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Advances in Catalytic Hydrogenation of Oil with Novel Catalytic Systems

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Abstract. Traditionally, nickel-based catalysts (e.g., Raney Ni or Ni/Al_2O_3) have been used due to their low cost and high activity. However, Ni catalysts tend to yield excessive saturation and trans-fat isomers, which are undesirable for health. In recent years, intensive research has focused on new catalytic systems to improve selectivity, activity, and environmental performance. This review briefly surveys conventional catalysts and then focuses on two classes of novel catalysts: advanced supported metal catalysts (including noble metals and promoted Ni catalysts) and bimetallic or alloy catalysts. For each system, the article discusses the hydrogenation mechanism, observed activity and selectivity (particularly toward cis monoenes), catalyst stability and regeneration, as well as industrial scale-up potential and environmental impact (e.g., trans-fat formation, energy requirements). Emerging catalyst-free technologies (e.g., plasma hydrogenation) are also highlighted. The paper concludes with perspectives on designing catalysts that meet food-industry demands (high cis-selectivity, low trans content) while minimizing energy use and harmful by-products.

Keywords: Catalytic Hydrogenation, Novel Catalytic Systems, cis-Selectivity, Bimetallic /Alloy Catalysts

1. Introduction

Hydrogenation of vegetable oils (triglycerides rich in C=C bonds) is a key process in food and chemical industries, converting liquid oils into semi-solid fats with extended shelf life and desired physical properties [1]. Industrially, oil is mixed with a metal catalyst (~0.05 wt%) in a batch reactor, hydrogen (15–50 psi) is introduced, and the temperature is raised (120–180°C) until the target iodine value (unsaturation degree) is reached [2]. Reactions include full saturation, partial hydrogenation, and double-bond migration, often leading to cis-trans isomerization [2]. For instance, oil containing linoleic acid (C18:2) undergoes stepwise addition to form monounsaturated (C18:1) intermediates and saturated stearic acid (C18:0), with concurrent bond reshuffling [1].

Historically, heterogeneous Ni catalysts (e.g., Raney Ni) have dominated fat hydrogenation due to high activity and conversion rates [1]. However, they exhibit modest selectivity, frequently over-hydrogenating and generating large amounts of trans fatty acids [2]. Though useful industrially (e.g., for lubricant precursors), trans fats are undesirable in foods, being linked to cardiovascular disease and insulin resistance [2]. Consequently, global health organizations are eliminating trans fats from food products [3]. Thus, modern catalysts must minimize trans-isomer formation and favor cis monoene retention.

This review critically examines advances in catalytic systems for edible oil hydrogenation, addressing the urgent need to eliminate harmful trans isomers while maintaining process efficiency. By synthesizing findings on novel catalysts (supported metals, bimetallic alloys) and emerging technologies, it provides insights for designing advanced hydrogenation processes. These insights are crucial for developing practical catalysts that simultaneously ensure consumer safety (low trans fat), enhance product quality (high cis-selectivity), and improve environmental sustainability (reduced energy/chemical consumption).

2. Literature review

Nickel catalysts (e.g., Raney Ni, Ni/Al_2O_3, Ni/SiO_2) remain the industrial standard for oil hydrogenation [2]. They exhibit high activity, particularly at elevated temperatures, enabling rapid conversion. Traditional nickel catalysts exhibit significant advantages, including high activity at elevated temperatures, fast conversion rates, good cycling stability, low cost, and widespread industrial applicability. However, they demonstrate low selectivity toward cis-monounsaturated products (e.g., oleic acid) and tend to produce substantial amounts of harmful trans fatty acids. Furthermore, they require relatively high hydrogen pressure and extended reaction times to achieve moderate conversion levels. Additional drawbacks include susceptibility to sintering at high temperatures, sensitivity to sulfur-containing impurities (leading to poisoning), and the need for additional steps to remove residual nickel in food-grade applications.

