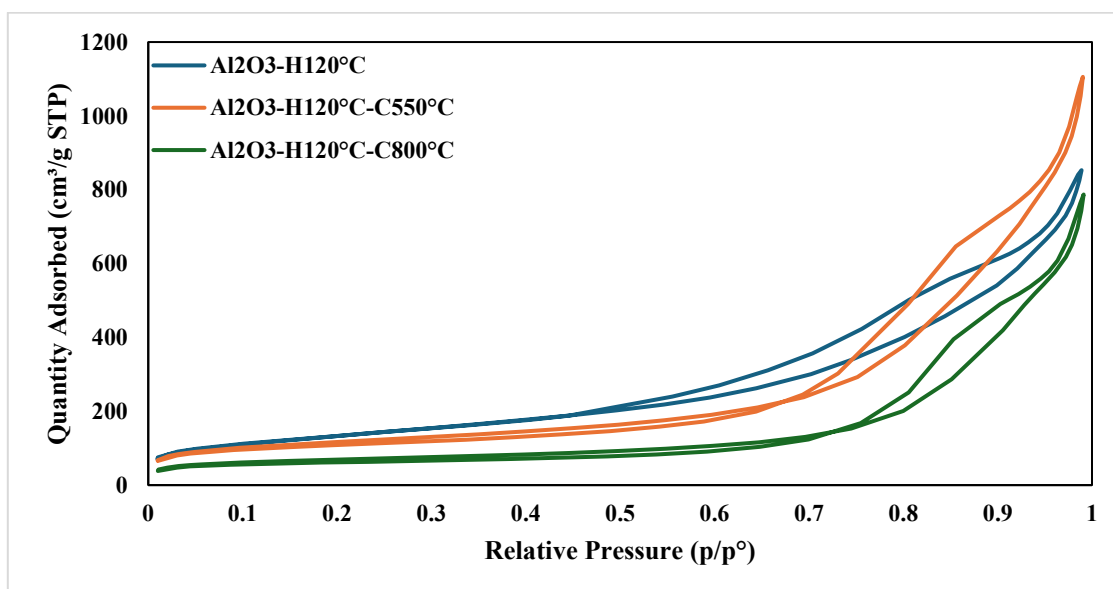


Figure 6: N₂ adsorption–desorption isotherms of Al₂O₃ synthesised by hydrothermal treatment at 120 °C (uncalcined, C550, C800).

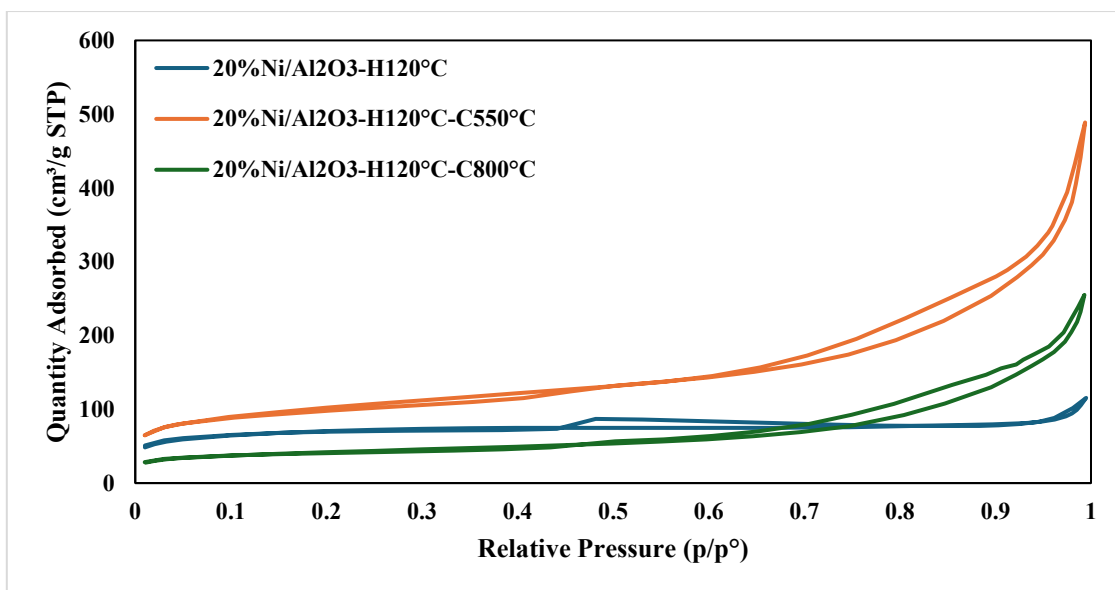


Figure 7: N_2 adsorption-desorption isotherms of 20%Ni/ Al_2O_3 catalysts based on H120 supports (uncalcined, C550, C800).

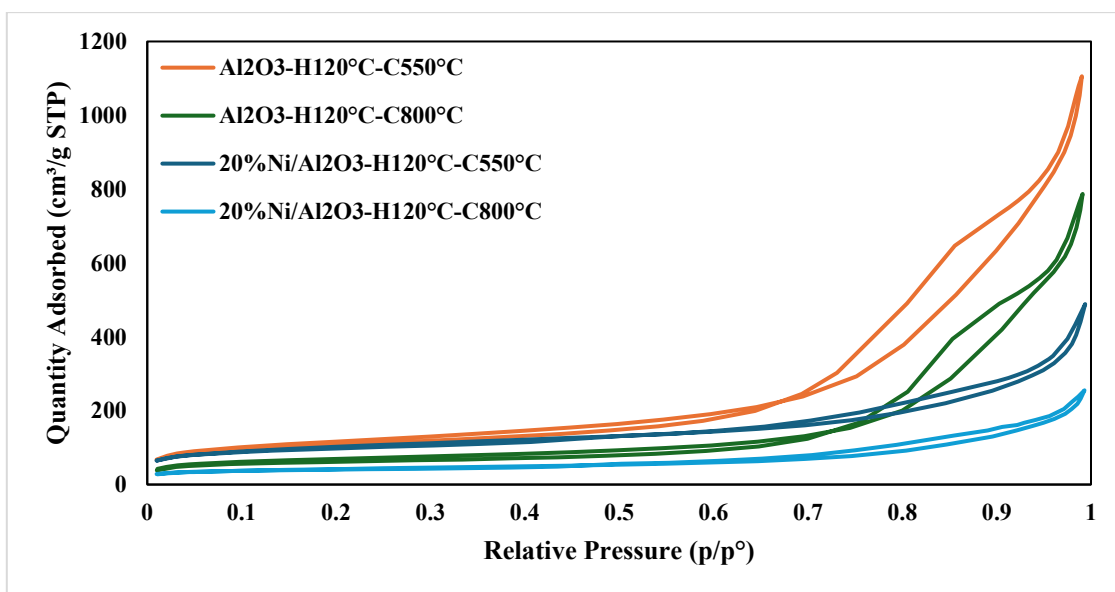


Figure 8: Comparative N_2 physisorption isotherms: Al_2O_3 -H120 vs. 20%Ni/ Al_2O_3 -H120.

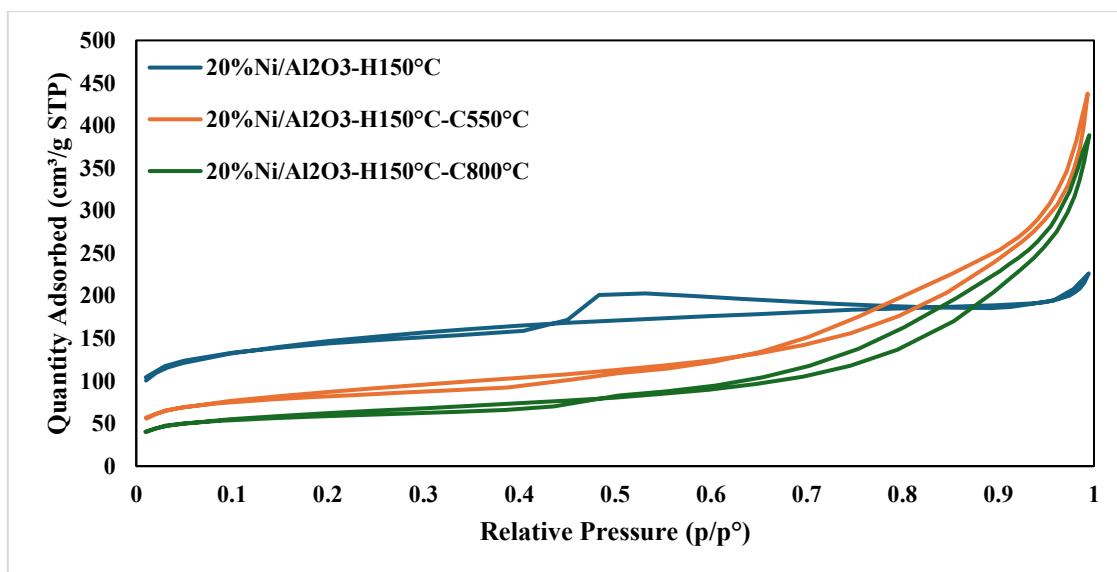


Figure 9: Comparative N_2 physisorption isotherms: 20%Ni/ Al_2O_3 -H150 series.

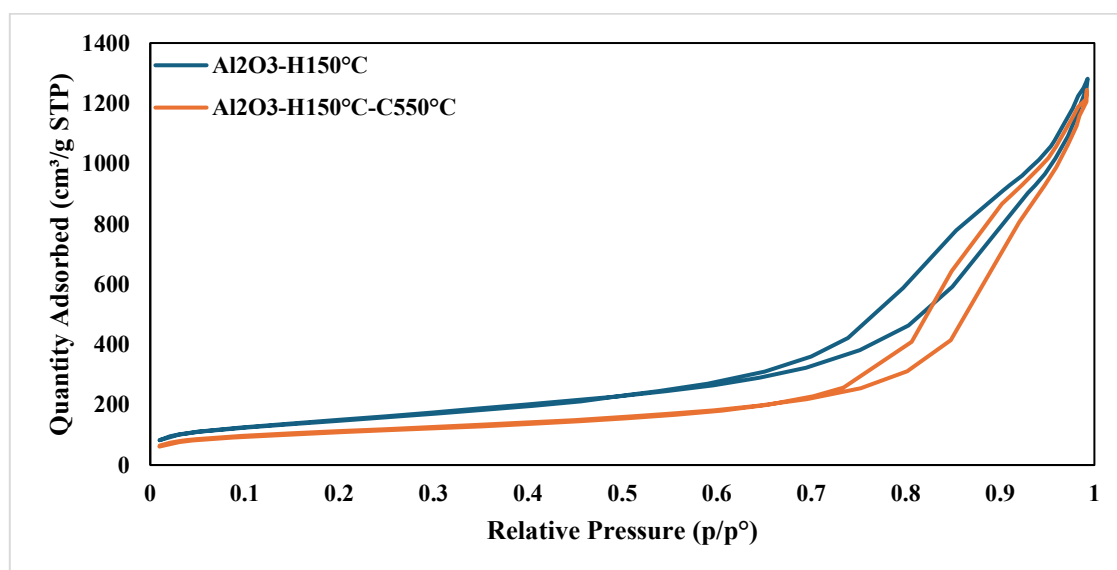


Figure 10: Comparative N_2 physisorption isotherms: Al_2O_3 -H150 series.

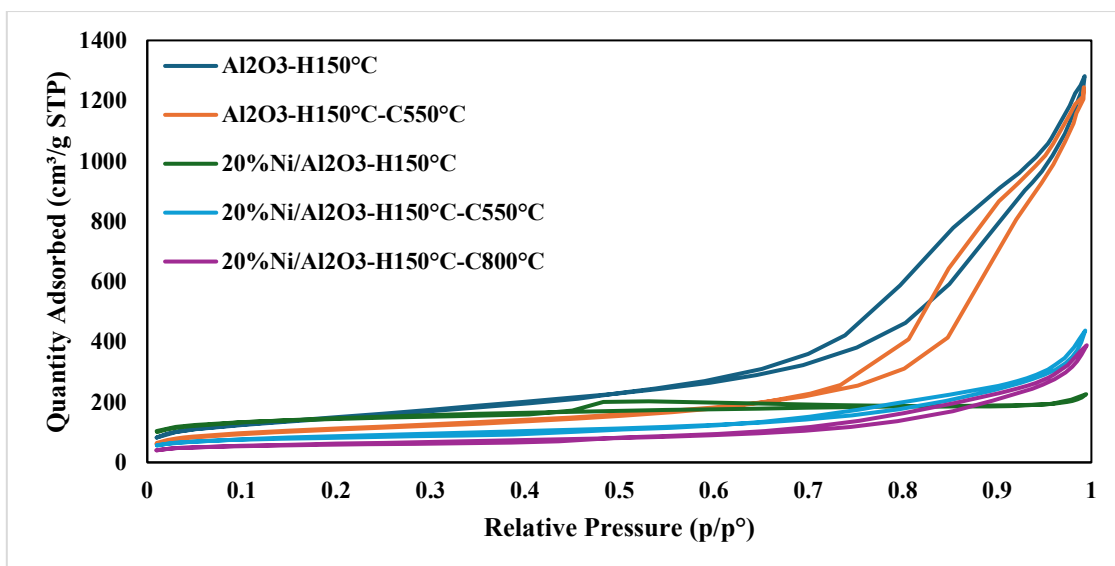


Figure 11: Comparative N_2 physisorption isotherms: Al_2O_3 -H150 vs. 20%Ni/ Al_2O_3 -H150.

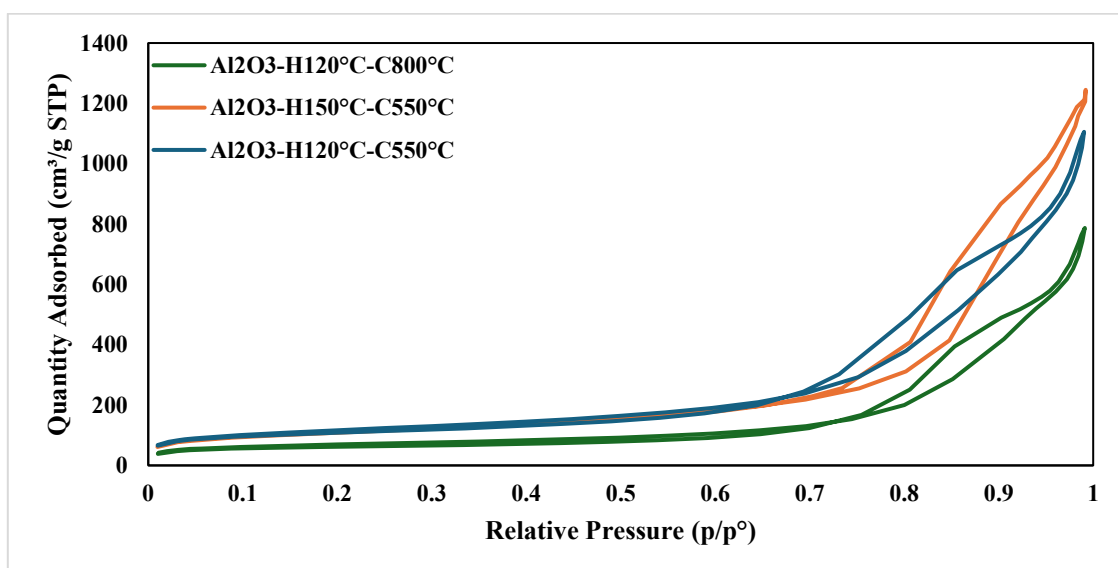


Figure 12: Comparative N_2 physisorption isotherms: H120 vs. H150 Al_2O_3 .

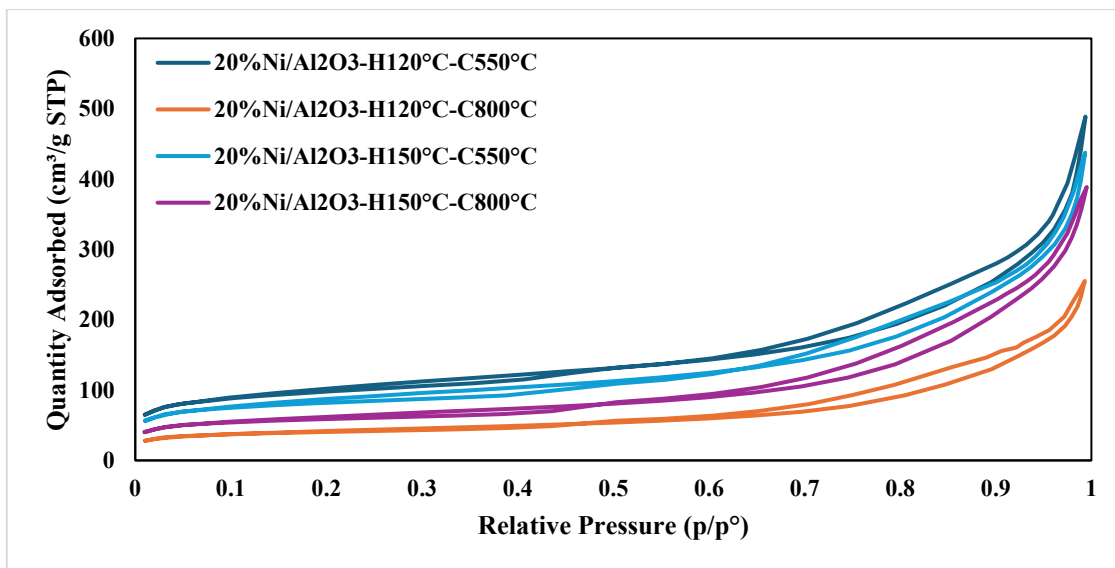


Figure 13: Comparative N_2 physisorption isotherms: H120 vs. H150 Ni/Al₂O₃.

5.1.1.2. XRD

XRD characterisation was performed on fresh and spent Al₂O₃ supports and 20%Ni/Al₂O₃ catalysts. The analysis focused on phase identification of the alumina support across synthesis conditions and on tracking Ni crystallite growth during catalytic testing.

Phase Identification of Al₂O₃

Uncalcined Al₂O₃ (both H120 and H150 series) presented XRD peaks consistent with pseudoboehmite (AlOOH), confirming the identity of the as-synthesised precursor (Figure 14).

Upon calcination:

- Calcination at 550 °C converted pseudoboehmite to γ -Al₂O₃, identified by its characteristic two-peak pattern (Figures 15 and 16).
- Calcination at 800 °C produced δ -Al₂O₃, recognisable by the splitting of the two γ -Al₂O₃ peaks into four peaks (Figures 15 and 16). This phase transformation is consistent with the literature: Al₂O₃ fully transitions from γ to δ at ~ 800 °C, remaining in this phase up to ~ 950 °C.

An unidentified peak at $2\theta \approx 41^\circ$ was observed in the H120 series and could not be assigned to any known phase; further investigation is warranted.

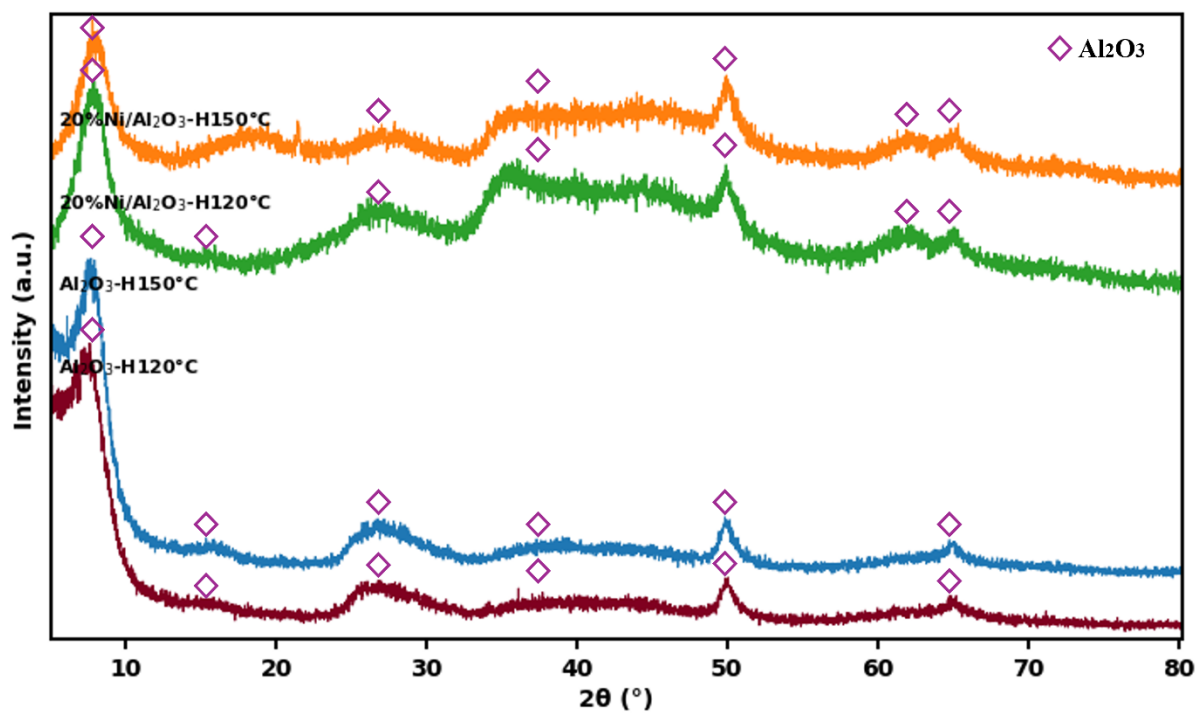


Figure 14: XRD diffractograms of uncalcined Al₂O₃ and 20%Ni/Al₂O₃ showing pseudoboehmite peaks.

