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Review

Recent Advancements in Catalysts for Petroleum Refining

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Abstract: In petroleum refining, catalysts are used to efficiently convert crude oil into valuable products such as fuels and petrochemicals. These catalysts are employed in a range of processes, including catalytic cracking, hydrotreating, and reforming to meet stringent fuel quality standards. This review explores recent advancements in refining catalysts, focusing on novel materials, enhanced synthesis methods, and their industrial applications. The development of nano-, hierarchically structured, and supported metal catalysts has led to significant improvements in catalyst selectivity, yield, and longevity. These innovations are particularly important for processes such as hydrocracking, fluid catalytic cracking, and catalytic reforming, where catalysts improve conversion rates, product quality, and environmental sustainability. Advances in synthesis techniques such as sol-gel processes, microwave-assisted synthesis, and atomic layer deposition have further optimized catalyst performance. Environmental considerations have also driven the development of catalysts that reduce harmful emissions, particularly sulfur oxides and nitrogen oxides while promoting green catalysis through the use of bio-based materials and recyclable catalysts. Despite these advancements, challenges remain, particularly in scaling novel materials for industrial use and integrating them with existing technologies. Future research should focus on the exploration of new catalytic materials, such as metal-organic frameworks and multi-functional catalysts, which promise to further revolutionize the refining industry. This review thus demonstrates the transformative potential of advanced catalysts in enhancing the efficiency and environmental sustainability of petroleum refining.

Keywords: petroleum refining; catalysts; nanocatalysts; fluid catalytic cracking; hydrocracking; catalytic reforming; green catalysis; sulfur removal

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1. Introduction

Petroleum refining involves the transformation of crude oil, a complex blend of hydrocarbons, into valuable products such as gasoline, diesel, jet fuel, and various petrochemicals [1,2]. In this process, catalysts are required to accelerate the associated chemical reactions, thus enhancing both the efficiency and selectivity of refining systems. Without catalysts, many refining processes would be economically impractical because they would require extremely high temperatures and/or pressures or long reaction times [3]. Catalysts also allow for more precise control over reaction pathways, maximizing the yield of desirable products from crude oil. This precision is especially crucial due to the variability in the composition of crude oil, which can range from light, sweet crudes to heavy, sour varieties, each of which requires distinct processing methods [4].

The continuous development of catalysts has been a driving force behind innovation in the refining industry [5]. In the early days of refining, simple acid-based catalysts were used, with progression toward more advanced and efficient catalytic systems over time. Modern refining processes heavily depend on catalysts such as zeolites, metal oxides, and mixed metal catalysts to promote specific reactions, including cracking, hydrocracking, and reforming [5,6]. These processes break down large hydrocarbon molecules into smaller, more valuable ones, remove impurities such as sulfur (S) and nitrogen (N), and rearrange molecular structures to enhance the quality of the resulting fuel. As such, catalysts not only influence the economic feasibility of refining operations but also the environmental impact of refining systems, with more efficient catalysts reducing both energy consumption and pollutant emissions [7].

In recent years, significant progress has been made in the development of petroleum refining catalysts due to the increasing demand for refined products and the introduction of stricter environmental regulations worldwide [8,9]. Of particular note has been the emergence of nanocatalysts, which offer precise control over catalytic reactions due to their high surface area and advantageous electronic properties [10]. Nanocatalysts have thus demonstrated their potential in hydrocracking and catalytic reforming, where they increase reaction rates and selectivity while minimizing the production of unwanted byproducts [11]. Their nanoscale design allows for the more precise tuning of their catalytic properties, leading to higher efficiency and lower operating costs.

Another significant area of innovation has been the development of hierarchically structured catalysts, which mimic the natural, multi-scale porosity found in biological and geological systems [12]. These catalysts employ a combination of micropores, mesopores, and macropores to optimize mass transfer and catalytic performance [13]. This design is particularly effective in processing large hydrocarbon molecules, improving the efficiency of processes such as fluid catalytic cracking (FCC), which is crucial for converting heavy crude oil fractions into lighter, more valuable products. Advances in synthesis methods, including sol-gel techniques and atomic layer deposition, now offer the precise control needed to fabricate complex catalytic structures [14,15].