Hydrogenation metrics: In an industrial batch process, for example, the partial hydrogenation of soybean oil—standard conditions include temperatures of approximately 150–180 °C, H_2 pressures of about 30 psi, and 5–10 wt% Ni (as metal) [2]. Under these conditions, unmodified Ni yields mostly saturated and trans-rich products. For example, Spiekermann et al. Report that while Ni catalysts achieve moderate conversion to monounsaturated fats, they yield low cis-selectivity and high trans fractions [1]. In contrast, palladium catalysts (discussed below) offer higher cis selectivity, albeit at a higher cost.

3. Supported monometallic catalysts

3.1. Overview of supported catalysts

To improve performance over pure Ni, researchers have explored supported monometallic catalysts, especially noble metals or Ni with promoters. The goal is to achieve higher cis-selectivity (and thus higher yields of desired monoenes like oleic acid) and/or milder operating conditions. Supported Pd and Pt catalysts are classic examples: they are more active for hydrogenation than Ni, and tend to hydrogenate unsaturations more quickly, reducing isomerization. Numwong et al. found that catalyst activity follows Pd > Pt >> Ni, and trans selectivity follows Pd >> Ni > Pt [4]. In practice, Pd and Pt catalysts on high-surface supports (C, Al_2O_3, SiO_2, zeolites, etc.) have been tested under relatively mild conditions (often <120 °C) for selective hydrogenation.

3.2. Typical catalyst

3.2.1. Palladium-based catalysts

Supported Pd catalysts (e.g., Pd/C, Pd/γ-Al_2O_3) exhibit high activity, rapidly hydrogenating linoleic and linolenic acids at near-ambient temperatures under high pressure. They show improved cis/transselectivity over Ni, with Pd/bentonite yielding products rich in cisoleic acid (IV ~70 at 25–70°C) while preserving olefin geometry [3]. Drawbacks include a tendency toward over-saturation (C18:0) during prolonged reactions, high cost, and stringent requirements for Pd removal from edible oils [3].

3.2.2. Platinum-based catalysts

Pt catalysts (e.g., Pt/γ-Al_2O_3) display hydrogenation activity between Pd and Ni (Pd > Pt > Ni) [4]. Though highly active and sintering-resistant on supports (ZSM-5, mesoporous carbons), Pt favors higher saturation than Pd, increasing stearic acid yield [4]. Their high cost limits food-industry applications despite promising lab-scale cis-selectivity.

3.2.3. Copper-based catalysts

Cu catalysts offer cost advantages but require higher temperatures (>200°C) than Ni [5]. Their moderated activity enables selective hydrogenation: preferential saturation of linoleic acid's first double bond promotes oleic acid accumulation while minimizing trans-fats [5]. This makes Cu suitable for producing low-transbio-lubricants, though slower kinetics demand extended reaction times [5].

3.2.4. Promoted Ni catalysts

Support engineering (MgO, CeO_2) or dopants significantly enhance Ni performance. Adding 1 wt% CeO_2 to Ni/SiO_2 increased active sites and altered fatty acid adsorption, boosting both conversion and cis-C18:1 selectivity [6]. Basic supports (e.g., Ni/MgO-SiO_2) reduce side reactions, demonstrating promoter-driven optimization of Ni's inherent activity [6].

Overall, supported monometallic catalysts expand the toolbox: using Pt or Pd enables low-temperature hydrogenation; using Cu or modified Ni allows control over extent of saturation. In all cases, achieving an optimal cis/trans ratio remains a key design goal.

4. Bimetallic and alloy catalysts

Bimetallic catalysts combine two metals to exploit synergistic effects. In fat hydrogenation, common approaches have been to alloy Ni with a second metal (noble or non-noble) to modify hydrogen adsorption and isomerization kinetics. Several recent studies exemplify promising bimetallic systems.