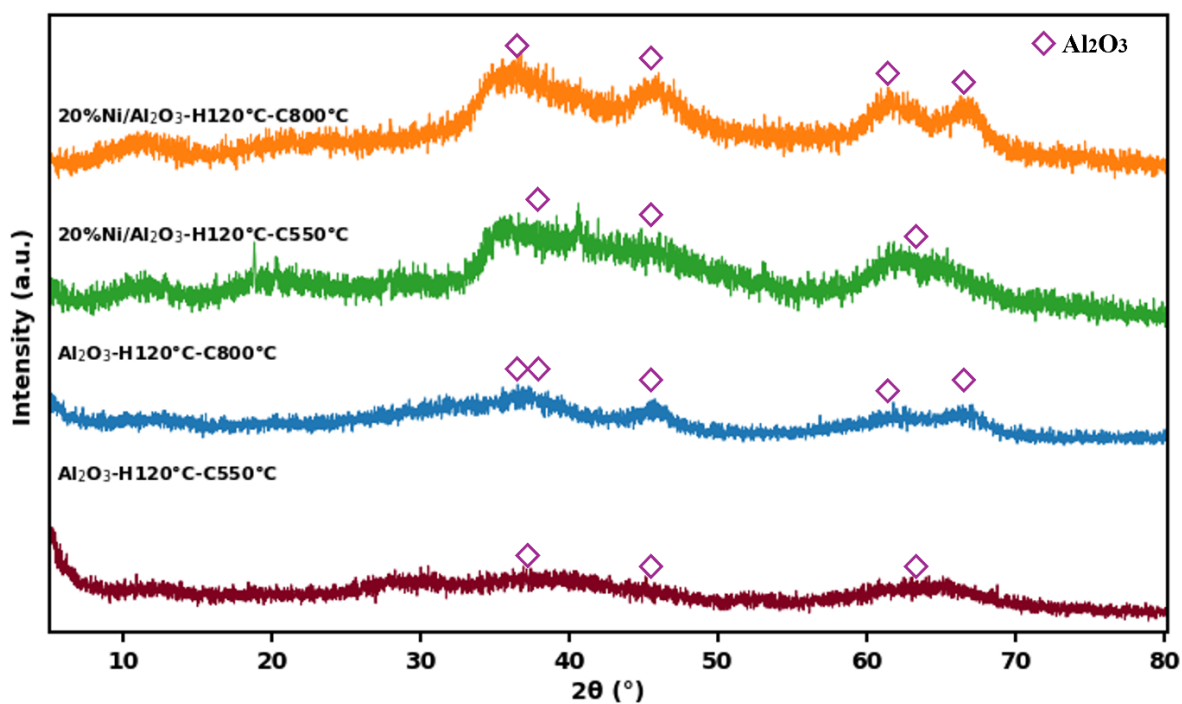


Figure 15: XRD diffractograms of Al₂O₃-H120 and 20%Ni/Al₂O₃-H120 (uncalcined, C550 γ-Al₂O₃, C800 δ-Al₂O₃).

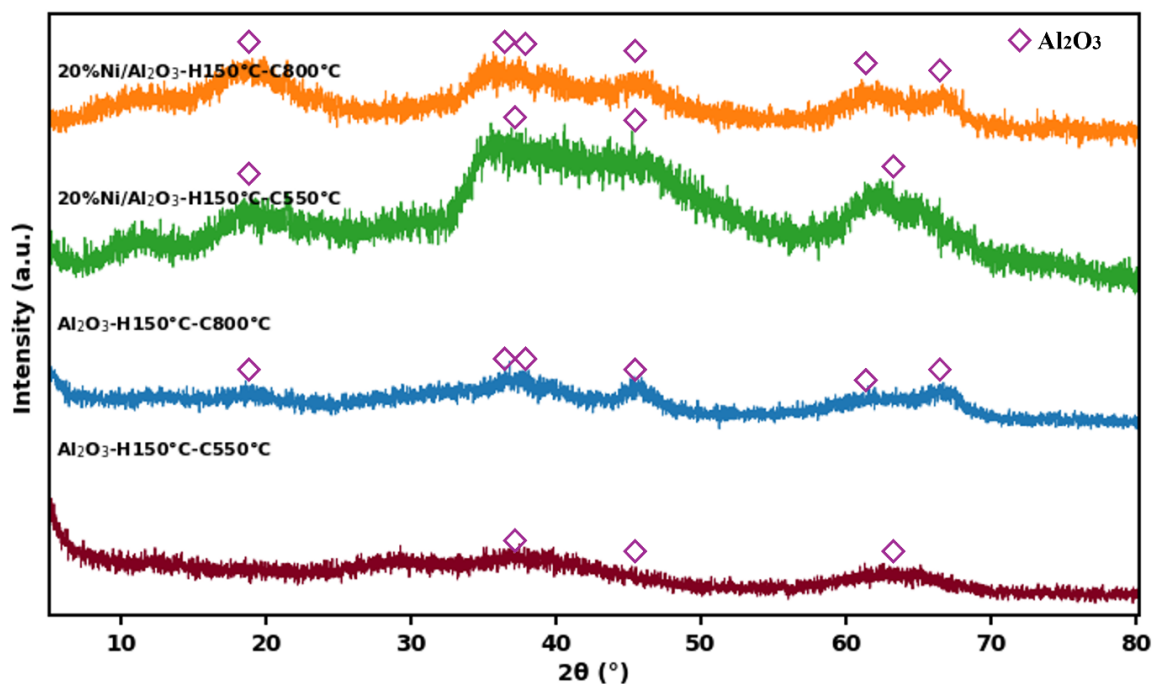


Figure 16: XRD diffractograms of Al_2O_3 -H150 and 20%Ni/ Al_2O_3 -H150 (uncalcined, C550 γ - Al_2O_3 , C800 δ - Al_2O_3).

Ni Phase in Fresh and Spent Catalysts

No Ni diffraction peaks were observed in fresh 20%Ni/ Al_2O_3 catalysts, implying that Ni was either amorphous or dispersed as crystallites below the XRD detection limit (~ 3 nm) (Figures 17 and 18). Ni^0 and NiO peaks emerged in spent catalyst diffractograms, confirming the presence of metallic Ni at the catalyst surface — consistent with the significant enhancement in NH_3 conversion over bare Al_2O_3 .

SiO_2 peaks were systematically detected in all spent catalyst diffractograms. This contamination is associated with the silica wool present in the reactor and warrants attention in future experimental design.

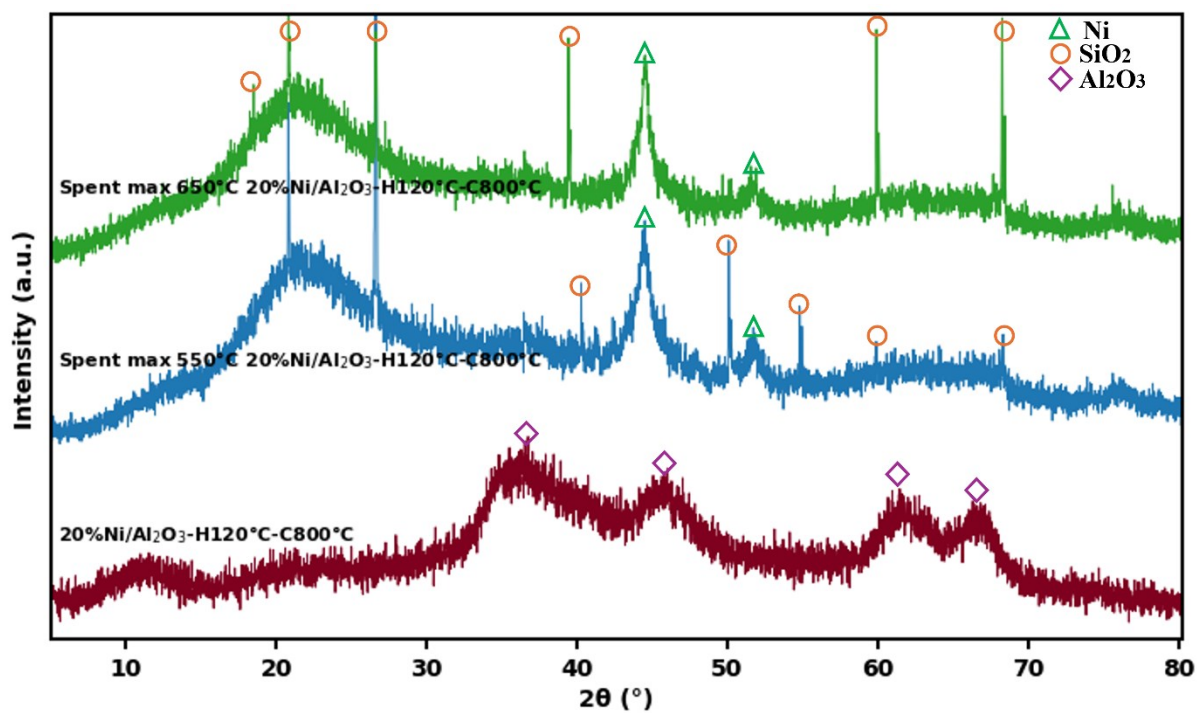


Figure 17: XRD diffractograms of fresh and spent 20%Ni/Al₂O₃-H120-C800 showing sharper Ni peaks for the 650 °C cycle.

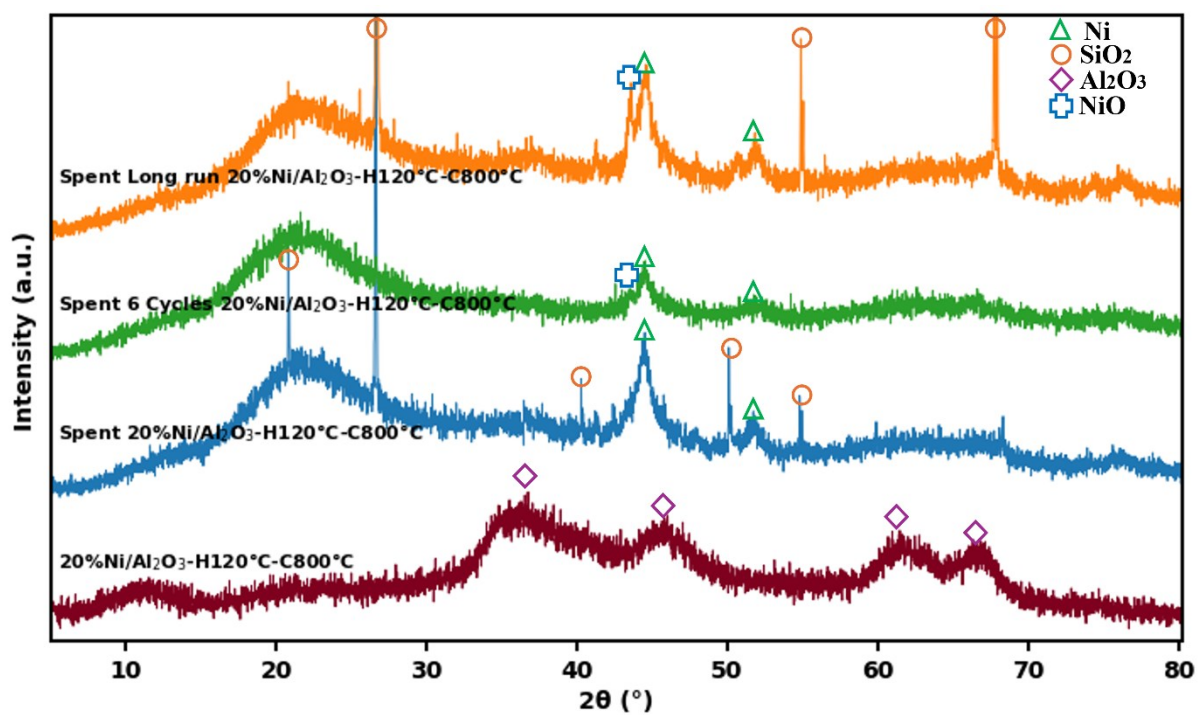


Figure 18: XRD diffractograms of spent 20%Ni/Al₂O₃-H120-C800 under different cycling conditions, showing the NiO peak in the 6-cycle and long-run samples.

Ni Crystallite Size and Sintering Behaviour

Ni crystallite sizes were determined by the Scherrer equation from spent catalyst diffractograms. The complete dataset is presented in Table 4.

Table 4: Ni crystallite size of spent catalysts at 650 °C and 550 °C

Catalyst / Condition	Ni Crystallite Size [nm]
<i>Spent 650 20%Ni/Al₂O₃ – H120</i>	23
<i>Spent 650 20%Ni/Al₂O₃ – H120 – C550</i>	19
<i>Spent 650 20%Ni/Al₂O₃ – H120 – C800</i>	15
<i>Spent 650 20%Ni/Al₂O₃ – H150</i>	24
<i>Spent 650 20%Ni/Al₂O₃ – H150 – C550</i>	24
<i>Spent 650 20%Ni/Al₂O₃ – H150 – C800</i>	23
<i>Spent 550 20%Ni/Al₂O₃ – H120</i>	18
<i>Spent 550 20%Ni/Al₂O₃ – H120 – C550</i>	14
<i>Spent 550 20%Ni/Al₂O₃ – H120 – C800</i>	14
<i>Spent long run 20%Ni/Al₂O₃ – H120 – C800</i>	14
<i>Spent 6 cycles 20%Ni/Al₂O₃ – H120 – C800</i>	18

Several key trends emerge from Table 4:

1. Effect of reaction temperature: operating at 650 °C versus 550 °C increased Ni crystallite size by 7–36 % across the catalyst series, with the H120-C800 sample showing the greatest resistance to sintering (smallest absolute crystallite size and lowest relative increase).
2. Effect of support phase: δ -Al₂O₃ (C800) consistently yielded the smallest Ni crystallite sizes after reaction at both temperatures, suggesting superior stabilisation of Ni dispersion relative to γ -Al₂O₃ (C550) and uncalcined pseudoboehmite, particularly at 650 °C.
3. Long run stability: a 62-h continuous run at 550 °C produced an identical crystallite size (14 nm) to a single 22 h temperature-ramped cycle (300–550 °C), indicating that cumulative thermal exposure did not accelerate sintering under these conditions.
4. Multi-cycle behaviour: performing 6 successive 22 h cycles on the same catalyst sample increased the crystallite size by 29 % (14 → 18 nm), reflecting gradual but limited sintering between each thermal cycle (exposure to oxidative conditions during shutdown/restart).

5.1.1.3. Catalytic Tests

Screening of Catalyst Variants

All 20%Ni/Al₂O₃ variants significantly outperformed the blank (Al₂O₃ alone) in NH₃ decomposition across the tested temperature range (Figure 19). The largest performance spread among catalyst variants was observed at 450 °C, where NH₃ conversion ranged from 29 % (20%Ni/Al₂O₃-H150-C550) to 37 % (20%Ni/Al₂O₃-H120-C800). At 550 °C, 20%Ni/Al₂O₃-H120-C800 reached a conversion of 96 %, marginally outperforming its peers, though the difference between all variants at this temperature approached the confidence interval of 0.5%.

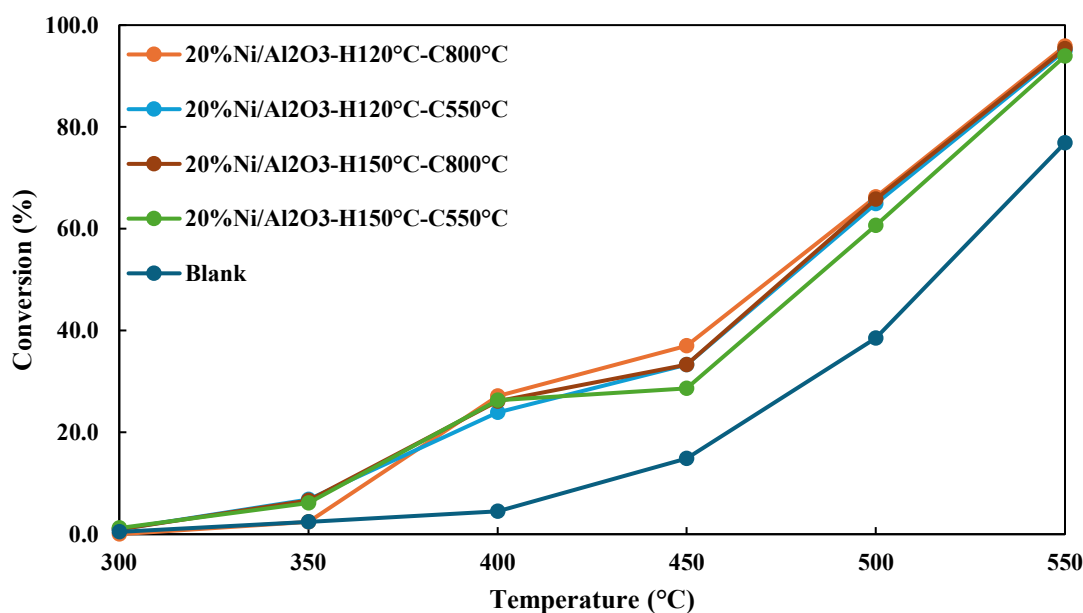


Figure 19: Catalytic tests with 20%Ni/Al₂O₃

Stability and Reusability of 20%Ni/Al₂O₃-H120-C800

The 20%Ni/Al₂O₃-H120-C800 catalyst was selected for extended stability testing based on its superior performance at 650 °C and the smallest post-reaction Ni crystallite size, both indicative of good thermal stability.

Multi-cycle testing (6 × 22 h cycles): NH₃ conversion at 550 °C was 97 % during the first two cycles and 96.5 % at the sixth cycle, representing a cumulative degradation of 0.5 % (Figure 20). The gradual decline is consistent with the progressive Ni sintering observed in the XRD data (Table 4), though the magnitude remains modest.

Long run (62 h at 550 °C): conversion remained stable at ~96.5 % throughout the test, and the post-reaction Ni crystallite size was identical to that of a single-cycle experiment (Figure 21). These results confirm that continuous operation at 550 °C is thermally less demanding than

repeated thermal cycling and that the catalyst possesses good intrinsic stability under steady-state conditions.

