American Journal of Chemical Engineering
2025, Vol. 13, No. 4, pp. 76-82
https://doi.org/10.11648/j.ajche.20251304.11

Review Article

Ammonia Synthesis over an Iron Catalyst with an Inverse Structure: A Comprehensive Review

Tsiye Tekleyohanis Hailemariam*

Department of Chemical Engineering, Debre Berhan University, Deber Berhan, Ethiopia

Abstract

Ammonia synthesis is a cornerstone of the chemical industry, critical for fertilizer production and global food security. The Haber-Bosch process, relying heavily on iron-based catalysts, has been optimized over the decades. However, conventional catalysts still face limitations related to reaction conditions, energy efficiency, and catalyst deactivation. This review focuses on recent advances in inverse structured iron catalysts a novel configuration where the support encapsulates the active iron phase, reversing the conventional catalyst design. This inverse approach promises improved dispersion, enhanced surface properties, and increased resistance to sintering and poisoning. The review explores the synthesis methods, structural characterization, mechanistic insights, and catalytic performance of inverse iron catalysts, comparing them with traditional systems. Finally, it addresses current challenges and outlines future directions in the development of sustainable and efficient ammonia synthesis technologies.

Keywords

Ammonia Synthesis, Inverse Catalyst, Iron Catalyst, Core-Shell Structure, Haber-Bosch, Catalytic Efficiency, Nitrogen Fixation, Catalyst Design

1. Introduction

Ammonia synthesis plays a critical role in modern industry, serving as the foundation for global fertilizer production and indirectly supporting global food security. The process is primarily carried out through the Haber-Bosch method, which has remained the industrial standard for over a century. This method facilitates the reaction between nitrogen and hydrogen gases to form ammonia, an essential compound used in agriculture, pharmaceuticals, and various chemicals [1].

The Haber-Bosch process, though highly effective, is energy-intensive and environmentally impactful. It accounts for approximately 1-2% of global energy consumption and is responsible for a notable share of industrial carbon emissions. A major factor contributing to this energy demand is the extreme reaction conditions required typically temperatures of 400-500 ℃ and pressures of 150-300 atmospheres. These harsh conditions are necessary due to the strong triple bond in nitrogen (N≡N), which makes its activation and subsequent conversion challenging [2].

Traditionally, the catalyst used in this process is magnetite-based iron (Fe_3O_4), promoted with materials such as potassium and alumina to enhance performance. These catalysts, while robust and cost-effective, often suffer from limitations such as sintering, deactivation by poisons, and poor performance under milder reaction conditions. Over time, these

*Corresponding author: tsiye.tekleyohanis2005@gmail.com (Tsiye Tekleyohanis Hailemariam)

Received: 15 July 2025; **Accepted:** 25 July 2025; **Published:** 13 August 2025

issues reduce their effectiveness and increase the cost and environmental burden associated with their use [3].

In recent years, researchers have focused on improving catalyst performance by exploring advanced designs, among which the "inverse catalyst structure" has garnered considerable attention. Unlike conventional catalysts, where metal particles sit atop support materials, inverse catalysts encapsulate the active metal (e.g., iron) within a permeable oxide shell or matrix. This inversion offers several potential benefits, including enhanced metal-support interaction, improved resistance to sintering and deactivation, and better control over surface chemistry [4].

The adoption of inverse catalyst structures in ammonia synthesis offers the possibility of operating the process at lower temperatures and pressures, thus reducing energy consumption and associated emissions. Additionally, the improved stability and performance of these catalysts may extend their lifespan and minimize downtime in industrial operations. While challenges remain in synthesizing these catalysts at scale and understanding their long-term behavior, the inverse catalyst design represents a promising frontier in the pursuit of greener, more efficient ammonia production technologies [5].

2. Conventional Iron Catalysts: A Brief Overview

Iron-based catalysts are the cornerstone of the Haber-Bosch process, which is the dominant method for industrial ammonia synthesis. These catalysts are primarily composed of iron (Fe), typically derived from magnetite (Fe_3O_4), and are promoted with small amounts of potassium (K), aluminum oxide (Al_2O_3), and calcium oxide (CaO). The promoters serve specific functions: potassium enhances electron donation to nitrogen molecules, aluminum oxide stabilizes the catalyst structure, and calcium oxide improves sintering resistance. These components are generally supported on porous materials to increase the active surface area available for the reaction [5].

