

BIMETALLIC CATALYST (CO-NI) FOR NaBH_4 REDUCTION OF NITROARENES, C=C UNSATURATION, AND REDUCTIVE AMINATION

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ABSTRACT

Bimetallic catalysts are of growing interest in sustainable chemistry, and the Co-Ni bimetallic system has shown great promise in facilitating selective reductions under mild conditions. Utilizing sodium borohydride (NaBH_4) as a reducing agent, Co-Ni catalysts significantly enhance reaction rates and selectivity for the reduction of nitroarenes, C=C unsaturation, and reductive amination reactions. The synergistic interaction between cobalt and nickel in these catalysts leads to improved activity, stability, and tunable reaction outcomes compared to their monometallic counterparts. This review explores the structural properties of Co-Ni catalysts, the mechanisms of NaBH_4 reductions, and their applications in various organic transformations. Additionally, challenges such as catalyst deactivation and future research directions in the development of Co-Ni catalysts are discussed.

Keywords: Sodium Borohydride, Nitroarene Reduction, Reductive Amination, Organic Synthesis,

1. INTRODUCTION

1.1 BIMETALLIC CATALYSIS: THE ROLE OF CO-NI SYSTEMS

Bimetallic catalysts, composed of two metals, exhibit superior catalytic properties compared to monometallic systems due to synergistic effects that enhance reactivity, selectivity, and stability. In particular, cobalt (Co) and nickel (Ni) as a bimetallic system have garnered attention for their ability to activate and transfer hydrogen under mild conditions, making them ideal candidates for reductions mediated by sodium borohydride (NaBH_4) [1,2].

The Co-Ni bimetallic system is especially appealing due to the earth-abundant, cost-effective nature of both metals. Additionally, their electronic and geometric complementarities allow

them to serve as excellent hydrogenation catalysts, capable of selectively reducing nitroarenes, unsaturated hydrocarbons, and intermediates in reductive amination processes [3].

1.2 WHY CO-NI FOR NaBH_4 -MEDIATED REACTIONS?

NaBH_4 is a widely used reducing agent in organic synthesis due to its ability to donate hydride ions under mild conditions, but its activity and selectivity are greatly enhanced by the presence of a suitable catalyst. Co-Ni bimetallic catalysts have been demonstrated to facilitate reductions in a more efficient and selective manner. This system combines the strength of cobalt in stabilizing intermediates with nickel's ability to efficiently transfer

hydride ions. Such synergism makes the Co-Ni system highly effective for the reduction of nitroarenes to amines, hydrogenation of C=C bonds, and reductive amination [3].

1.3 SCOPE AND STRUCTURE OF THIS REVIEW

This review focuses on the use of Co-Ni bimetallic catalysts in NaBH₄-mediated reductions. It covers the underlying mechanisms of key reactions such as nitroarene reduction, C=C unsaturation hydrogenation, and reductive amination. The design of Co-Ni catalysts, their surface properties, and their application in organic transformations are explored in depth. Finally, challenges in catalyst design, such as deactivation and sustainability, are discussed, alongside potential future directions.

2. HISTORICAL DEVELOPMENT OF CO-NI BIMETALLIC CATALYSTS

2.1 EARLY STUDIES ON CO-NI BIMETALLIC SYSTEMS

The interest in Co-Ni bimetallic systems began in the mid-20th century when early investigations into hydrogenation reactions revealed that combining cobalt and nickel led to improved activity and selectivity compared to monometallic systems. The development of Co-Ni catalysts for the reduction of unsaturated bonds and nitro groups followed soon after, especially in the context of industrial processes where inexpensive and abundant metals were desired [4].

2.2 THE ROLE OF NABH₄ IN CATALYTIC REDUCTIONS

NaBH₄ with its high hydride ion donation capacity, has long been used in organic synthesis for reduction reactions. The catalytic activity of Co-Ni in the presence of NaBH₄ was first demonstrated in the 1990s, where researchers showed that the bimetallic system could dramatically enhance the reduction of nitro compounds to amines under mild conditions. Since then, Co-Ni has been explored for various

reduction reactions due to its versatility and sustainability [5].

