

Intermetallic Compounds from Non-Noble Metals as Catalysts in the Electrochemical Reactions of Ammonia Synthesis [†]

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Abstract

Intermetallic compounds (IMCs) can be used to create catalysts with unsurpassed practical characteristics, including for demanding and stable electrochemical reactions such as nitrogen reduction (NRR), nitrate reduction (NO₃RR), and nitrite reduction (NO₂RR), which can serve as a replacement for the industrial Haber–Bosch process. An urgent task is to develop efficient electrocatalysts using low-cost base metals, with partial or complete replacement of noble metals. This short perspective review focuses primarily on the latest work from 2024–2025 and serves as a guide and starting point for a wide readership on the IMC applications of catalysts.

Keywords: intermetallic compounds (IMCs); electrocatalysis; ammonia synthesis; sustainable chemistry



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1. Introduction

Intermetallic compounds (IMCs), which have a homogeneous structure of active centers with controlled electronic structures and an atomic ensemble size, can be used to create catalysts with unsurpassed practical characteristics, including for demanding and stable electrochemical reactions such as nitrogen reduction (NRR), nitrate reduction (NO₃RR), and nitrite reduction (NO₂RR), which can serve as a replacement for the industrial Haber–Bosch process. An urgent task is to develop efficient electrocatalysts using low cost base metals, with partial or complete replacement of noble metals.

For this aim, we propose using IMCs based on base metals or base bimetals with some noble ones to maintain high efficiency.

This short perspective review focuses primarily on the latest work from 2024 to 2025 and serves as a guide and starting point for a wide readership on IMC applications of catalysts for NRR, NO₃RR, and NO₂RR.

2. IMCs in Nitrogen Reduction Reaction (NRR)

In [1], it was found that the introduction of boron into intermetallic carbide increases selectivity during the electrocatalytic fixation of N₂. In this case, isolated single B-sites

with electron deficiency in intermetallic carbide are rationally designed in such a way as to initiate a redistribution of charge density, ensuring good selectivity in NRR.

The Ni₃Mo intermetallic compound synthesized in [2] effectively accelerates the selective synthesis of ammonia. For this IMC, the active NRR centers are protected from competitive H-adsorption and slow down unwanted HER, providing highly selective NH₃ synthesis. The theoretical calculations are confirmed by experimental results in which Ni₃Mo demonstrates high NRR values with an NH₃ yield of $17.35 \pm 0.3 \mu\text{g h}^{-1} \text{cm}^{-2}$ at a potential of 0.35 V.

The synthesis of IMCs with a small size and defective structure is a difficult task. Due to optimized vacancies, atomic arrangement, and components, the intermetallic Pd₃Pb₂ demonstrates excellent nitrogen reduction rates among the IMCs (PdM (<10 nm) (M = Pb, Sn, In) studied in [3].

In Ref. [4], using density functional theory (DFT) to study the effect of Cu doping with Mn on NRR characteristics, it was shown that the inclusion of Mn in the Cu structure can significantly improve NRR characteristics. Due to the synergy between Cu and Mn and the nanoporous structure, the resulting np-CuMn alloy demonstrates a high ammonia yield of $28.9 \mu\text{g h}^{-1} \text{cm}^{-2}$, and the Faradaic efficiency is 9.83% at -0.3 V.

The present study [5] demonstrates the potential of IMCs in NRR compared to conventional alloys. The adsorption properties of nitrogen reduction intermediates were calculated. A significant result is the provision of a stabler inclined configuration of NNH adsorption on a hetero-metallic hollow surface and an increase in the strength of NH₂ adsorption on monatomic sites (an isolated Mo or Ta atom on the surface of Pd₃Mo or Cu₃Ta) due to the covalent effect, and Pd₃Mo is proposed as the best catalyst among the IMCs studied.

DFT prediction of three-metal cluster catalysts on a two-dimensional W₂N₃ substrate in NRR was performed [6]. The NiCu cluster has the best catalytic activity among all currently proposed catalysts. Clusters of Fe₃ and Fe₂Co are also suitable catalysts.