The catalytic process operates through a mechanism called dissociative adsorption, where nitrogen molecules (N_2) from the gas phase adsorb onto the catalyst surface and are split into individual nitrogen atoms. This is the most energy-intensive and rate-limiting step in ammonia synthesis due to the exceptionally strong triple bond (N≡N) that requires significant activation energy to break. Once dissociated, the nitrogen atoms react with adsorbed hydrogen to gradually form ammonia (NH_3), which then desorbs from the surface [6].

Despite their widespread industrial use, conventional iron catalysts suffer from several inherent limitations. One major issue is sintering, the agglomeration of iron particles at high temperatures, which reduces the catalyst's active surface area and thus its effectiveness. This leads to a decline in catalytic activity over time, requiring more frequent regeneration or replacement of the catalyst bed—an economically and operationally undesirable scenario [7].

Another challenge is catalyst poisoning, especially by impurities such as sulfur, oxygen, and water vapor in the feed gases. These contaminants bind strongly to the active iron sites, effectively blocking them from participating in the reaction. Even trace amounts of these poisons can significantly reduce catalyst performance, making feedstock purification a critical step in the process. Poisoning not only lowers activity but also accelerates catalyst deactivation [8].

Additionally, traditional iron catalysts have limited surface area, which restricts the number of active sites available for nitrogen and hydrogen interaction. Although promoters and porous supports help mitigate this issue to some extent, they do not completely overcome the fundamental limitations of the catalyst structure. These challenges underscore the need for innovative catalyst designs, such as inverse structures, that offer enhanced surface properties, improved resistance to deactivation, and superior catalytic efficiency under milder operational conditions [9].

3. Concept of Inverse Catalyst Structures

Inverse catalysts represent a significant departure from conventional catalyst architecture in heterogeneous catalysis. In traditional systems, metal nanoparticles are dispersed on the surface of oxide supports, such as alumina or silica, with the support serving primarily as a structural scaffold. However, in inverse catalysts, this arrangement is reversed: the active metal core, such as iron, is encapsulated within a thin, permeable oxide or support shell. This innovative structure provides unique physicochemical properties that can significantly enhance catalytic performance [10].

One of the key advantages of the inverse catalyst design is the enhanced interaction between the metal and the support. The encapsulating shell facilitates more uniform and intimate contact at the metal-support interface, allowing for improved charge transfer and modification of surface energy states. These interactions can lead to better activation of reactant molecules—such as nitrogen and hydrogen in ammonia synthesis—by optimizing adsorption and reaction pathways on the catalyst surface [11].

Another notable benefit of the inverse structure is protection against agglomeration and thermal degradation. High-temperature industrial processes like the Haber-Bosch reaction often cause sintering, where metal particles fuse together, reducing catalytic surface area. Inverse catalysts counter this problem by physically isolating metal cores within a protective shell, thereby maintaining particle dispersion and extending catalyst life, especially under harsh operating conditions [12].

Additionally, inverse catalysts allow for the modulation of electronic and adsorption properties. The nature and thickness of the oxide layer can be engineered to fine-tune electron density around the metal center. This in turn can influence the

adsorption strength and reaction kinetics of nitrogen and hydrogen species, crucial in determining the rate and efficiency of ammonia formation. The ability to modify these properties offers a pathway to operate under milder reaction conditions, reducing energy consumption [13].

Finally, the inverse catalyst structure offers controlled exposure of active sites, which is essential for both activity and selectivity. By designing the shell to be permeable or porous, reactant gases can diffuse through to reach the active metal core, while still limiting access of contaminants or poisons. This selective accessibility enhances the catalyst's resistance to deactivation and can also improve product yield. Overall, the inverse iron catalyst architecture offers a promising solution to overcome the limitations of traditional catalyst systems, pushing forward the development of more efficient and sustainable ammonia synthesis technologies [14].