4.1. Typical alloy systems

Bimetallic Ni catalysts exploit synergistic effects to enhance selectivity. For instance, Ni-Ag alloys (e.g., Ni-Ag/SBA-15) reduce hydrogenation strength through Ag dilution of Ni sites, which lowers H_2 dissociation rates. This suppression of over-hydrogenation, increases cis-C18:1 selectivity while limiting trans-fat formation [6]. Similarly, Ni-Pd-Ru/graphene systems leverage Pd/Ru to accelerate linolenic acid hydrogenation while Ni provides bulk activity. For cost-effective alternatives, Ni-Fe catalysts exhibit high hydrogenation activity and exceptional stability, demonstrating strong resistance to coke deactivation. As evidenced by Umenweke et al., Ni-Fe/ZrO_2 achieves near-quantitative conversions with minimal sintering, highlighting its industrial potential [6]. Ni-Co alloys, though less explored in fat hydrogenation, show promise in biofuel deoxygenation. Collectively, these alloys optimize Ni's inherent activity, while addressing selectivity (cis/transcontrol) and stability challenges.

Ni–Fe has gained attention: Umenweke et al. found that a 20%Ni–5%Fe catalyst supported on ZrO_2 gave a near-quantitative yield of hydrocarbons from a triglyceride feed [6]. While that study focused on deep hydrodeoxygenation of tristearin, it highlights that Ni–Fe promotes high hydrogenation activity and stability (strong Fe–Ni alloying may resist sintering). By analogy, Ni–Fe catalysts may achieve very high rates in hydrogenating unsaturated fats, potentially more so than monometallic Ni. The role of Fe is often to aid H_2 activation or alter Ni particle growth. In practice, Ni–Fe hydrogenation catalysts showed minimal deactivation by coke, suggesting good stability [6].

4.2. Mechanistic aspects

Bimetallic alloys operate by modifying adsorption energies. For example, adding a second metal that binds hydrogen weakly (e.g., Ag, Cu, or a small amount of a more expensive noble metal) can decrease the overall hydrogenation strength of Ni, improving selectivity. Conversely, a more active metal like Pd or Pt alloyed into Ni can boost activity. The alloying process can also create new ensembles on the surface. For example, on Ni–Ag surfaces, Ni sites are separated by Ag atoms, which alters the pathway of isomerization. Alloy catalysts can show unique kinetics: some Ni–Cu alloys had optimal acid site concentrations for fat conversion. Bimetallics are often more robust, as one metal can stabilize the other against sintering or poisoning [1].

4.3. Industrial potential and environmental performance

Bimetallic Ni catalysts offer a bridge between cheap Ni and costly noble metals. For example, even a small Pd content in Ni–Pd catalysts (or an Ag promoter) can dramatically improve performance at a modest incremental cost. These bimetallic catalysts can potentially be adapted to existing Ni-based reactors. One challenge is ensuring uniform alloying at scale. However, the literature shows many synthesis routes (co-impregnation, co-precipitation, sol-gel) to make nano-alloys.

By boosting cis-selectivity and reducing trans formation, bimetallic catalysts directly address health/environmental concerns of hydrogenated fats. For instance, Ni–Ag catalysts have been reported to produce significantly less trans fat than Ni alone. In terms of waste, bimetallic catalysts are still heterogeneous solids that can be filtered and reused. However, any added metals (Pd, Ag, etc.) must be non-toxic or removed from food products. Nickel generally considered safe in trace amounts post-processing, provided it is reduced to levels complying with food safety regulations. Some studies report good recyclability: e.g., Ni–Fe catalysts showed minimal loss of activity over repeated uses, hinting at high durability [7].

In summary, bimetallic catalysts are among the most promising new systems: they allow tuning of the hydrogenation properties without relying solely on expensive metals. The recent literature shows several Ni-based alloys achieving near-ideal performance (high conversion, high cis/low trans) in laboratory tests [3].

5. Emerging metal-free and novel systems

5.1. Metal-free catalysts

Apart from modifying metal catalysts, researchers have explored alternative approaches. One novel approach is catalyst-free hydrogenation using plasma. In non-thermal plasma reactors (e.g., dielectric barrier discharge), H_2 molecules can be activated by energetic electrons and directly hydrogenate oils at ambient temperature [1]. In a catalyst-free plasma, triglycerides passing through the plasma undergo hydrogenation. However, studies report that the process is highly unselective: virtually all unsaturated bonds react indiscriminately, yielding a mix of fully saturated fats and many new trans and polyunsaturated compounds [1]. Thus, while plasma hydrogenation remains an interesting concept for catalyst-free processing, it is currently impractical for selective fat hydrogenation due to its highly unselective nature [1].

