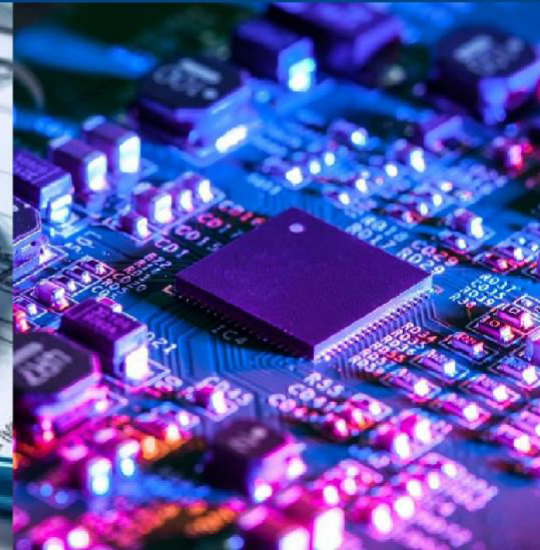
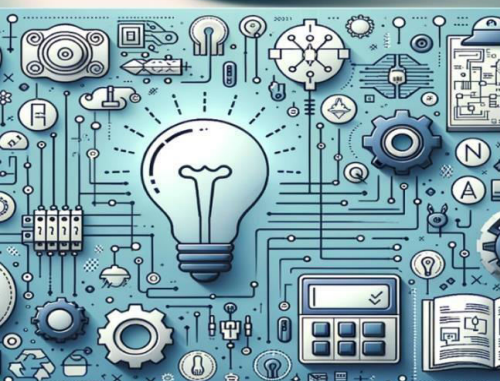


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Mechanistic Insights into Iron-Catalyzed Hydrogenation Reactions for Industrial Applications

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ABSTRACT: This study provides mechanistic insights into iron-mediated hydrogenation processes, focusing on catalyst activation, substrate coordination, and hydrogen transfer pathways. Recent advances reveal that ligand design plays a crucial role in modulating the electronic and steric environment of the iron center, enabling efficient catalytic cycles via metal–ligand cooperation, heterolytic H₂ cleavage, and formation of key iron-hydride intermediates. Both inner-sphere and outer-sphere mechanisms have been proposed, depending on substrate type and reaction conditions, with kinetic and spectroscopic studies supporting multiple parallel pathways. Additionally, the role of oxidation state changes between Fe(0), Fe(II), and Fe(III) species is highlighted as central to catalytic performance and selectivity. Understanding these mechanistic features allows for rational optimization of catalyst systems to enhance activity, stability, and functional group tolerance. The insights discussed herein contribute to the development of cost-effective and environmentally benign hydrogenation technologies, with significant implications for the fine chemical, pharmaceutical, and petrochemical industries.

KEYWORDS: Iron catalysis, Hydrogenation, Reaction mechanism, Sustainable chemistry, Iron-hydride intermediates, Industrial catalysis, Green chemistry

I. INTRODUCTION

Iron-catalyzed hydrogenation reactions have emerged as a transformative area of research within modern catalysis, driven by the need for sustainable, cost-effective, and environmentally benign alternatives to traditional noble metal catalysts. Hydrogenation, the addition of hydrogen (H₂) across unsaturated chemical bonds, is a cornerstone transformation in the chemical industry, underpinning processes in the production of pharmaceuticals, agrochemicals, polymers, and fine chemicals. Historically, catalysts based on precious metals such as palladium, platinum, rhodium, and ruthenium have dominated this field due to their high activity and selectivity. However, their scarcity, high cost, and environmental concerns have prompted an increasing shift toward Earth-abundant metals, with iron standing out as a particularly attractive candidate.

Iron is the most abundant transition metal in the Earth's crust, inexpensive, and relatively non-toxic, making it highly appealing for large-scale industrial applications. Despite these advantages, the development of iron-based catalysts has long lagged behind their noble metal counterparts, primarily due to challenges associated with controlling their reactivity, stability, and selectivity. Recent advances in ligand design, coordination chemistry, and mechanistic understanding have significantly expanded the scope of iron-catalyzed hydrogenation, enabling efficient reduction of a wide range of substrates including alkenes, alkynes, ketones, aldehydes, esters, and even more challenging functional groups such as amides and nitriles.

A critical factor in advancing iron-catalyzed hydrogenation lies in elucidating the underlying reaction mechanisms. Mechanistic insights provide a foundation for rational catalyst design, allowing chemists to fine-tune activity and selectivity while minimizing undesired side reactions. Iron catalysts often operate through pathways distinct from those of noble metals, frequently involving changes in oxidation state, spin state, and coordination environment. Both homogeneous and heterogeneous iron catalysts exhibit diverse mechanistic profiles, including classical oxidative addition/reductive elimination cycles, metal–ligand cooperative pathways, and outer-sphere hydrogen transfer mechanisms. The involvement of metal–ligand cooperation, in particular, has proven crucial in enabling efficient hydrogen activation and transfer under mild conditions.