4. Synthesis Methods for Inverse Iron Catalysts

The synthesis of inverse iron catalysts has garnered significant attention in recent years due to their potential to enhance ammonia synthesis efficiency. A key aspect of their performance lies in the method used to prepare them. Unlike conventional catalysts, inverse structures require precise control over the encapsulation of the active metal by a supporting shell. Several advanced techniques have been developed and optimized to achieve the desired core-shell architecture with appropriate porosity and structural integrity [15].

One widely used method is Atomic Layer Deposition (ALD), which allows for the layer-by-layer growth of a thin oxide shell around iron nanoparticles. ALD offers exceptional control over shell thickness and uniformity, ensuring that the iron core is evenly encapsulated while maintaining permeability for reactant gases. This technique also enables fine-tuning of surface properties, which is crucial for optimizing catalytic activity and stability under industrial conditions [16].

Another effective approach involves template-assisted synthesis, where iron nanoparticles are embedded in a templating matrix. After forming the shell structure, the template is selectively removed, leaving behind a porous oxide shell surrounding the iron core. This method is advantageous for creating well-defined pore networks that facilitate gas diffusion while protecting the active metal from sintering and poisoning [17].

Sol-gel encapsulation is another popular strategy, which involves hydrolysis and condensation of metal alkoxides in the presence of iron particles. This process forms a gel-like network that solidifies into a porous oxide shell upon drying and calcination. Sol-gel techniques are relatively simple and cost-effective, offering good control over the chemical composition and microstructure of the shell, though they may require post-treatment to optimize porosity and stability [18].

Lastly, precursor-controlled pyrolysis involves using a single-source precursor that contains both the metal and the support material in a chemically bonded form. Upon thermal treatment, the precursor decomposes to form the desired inverse structure. This method enables intimate mixing of components at the molecular level and can yield high-performance catalysts with strong metal-support interactions. However, controlling the final structure depends heavily on the choice of precursor and pyrolysis conditions [19].

In all these synthesis routes, the choice of parameters such as temperature, atmosphere, precursor concentration, and calcination time plays a critical role in determining the final properties of the catalyst. Shell porosity, thickness, and permeability are particularly important, as they directly affect reactant diffusion, accessibility to the active sites, and overall catalytic performance. Optimizing these parameters is essential for developing efficient and durable inverse iron catalysts for industrial ammonia synthesis [20].

5. Characterization of Inverse Structures

Analyzing inverse catalysts requires advanced characterization techniques to fully understand their structure, composition, and behavior under reaction conditions. Given their unique architecture where an active metal core is encapsulated within an oxide or support shell it is crucial to use tools that can resolve nanoscale features and capture both static and dynamic properties. These analyses are essential for verifying successful synthesis and optimizing performance for ammonia synthesis and other catalytic processes [21].

Transmission Electron Microscopy (TEM) is one of the most powerful tools for characterizing inverse catalysts. It allows direct visualization of the core-shell morphology, confirming the encapsulation of iron nanoparticles by the oxide layer. High-resolution TEM can also provide information about the crystallinity, particle size distribution, and interface between the core and the shell. These details are critical in evaluating the structural integrity and consistency of the synthesized catalysts [22].

X-ray Photoelectron Spectroscopy (XPS) is widely employed to analyze the surface composition and oxidation states of the elements present in the catalyst. Since the catalytic activity is heavily influenced by the chemical environment at the surface, XPS provides valuable insights into electronic interactions between the iron core and the surrounding shell. Changes in binding energies can reveal charge transfer processes and identify surface species that contribute to or inhibit catalytic function [23].

To assess the surface area and porosity, Brunauer-Emmett-Teller (BET) surface area analysis is used. This technique is important for determining how accessible the active sites are to reactant gases like nitrogen and hydrogen. A well-designed inverse catalyst should maintain a high surface area and optimal pore size distribution to allow efficient gas

diffusion through the shell and into the reactive core. BET analysis also helps correlate textural properties with catalytic performance [24].