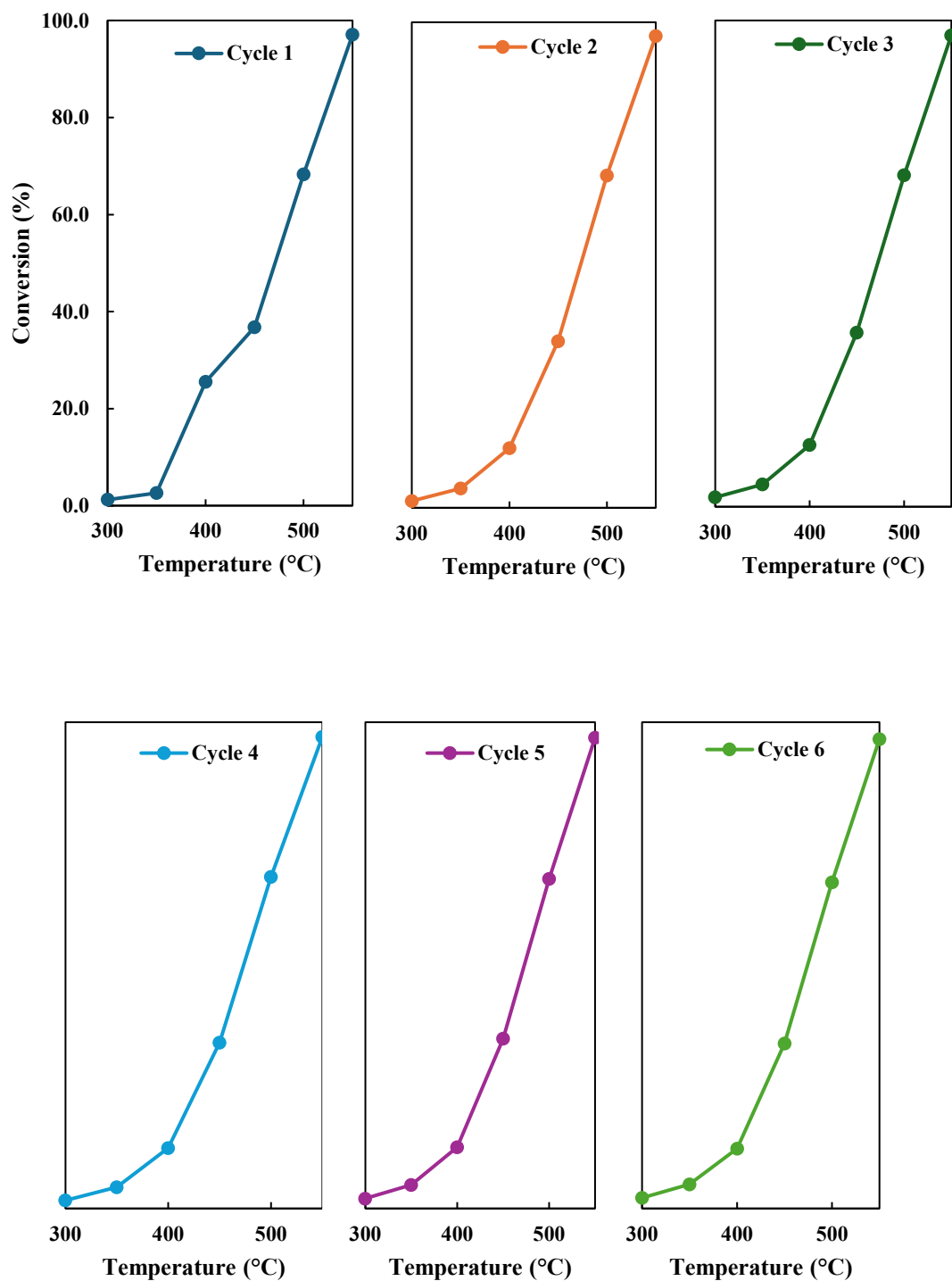


Figure 20: Catalytic tests with 20%Ni/Al₂O₃-H120°C-C800°C (6 successive cycles).

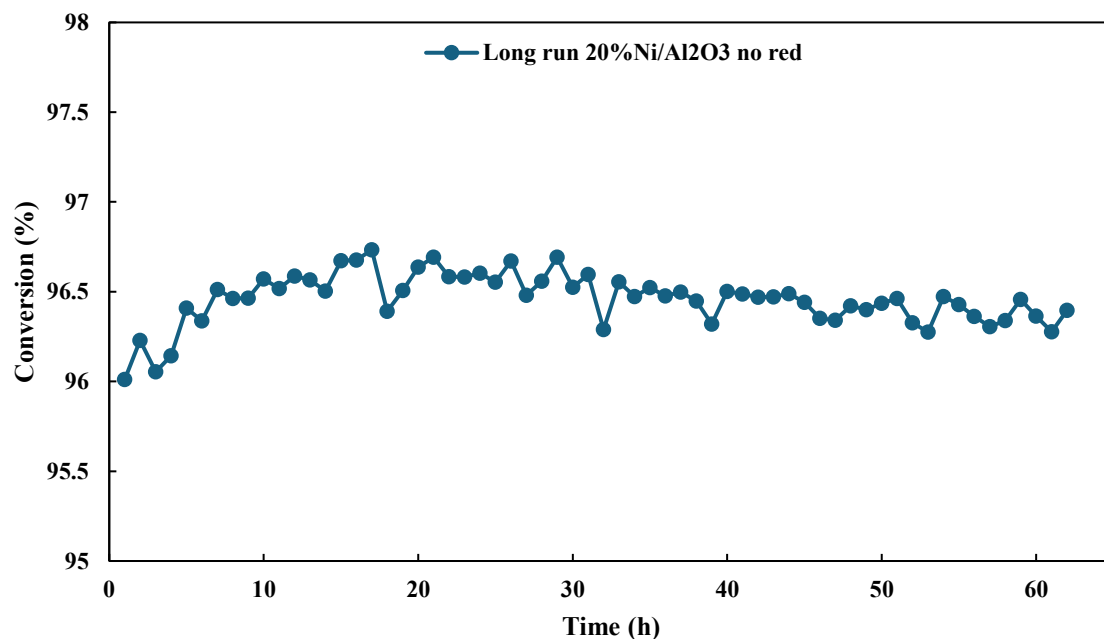


Figure 21: Catalytic test with 20%Ni/Al₂O₃-H120°C-C800°C (long run at 550 °C).

5.1.2. Discussion

Structural Evolution of the Al₂O₃ Support

Hydrothermal synthesis at both 120 and 150 °C produces pseudoboehmite as needle-like or platelet crystallites. Calcination at 550 °C transforms this precursor to γ -Al₂O₃, while calcination at 800 °C drives a complete phase transition to δ -Al₂O₃ — evidenced by the characteristic peak-splitting in XRD diffractograms. The progressive sintering that accompanies higher calcination temperatures contracts the specific surface area while widening the average pore diameter, reflecting a coarsening of the platelet aggregates into a more open architecture. This textural evolution is captured in the isotherm data by the gradual shift in the hysteresis loops to higher relative pressures and the decreased quantity of adsorbed N₂ in the BET region.

Interaction of Ni with the Al₂O₃ Pore Network

Ni deposition via NaBH₄ reduction invariably reduced textural properties across all supports. Beyond the simple dilution effect (~20 % from the Ni mass fraction), pore blocking by Ni particles and, in the case of uncalcined supports, a textural collapse of the pseudoboehmite framework were the primary contributors to specific surface area loss.

Calcined supports (γ - and δ -Al₂O₃) withstood the process conditions with comparatively minor textural damage: Ni settled into interplatelet gaps, preserving the slit-like mesopore character. The uncalcined pseudoboehmite, in contrast, was irreversibly transformed: its fragile platelet

stacking was disrupted by the alkaline medium and vigorous H₂ evolution, converting open slit pores to ink-bottle geometry. This finding underscores the critical importance of thermal pre-treatment before Ni deposition.

Ni Dispersion, Crystallite Stability, and Catalyst Selection

The absence of Ni peaks in fresh catalyst XRD patterns confirms that as-deposited Ni is either amorphous or finely dispersed below the detection limit. Formation of crystalline Ni⁰ and NiO occurs only upon reaction, with crystallite sizes increasing with temperature and cycle number. δ -Al₂O₃ (C800 support) demonstrated superior Ni stabilisation, particularly at 650 °C, producing the smallest post-reaction crystallite sizes. The mechanistic basis likely involves a stronger Ni- δ -Al₂O₃ interaction and a more rigid pore architecture that restricts Ni particle migration. At 550 °C, the advantage of δ -Al₂O₃ over γ -Al₂O₃ was negligible, suggesting that the stability criterion becomes decisive only at elevated temperatures.

Based on these results, 20%Ni/Al₂O₃-H120-C800 was selected as the reference catalyst for further investigation. Its advantages — highest NH₃ conversion at 550 °C, best resistance to crystallite growth, and stable performance over both long runs and multiple cycles — collectively justify this choice. The 0.5 % decline of performance over 6 cycles, while measurable, is acceptable for practical application, and continuous operation at 550 °C is preferred over repeated thermal cycling to minimise sintering.

5.2. Direct Reduction vs. Simultaneous Synthesis of 20%Ni/Al₂O₃

5.2.1. Results

Two distinct routes were investigated for introducing Ni into the Al₂O₃ support: (i) direct reduction of a Ni precursor onto pre-formed δ -Al₂O₃ using NaBH₄, and (ii) simultaneous synthesis, in which the Ni precursor is incorporated during the hydrothermal Al₂O₃ synthesis, followed by calcination at 800 °C. In both cases the Al₂O₃ support was prepared by hydrothermal treatment at 120 °C and calcined at 800 °C (H120-C800). The objective was to determine whether the structural integration of Ni into the support bulk (20%Ni/Al₂O₃-H120-C800 Sim) confers any advantage over surface deposition in terms of textural properties, Ni reducibility, dispersion, resistance to sintering, and ultimately catalytic performance.

5.2.1.1. N₂ Physisorption

Table 5 compares the textural properties of the bare δ -Al₂O₃ support with the two catalyst variants. Both synthesis routes produce mesoporous materials (average pore diameter 2–20 nm).

Table 5: Specific surface area, pore volume, and pore diameter of directly reduced and simultaneously synthesised catalysts.

Catalyst	Specific surface area [m ² /g]	Pore volume [cm ³ /g]	Pore width [nm]
Al ₂ O ₃ – H120 – C800	230	1.20	18.4
20%Ni/Al ₂ O ₃ – H120 – C800	140	0.38	13.4
20%Ni/Al ₂ O ₃ – H120 – C800 Sim	220	0.67	10.3

Simultaneous Synthesis

The simultaneously synthesised catalyst retained a specific surface area essentially identical to that of the bare Al₂O₃ support (220 vs. 230 m²/g, –4 %). This is expected: the synthesis steps are identical, with the sole addition of a Ni precursor to the hydrothermal solution. However, the inclusion of Ni into the forming pore network reduced both pore volume and pore diameter by approximately half compared to bare Al₂O₃.

Direct Reduction

Direct reduction led to a more substantial loss of surface area (-39% vs. bare Al_2O_3) and pore volume (-68%), though the average pore diameter remained larger (13.4 nm) than for the simultaneously synthesised catalyst (10.3 nm, -30%). This combination — larger but fewer and less voluminous pores — is consistent with surface pore blocking by deposited Ni particles rather than in-wall confinement.

Isotherm Comparison

Figure 22 confirms these trends at the isotherm level. All three samples exhibited Type IV(a) isotherms with hysteresis loops closing in the $0.6\text{--}0.75$ p/p° range and no saturation plateau, indicative of open mesopores spilling into the macropore boundary.

At low relative pressures ($p/p^\circ < 0.6$, including the BET region), the bare Al_2O_3 and the simultaneously synthesised catalyst produced nearly superimposed isotherms, confirming their near-identical specific surface areas. Above $p/p^\circ \approx 0.6$, the Al_2O_3 isotherm rose above the Sim variant in the capillary condensation region, reflecting the reduction in pore volume caused by the embedded Ni particles. The earlier hysteresis closure of Ni/ Al_2O_3 Sim ($p/p^\circ \approx 0.60$ vs. 0.75 for bare Al_2O_3) indicates that Ni incorporation introduced a population of narrower interparticle openings, likely smaller residual gaps around the embedded Ni particles, whereas the bare support retained a coarser interparticle geometry.

The directly reduced catalyst showed uniformly lower uptake across the entire isotherm relative to both other samples, consistent with the more severe loss of specific surface area and pore volume from surface pore blocking.

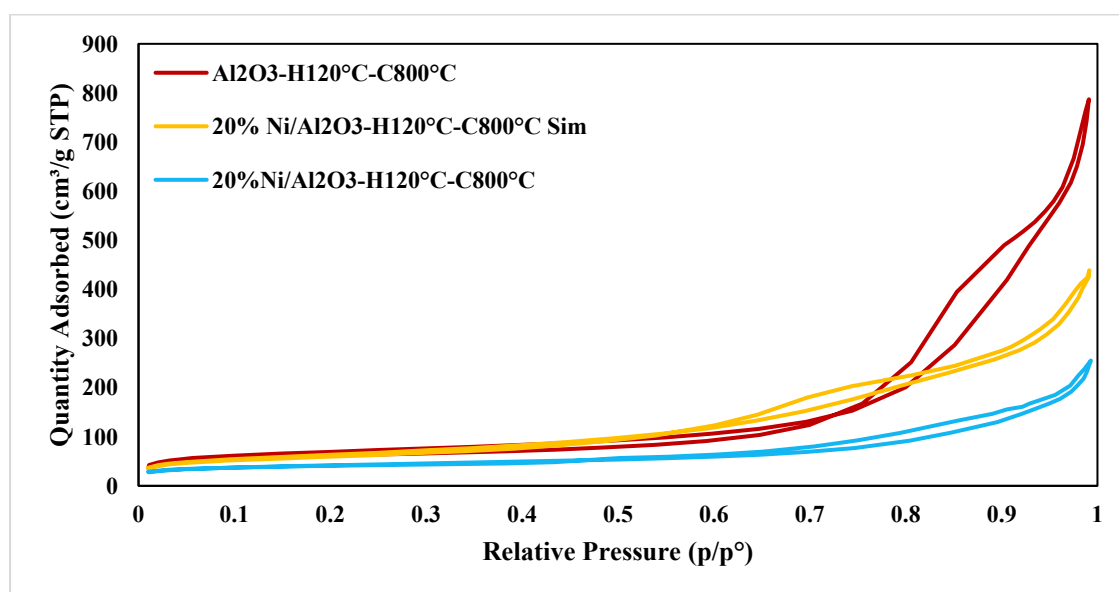


Figure 22: Isotherms of directly reduced and simultaneously synthesised catalysts.

5.2.1.2. XRD

Phase Identification

Both catalyst variants displayed the characteristic peaks of δ - Al_2O_3 inherited from the C800 calcination step (Figures 23 and 24). The key structural difference between the two routes lies in the Ni-containing phase:

- Direct reduction (20%Ni/ Al_2O_3 -H120-C800): no crystalline Ni peaks in the fresh catalyst, consistent with an amorphous or highly dispersed Ni phase. Ni^0 peaks emerged after reaction cycles.
- Simultaneous synthesis (20%Ni/ Al_2O_3 -H120-C800 Sim): multiple peaks corresponding to NiAl_2O_4 spinel were identified in both fresh and spent catalysts, confirming that calcination at 800 °C drove the incorporation of Ni into the Al_2O_3 lattice to form a thermally stable mixed oxide.

SiO_2 contamination peaks due to silica wool were again present in most spent catalysts, consistent with observations from Section 1.

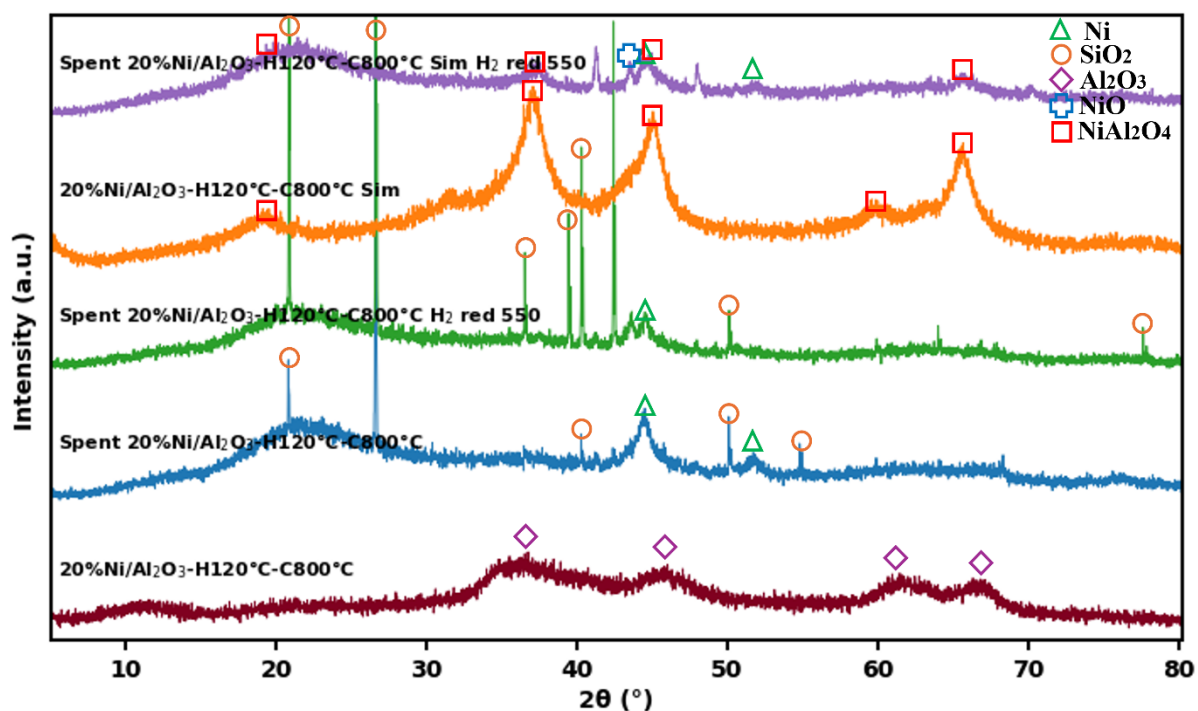


Figure 23: XRD diffractograms of fresh and spent directly reduced and simultaneously synthesised catalysts.

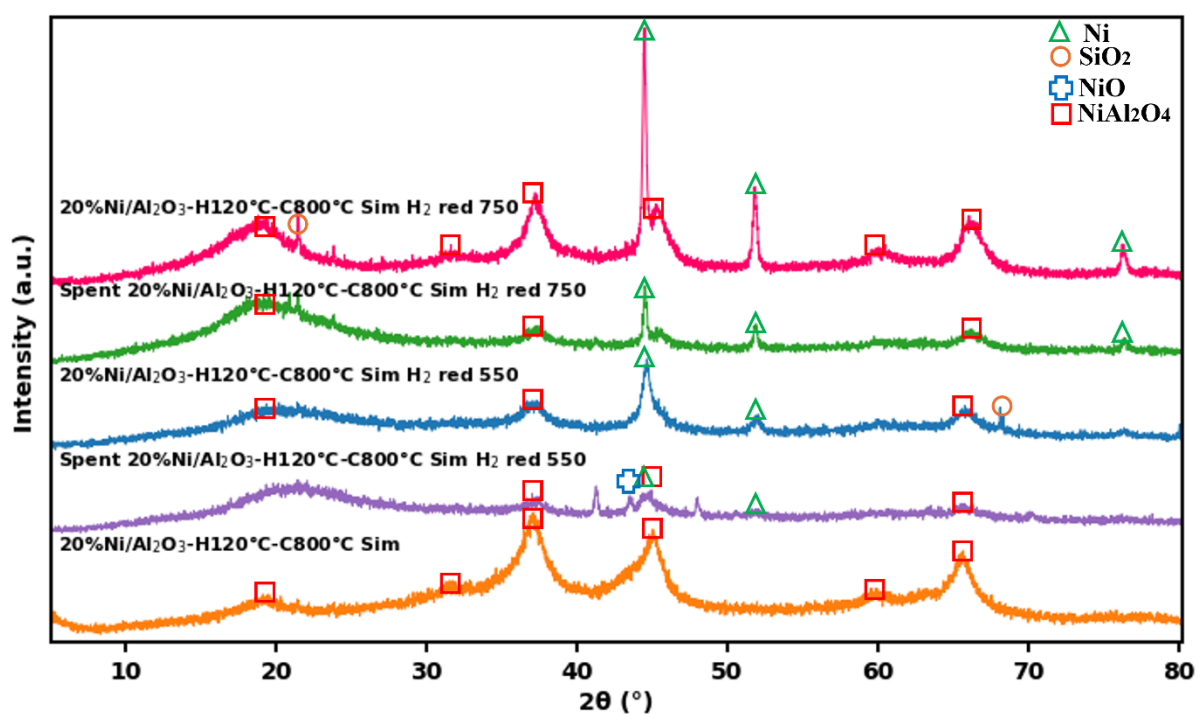


Figure 24: XRD diffractograms of fresh and spent (550 and 750 °C) simultaneously synthesised catalysts.

Ni Crystallite Growth

Table 6 summarises the Ni crystallite sizes at successive stages of preparation and reaction. Three key findings emerge:

Table 6: Ni crystallite size of spent directly reduced and simultaneously synthesised catalysts.

Catalyst / Condition	Ni Crystallite Size [nm]
<i>Spent 20%Ni/Al₂O₃ – H120 – C800</i>	14
<i>Spent 20%Ni/Al₂O₃ – H120 – C800 H₂ red 550</i>	23 ± 2
<i>20%Ni/Al₂O₃ – H120 – C800 Sim H₂ red 550</i>	15
<i>Spent 20%Ni/Al₂O₃ – H120 – C800 Sim H₂ red 550</i>	24
<i>20%Ni/Al₂O₃ – H120 – C800 Sim H₂ red 750</i>	34
<i>Spent 20%Ni/Al₂O₃ – H120 – C800 Sim H₂ red 750</i>	32

1. H₂ pre-reduction penalty (direct reduction): the 20%Ni/Al₂O₃-H120-C800 catalyst that underwent a H₂ reduction pre-treatment at 550 °C prior to catalytic testing developed Ni crystallites of 23 ± 2 nm after the reaction cycle — i.e. a 64 % increase relative to the same catalyst used without pre-treatment (14 nm). This strongly suggests that H₂ pre-reduction caused premature Ni sintering before the catalytic reaction even began.