The bimetallic single atomic Fe–Ru catalyst demonstrates an optimized Faradaic efficiency of 29.3%, as well as an NH₃ yield level of $43.9 \mu\text{g h}^{-1} \text{cm}^{-2}$, with an NRR at -0.2 V [7]. Calculations show that Fe acts as active nitrogen reduction centers.

In [8], the catalytic activity in the NRR of Ru-based Geisler alloys was investigated. The best result was shown by the Ru₂ScP alloy, which demonstrates high selectivity for NRR compared to hydrogen evolution reaction (HER).

In [9], a catalyst made of core–shell nanoparticles was developed, and Pd/Pd₁₆B₃ nanocrystals consisting of a core and shell demonstrate exceptional NRR values with a high NH₃ Faradaic efficiency of 30.8% and a yield of $0.81 \text{ mmol h}^{-1} \text{cm}^{-2}$.

As can be seen from the above works, studies on NRR are still characterized by relatively low values of both Faradaic efficiency and ammonia yield. The following studies were conducted for NO₃RR and NO₂RR.

3. IMC in Nitrate Reduction Reaction (NO₃RR/NO₂RR)

Ref. [10] discovered a new homoleptic superatom, Ag₂₀Cu₁₂, protected by alkynyl, and it provides a good example illustrating the relationship between the structure and characteristics of a bimetallic catalyst for NO₃RR and other electrocatalytic reactions involving multiple protons/electrons. Excellent catalytic properties with respect to NO₃RR are shown, as evidenced by the higher Faradaic efficiency (84.6%).

RuO_x clusters with a size of less than a nanometer [11] fixed on the metal Pd (RuO_x/Pd) are presented as a highly efficient NO₃RR catalyst providing a NH₃ Faradaic efficiency of 98.6% at a corresponding NH₃ yield of $23.5 \text{ mg h}^{-1} \text{cm}^{-2}$ at -0.5 V (RHE).

The $\text{Cu}_{2+1}\text{O}/\text{Ag-CC}$ heterostructural electrocatalyst provides a high NH_3 yield of $2.2 \text{ mg h}^{-1} \text{ cm}^{-2}$ and a significant ammonia Faradaic efficiency content of 85.03% in NO_3RR at a potential of -0.74 V (RHE) [12].

In a recent paper [13], an intermetallic AuCu_3 electrocatalyst with a high density of active sites for effective NO_3RR was developed and prepared. It is noteworthy that the Faradaic efficiency and ammonia yield at -0.9 V are 97.6% and $75.9 \text{ mg h}^{-1} \text{ cm}^{-2}$, respectively. Importantly, after 10 testing cycles, the stability of the catalyst is almost preserved.

Two main types of bimetallic nanocrystalline Pd-Cu structures, the heterostructure and the IMC, were synthesized in [14]. It was found that the Pd and Cu atoms are uniformly distributed over intermetallic Pd-Cu nanocrystals. The main result is that NO_3RR using a Pd-Cu catalyst is extremely sensitive to the bimetallic structures of the catalysts.

The non-equilibrium adsorption of intermediates and slow multielectron transport negatively affect the electrocatalytic characteristics of NO_3RR , creating obstacles to its practical application. Here [15] first analyzed the adsorption energies of three key intermediates, i.e., $^*\text{NO}_3$, $^*\text{NO}$ and $^*\text{H}_2\text{O}$, as well as d-band centers for 21 types of transition metals (IIIV and IB) - IMC based on Sb/Bi as electrocatalysts. Hexagonal CoSb IMCs have optimal adsorption equilibrium for key intermediates and exhibit outstanding electrocatalytic NO_3RR characteristics with a Faradaic efficiency of 96.3%.

In [16], the gallium-based IMC with an individual configuration of active centers for the electrochemical synthesis of ammonia were obtained. The body-centered cubic CoGa IMCs are evenly distributed on a substrate of reduced graphene oxide doped with nitrogen and provide excellent NO_3RR performance.

The configuration of atomically ordered intermetallic PdFe_3 nanoparticles into mesoporous carbon nanofibers as an effective NO_3RR catalyst is described, and a high of Faradaic efficiency (98.3%) is demonstrated. Field and theoretical analysis shows that the high efficiency of IMC is due to the synergistic effect of periodic interaction of neighboring sections of the Pd-Fe pair on an ordered (110) face through an accelerating proton repeater, where Fe sections demonstrate a preferred stabilization of the nitrogen-oxygen ratio [17].