5.2. Novel catalytic and environmentally benign systems

Other novel systems include membrane reactors (where hydrogen is permeated through a selective membrane into a catalyst bed) and photocatalytic hydrogenation. For example, immobilizing Ni on a polymer membrane has been shown to enhance single-batch productivity in pilot studies. Photocatalysts (e.g., semiconductor or dye-sensitized systems) have been used for small-molecule hydrogenations, but applying them to large triglycerides is still exploratory. Some research has demonstrated Frustrated Lewis Pairs (FLPs), which are metal-free systems capable of splitting H_2, but these have not yet been applied to vegetable oils. In essence, truly metal-free fat hydrogenation remains largely undeveloped beyond plasma.

Metal oxides like defect-engineered CeO_2 are potential catalysts: CeO_2 nanorods can hydrogenate α,β-unsaturated aldehydes by heterolytic H_2 activation [3]. While not directly used for triglycerides, such studies hint at the possibility of designing oxygen-rich materials that activate H_2 at defects, possibly enabling precious meal-free fats hydrogenation.

Overall, metal-free alternatives cut catalyst costs but face new issues (e.g., plasma/photochemistry has low selectivity/efficiency). For now, they only complement rather than replace advanced metal catalysts [8].

5.3. Future prospects and research directions

Fat hydrogenation is moving beyond traditional Ni catalysts (harsh conditions, high trans fats). Current research prioritizes high cis-monounsaturated yields under milder temperature and pressure to improve quality and energy efficiency. While supported noble-metal (Pd, Pt) and promoted Ni catalysts show exceptional lab performance, cost and scale-up challenges limit commercial adoption [2]. For example, $Pd/\gamma\text{-}Al_2O_3$ has been used for partial hydrogenation of palm oil to produce eco-friendly lubricants, but cost and scale-up challenges limit commercial adoption [9].

Bimetallic Ni-based catalysts (alloyed with Ag, Pd, Cu, or Fe) demonstrate particular promise, enabling tuned hydrogen binding for near-quantitative oleic acid production with minimal trans fats. Their compatibility with existing industrial units enhances feasibility. Future efforts should reduce isomerization, extend catalyst lifetime, boost sustainability by eliminating trans fats, cutting energy use and adopting non-toxic materials, and develop hybrid systems (e.g., membrane/photocatalyst plus tailored metal sites) for selective hydrogenation under mild conditions. Non-thermal plasma remains limited by selectivity issues. Ultimately, leveraging nanomaterial advances and mechanistic insights will be crucial for "greening" industrial fat hydrogenation.

6. Conclusion

This review explores recent advancements in the catalytic hydrogenation of vegetable oils, with a focus on the shift from traditional nickel-based catalysts to more efficient and selective alternatives. Nickel catalysts, while cost-effective, tend to produce excessive trans fats, which are undesirable for health. Supported noble metals like palladium and platinum offer improved cis-selectivity but come with high costs and scalability issues. Bimetallic catalysts, particularly nickel-based alloys, have shown potential in optimizing hydrogenation activity, improving selectivity, and reducing trans-fat formation, making them more feasible for industrial applications.

The research further points out that challenges remain in terms of cost and large-scale implementation. Emerging metal-free technologies, such as non-thermal plasma and photocatalytic hydrogenation, offer promising solutions but face limitations in selectivity and efficiency, making them unsuitable for large-scale applications at present. Developing cost-effective and sustainable catalytic systems is a necessity to minimize trans fats and improve selectivity, and reduce energy consumption. Ultimately, the future of catalytic hydrogenation lies in creating more efficient, scalable, and environmentally friendly catalysts that meet both industrial and health-related demands.

The study also has limitations. It focuses on the main catalysts based on the statistics and research, while completely ignoring practical industrial factors such as catalyst deactivation mechanisms, catalyst recycling processes, and the full-life-cycle environmental and economic costs of catalytic systems.

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