2. Simultaneous synthesis — mild pre-reduction (550 °C): H₂ pre-treatment at 550 °C partially reduced NiAl₂O₄, yielding 15 nm Ni crystallites before reaction. After one catalytic cycle, crystallites grew to 24 nm (+60 %), matching the post-reaction size of directly reduced catalysts.
3. Simultaneous synthesis — aggressive pre-reduction (750 °C): forcing reduction at 750 °C produced crystallites of 34 nm before any catalytic test. The post-reaction size (32 nm) was slightly smaller, within experimental uncertainty, suggesting that sintering was essentially complete during the pre-treatment step and no further significant coarsening occurred during the reaction.

5.2.1.3. H₂ Chemisorption

Ni Dispersion

H₂ chemisorption after H₂ pre-reduction at 550 °C was used to quantify accessible Ni surface sites. The results are presented in Table 7.

Table 7: Ni dispersion of directly reduced and simultaneously synthesised catalysts.

Catalyst	Ni dispersion [%]
20%Ni/Al₂O₃ – H120 – C800	1.5
20%Ni/Al₂O₃ – H120 – C800 New	1.3
20%Ni/Al₂O₃ – H120 – C800 Sim	0

The directly reduced catalyst showed a consistent Ni dispersion of 1.3–1.5 % across two independently synthesised Al₂O₃-H120-C800 batches, confirming the reproducibility of the synthesis protocol. Although modest in absolute terms, this measurable dispersion confirms the availability of surface Ni⁰ sites after mild H₂ pre-reduction.

In strong contrast, the simultaneously synthesised catalyst showed zero detectable Ni dispersion after the same 550 °C H₂ pre-treatment. This finding is decisive: H₂ pre-reduction at 550 °C is insufficient to reduce NiAl₂O₄ spinel to metallic Ni, leaving no accessible active sites for NH₃ decomposition.

H₂ Temperature-Programmed Reduction (H₂-TPR)

The H₂-TPR profiles (Figure 25) corroborate the chemisorption results by revealing the reduction temperature windows of both catalysts:

- 20%Ni/Al₂O₃-H120-C800 (direct reduction): reduction began at 300–400 °C and was nearly complete by 800 °C. This low onset temperature is characteristic of surface amorphous NiO or Ni species with weak-to-moderate metal–support interaction.
- 20%Ni/Al₂O₃-H120-C800 Sim (simultaneous synthesis): reduction was delayed to 600–700 °C, and the catalyst required temperatures well above 800 °C for complete reduction. This high-temperature requirement is typical of NiAl₂O₄ spinel, where strong Ni-O-Al covalent bonding inhibits H₂ access. At 750 °C — the highest pre-reduction temperature tested — the spinel was only partially reduced, and the resulting Ni crystallites (34 nm) already exhibited severe sintering.

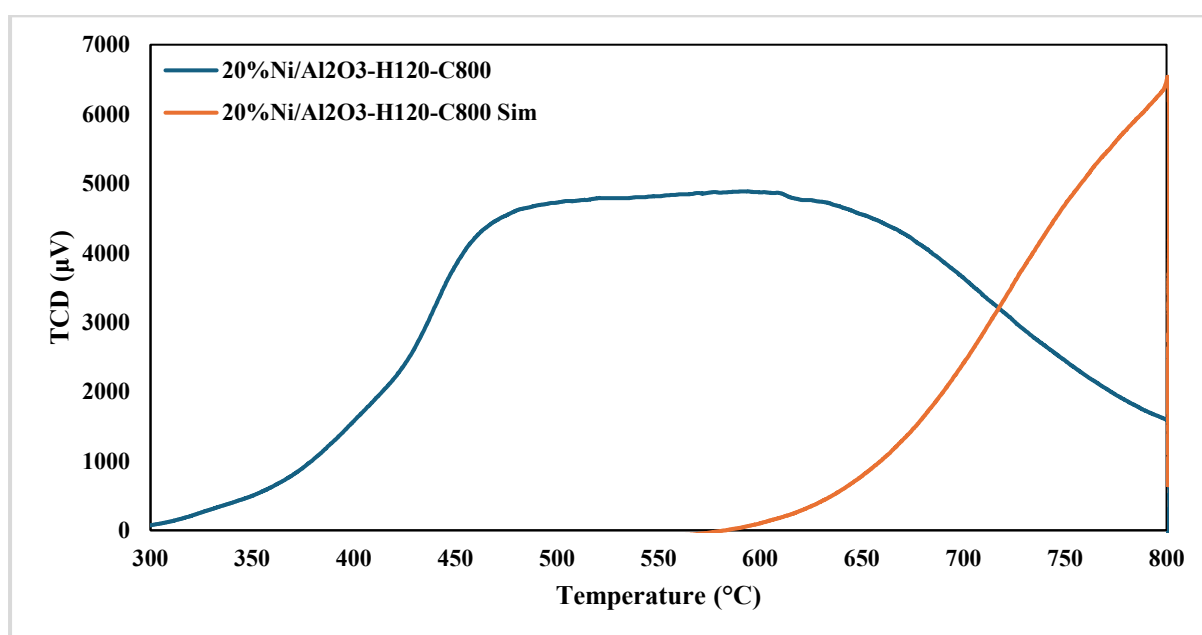


Figure 25: H₂-TPR of directly reduced and simultaneously synthesised catalysts.

5.2.1.4. XPS

XPS surface analysis was performed to determine the elemental composition of the catalyst's surface and to compare the Ni surface concentration between the two synthesis routes. Tables 8 and 9 present the atomic surface concentrations and the Ni/Al atomic ratio, respectively.

Table 8: Surface elemental contents of directly reduced and simultaneously synthesised catalysts.

Catalyst	O [%]	Al [%]	Ni [%]	B [%]	Cl [%]
20%Ni/Al ₂ O ₃ – H120 – C800 Sim	55.4	37.8	6.7	/	/
20% Ni/Al ₂ O ₃ – H120 – C800	56.5	32.2	6.0	4.1	1.3

Table 9: Ni/Al elemental ratio of directly reduced and simultaneously synthesised catalysts.

Catalyst	Ni/Al
20% Ni/Al₂O₃ – H120 – C800	0.18
20%Ni/Al₂O₃ – H120 – C800 Sim	0.18

Despite the fundamental difference in how Ni was incorporated, both catalysts exhibited an identical Ni/Al atomic surface ratio of 0.18. The absolute Ni and Al surface concentrations differed proportionally: the simultaneously synthesised catalyst showed slightly higher Ni content (6.7 at.%) and higher Al content (37.8 at.%) compared to the directly reduced catalyst (6.0 at.% Ni, 32.2 at.% Al), with the balance maintained by O.

The identical Ni/Al ratio confirms that the total Ni loading was equivalent on both catalysts' surfaces. The presence of B (4.1 at.%) and Cl (1.3 at.%) residues on the directly reduced catalyst is attributable to incomplete removal of NaBH₄ by-products during washing; these contaminants were absent on the simultaneously synthesised catalyst.

5.2.1.5. Catalytic Tests

Figure 26 compares the NH₃ conversion as a function of temperature for the directly reduced catalyst, the simultaneously synthesised one (at two pre-reduction temperatures), and a blank Al₂O₃ support.

The results clearly differentiate the two synthesis routes:

- 20%Ni/Al₂O₃-H120-C800 (direct reduction): NH₃ conversion reached 99 % at 550 °C, demonstrating excellent catalytic activity consistent with highly accessible metallic Ni sites.
- 20%Ni/Al₂O₃-H120-C800 Sim (H₂ pre-reduction at 550 °C): NH₃ conversion reached only 86 % at 550 °C — a 13 % deficit relative to direct reduction. Despite having nearly identical specific surface area, this catalyst was substantially less active owing to the inaccessibility of Ni locked within NiAl₂O₄ spinel.
- 20%Ni/Al₂O₃-H120-C800 Sim (H₂ pre-reduction at 750 °C): NH₃ conversion at 550 °C was 78 %, only 1 % above the blank (77 %), close to indistinguishable from a Ni-free support. The massive sintering induced by 750 °C pre-reduction (crystallite size 34 nm) rendered the catalyst essentially inactive.

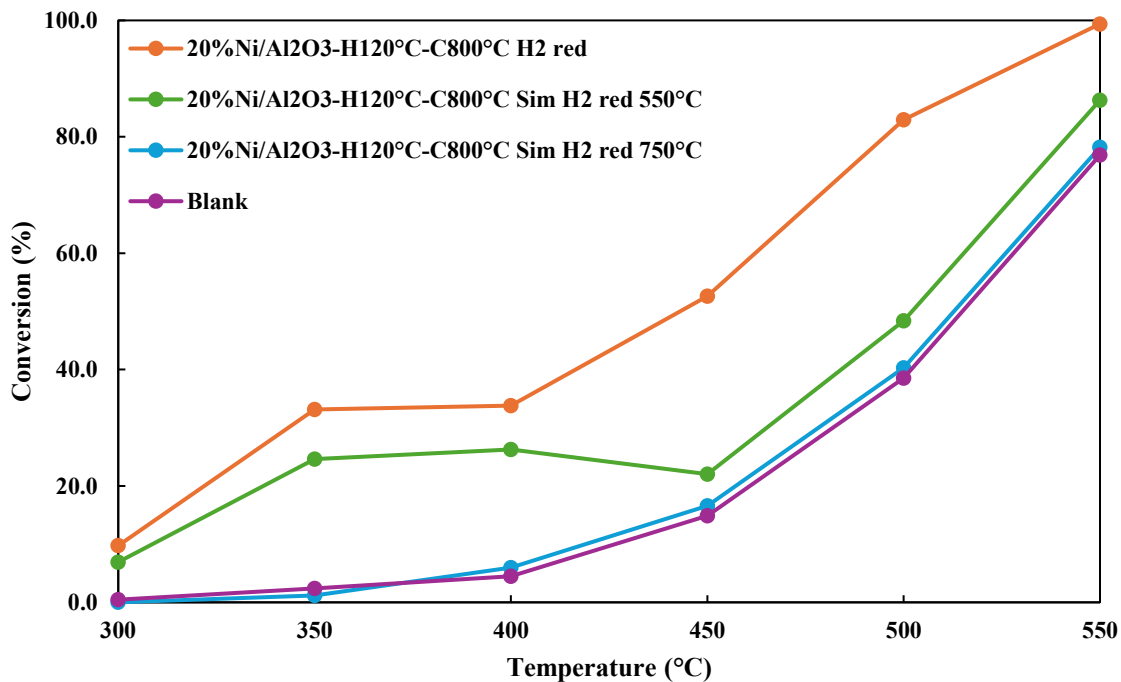


Figure 26: Catalytic tests with directly reduced and simultaneously synthesised catalysts.

5.2.2. Discussion

Structural Role of the Synthesis Route

The two synthesis routes produce fundamentally different Ni environments within the δ -Al₂O₃ matrix. In simultaneous synthesis, Ni ions are present during the hydrothermal network formation and are subsequently incorporated into the Al₂O₃ lattice upon calcination at 800 °C, forming NiAl₂O₄ spinel. The pore network organises itself around these particles with NiO/NiAl₂O₄ particles being embedded within the pore walls, preserving most of the surface area but narrowing the pores. In direct reduction, pre-formed Ni particles are deposited onto an already-structured support, occupying existing pores and causing surface blocking — a more disruptive process texturally but one that leaves Ni in a surface-accessible, reducible state.

The Reducibility Bottleneck of Simultaneous Synthesis

The decisive limitation of simultaneous synthesis is the formation of NiAl₂O₄ spinel during calcination at 800 °C. This mixed oxide phase exhibits a reduction onset above 600 °C and requires temperatures well beyond 800 °C for complete reduction to Ni⁰. Therefore:

- H₂ pre-reduction at 550 °C failed to generate any accessible Ni⁰ sites (H₂ chemisorption = 0 %), yet the reaction cycle still achieved 86 % NH₃ conversion at 550 °C — suggesting that partial *in-situ* reduction during the reaction itself generated a limited amount of active Ni, but far less than the directly reduced catalyst.

- H₂ pre-reduction at 750 °C did partially reduce the spinel, but at the cost of producing sintered crystallites (34 nm) that dramatically diminished active surface area. The resulting performance was indistinguishable from the blank.

This reducibility bottleneck cannot be resolved by simply raising the pre-treatment temperature: doing so inexorably trades reducibility for sintering. The NiAl₂O₄ phase thus represents an intrinsic incompatibility between simultaneous synthesis and δ -Al₂O₃ calcined at 800 °C.

Surface Composition and Active Site Accessibility

XPS confirmed that both routes deliver the same Ni/Al surface ratio (0.18), ruling out differences in total Ni loading as an explanatory variable. The performance gap is therefore entirely attributable to the accessibility and reducibility of Ni, not to its bulk concentration.

Conclusion: Selection of Direct Reduction

Direct reduction of Ni onto δ -Al₂O₃-H120-C800 using NaBH₄ was selected as the optimal synthesis route. Despite causing greater textural degradation than simultaneous synthesis, it yields a catalyst with accessible, reducible Ni surface sites that cannot be achieved via the simultaneous route without prohibitive sintering. The 99 % NH₃ conversion at 550 °C delivered by the directly reduced catalyst — versus 86 % for the best-performing Sim variant and 77 % for the blank — unambiguously validates this choice.

5.3. Praseodymium Promotion of Ni/Al₂O₃ Catalysts for NH₃ Decomposition: Synthesis Optimisation

5.3.1. Results

Optimisation of the Pr–Ni Direct Reduction Sequence

This section investigates how the order and mode of Pr and Ni addition by direct reduction onto Al₂O₃-H120-C800 affects the textural, structural, and catalytic properties of the resulting catalysts. Three preparation routes are compared: (i) simultaneous direct reduction of Pr and Ni (denoted Sim), (ii) successive reduction of Pr first followed by Ni, and (iii) successive reduction of Ni first followed by Pr. All Pr-containing catalysts in this section were prepared using Al₂O₃-H120-C800 New as the support, which originates from a different batch than the reference Al₂O₃-H120-C800, and comparisons are made accordingly.

5.3.1.1. N₂ Physisorption

Table 10: Specific surface area, pore volume, and pore diameter of Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts.

Catalyst	Specific surface area [m ² /g]	Pore volume [cm ³ /g]	Pore width [nm]
Al ₂ O ₃ – H120 – C800	230	1.20	18.4
20%Ni/Al ₂ O ₃ – H120 – C800	140	0.38	13.4
Al ₂ O ₃ – H120 – C800 New	220	0.99	15.8
5%Pr20%Ni Sim/Al ₂ O ₃ – H120 – C800	190	0.60	12.2
20%Ni5%Pr/Al ₂ O ₃ – H120 – C800	210	0.65	11.1

All samples exhibited Type IV(a) isotherms with capillary condensation, no plateau, and H3-type hysteresis with partial H1 character in the loop body, indicative of mesoporous materials with a broad pore-size distribution (Figure 27). The isotherms of the two Pr-containing catalysts overlapped with that of the bare Al₂O₃ New support up to a relative pressure of 0.6 p/p°, including the BET region, suggesting that the addition of Pr largely preserves the specific surface area. This behaviour contrasts with 20%Ni/Al₂O₃, for which a significant decrease in specific surface area relative to its bare support was observed.

Simultaneous addition of Pr and Ni reduced the specific surface area by 14% relative to the bare Al₂O₃ New support, compared to only 5% for the successive Pr-then-Ni route (Table 10). In terms of pore volume, the simultaneous route led to a 39% decrease versus 34% for the successive route; the latter therefore retains marginally superior textural properties despite

undergoing two separate NaBH_4 treatments. The mean pore width decreased by 23% and 30% for simultaneous and successive addition, respectively, with the larger relative loss in pore diameter for the successive route attributable to a widened pore-size distribution arising from partial pore-neck narrowing during the second reduction step.

In the capillary condensation regime, the bare Al_2O_3 New isotherm rose to higher relative adsorption than its Pr-containing counterparts, confirming that pore volume decreases upon loading. The hysteresis loop of the successive Pr–Ni sample closed at a lower relative pressure ($\sim 0.5 \text{ p/p}^\circ$) than the simultaneous sample ($\sim 0.6 \text{ p/p}^\circ$), indicative of a greater proportion of ink-bottle pores and a broader pore-size distribution in the successive route.

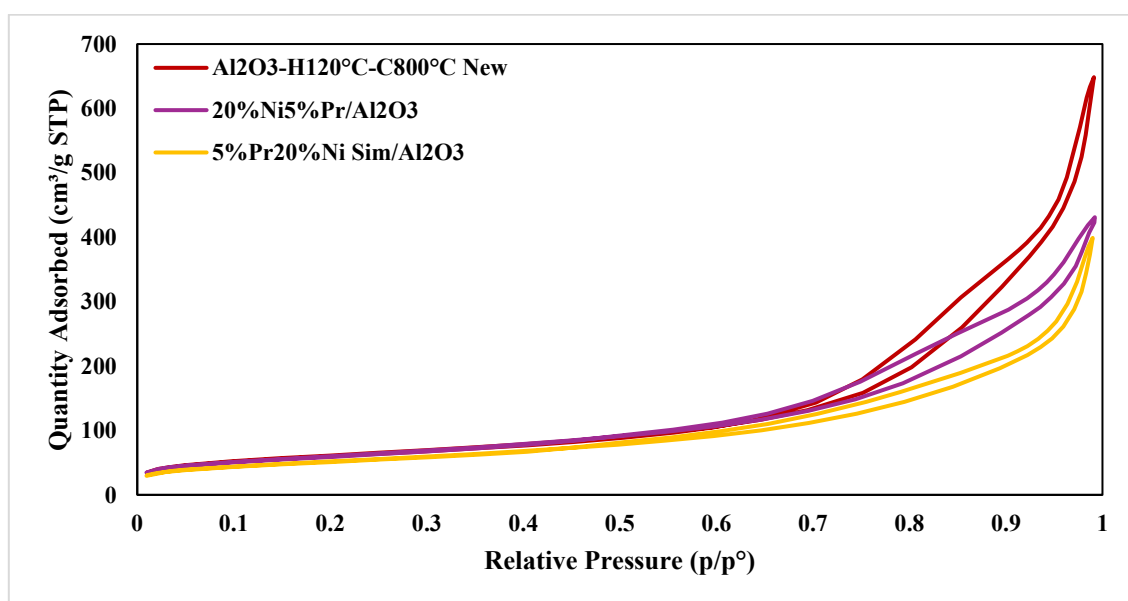


Figure 27: Isotherms of $\text{Ni}/\text{Al}_2\text{O}_3$ and $\text{NiPr}/\text{Al}_2\text{O}_3$ catalysts.

5.3.1.2. XRD

Prior to catalytic testing, the diffractograms of all fresh catalysts showed only peaks characteristic of $\delta\text{-Al}_2\text{O}_3$, with no discernible Ni or Pr crystalline phases, consistent with a highly dispersed or amorphous state of the deposited species (Figure 28).

After catalytic testing, Ni metallic peaks emerged in all spent catalysts. The sharpest Ni peak was observed for the successive Pr-onto-Ni/ Al_2O_3 sample, while the simultaneous Pr–Ni reduction yielded the broadest peak, indicating the smallest crystallite size (15 nm) in that series. The reference 20%Ni/ Al_2O_3 New showed a Ni crystallite size of 21 nm after a standard catalytic cycle reaching 550 °C (Table 11).

When a H₂ reduction pre-treatment at 550 °C was applied, the Ni crystallite size of 5%Pr20%Ni Sim/Al₂O₃ decreased by 20% (from 15 to 12 nm), while 20%Ni5%Pr/Al₂O₃ showed only a 9.5% decrease (from 21 to 19 nm). An extended long-run test at 550 °C for 62 h resulted in a 9.5% increase in Ni crystallite size relative to the standard 22 h temperature-ramp cycle, suggesting moderate but non-catastrophic sintering under prolonged operation. Several SiO₂ peaks, attributed to silica wool contamination from the reactor, were identified in all spent-catalyst diffractograms (Figures 29 and 30).

Table 11: Ni crystallite size of Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts.