The authors [18] note that bimetallic compounds based on copper (BMC) are attractive NO_3RR catalysts due to their high selectivity for nitrates, but their disordered crystal structure limits their kinetics and durability. The highly ordered Ga-Cu₃N catalyst provides an impressive 96.48% Faradaic efficiency and a stable yield of $24.36 \text{ mg h}^{-1} \text{ cm}^{-2}$. The rapid formation of active hydrogen ($^*\text{H}$) and the low energy barrier at the edges of Ga-Cu intermetallides are confirmed by both theoretical calculations and dynamic experiments.

Ref. [19] provides valuable guidance on the development of high-entropy metal catalysts with well-defined active centers, paving the way for the precise synthesis of highly efficient electrocatalysts for use in energy catalysts involving complex reaction processes. The FeCoNiGeSb (high-entropy alloy) is used as an electrocatalyst for the conversion of NO_3^- to NH_3 , which has a high Faradaic efficiency content (97.6%) and exceptional long-term stability at -0.30 V , as well as an NH_3 yield of $7.5 \text{ mg h}^{-1} \text{ cm}^{-2}$ at -0.40 V . DFT calculations show that the Fe, Co, and Ni centers enhance NO_3^- adsorption and synergistically reduce energy barriers to the reaction pathways. The introduction of Ge and Sb elements suppresses the competing evolution of hydrogen.

In conclusion, we will consider the work of the authors in [20], who focused on the synthesis, characterization, and testing for NO_3RR of a series of electrocatalysts based on two-component cobalt alloys using inexpensive non-noble metals, Co, Fe, Cr, and Si. Unexpectedly, it turned out that the sample containing the intermetallic compound of the composition Co_2Si turned out to be the most highly effective. The Faradaic efficiency of 80.8% at $E = -0.585 \text{ V}$ (RHE) and the ammonia yield of $22.3 \text{ } \mu\text{mol h}^{-1} \text{ cm}^{-2}$ at $E = -0.685 \text{ V}$ (RHE) indicate the progressive role of IMC as the main active component of

the electrocatalyst (Figure 1). This work can serve primarily as a starting point for future studies of electrocatalytic conversion reactions in the production of ammonia using IMC catalysts containing non-noble metals.

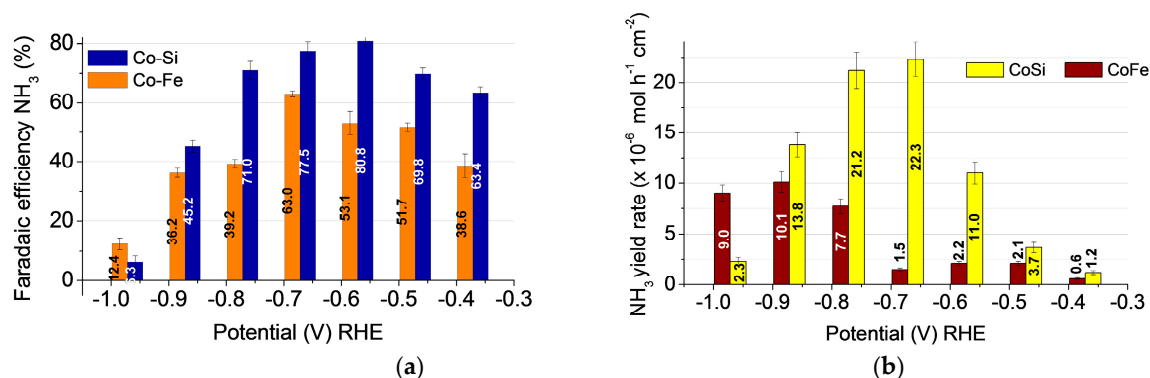


Figure 1. The results of the NO₃RR study at different potentials: (a) the resulting general FE-graph, and (b) ammonia yield rate. Adapted from [20].

4. Conclusions

The results show the advantages of using electrocatalysts in the form of IMCs, which demonstrate increased Faradaic efficiency values and ammonia yield rates. Thus, we can conclude the following:

The main research directions in world science are related to the search for new electrocatalysts.