In addition to the focus on material and structural design, the environmental performance of refining catalysts has received greater attention. Because the carbon footprint of the refining industry has faced increasing scrutiny, efforts to develop greener catalysts that are both efficient and sustainable have [16]. This includes the use of bio-based materials, minimizing hazardous waste during catalyst production, and designing catalysts that can be easily regenerated or recycled [17,18]. These innovations are required to align the refining industry with global sustainability objectives.

This review aims to provide a comprehensive examination of recent advancements in petroleum refining catalysts, covering both their foundational scientific principles and practical applications. We begin by exploring the critical roles catalysts play in the refining process, followed by an analysis of innovations in catalyst design, including nanocatalysts, hierarchically structured catalysts, and environmentally sustainable catalysts. Case studies illustrate the industrial implementation of these innovations, emphasizing their contributions to enhanced efficiency, product quality, and sustainability. Major areas of focus include the fundamental concepts underlying catalyst design, recent technological developments in material design and synthesis methods, efforts to enhance the catalytic selectivity, yield, and stability, and strategies for reducing the environmental impact. The final sections examine the real-world applications of advanced catalysts, current challenges, and future research directions. This structured approach ensures that the review will be an invaluable resource for researchers and industry professionals, offering a detailed understanding of the current state of petroleum refining catalysts and their future possibilities.

2. Fundamentals of Petroleum Refining Catalysts

Petroleum refining is centered around the activity of catalysts, which drive the chemical processes needed to turn crude oil into useful products [19,20]. These catalysts are carefully designed to promote specific reactions, allowing refiners to improve the quantity and quality of final products while reducing waste and energy usage [21]. The effectiveness of these catalysts depends on their composition and structure and the specific processes they are intended to promote [22,23]. By recognizing the different types of catalysts used in refining, it is possible to understand how advancements in catalyst technology can be employed to enhance refining efficiency and sustainability.

2.1. Types of Catalyst Used in Refining

Petroleum refining systems use various catalysts, each designed for specific processes within the refinery. Catalyst selection depends on a variety of factors, such as the characteristics of the feedstock, the desired products, and the operational parameters of the refinery. Refining catalysts can be categorized into three main groups: zeolite-based, metal-based, and mixed metal-oxide catalysts [18,24]. Each type has unique qualities and applications that contribute to the overall refining process (Table 1).

2.1.1. Zeolite-Based Catalysts

Zeolite-based catalysts are widely used in petroleum refining, especially in FCC and hydrocracking processes (Table 1). Zeolites are crystalline aluminosilicates with a highly organized microporous structure that provides a large surface area and distinct active sites for catalytic processes [15,25]. The unique structure of zeolites allows them to act as molecular sieves, selectively breaking down large hydrocarbon molecules into smaller, more valuable compounds such as gasoline and olefins. The acidity of zeolites, which can be adjusted by changing their chemical composition, is a critical factor in determining their catalytic efficiency. For example, Y-zeolite catalysts in FCC have demonstrated conversion rates of up to 80% and gasoline yields of up to 50% [26]. However, coke formation (a carbonaceous deposit that deactivates catalysts) remains a limitation, with the observed coke yield reaching 10%, thus requiring frequent regeneration cycles to maintain efficiency [27]. Strategies to overcome these challenges include the development of hierarchically structured zeolites with micro-, meso-, and macropores, which improve mass transport and reduce deactivation [28]. Process intensification techniques, such as incorporating continuous regeneration cycles, have also been explored to extend the active lifespan of zeolite catalysts under industrial conditions [29]. Because of their ability to operate under harsh conditions and their resistance to deactivation, zeolite catalysts are important components of refining processes that focus on maximizing the yields of light products [30].

2.1.2. Metal-Based Catalysts

Metal-based catalysts are generally employed in refining processes that involve hydrogenation, dehydrogenation, and other reactions that require the addition or removal of hydrogen (Table 1). These catalysts typically consist of transition metals such as platinum, palladium, nickel, and cobalt, often supported on an inert substrate such as alumina (Al_2O_3) or silica (SiO_2) [31,32]. For example, in catalytic reforming, platinum-based catalysts (e.g., Pt/Al_2O_3) improve the octane rating of gasoline by promoting the dehydrogenation of naphthenes into aromatic compounds [33]. Platinum-based catalysts in catalytic reforming can achieve octane ratings up to 95 RON, which is critical for high-quality gasoline production [34]. However, platinum catalysts are costly, and sulfur poisoning can reduce their lifespan, requiring sulfur-resistant modifications to extend operational stability [35]. Metal-based catalysts offer a hydrogenation and dehydrogenation performance that is superior to zeolite-based catalysts, making them ideal for hydroprocessing. While base metals such as nickel represent a more economical option, they typically require more frequent regeneration. Alloying and sulfur-tolerant catalysts have thus been explored to improve durability in sulfur-rich environments [36,37].