Catalyst	Ni crystallite size [nm]
<i>Spent 20%Ni/Al₂O₃ – H120 – C800</i>	14
<i>Spent 20%Ni/Al₂O₃ – H120 – C800 New</i>	21
<i>Spent 5%Pr20%Ni/Al₂O₃ – H120 – C800</i>	20
<i>Spent 5%Pr20%Ni Sim/Al₂O₃ – H120 – C800</i>	15
<i>Spent 20%Ni5%Pr/Al₂O₃ – H120 – C800</i>	21
<i>Spent 5%Pr20%Ni/Al₂O₃ – H120 – C800 H₂ red</i>	22
<i>Spent 5%Pr20%Ni Sim/Al₂O₃ – H120 – C800 H₂ red</i>	12
<i>Spent 20%Ni5%Pr/Al₂O₃ – H120 – C800 H₂ red</i>	19
<i>Spent long run 20%Ni5%Pr/Al₂O₃ – H120 – C800</i>	23

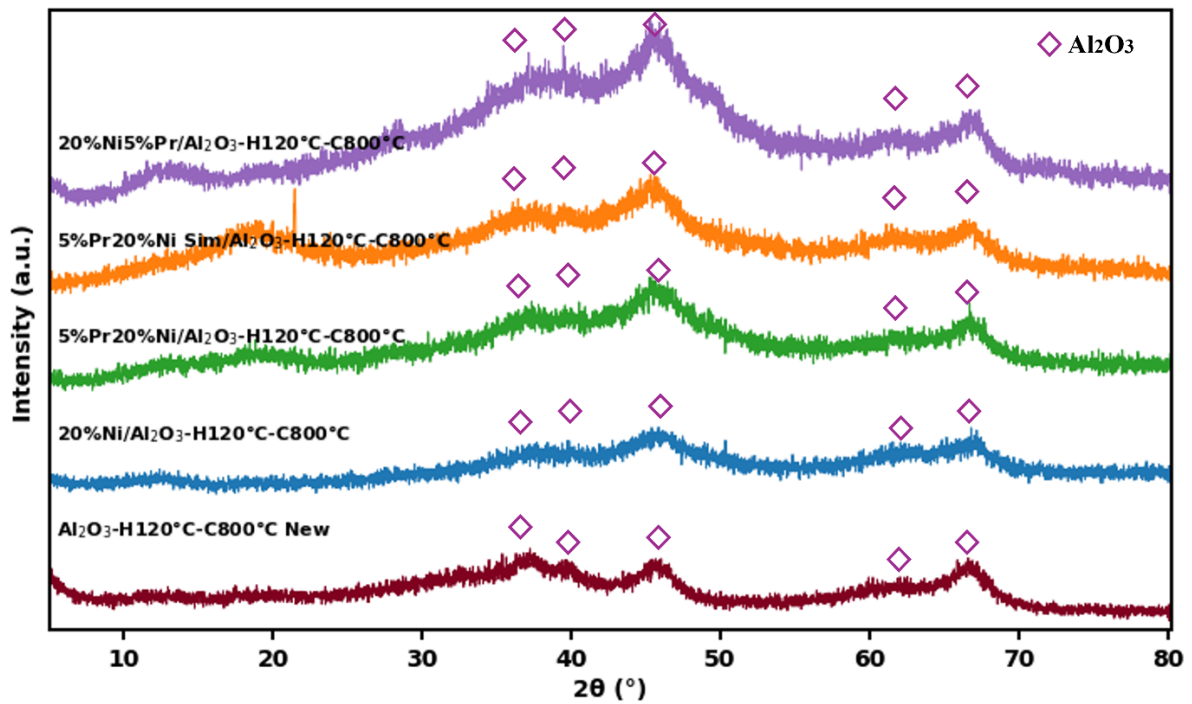


Figure 28: XRD diffractograms of Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts.

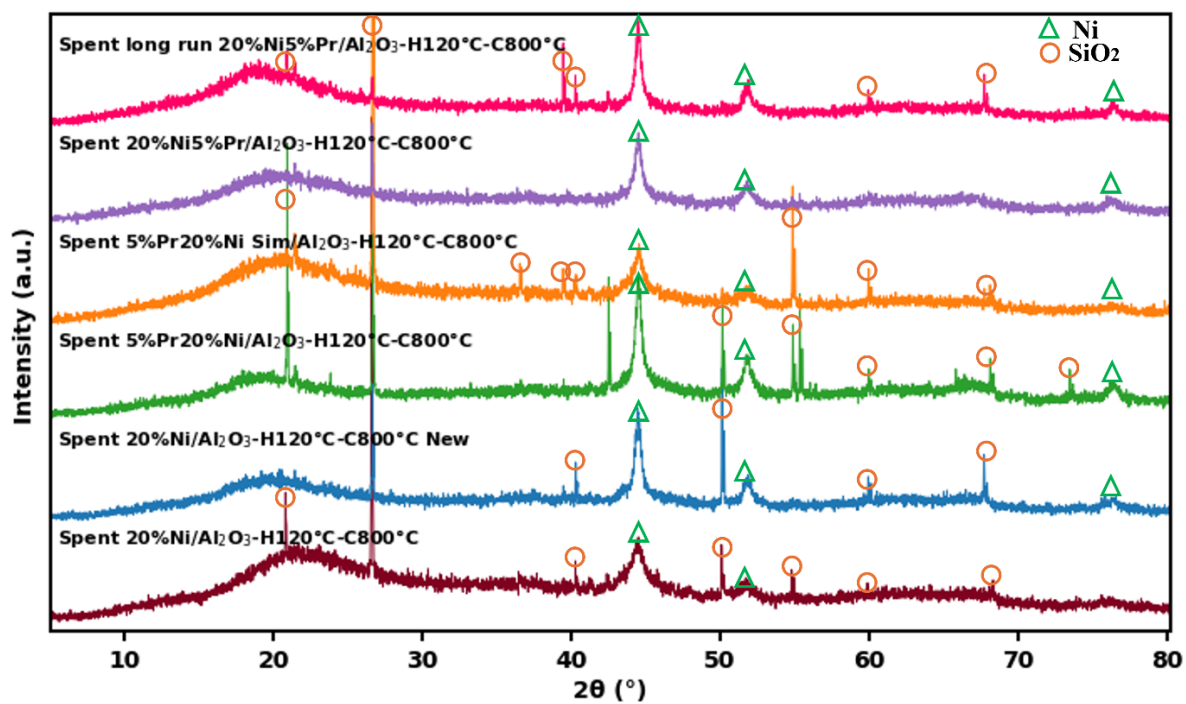


Figure 29: XRD diffractograms of spent Ni/ Al_2O_3 and NiPr/ Al_2O_3 catalysts.

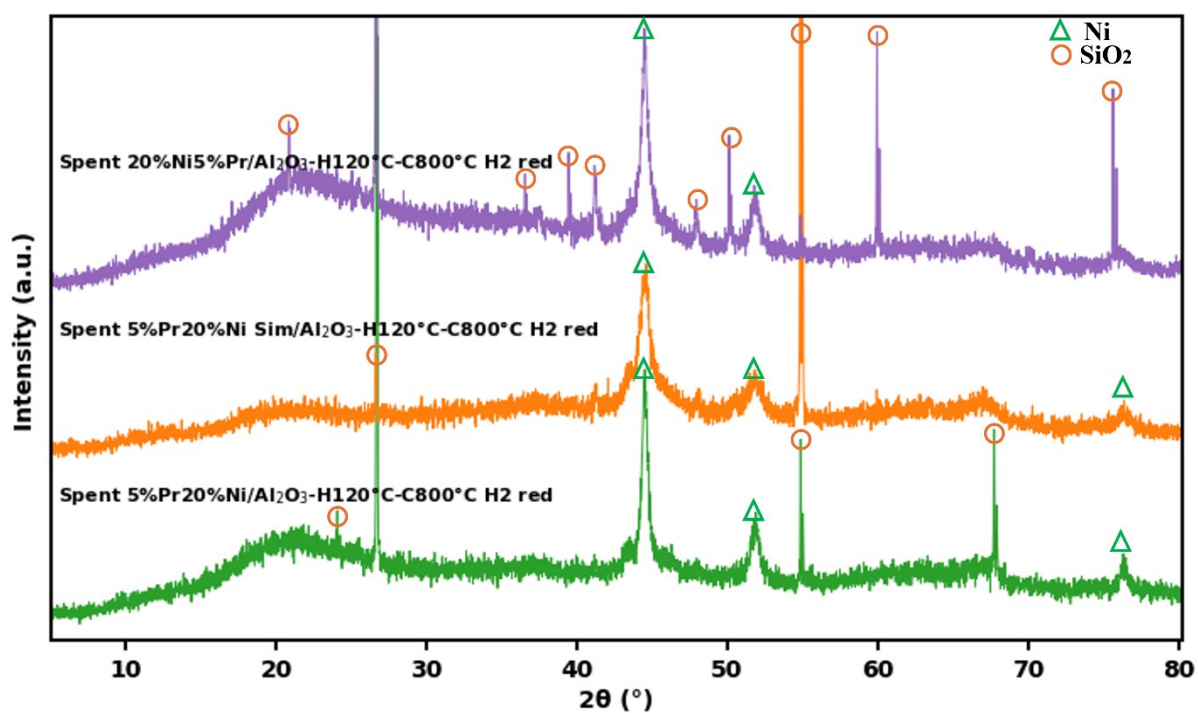


Figure 30: XRD diffractograms of spent NiPr/ Al_2O_3 catalysts with H_2 reduction.

5.3.1.3. H₂ Chemisorption

Despite H₂ reduction pre-treatment, negligible Ni dispersion was measured for all Pr-containing catalysts by pulsed H₂ chemisorption (Table 12). The 5%Pr20%Ni Sim/Al₂O₃ sample showed a residual dispersion of 0.1%, whereas no chemisorption was detected for the remaining two Pr variants. The reference 20%Ni/Al₂O₃ New retained a dispersion of 1.3%. These anomalously low values suggest that Pr may partially block Ni surface sites or that the H₂ reduction was insufficient to expose the Ni surface in the presence of Pr. Logistical constraints prevented repetition of these measurements.

Table 12: Ni dispersion of Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts.

Catalyst	Ni dispersion [%]
20%Ni/Al₂O₃ – H120 – C800 New	1.3
5%Pr20%Ni Sim/Al₂O₃ – H120 – C800	0.1
20%Ni5%Pr/Al₂O₃ – H120 – C800	0
5%Pr20%Ni/Al₂O₃ – H120 – C800	0

5.3.1.4. XPS

XPS analysis revealed that the O content of fresh catalysts was lower (56–61%) than that of spent catalysts (65–66%), with the inverse trend observed for Al (Table 13). This is consistent with partial oxidation of surface species and a reduction in the proportion of metallic elements at the surface after catalytic use.

Table 13: Surface elemental contents of Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts.

Catalyst	O [%]	Al [%]	Ni [%]	Pr [%]	B [%]	Cl [%]
Spent 20% Ni/Al₂O₃ – H120 – C800 New	65.9	26.9	2.3	/	4.3	0.5
20% Ni/Al₂O₃ – H120 – C800	56.5	32.2	6.0	/	4.1	1.3
Spent 20%Ni5%Pr/Al₂O₃ – H120 – C800	65.5	27.9	2.2	0.6	3.4	0.3
5%Pr20%Ni Sim/Al₂O₃ – H120 – C800	60.1	31.9	4.6	0.7	2.0	0.8
20%Ni5%Pr/Al₂O₃ – H120 – C800	59.4	32.5	5.2	0.6	1.7	0.6
5%Pr/Al₂O₃ – H120 – C800	60.8	37.5	/	0.9	0.6	0.3
5%Pr20%Ni/Al₂O₃ – H120 – C800	65.6	29.8	3.2	1.4	0.0	0.0

Among the three fresh Pr-containing catalysts, 20%Ni5%Pr/Al₂O₃ — where Ni was deposited onto a pre-formed Pr/Al₂O₃ support — showed the highest surface Ni content (5.2%) and the highest Ni/Al ratio (0.16). Conversely, the highest surface Pr content was found for the

successive Pr-onto-Ni/Al₂O₃ route (Pr: 1.4%), consistent with Pr being deposited as the last step and therefore preferentially exposed at the outermost surface layers. The Pr/Al ratio was twice as high for 5%Pr20%Ni/Al₂O₃ (0.046) as for 5%Pr/Al₂O₃ (0.023), suggesting that the presence of Ni influences the surface redistribution of Pr.

After catalytic testing, the Ni/Al ratio decreased while the Pr/Al and Pr/Ni ratios increased, indicating preferential migration of Ni into the bulk or partial coverage by Pr-containing species under reaction conditions (Table 14).

Table 14: Surface elemental content ratios of Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts.

Catalyst	Pr/Al	Ni/Al	Pr/Ni
Spent 20% Ni/Al₂O₃ – H120 – C800 New	/	0.09	/
20% Ni/Al₂O₃ – H120 – C800	/	0.18	/
Spent 20%Ni5%Pr/Al₂O₃ – H120 – C800	0.023	0.08	0.292
5%Pr20%Ni Sim/Al₂O₃ – H120 – C800	0.022	0.14	0.155
20%Ni5%Pr/Al₂O₃ – H120 – C800	0.019	0.16	0.119
5%Pr/Al₂O₃ – H120 – C800	0.023	/	/
5%Pr20%Ni/Al₂O₃ – H120 – C800	0.046	0.11	0.426

The Ni 2p binding energy was marginally lower for 20%Ni5%Pr/Al₂O₃ (856.2 eV) than for the other Pr-containing samples (856.6–856.8 eV), which may reflect a slightly modified electronic environment of Ni when in direct contact with a Pr oxide interlayer (Figure 31).

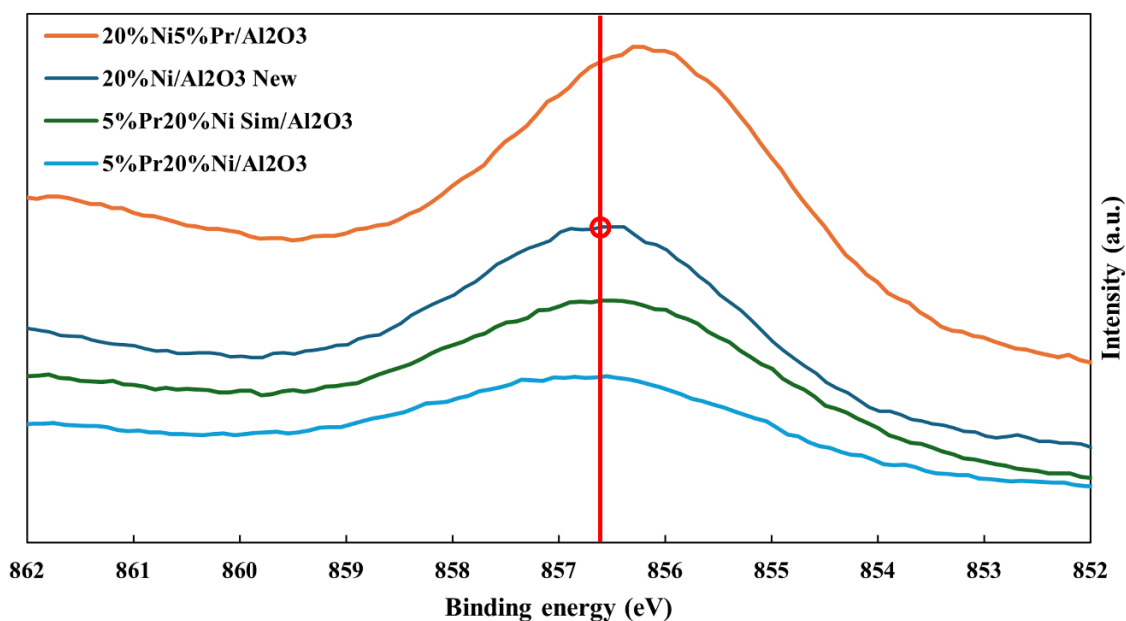


Figure 31: Ni binding energy of Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts.

5.3.1.5. Catalytic Tests

According to Figures 32 and 33, in the case of an absence of H₂ reduction pre-treatment (no red), the NH₃ conversion at 550 °C with 20%Ni/Al₂O₃ New was 92.4 % compared to 92.1 % when Pr and Ni were simultaneously directly reduced onto Al₂O₃. In the case of Pr directly reduced onto Ni/Al₂O₃, this value stood at 94.0 % compared to 94.2 % in the case of Ni directly reduced onto Pr/Al₂O₃.

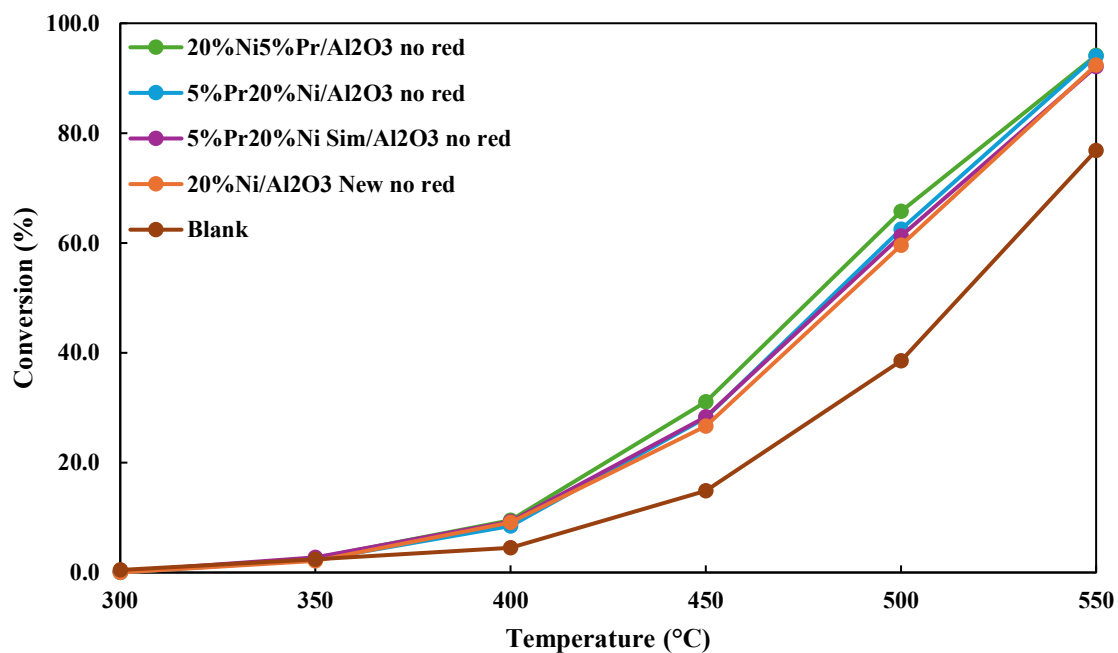


Figure 32: Catalytic tests with Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts.

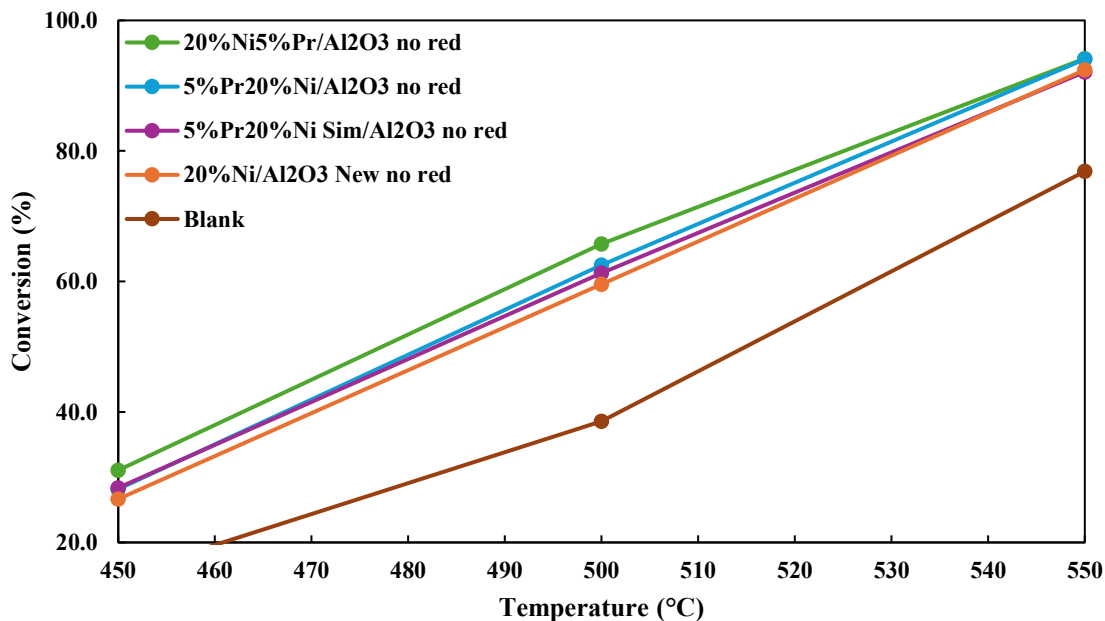


Figure 33: Catalytic tests with Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts.