The catalysts for the reactions under consideration, i.e., NRR, NO₃RR, and NO₂RR, should be sufficiently competitive in cost and free of noble metals.

Non-noble metal-based IMCs meet the above criteria.

IMCs (especially those based on non-noble metals) as electrocatalysts for NRR, NO₃RR, and NO₂RR are currently relatively poorly studied.

IMCs are, independently, of particular interest in terms of studying their processes, as due to the peculiarities of the structure and nature of the bond, in many cases, they demonstrate the effects of single-atom catalysts (SACs).

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References

- Wen, Y.; Zhuang, Z.; Zhu, H.; Hao, J.; Chu, K.; Lai, F.; Zong, W.; Wang, C.; Ma, P.; Dong, W.; et al. Isolation of Metalloid Boron Atoms in Intermetallic Carbide Boosts the Catalytic Selectivity for Electrocatalytic N₂ Fixation. *Adv. Energy Mater.* **2021**, *11*, 2102138. [CrossRef]
- Zhou, H.Y.; Qu, Y.B.; Fan, Y.C.; Wang, Z.L.; Lang, X.Y.; Li, J.C.; Jiang, Q. Multi-site intermetallic Ni₃Mo effectively boosts selective ammonia synthesis. *Appl. Catal. B Environ.* **2023**, *339*, 123133. [CrossRef]