Common metal-based catalysts for hydrotreating include Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3, where cobalt or nickel acts as the active metal, with Al_2O_3 providing stability and a high surface area for reactions. These catalysts have shown sulfur removal efficiencies of over 90%, enabling refiners to meet ultra-low sulfur fuel standards [38]. However, sensitivity to impurities such as nitrogen can still lead to deactivation over time, impacting long-term performance. Advances in support materials, such as Al_2O_3 and SiO_2, have also improved metal dispersion, enhancing catalyst stability and extending operational lifespans [39]. Moreover, adding sulfur-tolerant components has proven effective in improving the durability of metal-based catalysts under refining conditions [40]. The choice of metal and its distribution on the support material are crucial factors that influence the catalyst's effectiveness, selectivity, and resistance to impurities.

2.1.3. Mixed Metal-Oxide Catalysts

Mixed metal-oxide catalysts are a diverse family of materials used in various refining processes under high pressures and temperatures, such as hydrodesulfurization (HDS), hydrodenitrogenation, and residual hydrocarbon oxidation (Table 1). These catalysts consist of combinations of metal oxides, such as cobalt-molybdenum (Co-Mo/Al_2O_3) or nickel-molybdenum (Ni-Mo/Al_2O_3), often supported by aluminum [41,42]. The synergy between the metal oxides enhances the catalyst's activity and stability, making it well-suited for processes that require the removal of sulfur and nitrogen molecules from heavy crude fractions. In these catalysts, the interaction between Co or Ni with molybdenum oxide (MoO_3) on an Al_2O_3 support enhances the hydrogenation properties needed for effective removal. In hydrodesulfurization, Co-Mo/Al_2O_3 catalysts demonstrate removal rates of between 85 and 95% depending on the process conditions and feed composition. Although effective, these catalysts are prone to deactivation due to the accumulation of impurities, thus they require periodic regeneration.

To overcome these challenges, new synthesis techniques, such as atomic layer deposition (ALD) and sol-gel processes, have been employed to create catalysts with improved structural stability and resistance to deactivation [43]. Additionally, advancements in regenerable mixed metal-oxide formulations allow for periodic regeneration, ensuring sustained sulfur removal. As such, mixed metal-oxide catalysts are particularly valuable for systems aiming to comply with strict environmental regulations. Advancements in synthesis processes also allow for the precise adjustment of catalyst properties, enhancing their performance and longevity under demanding industrial refining conditions [42,44].

Table 1. Comparison of the three main catalyst types and their applications.

Catalyst Type	Composition	Applications	Operating Conditions	Advantages	Disadvantages	References
Zeolite-based	Crystalline aluminosilicates	FCC, hydrocracking	High temperature (500–700 °C), moderate pressure	High selectivity, resistance to deactivation	Limited ability to handle heavy feedstocks, coke formation	[45]
Metal-based	Transition metals such as Pt, Pd, and Ni	Catalytic reforming, hydrotreating	High temperature (400–600 °C), high pressure	High activity for hydrogenation/dehydrogenation, excellent selectivity	Expensive, sensitive to sulfur poisoning	[46]
Mixed Metal Oxide-based	Combinations of metal oxides (e.g., Co-Mo)	HDS, hydrodenitrogenation	High temperature (300–500 °C), high pressure (100–200 bar)	Good stability, effective in removing S and N compounds	Can suffer from deactivation due to impurities, relatively high cost	[47]

2.2. Key Catalytic Processes in Petroleum Refining

The efficient conversion of crude oil into useful products such as fuels and petrochemicals relies on catalytic reactions. Specific catalysts are essential for accelerating chemical reactions that break down complex hydrocarbons, modify their structural arrangements, or eliminate impurities [2,48]. FCC, hydrocracking, and catalytic reforming are three of the most important catalytic processes in petroleum refining (Figure 1). Each of these processes targets different crude oil fractions and contributes to the overall efficiency and production of high-quality finished products [49,50]. However, these processes also face several technical issues, including catalyst deactivation due to coke formation and difficulties handling variable feedstock compositions, and meeting increasingly stringent environmental regulations. Addressing these challenges is critical to maintaining process efficiency and extending the lifetime of catalysts, particularly because refiners work with heavier and more sulfur-rich crude sources.