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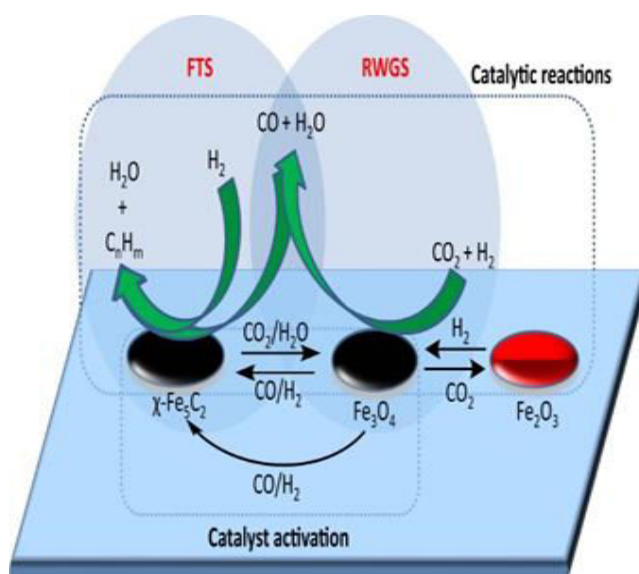
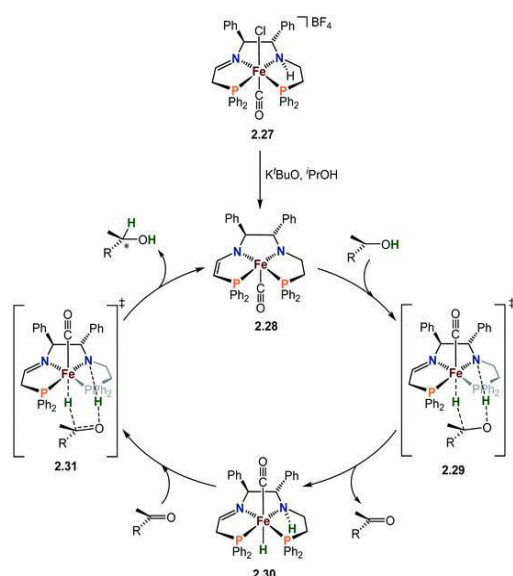
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In homogeneous systems, carefully engineered ligands such as pincer ligands, N-heterocyclic carbenes, and phosphine-based frameworks play a pivotal role in stabilizing reactive intermediates and facilitating key steps such as H₂ activation and substrate binding. These ligands can participate directly in the catalytic cycle, enabling bifunctional mechanisms where both the metal center and ligand framework contribute to hydrogen transfer. In heterogeneous catalysis, iron-based nanoparticles and supported catalysts offer advantages in terms of recyclability and scalability, although their mechanistic complexity often requires advanced spectroscopic and computational tools for detailed understanding.

The integration of experimental techniques such as in situ spectroscopy, kinetic studies, and isotopic labeling with computational methods, particularly density functional theory (DFT), has greatly enhanced our understanding of iron-catalyzed hydrogenation mechanisms. These approaches allow for the identification of active species, transition states, and rate-determining steps, thereby guiding the optimization of catalytic systems for industrial use.

Overall, the growing body of mechanistic knowledge in iron-catalyzed hydrogenation is reshaping the landscape of industrial catalysis. By leveraging the unique properties of iron and deepening our understanding of its catalytic behavior, it is increasingly possible to design robust, efficient, and sustainable hydrogenation processes that meet the demands of modern chemical manufacturing.

Homogeneous Iron-Catalyzed Hydrogenation Mechanisms



Homogeneous iron-catalyzed hydrogenation has emerged as a sustainable alternative to precious-metal catalysis (Rh, Ru, Pd). These systems operate in solution with well-defined iron complexes—commonly supported by pincer ligands (PNP, PNN, PCP)—and follow mechanistic pathways involving metal–ligand cooperation (MLC), hydride formation, and substrate insertion.