3. Wang, Z.; Liu, J.; Wu, X.; Nie, N.; Zhang, D.; Li, H.; Zhao, H.; Lai, J.; Wang, L. Engineering ordered vacancies and atomic arrangement over the intermetallic PdM/CNT (M = Pb, Sn, In) nanocatalysts for synergistically promoting electrocatalysis N₂ fixation. *Appl. Catal. B Environ.* **2022**, *314*, 121465. [\[CrossRef\]](#)
4. Cui, Y.; Dong, A.; Qu, Y.; Zhang, J.; Zhao, M.; Wang, Z.; Jiang, Q. Theory-guided design of nanoporous CuMn alloy for efficient electrocatalytic nitrogen reduction to ammonia. *Chem. Eng. J.* **2021**, *426*, 131843. [\[CrossRef\]](#)
5. Zhou, J.; Chen, X.; Guo, M.; Hu, W.; Huang, B.; Yuan, D. Enhanced catalytic activity of bimetallic ordered catalysts for nitrogen reduction reaction by perturbation of scaling relations. *ACS Catal.* **2023**, *13*, 2190–2201. [\[CrossRef\]](#)
6. Chen, S.; Gao, Y.; Wang, W.; Prezhdo, O.V.; Xu, L. Prediction of Three-Metal Cluster Catalysts on Two-Dimensional W₂N₃ Support with Integrated Descriptors for Electrocatalytic Nitrogen Reduction. *ACS Nano* **2023**, *17*, 1522–1532. [\[CrossRef\]](#) [\[PubMed\]](#)
7. Liu, M.; Zhang, S.; Chen, M.; Zhou, S.; Wu, L. An isolated bimetallic Fe–Ru single-atom catalyst for efficient electrochemical nitrogen reduction. *J. Mater. Chem. A* **2023**, *11*, 14900–14910. [\[CrossRef\]](#)
8. Chen, X.; Zhou, J.; Hu, W.; Huang, B.; Yuan, D. Highly efficient Ru-based Heusler alloys for nitrogen reduction reaction: Breaking scaling relations and regulating potential determining steps. *Appl. Surf. Sci.* **2024**, *655*, 159686. [\[CrossRef\]](#)
9. Wen, Y.; Wang, T.; Hao, J.; Zhuang, Z.; Gao, G.; Lai, F.; Lu, S.; Wang, X.; Kang, Q.; Wu, G.; et al. A Coherent Pd–Pd₁₆B₃ Core–Shell Electrocatalyst for Controlled Hydrogenation in Nitrogen Reduction Reaction. *Adv. Funct. Mater.* **2024**, *34*, 2400849. [\[CrossRef\]](#)
10. Ma, G.; Sun, F.; Qiao, L.; Shen, Q.; Wang, L.; Tang, Q.; Tang, Z. Atomically precise alkynyl-protected Ag₂₀Cu₁₂ nanocluster: Structure analysis and electrocatalytic performance toward nitrate reduction for NH₃ synthesis. *Nano Res.* **2023**, *16*, 10867–10872. [\[CrossRef\]](#)
11. Li, X.; Shen, P.; Li, X.; Ma, D.; Chu, K. Sub-nm RuO_x Clusters on Pd Metallene for Synergistically Enhanced Nitrate Electroreduction to Ammonia. *ACS Nano*. **2023**, *17*, 1081–1090. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Liu, Y.; Yao, X.-M.; Liu, X.; Liu, Z.; Wang, Y.-Q. Cu₂₊₁O/Ag Heterostructure for Boosting the Electrocatalytic Nitrate Reduction to Ammonia Performance. *Inorg. Chem.* **2023**, *62*, 7525–7532. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Zhou, S.; Dai, Y.; Song, Q.; Lu, L.; Yu, X. Efficient Electrochemical Nitrate Removal by Ordered Ultrasmall Intermetallic AuCu₃ via Enhancing Nitrate Adsorption. *ACS Appl. Mater. Interfaces* **2024**, *16*, 20551–20558. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Zhang, Z.; Li, W.; Zheng, C.; Chen, K.; Pang, H.; Shi, W.; Lu, J. Insight into the bimetallic structure sensibility of catalytic nitrate reduction over Pd–Cu nanocrystals. *J. Environ. Sci.* **2025**, *149*, 221–233. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Ma, C.; Zhang, H.; Xia, J.; Zhu, X.; Qu, K.; Feng, F.; Han, S.; He, C.; Ma, X.; Lin, G.; et al. Screening of Intermetallic Compounds Based on Intermediate Adsorption Equilibrium for Electrocatalytic Nitrate Reduction to Ammonia. *J. Am. Chem. Soc.* **2024**, *146*, 20069–20079. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Zhang, H.; Ma, C.; Wang, Y.; Zhu, X.; Qu, K.; Ma, X.; He, C.; Han, S.; Liu, A.; Wang, Q.; et al. Transition Metal–Gallium Intermetallic Compounds with Tailored Active Site Configurations for Electrochemical Ammonia Synthesis. *Angew. Chem. Int. Ed. Engl.* **2024**, *63*, e202409515. [\[CrossRef\]](#) [\[PubMed\]](#)
17. Xie, M.; Zhu, G.; Yang, H.; Liu, B.; Li, M.; Qi, C.; Wang, L.; Jiang, W.; Qiu, P.; Luo, W. Periodic Adjacent Pd–Fe Pair Sites for Enhanced Nitrate Electroreduction to Ammonia via Accelerating Proton Relay. *Adv. Energy Mater.* **2024**, 2401717. [\[CrossRef\]](#)
18. Wang, P.; Liu, C.; Rao, L.; Tao, W.; Huang, R.; Huang, P.; Zhou, G. Transient heating synthesis of a highly ordered Ga–Cu intermetallic antiperovskite for efficient ammonia electrosynthesis and ultrastable zinc–nitrate fuel cells. *Energy Environ. Sci.* **2024**, *17*, 6698–6706. [\[CrossRef\]](#)
19. Ma, X.; Ma, C.; Wang, Y.; Xia, J.; Han, S.; Zhang, H.; He, C.; Feng, F.; Lin, G.; Cao, W.; et al. Precise Control of Active Site Configurations in High-Entropy Intermetallic Compounds for Electrocatalytic Nitrate Reduction to Ammonia. *Angew. Chem. Int. Ed. Engl.* **2025**, *64*, e202502333. [\[CrossRef\]](#) [\[PubMed\]](#)
20. Kuznetsova, I.; Kultin, D.; Lebedeva, O.; Nesterenko, S.; Murashova, E.; Kustov, L. Intermetallic Compound and Solid Solutions of Co₇₅Me₂₅ (Me: Si, Fe, Cr) as Catalysts for the Electrochemical Reaction of Nitrate Conversion to Ammonia. *Int. J. Mol. Sci.* **2025**, *26*, 1650. [\[CrossRef\]](#) [\[PubMed\]](#)

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