3. MECHANISMS OF NABH₄ REDUCTIONS WITH CO-NI BIMETALLIC CATALYSTS

3.1 REDUCTION OF NITROARENES

The reduction of nitroarenes to aromatic amines is an essential transformation in the production of fine chemicals, pharmaceuticals, and polymers. The Co-Ni system, when used with NaBH₄, significantly enhances the selectivity and efficiency of this reduction.

- **Mechanistic Pathway:** The reduction proceeds through a stepwise pathway, involving the adsorption of the nitroarene onto the Co-Ni catalyst surface. Cobalt stabilizes the adsorption of the nitro group, while nickel facilitates the hydride transfer from NaBH₄, leading to the formation of intermediate species like nitrosoarenes and hydroxylamines. These intermediates are rapidly reduced to the corresponding amine due to the high activity of the Co-Ni system [6,7].
- **Synergistic Effect:** Cobalt plays a crucial role in stabilizing the intermediates, preventing over-reduction to undesirable by-products. Nickel enhances the reduction step by improving the efficiency of hydride transfer, resulting in a highly selective and fast conversion to amines.
- **Case Study: Co-Ni/Alumina:** Co-Ni supported on alumina has been reported to offer excellent performance in the reduction of nitroarenes. The alumina support enhances the dispersion of active Co-Ni particles, allowing for greater surface interaction and leading to higher turnover frequencies.

3.2 HYDROGENATION OF C=C UNSATURATION

The hydrogenation of C=C unsaturated bonds is an important reaction in the production of

saturated hydrocarbons and industrial chemicals. Co-Ni bimetallic catalysts are highly effective in promoting this transformation when NaBH_4 is used as a hydrogen source [8].

- Mechanistic Insights:** The C=C bond is activated upon adsorption onto the catalyst surface, with cobalt assisting in the interaction of the unsaturated substrate, while nickel facilitates the transfer of hydride ions. The dual activity of Co and Ni allows for a fast and selective hydrogenation of C=C bonds to alkanes without over-reduction of other functional groups.

- Selectivity Control:** The ratio of Co to Ni in the bimetallic catalyst can be fine-tuned to achieve high selectivity. Increasing the nickel content enhances hydride transfer and accelerates the reaction, while cobalt ensures that unsaturated bonds are selectively hydrogenated without unwanted side reactions [9,10].

- Example: Co-Ni/Carbon Catalysts:** Co-Ni supported on carbon has been shown to effectively hydrogenate alkenes and conjugated alkenes under mild conditions, demonstrating excellent selectivity toward the desired saturated products.

3.3 REDUCTIVE AMINATION

Reductive amination is a critical synthetic route for the formation of amines from carbonyl compounds and amines. The Co-Ni bimetallic system, in combination with NaBH_4 , facilitates this transformation by promoting the reduction of the imine intermediate [7].

- Mechanistic Pathway:** The reaction involves the formation of an imine (Schiff base) intermediate from the carbonyl compound and amine, which is then reduced by NaBH_4 in the presence of the Co-Ni catalyst. Nickel accelerates the reduction of the imine, while cobalt aids in stabilizing the reaction intermediates.

- Efficiency of Co-Ni:** The bifunctional nature of Co-Ni allows for rapid imine formation followed by fast reduction to the desired amine. This makes

Co-Ni systems particularly useful for producing amines with high selectivity.

- Case Study: Co-Ni/Graphene Oxide:** Recent studies have shown that Co-Ni supported on graphene oxide offers enhanced performance for reductive amination reactions, particularly in aqueous media. The high dispersion of Co-Ni particles on graphene oxide facilitates faster reaction rates and higher selectivity toward the desired amines.

4. COMPARATIVE PERFORMANCE OF CO-NI BIMETALLIC CATALYSTS WITH MONOMETALLIC AND OTHER CATALYSTS:

4.1 CATALYTIC ACTIVITY

Co-Ni bimetallic catalysts demonstrate superior activity compared to monometallic (Co or Ni) and other non-noble systems. The synergistic interaction between Co and Ni enhances the electronic properties, facilitating better adsorption of reactants and hydrogen activation. This results in higher reaction rates, particularly in NaBH_4 reduction of nitroarenes and reductive amination. In contrast, monometallic Co or Ni exhibits moderate activity but lacks this synergy. Noble metals like Pt and Pd are more active but costly and less sustainable [8, 9].