Finally, in situ and operando spectroscopic techniques, such as Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and X-ray Absorption Spectroscopy (XAS), are employed to gain real-time mechanistic insights during the catalytic reaction. These tools allow researchers to monitor surface intermediates, oxidation states, and changes in coordination environments under actual reaction conditions. Understanding the dynamic behavior of inverse catalysts under working environments is crucial for improving their design and stability [25].

In summary, a combination of structural, chemical, and in situ analytical techniques is essential to comprehensively evaluate inverse iron catalysts. These methods not only confirm the successful synthesis of core-shell architectures but also provide critical information on how these materials behave during ammonia synthesis. Such multi-faceted analysis guides further optimization and development of next-generation catalysts with improved efficiency and durability [26].

6. Catalytic Performance and Reaction Mechanism

Inverse iron catalysts have demonstrated remarkable performance improvements over conventional iron-based catalysts in ammonia synthesis. One of the most significant advantages is their ability to lower the activation energy required for nitrogen (N_2) dissociation, which is the rate-limiting step in the Haber-Bosch process. The altered surface electronic structure created by the intimate contact between the iron core and the oxide shell promotes more efficient nitrogen activation, thereby enhancing the overall reaction rate under milder operating conditions [27].

Another key benefit is the increased turnover frequency (TOF), which measures the number of ammonia molecules produced per active site per unit time. Inverse catalysts exhibit higher TOF compared to traditional iron catalysts, largely due to improved accessibility of reactive sites and the favorable metal-support interactions that modulate adsorption energies. This translates into higher catalytic efficiency and greater ammonia yield, even at reduced pressures and temperatures [28].

Resistance to sintering and poisoning is also significantly improved in inverse catalyst structures. The oxide shell acts as a physical barrier, minimizing the mobility and aggregation of iron nanoparticles, which is a common problem at high operating temperatures. Moreover, the encapsulating layer helps shield the active sites from impurities such as sulfur or oxygen that could otherwise bind irreversibly and deactivate the catalyst. This enhanced durability reduces the need for frequent regeneration or replacement [18].

Another advantage lies in the improved recyclability and long-term stability of inverse catalysts. Their robust structure allows them to retain catalytic activity over multiple reaction cycles, even under thermally harsh conditions. The shell design also ensures that the catalyst maintains its structural and functional integrity over time, which is critical for continuous industrial-scale ammonia production [8].

Finally, the selective diffusion properties of the oxide shell further optimize catalyst performance. The shell is designed to be permeable to small reactant molecules like N_2 and H_2, while restricting the diffusion of larger or harmful species. This controlled access not only protects the active sites but also contributes to consistent catalytic behavior over extended operation. In sum, inverse iron catalysts offer a superior combination of activity, durability, and efficiency, positioning them as a promising alternative to conventional systems for sustainable ammonia synthesis [17].

7. Comparative Analysis with Conventional Catalysts

Table 1. *Comparative Analysis with Conventional Catalysts [7].*

Feature	Traditional Iron Catalyst	Inverse Iron Catalyst
Surface Area	Traditional iron catalysts typically have a moderate surface area, often limited by particle agglomeration and sintering over time. The active iron sites are generally exposed on porous supports but can become less accessible due to catalyst degradation and surface restructuring during operation.	Inverse iron catalysts have the potential for higher surface area due to their unique core-shell architecture. The encapsulating oxide shell can be engineered with controlled porosity, preserving nanoparticle dispersion and preventing agglomeration. This enhances the accessible active surface area, improving reactant adsorption and catalytic turnover.
Sintering Resistance	Traditional catalysts suffer from moderate resistance to sintering. Under the harsh high-temperature conditions of ammonia synthesis, iron nanoparticles tend to grow and aggregate, reducing active surface sites and lowering catalyst effectiveness over time.	Inverse catalysts exhibit high sintering resistance as the oxide shell physically confines the iron core, preventing nanoparticle migration and growth. This encapsulation significantly improves thermal stability, maintaining catalytic activity even after prolonged exposure to elevated temperatures.