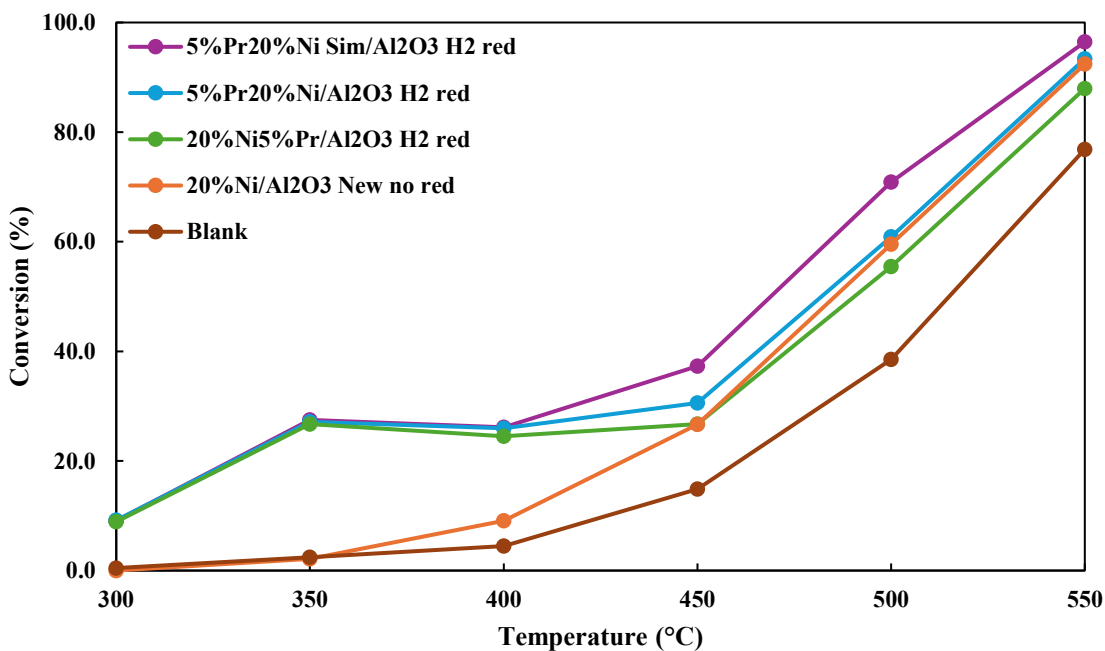


Figure 34: Catalytic tests with Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts with H₂ reduction.

However, according to Figure 34 illustrating the case of a H₂ reduction pre-treatment (H₂ red), 5%Pr20%Ni Sim/Al₂O₃ showed an NH₃ conversion at 550 °C of 96.5 %. This value was 9.5 % higher than for 20%Ni5%Pr/Al₂O₃ at 88.0 %.

With 5%Pr20%Ni/Al₂O₃ after a H₂ reduction pre-treatment, the NH₃ conversion at 550 °C reached 93.5 % compared to 92.5 % for 20%Ni/Al₂O₃ New without a pre-treatment.

No reaction was performed with 20%Ni/Al₂O₃ New having undergone a H₂ reduction pre-treatment.

In this case, the NH₃ conversion at 550 °C with 5%Pr20%Ni Sim/Al₂O₃ was 25 % higher than the blank, whereas 20%Ni5%Pr/Al₂O₃ was only 14 % higher than the blank.

5.3.2. Discussion

Rare-earth oxides such as Pr₂O₃ are known to act as structural stabilisers for Al₂O₃ by decorating the surface and pinning grain boundaries, suppressing sintering and specific surface area loss. The present results are consistent with this role: both Pr-containing catalysts preserved the specific surface area of the Al₂O₃ New support to a significantly greater extent than 20%Ni/Al₂O₃. Since the reduction potential of Pr³⁺ is too negative for reduction by NaBH₄ under aqueous conditions, Pr most likely deposited as a dispersed hydroxide or oxide phase rather than in its metallic form. A dispersed rare-earth oxide coating on the pore walls helps maintain the open pore structure and prevents pore collapse under the alkaline, gas-evolving conditions of NaBH₄ reduction.

The sequential addition of Pr followed by Ni retained marginally superior textural properties compared to simultaneous addition, even though it involved two NaBH₄ treatments. This can be interpreted as Pr forming a more complete protective coating prior to Ni deposition, thereby preventing direct Ni–Al₂O₃ contact. In the simultaneous route, competition between Ni and Pr for surface sites may have led to incomplete coverage of the support by Pr, resulting in a slightly greater loss of specific surface area.

Conversely, simultaneous Pr–Ni deposition promotes a more intimate Ni–Pr interaction, which appears to enhance Ni reducibility under H₂ pre-treatment — evidenced by the markedly higher NH₃ conversion of 5%Pr20%Ni Sim/Al₂O₃ after such treatment. The higher Ni/Al ratio of 20%Ni5%Pr/Al₂O₃, combined with its lower Ni binding energy (856.2 eV), suggests that placing Ni on a pre-formed Pr/Al₂O₃ surface also modifies the Ni electronic state, potentially through a metal–support interaction with Pr oxide acting as an oxygen-donor promoter. Notwithstanding, the absence of a pre-treatment H₂-TPR for 5%Pr20%Ni Sim/Al₂O₃ and a corresponding catalytic reference for Ni/Al₂O₃ New limits the strength of this conclusion.

Given the superiority of 20%Ni5%Pr/Al₂O₃ without pre-treatment, this preparation sequence was retained for the subsequent Pr-loading optimisation study.

5.4. Pr Loading Optimisation

5.4.1. Results

Building on the conclusion that successive Pr-then-Ni direct reduction is the preferred preparation route, this section systematically evaluates four Pr loadings — 1%, 3%, 5%, and 7% by weight relative to Al_2O_3 — in 20%NiX%Pr/ Al_2O_3 -H120-C800 Final catalysts. A separate Al_2O_3 Final support, issued from the same sol-gel and hydrothermal synthesis batch as the original Al_2O_3 used throughout this work but calcined at a different time (same protocol), was used; its textural properties are sufficiently close to enable valid comparisons with the 20%Ni/ Al_2O_3 reference.

5.4.1.1. N_2 Physisorption

All Pr-containing catalysts showed higher specific surface areas, pore volumes, and pore diameters than 20%Ni/ Al_2O_3 , confirming the textural-promotion role of Pr across all loadings investigated. The specific surface area remained relatively constant between 190 and 210 m^2/g regardless of Pr loading, representing an average decrease of only $\sim 20\%$ relative to the bare Al_2O_3 Final (250 m^2/g) compared to a 39% decrease for 20%Ni/ Al_2O_3 (230 $\rightarrow$ 140 m^2/g vs. the original reference support). Even a 1% Pr loading was sufficient to partially preserve the pore volume and surface area, with isotherms in both the BET and condensation regions lying above those of 20%Ni/ Al_2O_3 (Table 15).

Table 15: Specific surface area, pore volume, and pore diameter of Ni/ Al_2O_3 and NiPr/ Al_2O_3 catalysts with different loadings.

Catalyst	Specific surface area [m^2/g]	Pore volume [cm^3/g]	Pore width [nm]
$\text{Al}_2\text{O}_3 - \text{H120} - \text{C800}$	230	1.20	18.4
20%Ni/ $\text{Al}_2\text{O}_3 - \text{H120} - \text{C800}$	140	0.38	13.4
$\text{Al}_2\text{O}_3 - \text{H120} - \text{C800 Final}$	250	1.25	18.8
20%Ni1%Pr/ $\text{Al}_2\text{O}_3 - \text{H120} - \text{C800 Final}$	200	0.54	12.4
20%Ni3%Pr/ $\text{Al}_2\text{O}_3 - \text{H120} - \text{C800 Final}$	200	0.54	12.8
20%Ni5%Pr/ $\text{Al}_2\text{O}_3 - \text{H120} - \text{C800 Final}$	210	0.61	13.4
20%Ni7%Pr/ $\text{Al}_2\text{O}_3 - \text{H120} - \text{C800 Final}$	190	0.69	15.0

A clear trend of increasing pore volume with Pr loading was observed in the condensation region: the 7%Pr catalyst retained the highest pore volume (0.69 cm³/g), and the 3%Pr and 1%Pr catalysts yielded identical, lower pore volumes (0.54 cm³/g). The decrease in pore volume relative to the bare support ranged from 45% at 7%Pr to 57% at 1% and 3%Pr, while the decrease in pore width ranged from 20% at 7%Pr to 34% at 1%Pr. These trends indicate that higher Pr loadings more effectively protect the Al₂O₃ pore structure against blockage during NaBH₄ reduction.

For all samples except the 7%Pr catalyst, the hysteresis loop closed around a relative pressure of 0.5 p/p°, indicating a minor proportion of ink-bottle pores and a pore-size distribution broadened by the reduction process. The 7%Pr catalyst exhibited loop closure near 0.7 p/p°, in line with the bare Al₂O₃ Final, suggesting that at this loading Pr provides sufficient pore-neck protection to largely prevent the narrowing observed at lower loadings.

The isotherms related to these samples are available in the Appendices section.

5.4.1.2. XRD

Fresh catalyst diffractograms displayed only δ -Al₂O₃ peaks; no crystalline Ni, NiO, or Pr phases were detected, consistent with the highly dispersed state of the deposited species. After catalytic testing with H₂ pre-treatment at 550 °C, Ni metallic peaks were present in all spent catalysts. The Ni crystallite size was non-monotonic with Pr loading, with the highest value at 5%Pr (16 nm) and the lowest at 3%Pr (12 nm) (Table 16). Compared to the spent 20%Ni/Al₂O₃ reference after H₂ pre-treatment (23 ± 2 nm), the 5%Pr-containing catalyst showed a 30% smaller Ni crystallite size, demonstrating that Pr effectively inhibits sintering under these conditions.

A NiO peak was identified in the diffractogram of the 5%Pr long-run spent catalyst (62 h, 550 °C, no pre-treatment), partially overlapping with the Ni peak and suggesting incomplete reduction during the long-run test. The Ni peak was sharpest for the long-run test and for the 7%Pr single-cycle sample, and broadest for the 1%Pr single-cycle sample. Long-run tests without H₂ pre-treatment yielded lower Ni crystallite sizes (13–14 nm) than the single-cycle tests with pre-treatment, which is discussed below in the context of H₂-induced sintering.

The XRD diffractograms related to these samples are available in the Appendices section.

Table 16: Ni crystallite size of spent Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts with different loadings.

Catalyst	Ni crystallite size [nm]
Spent 20%Ni/Al₂O₃ – H120 – C800	14
Spent 20%Ni/Al₂O₃ – H120 – C800 H₂ red 550	23 ± 2
Spent 20%Ni1%Pr/Al₂O₃ – H120 – C800 Final H₂ red	13
Spent 20%Ni3%Pr/Al₂O₃ – H120 – C800 Final H₂ red	12
Spent 20%Ni5%Pr/Al₂O₃ – H120 – C800 Final H₂ red	16
Spent 20%Ni7%Pr/Al₂O₃ – H120 – C800 Final H₂ red	14
Spent long run 20%Ni5%Pr/Al₂O₃ – H120 – C800 Final	13
Spent long run 20%Ni/Al₂O₃ – H120 – C800	14

5.4.1.3. H₂ Chemisorption

In these samples, the 3%Pr catalyst exhibited the highest dispersion (1.6%), marginally exceeding that of 20%Ni/Al₂O₃ (1.5%), while the 7%Pr catalyst showed the lowest (0.3%) (Table 17). The 1%Pr and 5%Pr catalysts yielded 1.1%, i.e. 27% below the reference. These results suggest that moderate Pr loadings (3%) can sustain or slightly improve Ni accessibility, whereas high Pr loadings (7%) may partially block Ni surface sites.

Table 17: Ni dispersion of Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts with different loadings.

Catalyst	Ni dispersion [%]
20%Ni/Al₂O₃ – H120 – C800	1.5
20%Ni1%Pr/Al₂O₃ – H120 – C800 Final	1.1
20%Ni3%Pr/Al₂O₃ – H120 – C800 Final	1.6
20%Ni5%Pr/Al₂O₃ – H120 – C800 Final	1.1
20%Ni7%Pr/Al₂O₃ – H120 – C800 Final	0.3

Figure 35 illustrates the H₂-TPR of the Ni- versus Ni & Pr-containing catalysts. 20%Ni/Al₂O₃-H120-C800 reduction initiated in the 300 – 400 °C range, whereas for 20%Ni5%Pr/Al₂O₃ Final, that range was higher at 350 – 450 °C. However, the Ni & Pr-containing catalyst was closer to full reduction at 800 °C than its Ni-containing counterpart.

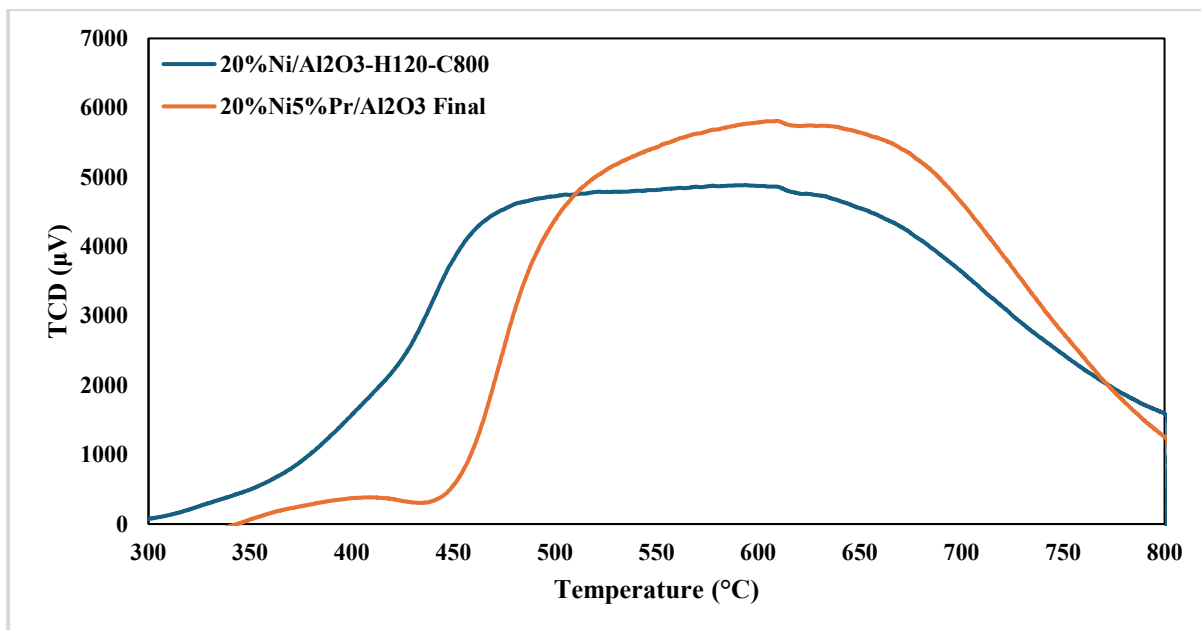


Figure 35: H_2 -TPR of Ni/Al_2O_3 and $NiPr/Al_2O_3$ catalysts.

5.4.1.4. XPS

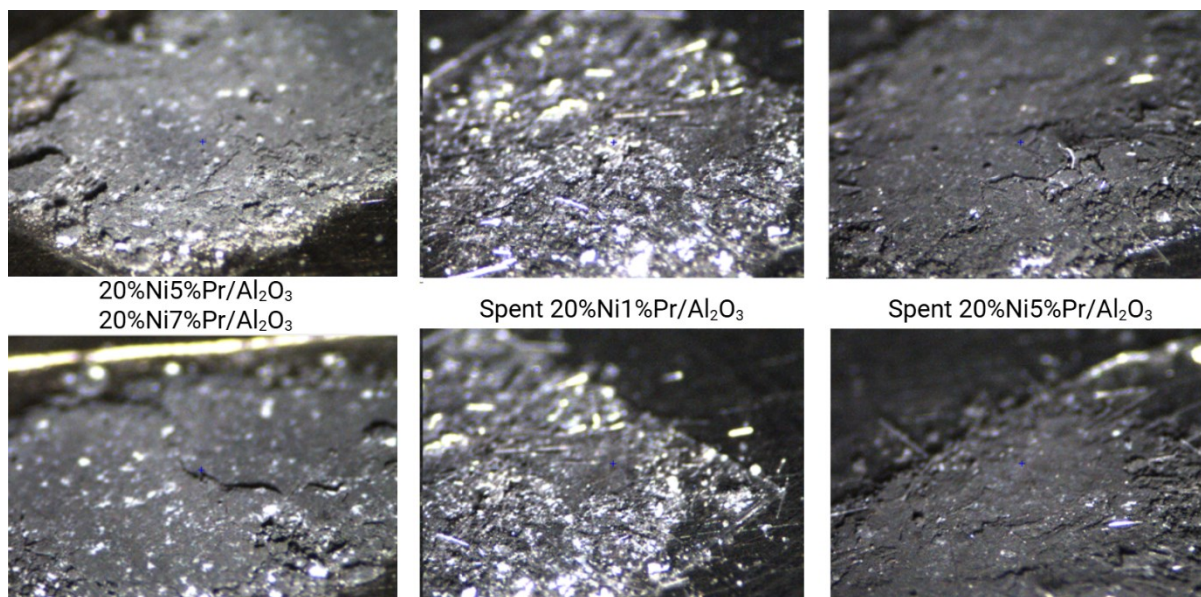


Figure 36: Pictures of fresh and spent $NiPr/Al_2O_3$ catalysts.

The O and Al contents of all fresh samples were tightly grouped (O: 56–58%, Al: 22–23%), indicating consistent surface compositions (Table 18). The Ni content was highest for the 5%Pr catalyst (4.6%) and showed no monotonic trend with Pr loading. Increasing Pr loadings led to proportionally higher Pr surface content (from 0.1% at 1%Pr to 0.8% at 7%Pr) (Table 19), consistent with the bulk ICP-OES data (Table 20). The Ni/Al ratio was highest at 5%Pr (0.21),

exceeding even the Ni/Al₂O₃ reference (0.16 for New batch), and the Pr/Al ratio increased proportionally with loading from 0.005 (1%Pr) to 0.037 (7%Pr).

After catalytic testing, the Ni content decreased for all loadings except 1%Pr, and the B content increased (from ~2% to ~4%), consistent with partial re-oxidation or surface restructuring under reaction conditions. The Pr/Al and Pr/Ni ratios increased upon use, suggesting Pr enrichment at the surface relative to Ni, possibly via Ni migration into the bulk (Table 19). The Si content in spent samples was significant (up to 3.1%) and attributed to silica wool contamination.

Table 18: Surface elemental contents of fresh and spent Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts with different loadings.

Catalyst	O [%]	Al [%]	Ni [%]	Pr [%]	B [%]	N [%]	Cl [%]	Si [%]	Fe [%]
20%Ni1%Pr/Al₂O₃ – H120 – C800 Final	57.6	22.3	3.8	0.1	2.1	0.2	0.1	/	0.6
20%Ni3%Pr/Al₂O₃ – H120 – C800 Final	57.9	23.4	2.8	0.3	1.7	/	0.1	/	0.6
20%Ni5%Pr/Al₂O₃ – H120 – C800 Final	56.8	22.1	4.6	0.6	2.1	/	0.1	/	0.4
20%Ni7%Pr/Al₂O₃ – H120 – C800 Final	56.0	21.9	3.8	0.8	2.0	/	0.0	/	0.3
Spent 20%Ni1%Pr/Al₂O₃ – H120 – C800 Final	55.4	19.2	5.2	0.12	4.4	0.9	/	3.1	/
Spent 20%Ni3%Pr/Al₂O₃ – H120 – C800 Final	57.4	22.4	2.5	0.39	3.7	0.2	/	1.7	0.2
Spent 20%Ni5%Pr/Al₂O₃ – H120 – C800 Final	55.9	22.2	3.5	0.64	4.1	0.4	/	0.8	0.2
Spent 20%Ni7%Pr/Al₂O₃ – H120 – C800 Final	57.1	22.1	1.9	0.87	4.2	0.2	/	1.5	/
20% Ni/Al₂O₃ – H120 – C800 New	57.4	23.1	3.8	/	1.6	0.1	0.1	/	0.6
20% Ni/Al₂O₃ – H120 – C800	55.8	21.3	6.1	/	2.3	0.1	0.1	/	0.6

Table 19: Surface elemental content ratios of Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts with different loadings.