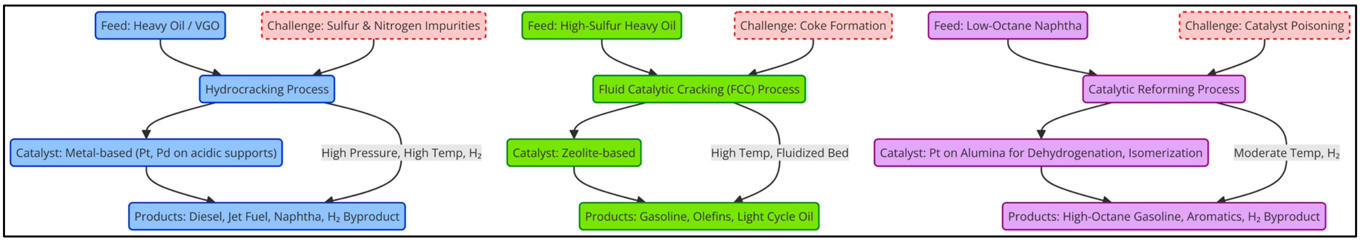

Figure 1. Schematic of key catalytic processes in petroleum refining: hydrocracking, fluid catalytic cracking (FCC), and catalytic reforming. Details about the figures are provided in Appendix A.

2.2.1. Hydrocracking

Hydrocracking converts heavy crude oil fractions into more valuable products such as jet fuel, naphtha, and diesel [51,52]. This process involves breaking down large hydrocarbon molecules through catalytic cracking in the presence of hydrogen at high pressures and temperatures. The catalyst, which is typically a metal or metal oxide on an acidic carrier, helps break the carbon–carbon bonds of the hydrocarbons while hydrogenating the resulting fragments to stabilize them. Metal-based hydrocracking catalysts, such as Ni-Mo on Al_2O_3, have exhibited conversion efficiencies of up to 90%, with middle distillate yields reaching 60% under optimal conditions [53]. However, a significant limitation is deactivation due to nitrogen impurities, which can poison the active sites over time, impacting catalyst longevity. Nevertheless, hydrocracking is a highly adaptable process that allows refiners to optimize the production of specific products based on market demand by adjusting the process conditions. It is essential for meeting strict environmental regulations by producing clean fuels with a low sulfur content [54].

2.2.2. Fluid Catalytic Cracking (FCC)

FCC optimizes the production of gasoline and other lighter products from heavy crude oil fractions such as vacuum gas oil [55,56]. The process uses a zeolite-based catalyst that is finely powdered and suspended in a fluidized state, allowing it to mix thoroughly with the feedstock. The high temperatures in the FCC unit facilitate the catalytic breakdown of large, complex hydrocarbon molecules into smaller, more valuable ones such as gasoline, olefins, and light cycle oil [57]. Advanced FCC catalysts, especially rare earth-stabilized Y-zeolites, have achieved gasoline yields of 45–55% while maintaining high selectivity. However, coke formation on the catalyst remains a limitation, with 5–10% of the feed typically converted to coke, necessitating frequent regeneration [58]. FCC units also struggle to effectively handle variable, sulfur-rich feedstocks, which can lead to catalyst deactivation and environmental concerns. To address these issues, advanced FCC catalysts with improved coke and sulfur resistance have been developed, along with feedstock pre-treatment methods to reduce impurities before cracking. Compared to hydrocracking, FCC with zeolite catalysts is more effective for cracking heavier feedstocks but has a higher tendency for coke formation. This limits the catalyst's lifespan and may require more frequent regeneration [59]. Advanced FCC catalysts and feedstock pre-treatment strategies have been developed to improve coke and sulfur resistance, enhancing the variety of feedstocks that can be used and extending the catalyst's longevity [60].