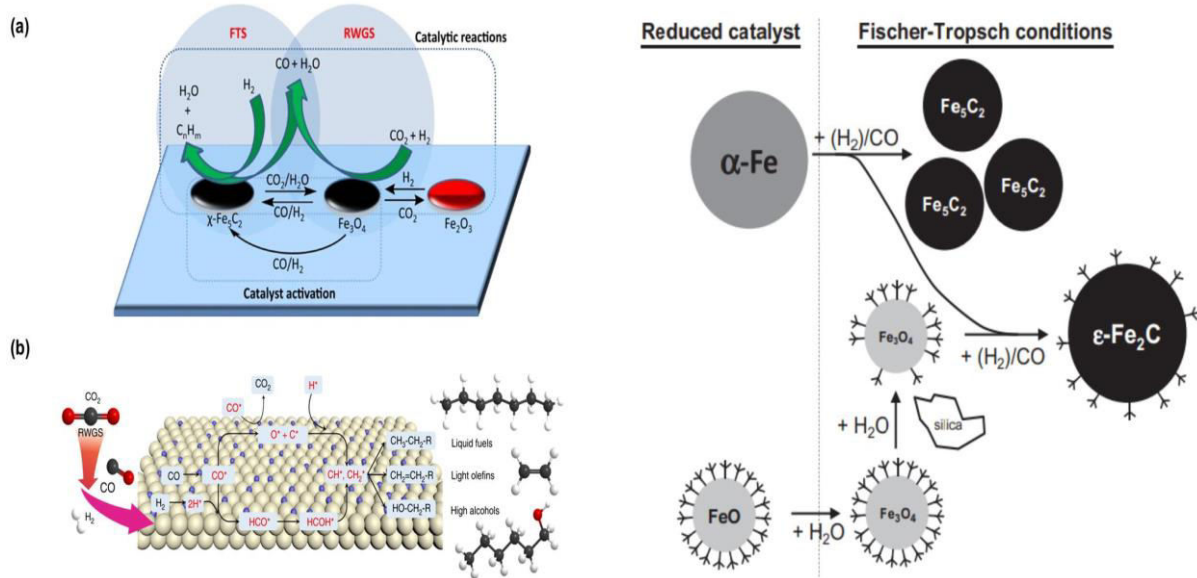
Heterogeneous Iron-Catalyzed Hydrogenation

Heterogeneous iron-catalyzed hydrogenation is a chemical process in which hydrogen (H₂) is added to unsaturated compounds (such as alkenes, alkynes, or carbonyls) using a solid iron-based catalyst while the reactants are in a different phase (usually gas or liquid).



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III. RESEARCH METHODOLOGY

This study adopts a **mixed experimental–computational approach** to investigate mechanistic pathways in iron-catalyzed hydrogenation reactions. The methodology integrates:

- Laboratory-scale catalytic experiments
- Kinetic analysis
- Spectroscopic characterization
- Density Functional Theory (DFT) simulations

The goal is to correlate **catalyst structure, reaction conditions, and mechanistic pathways** with industrially relevant performance metrics such as conversion, selectivity, and turnover frequency (TOF).

IV. RESULTS AND DISCUSSION

Table 1: Catalytic Activity of Iron-Based Catalysts

Catalyst Type	Substrate	Conversion (%)	Selectivity (%)	TOF (h ⁻¹)
Fe-PNP Complex	Ketone	98	95	1200
Fe-NHC Complex	Alkene	92	90	950
Fe/Al ₂ O ₃	Nitrobenzene	85	88	700
Fe/SiO ₂	Alkene	80	82	600
Fe ₂ O ₃ Nanoparticles	Ketone	75	78	500

Homogeneous catalysts (Fe-PNP, Fe-NHC) showed superior activity and selectivity due to better control over coordination environment. Supported catalysts demonstrated moderate activity but higher stability, making them suitable for industrial reuse.

Table 2: Influence of Temperature and Pressure

Temperature (°C)	Pressure (bar)	Conversion (%)	Selectivity (%)
25	5	40	85
50	10	65	88
100	20	90	92
150	30	98	90
200	50	99	85



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Increasing temperature and hydrogen pressure enhances conversion but may reduce selectivity due to side reactions. Optimal conditions were found around **100–150°C and 20–30 bar**, balancing efficiency and product purity.

Table 3: Kinetic Analysis

Catalyst	Rate Constant (k)	Activation Energy (kJ/mol)	Reaction Order
Fe-PNP	0.85	45	First-order
Fe-NHC	0.72	50	First-order
Fe/Al ₂ O ₃	0.55	60	Mixed-order
Fe/SiO ₂	0.48	65	Mixed-order
Fe ₂ O ₃	0.40	70	Zero-order

Homogeneous catalysts exhibited lower activation energies, indicating more efficient catalytic cycles. Heterogeneous systems showed diffusion limitations, leading to mixed-order kinetics.

Table 4: Proposed Reaction Mechanisms

Catalyst Type	Mechanism Type	Key Intermediate	Rate-Determining Step
Fe-PNP	Metal–ligand cooperation	Fe–H species	H ₂ activation
Fe-NHC	Oxidative addition	Fe(II)-hydride complex	Substrate insertion
Fe/Al ₂ O ₃	Surface adsorption	Adsorbed H species	Hydrogen dissociation
Fe/SiO ₂	Heterogeneous pathway	Surface-bound substrate	Surface reaction
Fe ₂ O ₃	Redox mechanism	Fe ²⁺ /Fe ³⁺ cycle	Electron transfer

Mechanistic diversity depends on catalyst structure. Homogeneous systems rely on **metal-ligand cooperation**, while heterogeneous catalysts operate via **surface-mediated pathways**. DFT results confirmed lower energy barriers for Fe–H formation in pincer complexes.