Catalyst	Pr/Al	Ni/Al	Pr/Ni
20%Ni1%Pr/Al₂O₃ – H120 – C800 Final	0.005	0.17	0.027
20%Ni3%Pr/Al₂O₃ – H120 – C800 Final	0.014	0.12	0.113
20%Ni5%Pr/Al₂O₃ – H120 – C800 Final	0.025	0.21	0.122
20%Ni7%Pr/Al₂O₃ – H120 – C800 Final	0.037	0.17	0.215
Spent 20%Ni1%Pr/Al₂O₃ – H120 – C800 Final	0.006	0.27	0.023
Spent 20%Ni3%Pr/Al₂O₃ – H120 – C800 Final	0.017	0.11	0.154
Spent 20%Ni5%Pr/Al₂O₃ – H120 – C800 Final	0.029	0.16	0.182
Spent 20%Ni7%Pr/Al₂O₃ – H120 – C800 Final	0.039	0.09	0.455
20% Ni/Al₂O₃ – H120 – C800 New	/	0.16	/
20% Ni/Al₂O₃ – H120 – C800	/	0.29	/

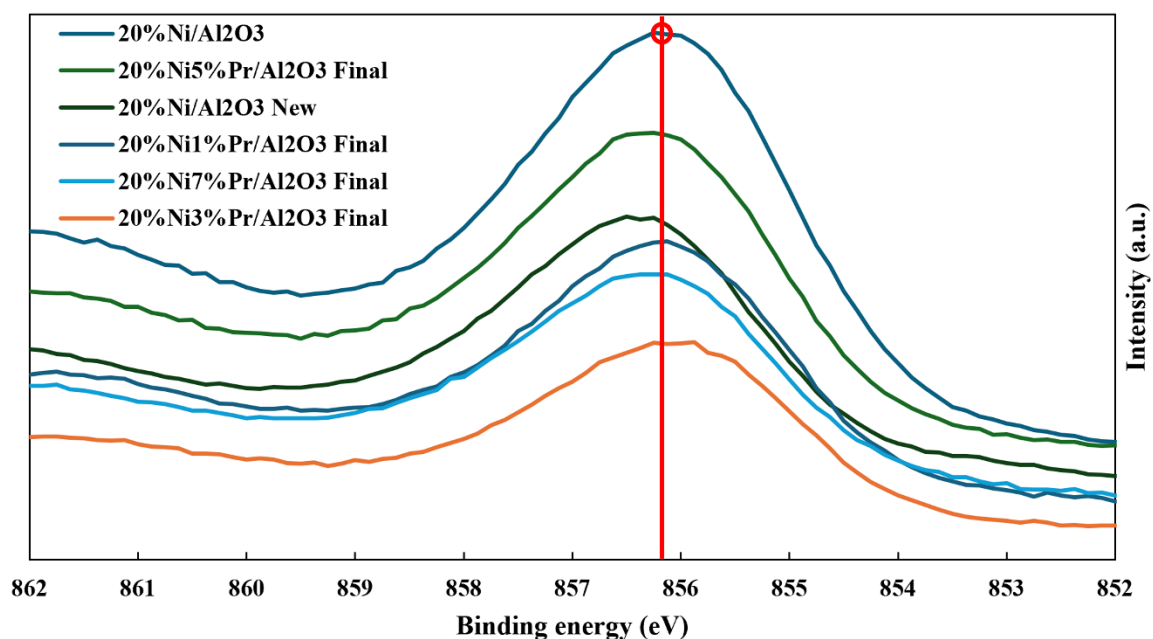


Figure 37: Ni binding energy of Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts with different loadings.

XPS of the binding energy region of the Ni_{2p 3/2} orbital revealed a peak near 856 eV (Ni²⁺) in fresh catalysts (Figure 37) and an additional peak at ~852.7 eV (Ni⁰) in spent catalysts (Figure 38). The intensity of the Ni⁰ peak decreased with increasing Pr loading, indicating that higher Pr loadings suppress the surface concentration of metallic Ni in spent catalysts — consistent with partial site blocking or lower Ni reducibility at high Pr content. The Ni binding energy across samples ranged from 856.1 eV (3%Pr) to 856.3–856.4 eV (5–7%Pr and Ni/Al₂O₃), with no systematic trend beyond instrument-level variability.

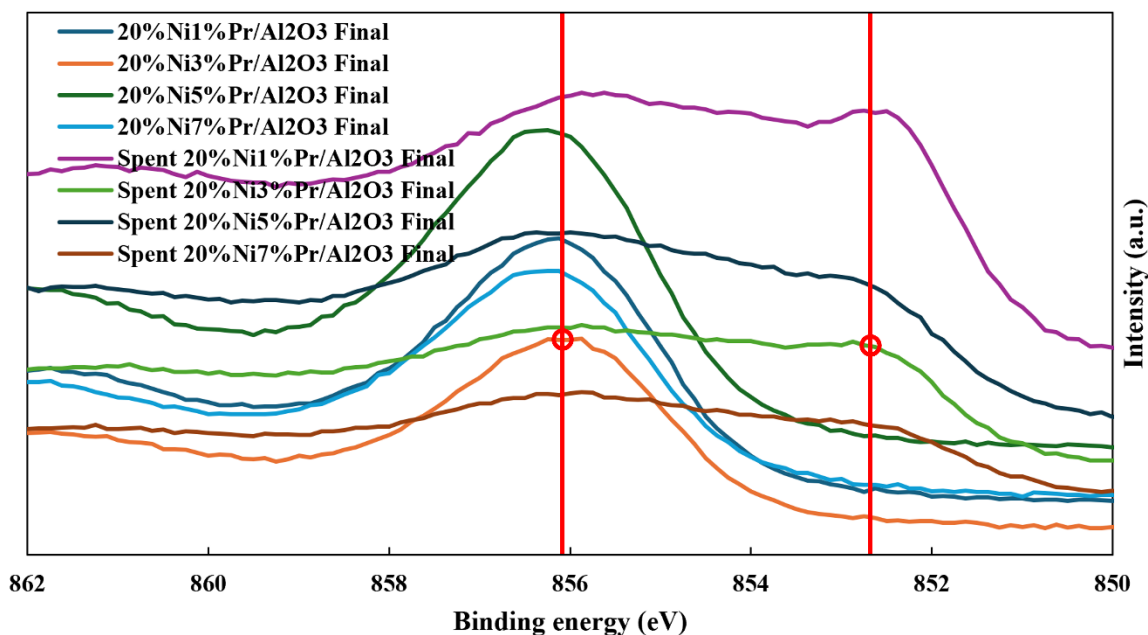


Figure 38: Ni binding energy of spent and fresh NiPr/Al₂O₃ catalysts with different loadings.

5.4.1.5. ICP-OES

The Pr bulk content increased proportionally with nominal loading from 0.53 ± 0.02 at.% (1%Pr) to 4.24 ± 0.07 at.% (7%Pr), confirming monotonic incorporation of Pr during synthesis (Table 20). The Ni content was largely consistent across loadings (~ 15.5 – 16.4 at.%), as expected given a fixed 20 wt% nominal Ni loading. The 3%Pr sample showed unusually high variability in Ni content (16.41 ± 1.97 at.%), which exceeds the variability observed for other loadings and may reflect inhomogeneous NaBH₄ addition during synthesis. This measurement should be repeated to confirm the value; due to time constraints, the reported average was retained.

Table 20: Bulk elemental contents of NiPr/Al₂O₃ catalysts with different loadings.

Catalyst	Al [%]	Ni [%]	Pr [%]
20%Ni7%Pr/Al ₂ O ₃ – H120 – C800 Final	18.60 ± 0.98	15.92 ± 0.31	4.24 ± 0.07
20%Ni5%Pr/Al ₂ O ₃ – H120 – C800 Final	18.63 ± 1.09	16.01 ± 0.10	2.78 ± 0.09
20%Ni3%Pr/Al ₂ O ₃ – H120 – C800 Final	17.88 ± 0.43	16.41 ± 1.97	1.81 ± 0.25
20%Ni1%Pr/Al ₂ O ₃ – H120 – C800 Final	18.51 ± 0.25	15.54 ± 0.44	0.53 ± 0.02

5.4.1.6. Catalytic Tests

All temperature-ramp catalytic tests in this section employed a H₂ reduction pre-treatment at 550 °C, consistent with the protocol identified in Section 5.3. as most discriminating between Pr-containing catalysts.

A 5%Pr loading was found to be optimal across the 450–550 °C temperature range. The 20%Ni5%Pr/Al₂O₃ Final catalyst achieved 98.7% NH₃ conversion at 550 °C under a space velocity of 6000 mL(NH₃)·g(cat)⁻¹·h⁻¹, compared to 99.4% for 20%Ni/Al₂O₃ prepared from the initial Al₂O₃ batch (Figure 39). Catalysts with 1%, 3%, and 7%Pr loading showed significantly lower and mutually similar performance at 550 °C (94.8–97.6%), while the 3%Pr sample displayed an anomalously high conversion at 400 °C (38.7%) relative to Ni/Al₂O₃ (31.4%).

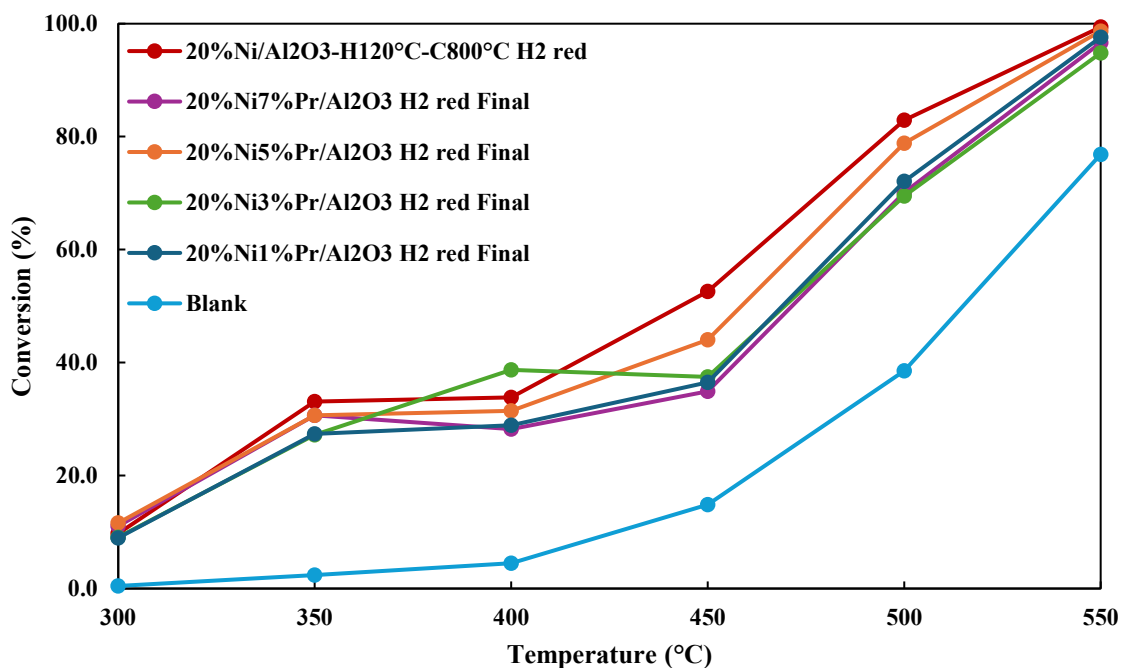


Figure 39: Catalytic tests with Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts with H₂ reduction.

Increasing the gas hourly space velocity (GHSV) from 6000 to 30 000 mL(NH₃)·g(cat)⁻¹·h⁻¹ for 20%Ni5%Pr/Al₂O₃ Final did not affect NH₃ conversion below 400 °C (Figure 40). At 450 °C, however, the high-GHSV test yielded a conversion of 26% versus 44% at low GHSV, representing a 41% relative decrease, consistent with a mass-transfer or contact-time limitation at intermediate temperatures.

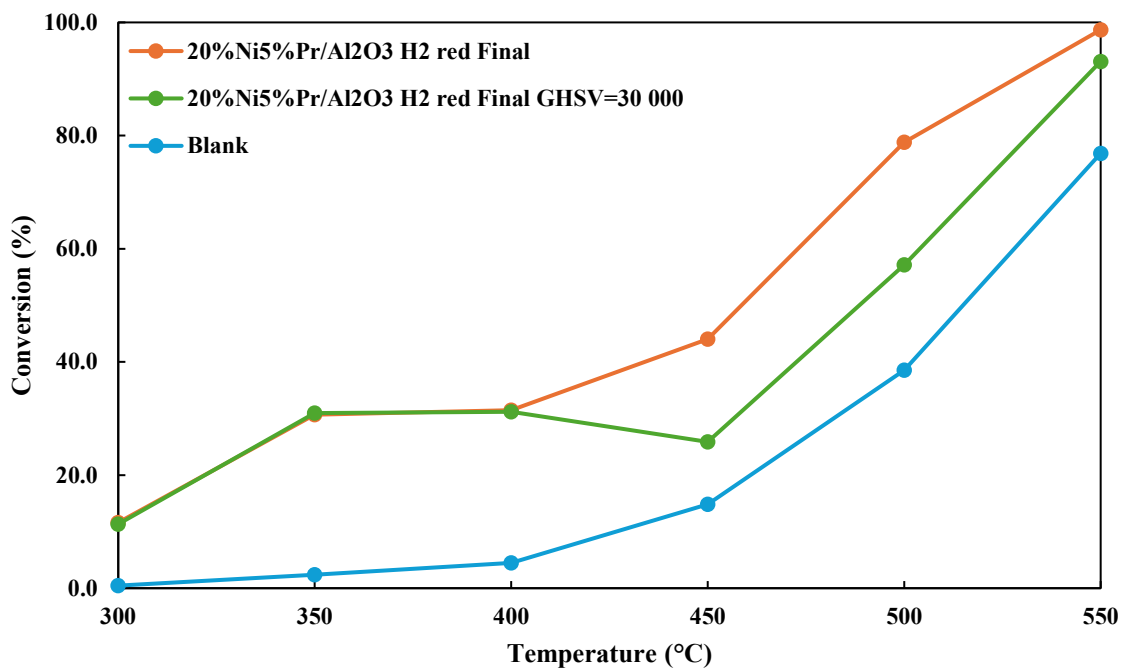


Figure 40: Catalytic tests with a NiPr/Al₂O₃ catalyst with H₂ reduction under different GHSV.

Long-run stability tests at 550 °C for 62 h confirmed that both 20%Ni5%Pr/Al₂O₃ Final (average conversion: 97.6%) and 20%Ni/Al₂O₃ (average: 96.5%) maintained stable activity over the course of the experiment, with no evidence of significant deactivation (Figure 41). These results demonstrate the long-term viability of Pr-promoted Ni/Al₂O₃ catalysts for NH₃ decomposition.

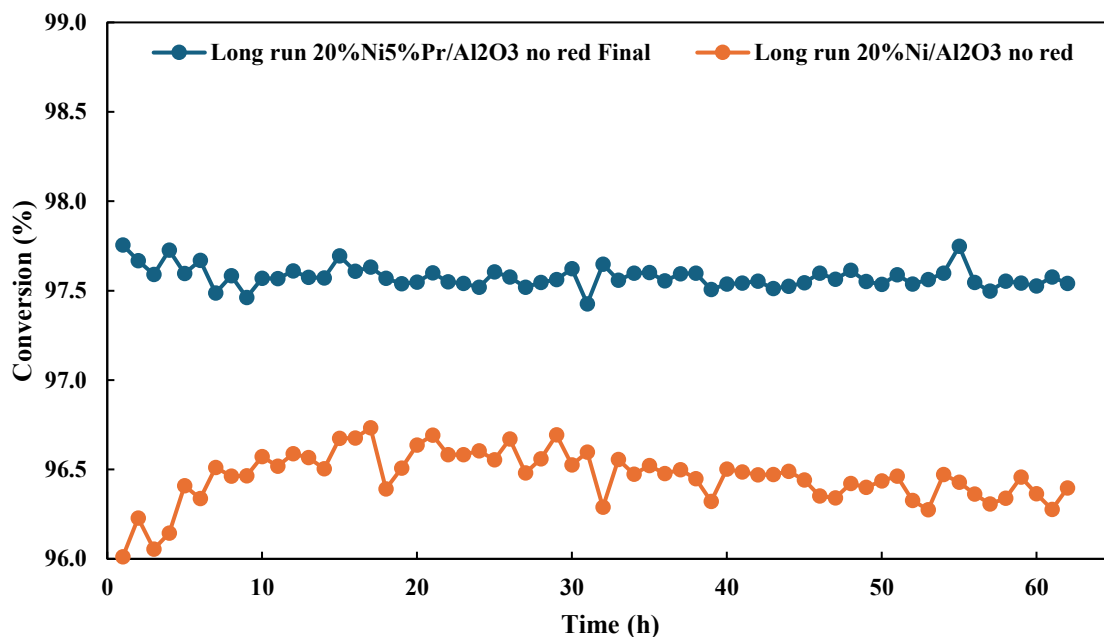


Figure 41: Long run catalytic tests with Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts.

5.4.2. Discussion

The present results confirm that Pr acts as a textural promoter across all loadings investigated, preserving the specific surface area and pore volume of the Al₂O₃ support to a greater extent than unpromoted Ni/Al₂O₃. Increasing the Pr loading monotonically raised the pore volume of the final catalyst, consistent with a more extensive coverage of the pore walls by a Pr oxide phase that prevents pore-neck blockage during NaBH₄ reduction.

H₂ pre-treatment was found to promote Ni sintering, as evidenced by the larger Ni crystallite sizes of pre-treated spent catalysts relative to those subjected to long-run tests without pre-treatment. Nevertheless, the enhanced fraction of metallic Ni accessible after H₂ pre-treatment — the catalytically active phase — more than compensates for the larger crystallite size, resulting in higher NH₃ conversion. This trade-off highlights the importance of characterising both Ni crystallite size and metallic Ni surface availability when evaluating catalyst performance.

The non-monotonic variation of Ni dispersion and XPS Ni/Al ratio with Pr loading, with a maximum at 3% and 5%, respectively, suggests that moderate Pr additions optimise the balance between textural protection and Ni accessibility. At 7%Pr, the marked drop in Ni dispersion (0.3%) and the decrease in the surface Ni⁰ peak intensity in spent catalysts indicate that

excessive Pr loading increasingly blocks Ni surface sites, offsetting the textural benefits of higher pore volumes.

The finding that the 3%Pr catalyst gave the highest Ni dispersion (1.6%) yet did not translate to superior catalytic performance at 550 °C suggests that factors beyond dispersion — such as Ni–Pr electronic interactions, reducibility, and pore accessibility — govern the turnover at high temperatures. The slightly lower Ni binding energy of the 3%Pr catalyst compared to Ni/Al₂O₃ (856.1 vs. 856.4 eV) may reflect a subtle electronic promotion that is superseded by other effects at lower Pr loadings.

ICP-OES confirmed that the nominal Pr loadings were achieved in the bulk, ruling out significant Pr leaching during synthesis. The higher Ni bulk content of the 3%Pr sample (~16.4 at.%), while within the range of its Pr-containing counterparts, may partly account for its anomalous catalytic behaviour at 400 °C and elevated Ni dispersion.

Overall, a Pr loading of 5% by weight relative to Al₂O₃, deposited by successive direct reduction followed by Ni reduction, represents the optimal compromise between textural preservation, Ni accessibility, and catalytic performance for NH₃ decomposition over 20%Ni/Al₂O₃-H120-C800 catalysts. Long-run stability at 550 °C further confirms the suitability of this formulation for sustained operation.

6. Conclusion

Rare earths, such as praseodymium, have been evaluated for their potential to improve the reaction mechanism of ammonia decomposition at the rate determining step by acting as electron donors, and the improving the reducibility of Ni.

At first, Al_2O_3 was synthesised by a sol-gel process according to varying parameters to determine the most optimal settings for the ammonia decomposition reaction. Al_2O_3 with hydrothermal synthesis at 120 °C and calcination at 800 °C was found to yield the highest ammonia conversion at 550 °C.

Two Ni addition methods were evaluated. It was determined that the direct reduction of Ni onto Al_2O_3 , using NaBH_4 as a reducing agent, was more optimal than the incorporation of Ni into the bulk of Al_2O_3 by simultaneous synthesis.