Feature	Traditional Iron Catalyst	Inverse Iron Catalyst
Poison Resistance	The susceptibility to poisoning by impurities such as sulfur or oxygen is a notable limitation of traditional iron catalysts. These contaminants adsorb strongly on active sites, leading to irreversible deactivation and frequent catalyst regeneration or replacement.	Inverse catalysts offer improved poison resistance because the protective shell acts as a selective barrier, reducing direct exposure of active iron sites to contaminants. This selective permeability extends catalyst life and reduces downtime due to poisoning effects.
Catalyst Lifetime	Due to sintering, poisoning, and structural degradation, traditional iron catalysts typically have a limited operational lifetime, necessitating periodic regeneration and replacement that increase operational costs.	The enhanced stability and protective encapsulation confer prolonged catalyst lifetime in inverse catalysts. The structural integrity and resistance to deactivation mechanisms translate into sustained activity over many reaction cycles, improving process economics and reliability.
Reaction Conditions	Traditional catalysts require high temperatures (400-500 ℃) and high pressures (150-300 atm) to achieve sufficient ammonia synthesis rates, which contributes to significant energy consumption and capital costs.	Inverse catalysts enable ammonia synthesis at potentially milder conditions by lowering the activation barrier for nitrogen dissociation and enhancing catalytic efficiency. This can reduce energy inputs and improve overall process sustainability.
Cost	Manufacturing traditional iron catalysts is generally low cost, benefiting from established production methods, inexpensive raw materials, and wide industrial experience.	The complexity of synthesizing inverse catalysts due to advanced techniques like atomic layer deposition or sol-gel encapsulation and the need for high-purity materials result in moderate costs. However, these costs could be offset by improved performance and longevity.

8. Challenges and Limitations

While inverse structured iron catalysts offer significant advantages for ammonia synthesis, they are not without challenges. One of the most pressing issues is scalability in synthesis. Many of the techniques used to produce these catalysts such as atomic layer deposition (ALD), sol-gel encapsulation, or template-assisted methods are inherently complex, time-consuming, and resource-intensive. Scaling these processes from laboratory to industrial scale without compromising structural uniformity and performance remains a major hurdle [7].

Another persistent difficulty lies in the precise control of shell porosity and thickness. The encapsulating layer must strike a delicate balance: it must be thick enough to protect the iron core from sintering and poisoning, yet porous enough to allow unhindered diffusion of nitrogen and hydrogen molecules to the active sites. Achieving this level of control consistently across large catalyst batches is technically challenging and affects catalyst reproducibility and performance uniformity [8].

Moreover, there is still a limited understanding of long-term deactivation mechanisms in inverse catalysts. While early studies show improved stability, the exact factors that contribute to gradual loss of activity over extended cycles such as structural collapse, pore blockage, or subtle changes in electronic properties are not fully understood. This gap in knowledge hinders the ability to predict lifespan and to engineer catalysts for prolonged industrial use with confidence [9].

Material compatibility and cost are also key concerns, especially when considering integration into existing industrial processes. Some of the oxides or precursors used in inverse structures may not align with the harsh operating environments or with current reactor designs. Additionally, high-purity precursors and sophisticated synthesis techniques can drive up costs, making these catalysts less economically viable unless performance gains are substantial enough to justify the investment [10].

In summary, while inverse iron catalysts hold strong potential for revolutionizing ammonia synthesis through enhanced efficiency and stability, they face significant barriers that must be addressed for industrial adoption. Future research should focus not only on improving catalytic performance but also on developing scalable, cost-effective synthesis methods, enhancing understanding of degradation pathways, and optimizing shell structures for both function and durability. Overcoming these obstacles is essential to realize the full potential of inverse catalyst technologies on a commercial scale [11].

9. Future Outlook and Research Directions

To complement design advancements, operando spectroscopic studies are becoming increasingly valuable for unraveling the real-time behavior of inverse catalysts under reaction conditions. Techniques such as operando DRIFTS, XAS, and environmental TEM enable researchers to observe structural and electronic changes, identify active sites, and monitor deactivation mechanisms. These insights are essential for guiding rational catalyst improvement and for validating

theoretical predictions with practical data [12].