2.2.3. Catalytic Reforming

Catalytic reforming is used to convert low-octane naphtha into high-octane gasoline components and aromatic hydrocarbons, which, in turn, are employed to produce high-quality fuels and petrochemicals [61,62]. During catalytic reforming, hydrocarbon molecules are rearranged through dehydrogenation, isomerization, and cyclization processes facilitated by a metal-based catalyst, often platinum. In Pt/Al_2O_3 catalysts, platinum acts as the active metal, while the Al_2O_3 support provides stability and a high surface area, facilitating the interaction with the hydrocarbon feed molecules. One key challenge in catalytic reforming is maintaining catalyst stability and activity in the presence of impurities such as sulfur, which can poison the catalyst and reduce efficiency. This sulfur-sensitive nature of Pt-based catalysts requires sulfur-tolerant modifications or periodic regeneration cycles to prevent deactivation and maintain catalytic performance [63]. Techniques such as using sulfur-tolerant catalysts and applying periodic regeneration cycles have helped to address these issues, prolonging the catalyst's operating life and maintaining its efficiency [64]. Additionally, catalytic reforming produces hydrogen as a byproduct, which can be used in other refining processes such as hydrocracking and hydrotreating [65].

Catalytic reforming in modern refineries enhances gasoline quality and yields valuable byproducts, contributing to fuel output and refinery efficiency. However, the combined use of metal-based catalysts such as Pt/Al_2O_3 with sulfur-tolerant modifications highlights the importance of carefully selecting the catalyst composition to optimize reforming reactions while maintaining durability under industrial conditions. For example, Pt/CeO_2-Al_2O_3 catalysts have demonstrated enhanced sulfur tolerance and stability, making these catalysts particularly effective in sulfur-rich environments [66]. Additionally, research on bimetallic Pt–Ru catalysts has demonstrated that the alloyed structure improves sulfur resistance, with the ability to regenerate through hydrogen treatment [67].

Catalytic reforming, in addition to FCC and hydrocracking, enables the conversion of heavy and less valuable fractions of crude oil into lighter, higher-value products (Figure 1). This ensures that refineries can meet market demands while optimizing resource use and complying with environmental regulations [68]. Continuous improvement of these processes through advancements in catalyst technology can ensure the growth and sustainability of the refining sector.

3. Recent Technological Advancements in Refining Catalysts

Recent innovations in catalyst technology for petroleum refining processes have focused on the development of novel catalytic materials and improving synthesis methods [69]. These advancements are driven by the need to process a wider range of complex feedstocks while meeting strict environmental regulations and responding to market demands for higher-quality products.

3.1. Novel Catalytic Materials

Various innovative catalytic materials that enhance refinery performance have recently been reported. Nanocatalysts have received significant attention due to their unique characteristics resulting from their nanoscale dimensions [70,71]. These catalysts offer a high surface area-to-volume ratio, which effectively increases the number of active sites available for reactions [72]. Nanocatalysts are particularly effective in hydrocracking applications due to their high surface area-to-volume ratio, which significantly increases the number of active sites and allows for more efficient hydrocarbon cracking. This leads to higher conversion rates and stronger selectivity for diesel and jet fuel products [73,74]. Moreover, their nanoscale properties allow for finer control over the shape and size of individual particles, which directly impacts the stability and distribution of the active sites, minimizes undesirable byproduct formation, and enhances catalyst longevity under hydrocracking conditions [75,76].

Hierarchically structured catalysts, which are characterized by a combination of micro-, meso-, and macropores, resemble the natural porous structures found in biological and geological materials and represent a substantial advancement in catalyst design (Figure 2). The hierarchical porosity improves mass transport within the catalyst, enhancing access to active sites, particularly for large hydrocarbon molecules. This leads to enhanced catalytic performance in processes such as FCC, where the efficient decomposition of heavy feedstocks is essential [57,75]. Adjusting the pore architecture of these catalysts can also enhance catalytic activity and stability in refining processes across various operating conditions.