4.2 SELECTIVITY

Co-Ni catalysts offer improved selectivity, efficiently reducing nitro groups without over-hydrogenating unsaturated compounds. The balanced interaction of the metals minimizes side reactions by stabilizing intermediates. Monometallic catalysts often display poorer selectivity due to unoptimized adsorption energies, while noble metals achieve high selectivity but are prone to poisoning in the presence of contaminants.

4.3 STABILITY AND REUSABILITY

The bimetallic configuration enhances catalyst stability, reducing leaching and sintering during reactions. Co-Ni catalysts maintain activity over

multiple cycles, unlike monometallic systems, which degrade faster. While noble metals are inherently stable, their high cost and scarcity limit their use in large-scale applications.

4.4 COST AND SUSTAINABILITY

Co-Ni catalysts strike a balance between performance and affordability, making them an attractive choice for industrial processes. They avoid the prohibitive costs of noble metals and outperform cheaper non-noble systems in efficiency and durability [10,11].

5. TYPES OF CO-NI BIMETALLIC CATALYSTS

5.1 SUPPORTED CO-NI CATALYSTS

Supported Co-Ni catalysts are widely used due to their increased stability, high surface area, and enhanced dispersion of active metal sites. Common supports include carbon, alumina, and silica, each providing unique advantages in different reactions.

Example: Co-Ni/Carbon Nanotubes (CNTs): Co-Ni supported on CNTs has shown superior performance in nitroarene reduction due to the enhanced electron transfer capabilities of carbon nanotubes, which promote faster hydride transfer from NaBH_4 [12].

5.2 ALLOY CO-NI CATALYSTS

Alloying cobalt and nickel at the atomic level provides unique electronic and geometric properties that improve catalytic performance. The alloyed Co-Ni structure offers improved stability and reactivity, making it ideal for industrial applications.

Example: Co-Ni Alloys for C=C Hydrogenation: Alloyed Co-Ni catalysts have been widely used for selective hydrogenation of unsaturated hydrocarbons, demonstrating high selectivity toward the desired products.

6. APPLICATIONS OF CO-NI CATALYSTS IN ORGANIC SYNTHESIS

6.1 FINE CHEMICALS AND PHARMACEUTICALS

Co-Ni bimetallic catalysts are widely used in the fine chemicals and pharmaceutical industries for the selective reduction of nitroarenes and reductive amination. The high selectivity and efficiency of Co-Ni systems make them ideal for producing intermediates used in drug synthesis and the manufacture of fine chemicals [6].

Case Study: Co-Ni catalysts have been successfully employed in the production of aromatic amines, which are important precursors for pharmaceutical compounds, dyes, and pigments.

6.2 ENVIRONMENTAL CATALYSIS

Co-Ni systems also play a role in environmental applications, such as the degradation of toxic nitroaromatic compounds in wastewater treatment. The ability of Co-Ni catalysts to reduce nitro compounds to less toxic amines under mild conditions makes them attractive for green chemistry applications [12].

7. CHALLENGES AND FUTURE DIRECTIONS

7.1 CATALYST DEACTIVATION

While Co-Ni bimetallic catalysts are highly active, they are susceptible to deactivation due to metal leaching, sintering, or poisoning by reaction intermediates. Future research is focused on improving catalyst stability by developing new support materials and protective coatings [13].

7.2 SCALABILITY AND ECONOMIC CONSIDERATIONS

Despite their advantages, the scalability of Co-Ni catalysts for industrial applications remains a challenge. Further research is needed to improve the cost-effectiveness of these systems while maintaining their high performance [14,15].

7.3 TOWARD GREENER CHEMISTRY

Co-Ni catalysts offer significant potential for greener chemical processes. Future developments aim to enhance their recyclability, reduce solvent usage, and increase their efficiency in aqueous media, aligning with the principles of sustainable chemistry.

8. CONCLUSION

Co-Ni bimetallic catalysts have emerged as powerful tools in NaBH_4 -mediated reductions, providing exceptional activity and selectivity for nitroarene reduction, C=C hydrogenation, and reductive amination. The synergistic interaction between cobalt and nickel enables efficient hydride transfer and precise control over reaction pathways. Continued advancements in Co-Ni catalyst design, coupled with a focus on sustainability and cost-effectiveness, are expected to expand their applications in both industrial and academic settings.

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