Another critical area is the integration of inverse catalysts with green hydrogen sources, such as those derived from water electrolysis powered by renewable energy. By coupling high-performance inverse catalysts with sustainable hydrogen inputs, it becomes possible to realize low-carbon or even carbon-neutral ammonia production. This aligns with global goals for decarbonizing the chemical industry and reducing the environmental footprint of fertilizer and energy sectors [13].

Innovative materials development is also on the horizon, particularly through the design of hybrid catalysts that combine inverse structures with promoters like ruthenium (Ru), molybdenum (Mo), or alkali metals. These combinations can enhance nitrogen activation, modify adsorption properties, and further reduce operating pressures and temperatures. The synergistic effects of promoters with the inverse core shell design offer a versatile platform for tuning performance across a range of operating conditions [14].

Finally, successful transition to industrial application will require comprehensive life cycle and techno-economic assessments. These evaluations help quantify the environmental and economic benefits of inverse catalysts compared to conventional systems. They also guide process engineers and decision-makers in identifying the most viable implementation strategies, considering factors such as raw material availability, energy consumption, scalability, and end-of-life recyclability [15].

10. Conclusion

Inverse structured iron catalysts represent a transformative advancement in the field of ammonia synthesis, addressing long-standing limitations of conventional catalysts used in the Haber-Bosch process. Traditional iron-based systems require high temperatures and pressures due to the challenging dissociation of the nitrogen molecule (N≡N bond). In contrast, inverse catalysts comprising an iron core encapsulated by a thin, porous oxide or support shell offer improved performance by modulating surface electronic properties and enhancing metal-support interactions. These features lead to lower activation energy for nitrogen dissociation, higher turnover frequency, and enhanced resistance to sintering and poisoning.

The encapsulating layer not only protects the active iron sites from agglomeration and degradation but also allows selective diffusion of reactants, thus preserving activity over longer operational periods. Additionally, inverse catalysts exhibit greater structural stability and recyclability, which are critical for long-term industrial use. Despite these advantages, challenges remain. Synthesizing inverse catalysts at scale with controlled porosity and shell thickness is complex, and the long-term deactivation mechanisms under industrial conditions are not yet fully understood. Furthermore, issues related to material cost, compatibility with existing reactors, and process economics must be addressed.

To fully realize the potential of inverse iron catalysts, interdisciplinary collaboration is essential. Advancements in materials science can lead to more robust synthesis methods and hybrid designs incorporating promoters. Surface chemistry offers insights into reaction mechanisms and deactivation pathways, while process engineering ensures the integration of these materials into scalable, energy-efficient systems. Emerging tools such as machine learning, operando spectroscopy, and life-cycle assessment will further accelerate innovation and commercialization. With continued research and development, inverse structured iron catalysts could become a cornerstone of next-generation, sustainable ammonia production technologies, significantly reducing energy consumption and environmental impact while meeting growing global demand.

Abbreviations

ALD	Atomic Layer Deposition
BET	Brunauer-Emmett-Teller
CaO	Calcium Oxide
CeO_2	Cerium Dioxide
CLO	Course Learning Outcome *(if used in teaching contexts, mentioned elsewhere)*
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
Fe	Iron
$Fe@Al_2O_3$	Iron Encapsulated in Alumina
$Fe@CeO_2$	Iron Encapsulated in Ceria
Fe_3O_4	Magnetite (Iron Oxide)
H_2	Hydrogen
JACS	Journal of the American Chemical Society
K	Potassium
LiH	Lithium Hydride
MXenes	Transition Metal Carbides/Nitrides
N_2	Nitrogen
NH_3	Ammonia
N≡N	Triple Bond in Nitrogen Molecule
Ru	Ruthenium
SMSI	Strong Metal-Support Interaction
TEM	Transmission Electron Microscopy
TOF	Turnover Frequency
XAS	X-ray Absorption Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
ZrO_2	Zirconium Dioxide

Author Contributions

Tsiye Tekleyohanis Hailemariam is the sole author. The author read and approved the final manuscript.

Conflicts of Interest

The author declares no conflicts of interest.

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