The potential of Pr as dopant was initially assessed by adding it to the catalyst in different orders. Adding Pr onto Al_2O_3 by direct reduction followed by adding Ni onto Pr/ Al_2O_3 yielded the highest ammonia conversion in the absence of a pre-treatment. However, adding Ni and Pr simultaneously in a single direct reduction step yielded the absolute highest ammonia conversion in the case of a H_2 reduction pre-treatment.

Further research determined that 5 % was the optimal Pr loading for catalysts made by directly reducing Ni onto Pr/ Al_2O_3 . Such catalysts performed slightly less well than Ni/ Al_2O_3 in 22h reaction cycles at temperatures increasing from 300 °C to 550 °C with a H_2 reduction pre-treatment. However, the opposite was true in the case of 62h catalytic tests at 550 °C with no pre-treatment.

In conclusion, Pr is a dopant which results in a slight improvement in the performance of the Ni/ Al_2O_3 catalysts under specific conditions. However, further research is required to truly identify the catalyst synthesis method using Pr which yields the best performance.

7. Perspectives

A great deal of experiments could have been carried through to provide more robust results and more accurate comparisons. Due to the relatively short duration of a master's thesis, those experiments could not be performed.

In the case that someone would take on the responsibility of furthering the research on the topic of ammonia decomposition over praseodymium-doped nickel catalysts, here are a few suggestions and advice based on what could have been improved during this research project.

Once the right Al_2O_3 formula had been identified, larger quantities of it should have been made in a single batch to make robust comparisons over the entirety of the project.

In some cases, the remaining quantity of sample was insufficient to perform N_2 physisorption characterisation. This wouldn't have occurred if more Al_2O_3 support had been available to make each catalyst in sufficient quantities to perform every required test.

Furthermore, in some cases, no robust N_2 physisorption data could be obtained due to leaks or measurement inefficiencies. Either the samples were not rerun after the failed test, or their textural properties simply weren't characterised at all. In all such cases, the limiting factor was time, even though experiments were performed intensely from early September through mid-May.

More H_2 -TPR could have been performed on the various catalyst samples. The *Support Synthesis Optimisation* section lacked this kind of information which could have been relevant.

$\text{Ni}/\text{Al}_2\text{O}_3$ Final could have been synthesised to accurately to compare its performance to the Pr-containing catalysts.

6 successive cycles could have been performed on a single sample of $20\%\text{Ni}5\%\text{Pr}/\text{Al}_2\text{O}_3$ Final to assess its reusability.

Long run tests could have been performed with a H_2 reduction pre-treatment for accurate comparison with cycles that were performed under such conditions.

$5\%\text{Pr}20\%\text{Ni Sim}/\text{Al}_2\text{O}_3$ could have been chosen as the candidate for testing different Pr loadings. It was only found out later in the research project that, when an H_2 reduction pre-treatment was performed, the performance of the catalyst was higher than $20\%\text{Ni}5\%\text{Pr}/\text{Al}_2\text{O}_3$.

Finally, a critical test that could not be performed is the integration of Pr into the bulk of Al_2O_3 by simultaneous sol-gel synthesis, followed by Ni direct reduction.

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9. Appendices

9.1. N₂ Physisorption from Pr Loading Optimisation

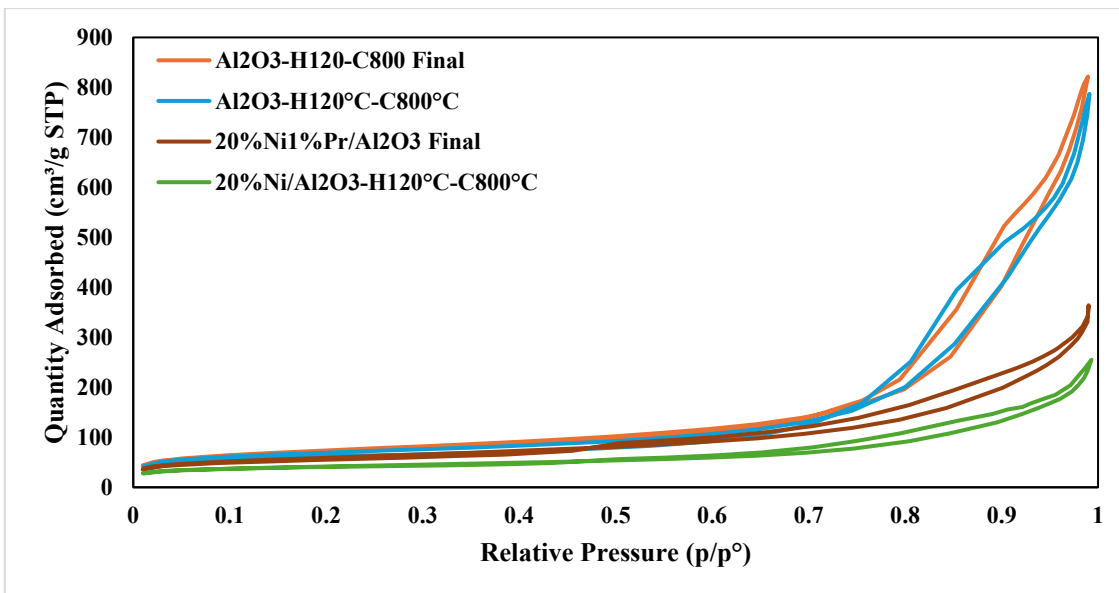


Figure 42: Isotherms of Al₂O₃, Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts.

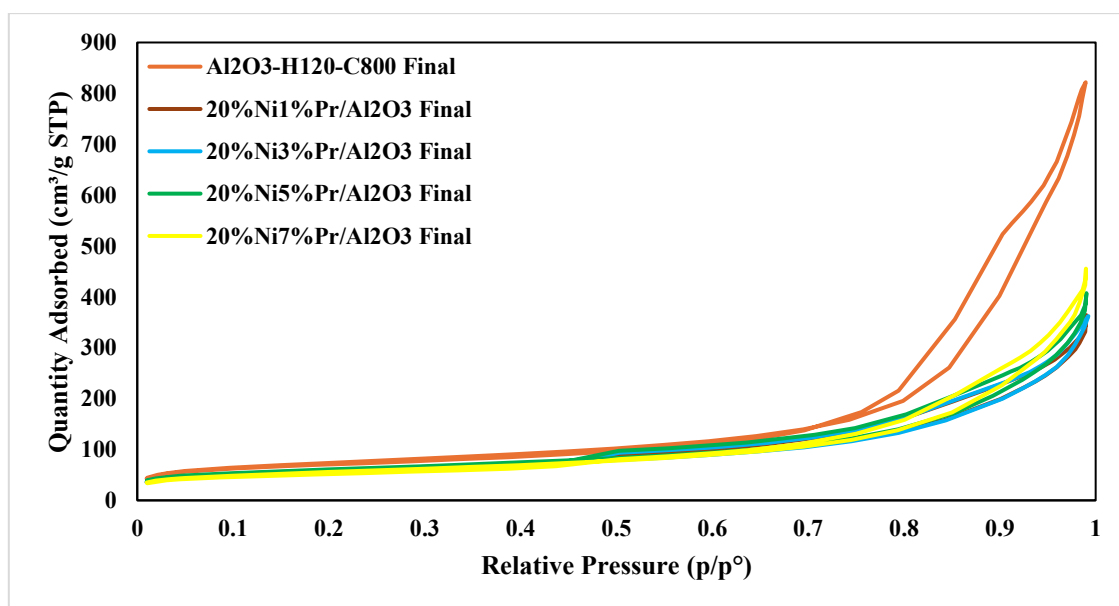


Figure 43: Isotherms of Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts with 1%, 3%, 5%, and 7%Pr loadings.

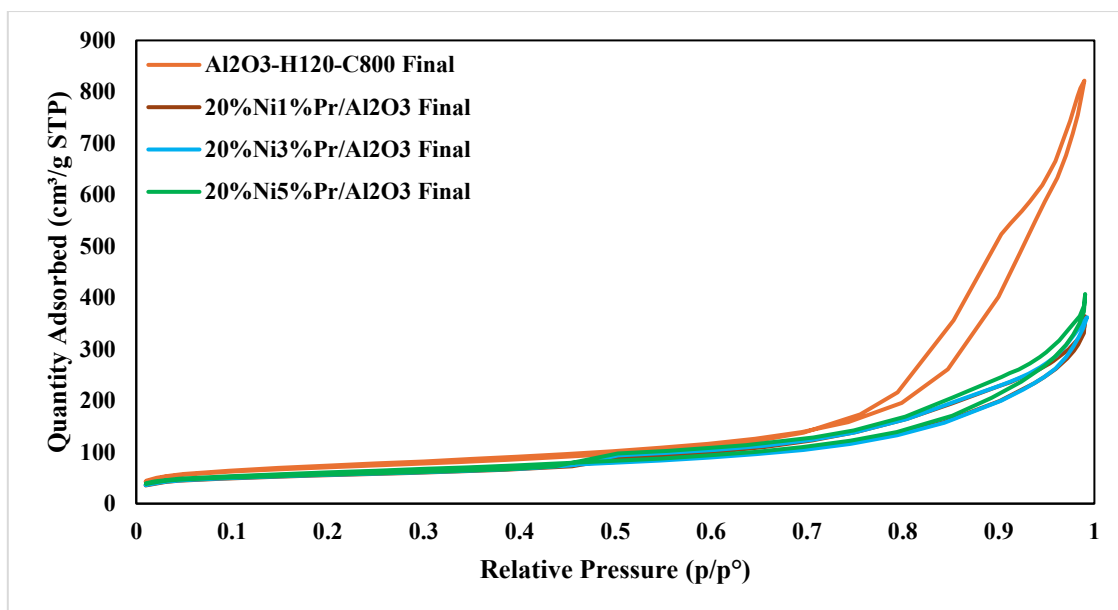


Figure 44: Isotherms of Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts with 1%, 3%, and 5%Pr loadings

9.2. XRD Diffractograms from Pr Loading

Optimisation

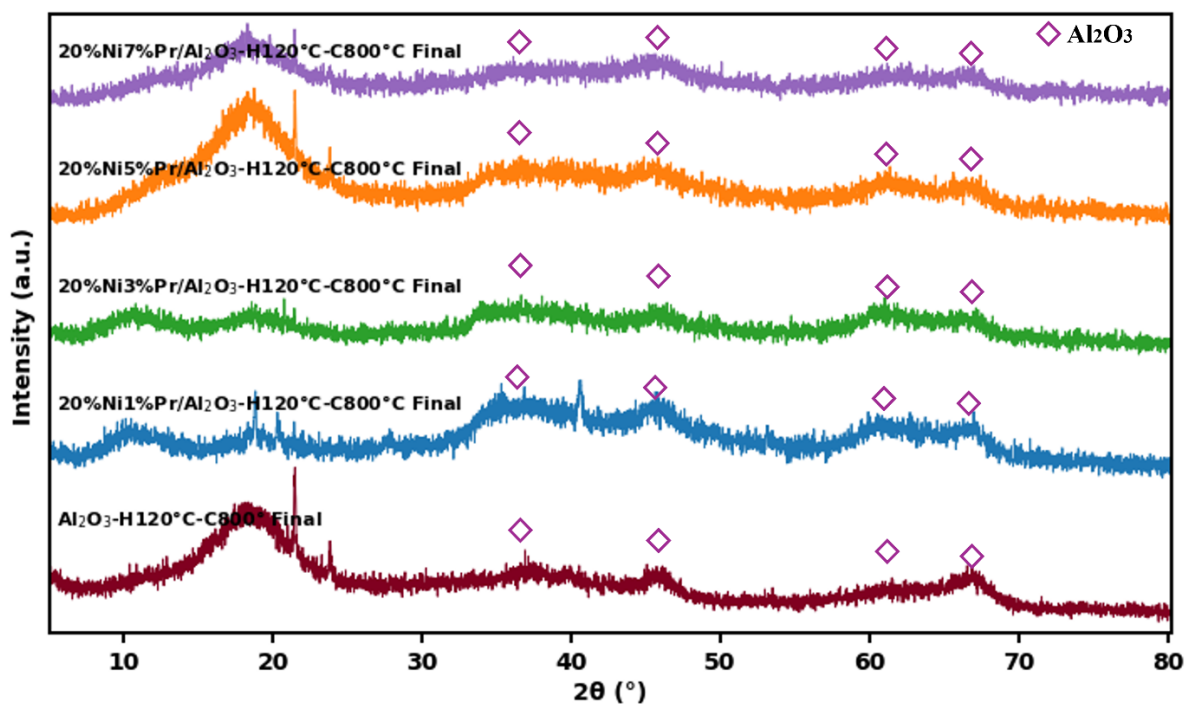


Figure 45: XRD diffractograms of Al₂O₃ and NiPr/Al₂O₃ catalysts with different loadings.

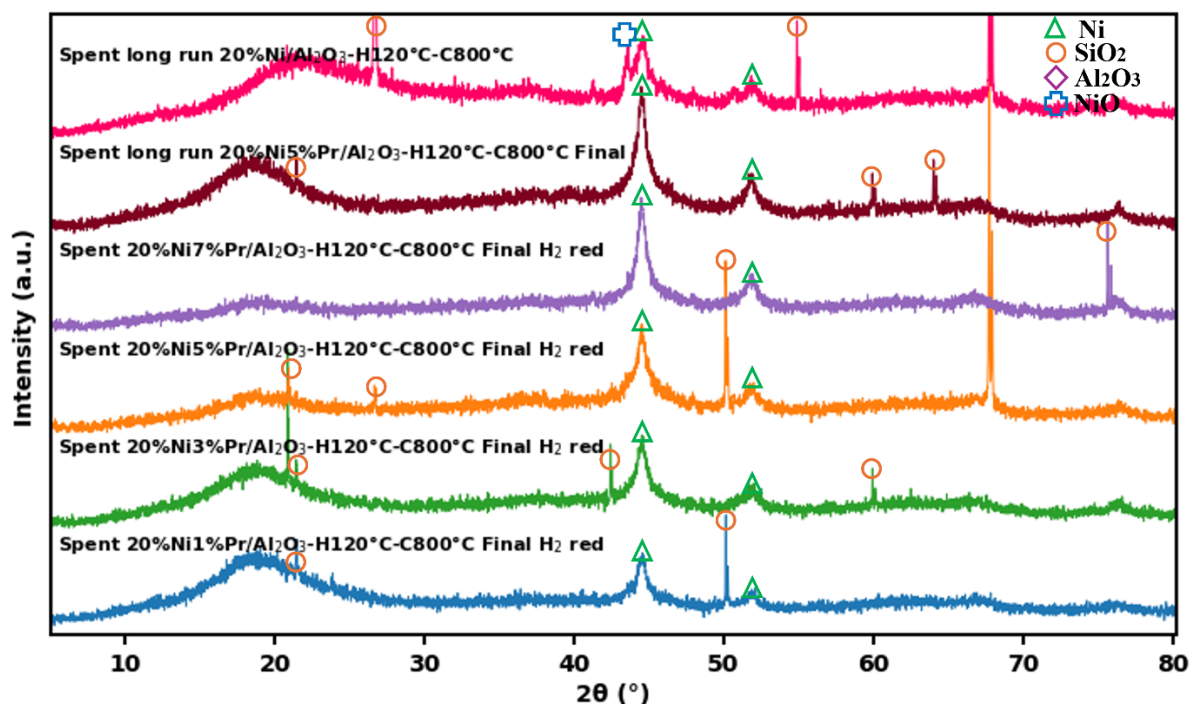


Figure 46: XRD diffractograms of spent Ni/Al₂O₃ and NiPr/Al₂O₃ catalysts with different loadings.

9.3. Catalytic Tests from Pr Loading Optimisation

Catalytic tests revealed that 20%Ni5%Pr/Al₂O₃ from the New batch performed less well (88%) than its counterpart from the Final batch (98.7%) at 550 °C after a H₂ reduction pre-treatment (Figure 47).

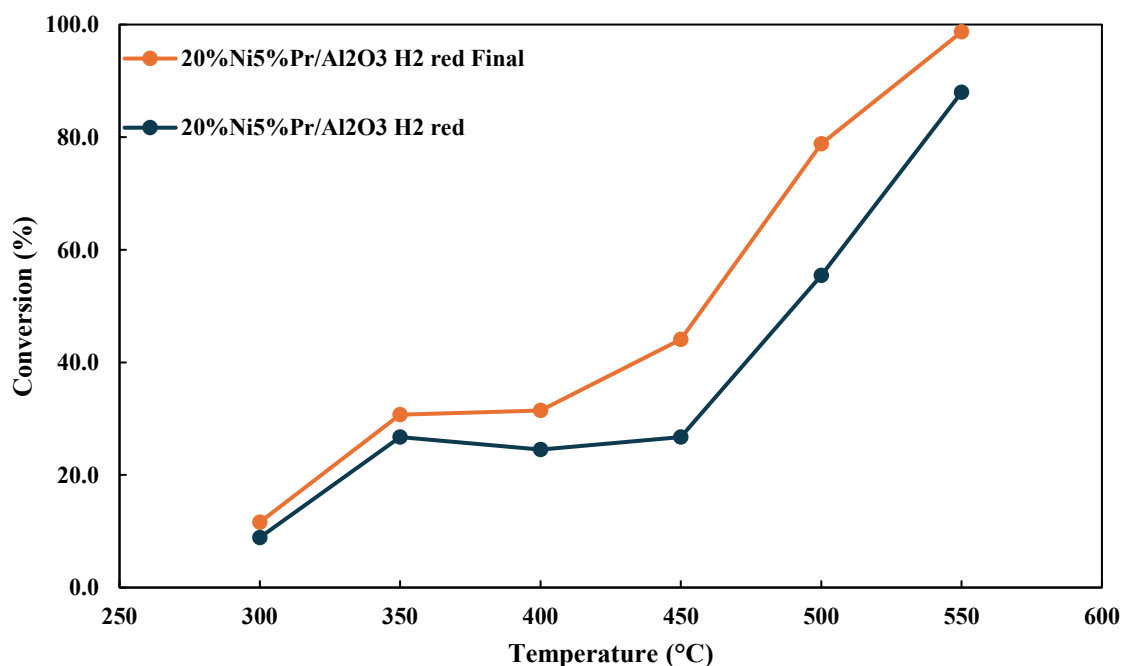


Figure 47: Catalytic tests with 2 NiPr/Al₂O₃ catalysts made using Al₂O₃ from different batches.

Ammonia decomposition over praseodymium-doped nickel catalysts

Ivaylo JANKOVSKI

This research project investigated catalysts to increase the conversion of ammonia into hydrogen at low temperatures. Ammonia can be produced from hydrogen in regions that possess the abundant and cheap renewable energy sources required to do so sustainably at scale. The low volumetric energy density of hydrogen makes it challenging to transport economically over long distances. Ammonia can be used as a hydrogen carrier thanks to its high energy density and a pre-existing infrastructure.

However, the decomposition of ammonia into hydrogen is an endothermic process. A catalyst is required to decrease the temperature at which this reaction is performed. Ni/Al₂O₃ catalysts are known to be effective and cheap catalysts to perform the ammonia decomposition reaction.

Rare earths, such as praseodymium, have the potential to improve the reaction mechanism at the rate determining step by acting as electron donors, and could improve the reducibility of Ni.

At first, Al₂O₃ was synthesised by a sol-gel process according to varying parameters to determine the most optimal settings for the ammonia decomposition reaction. Al₂O₃ with hydrothermal synthesis at 120 °C and calcination at 800 °C was found to yield the highest ammonia conversion at 550 °C.

Two Ni addition methods were evaluated. It was determined that direct reduction of Ni onto Al₂O₃, using NaBH₄ as a reducing agent, was more optimal than incorporation Ni into the bulk of Al₂O₃ by simultaneous synthesis.

The potential of Pr as dopant was initially assessed by adding it to the catalyst in different orders. Adding Pr onto Al₂O₃ by direct reduction followed by adding Ni onto Pr/Al₂O₃ yielded the highest ammonia conversion in the absence of a pre-treatment. However, adding Ni and Pr simultaneously in a single direct reduction step yielded the absolute highest ammonia conversion in the case of a H₂ reduction pre-treatment.

Further research determined that 5 % was the optimal Pr loading for catalysts made by directly reducing Ni onto Pr/Al₂O₃. Such catalysts performed slightly less well than Ni/Al₂O₃ in 22h reaction cycles at temperatures increasing from 300 °C to 550 °C with a H₂ reduction pre-treatment. However, the opposite was true in the case of 62h catalytic tests at 550 °C with no pre-treatment.

In conclusion, Pr is a dopant which results in a slight improvement in the performance Ni/Al₂O₃ catalysts under specific conditions. However, further research is required to truly identify the catalyst synthesis method using Pr which yield the best performance.