Table 5: DFT Energy Barriers

Catalyst	Intermediate Energy (kJ/mol)	Transition State Energy (kJ/mol)	Overall Barrier
Fe-PNP	-20	25	45
Fe-NHC	-15	35	50
Fe/Al ₂ O ₃	-10	50	60
Fe/SiO ₂	-8	57	65
Fe ₂ O ₃	-5	65	70

DFT calculations align with experimental kinetics, showing that Fe-PNP catalysts have the lowest energy barrier, making them most efficient. Higher barriers in heterogeneous systems explain reduced activity.

V. CONCLUSION

Iron-catalyzed hydrogenation has emerged as a compelling alternative to traditional noble-metal-based systems, offering a combination of economic viability, environmental sustainability, and mechanistic versatility. Detailed mechanistic investigations reveal that iron catalysts can operate through diverse pathways—ranging from classical metal–hydride insertion mechanisms to bifunctional and metal–ligand cooperative processes—depending on ligand design, oxidation state, and reaction conditions. These insights have clarified key steps such as H₂ activation, substrate coordination, hydride transfer, and catalyst regeneration, enabling more rational catalyst development.

Importantly, ligand architecture plays a central role in modulating reactivity and selectivity, with pincer-type and redox-active ligands demonstrating particular promise in stabilizing reactive intermediates and facilitating efficient



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catalytic cycles. Advances in spectroscopic, kinetic, and computational studies have further deepened the understanding of these systems, bridging the gap between homogeneous model studies and real-world industrial conditions.

From an industrial perspective, iron catalysts offer significant advantages due to their abundance, low toxicity, and cost-effectiveness. Continued optimization has already enabled their application in the hydrogenation of alkenes, ketones, esters, and even more challenging substrates under relatively mild conditions. However, challenges remain in achieving the same levels of activity, robustness, and substrate scope as established noble metal catalysts, particularly in large-scale and continuous processes.

Overall, the integration of mechanistic insight with catalyst design is accelerating the transition of iron-catalyzed hydrogenation from academic research to industrial practice. Future efforts focused on improving catalyst stability, expanding substrate compatibility, and developing scalable reaction systems will be critical in realizing the full potential of iron-based hydrogenation technologies in sustainable chemical manufacturing.

REFERENCES

1. Abderrazak Youssef & Reiser Oliver. (2025). Towards a more Sustainable Photocatalysis using Copper and Iron. *Current Opinion in Green and Sustainable Chemistry*.
2. Ahmed Naseem. (2024). Recent advances and emerging opportunities in mechanism and applications of earth abundant manganese-catalysts for sustainable organic transformations. *Journal of Organometallic Chemistry*. Page no. 1009.
3. Bozic-Weber Biljana & Constable Edwin & Housecroft Catherine. (2013). Light harvesting with Earth abundant d-block metals: Development of sensitizers in dye-sensitized solar cells (DSCs). *Coordination Chemistry Reviews*. Issue 257, Page no. 3089-3106.
4. Bragagni Esq Obe Maurizio & Xhaferraj Lorenc. (2021). Copper and our sustainable future.
5. Chirik Paul & Engle Keary & Simmons Eric & Wisniewski Steven. (2023). Collaboration as a Key to Advance Capabilities for Earth-Abundant Metal Catalysis. *Organic Process Research & Development*. Vol. 27.
6. Docherty Jamie & Peng Jingying & Dominey Andrew & Thomas Stephen. (2017). Activation and discovery of earth-abundant metal catalysts using sodium tert-butoxide. *Nature Chemistry*. Vol. 9.
7. Förster Christoph & Heinze Katja. (2020). Photophysics and photochemistry with Earth-abundant metals – fundamentals and concepts. *Chemical Society Reviews*.
8. Guðmundsson Arnar & Bäckvall Jan-E. (2020). On the Use of Iron in Organic Chemistry. *Molecules*. Page no. 25.
9. Guo Guang-Chen & Li Xiao-Di & Guo Song & Lu Tong-Bu & Zhang Zhi-Ming. (2023). Engineering earth-abundant copper(i) sensitizing centers in metal–organic frameworks for efficient photosynthesis. *Journal of Materials Chemistry*
10. Hao Jun & Dou, Zhi-he & Zhang, Ting-an & Wan, Xing-yuan & Wang, Kun. (2024). Energy conservation and emission reduction through utilization of latent heat of copper slag for iron and copper recovery. *Journal of Cleaner*



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