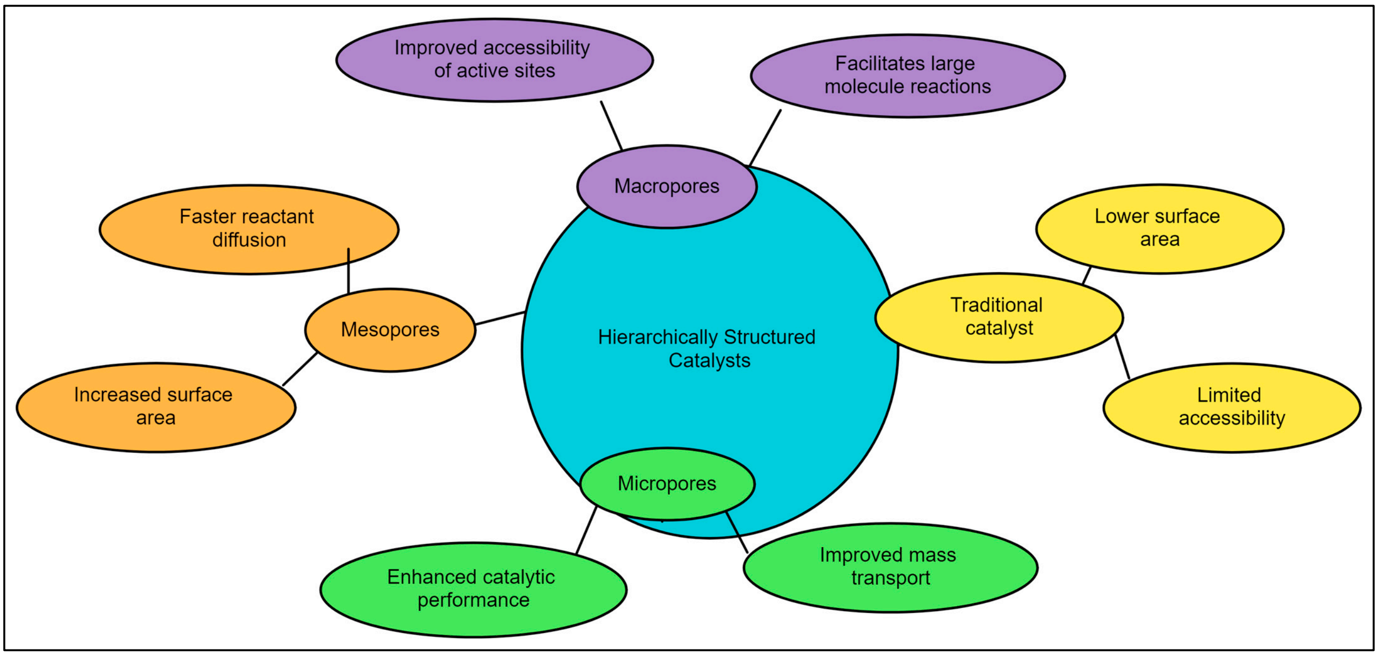

Figure 2. Schematic diagram of the characteristics of hierarchically structured catalysts.

Significant progress has also been made in the development of supported metal catalysts, where metal nanoparticles are coated onto a support medium [77,78]. These catalysts offer the dual advantage of high activity due to the metal catalysts and stability due to the support material, usually an oxide such as Al_2O_3 or SiO_2. Recent advancements have focused on improving the dispersion and stability of metal particles as a means to improve long-term catalyst performance. Supported metal catalysts are widely used in processes such as hydrotreating and catalytic reforming to enhance the hydrogenation and dehydrogenation reactions necessary to produce clean fuels and high-octane gasoline components [79,80]. The synthesis and characterization of these catalysts have been improved, leading to more efficient and durable systems capable of operating under the harsh conditions of modern refineries.

3.2. *Advanced Synthesis Methods*

The development of advanced synthesis methods is required to realize the full potential of novel catalytic materials. Sol-gel techniques have emerged as a viable option for producing highly homogeneous and finely structured catalysts. The sol-gel process converts a system from a colloidal solution to a solid gel phase. This approach enables precise control over the composition, particle size, and porosity of the catalyst, resulting in materials with outstanding catalytic capabilities [81,82]. Sol-gel processes are particularly useful in creating mixed metal-oxide and hierarchical catalysts, where uniformity and fine-tuning of the catalyst structure are required for effective performance [81].

Microwave-assisted synthesis is a new method for producing refining catalysts. This technique uses microwave radiation to quickly heat the reactants, leading to shorter reaction times and more consistent particle production. The precise control over the heating process at the molecular level results in catalysts with a higher surface area, crystallinity, and active site dispersion. Microwave-assisted synthesis has been particularly successful in developing nanocatalysts and supported metal catalysts, where managing the particle size and distribution enhances catalytic activity and stability [83].

ALD is one of the most advanced catalyst synthesis processes, especially for the production of supported metal catalysts, offering precise control over the thickness and composition of the active layers (Figure 3). ALD is a vapor-phase process in which thin layers of a material are sequentially deposited onto a substrate [84], thus producing highly uniform and conformal coatings with the active metal uniformly dispersed throughout the support material. ALD can be used to fabricate next-generation catalysts with customized features, such as stronger resistance to sintering and longevity under the demanding operating conditions associated with petroleum refining [85].

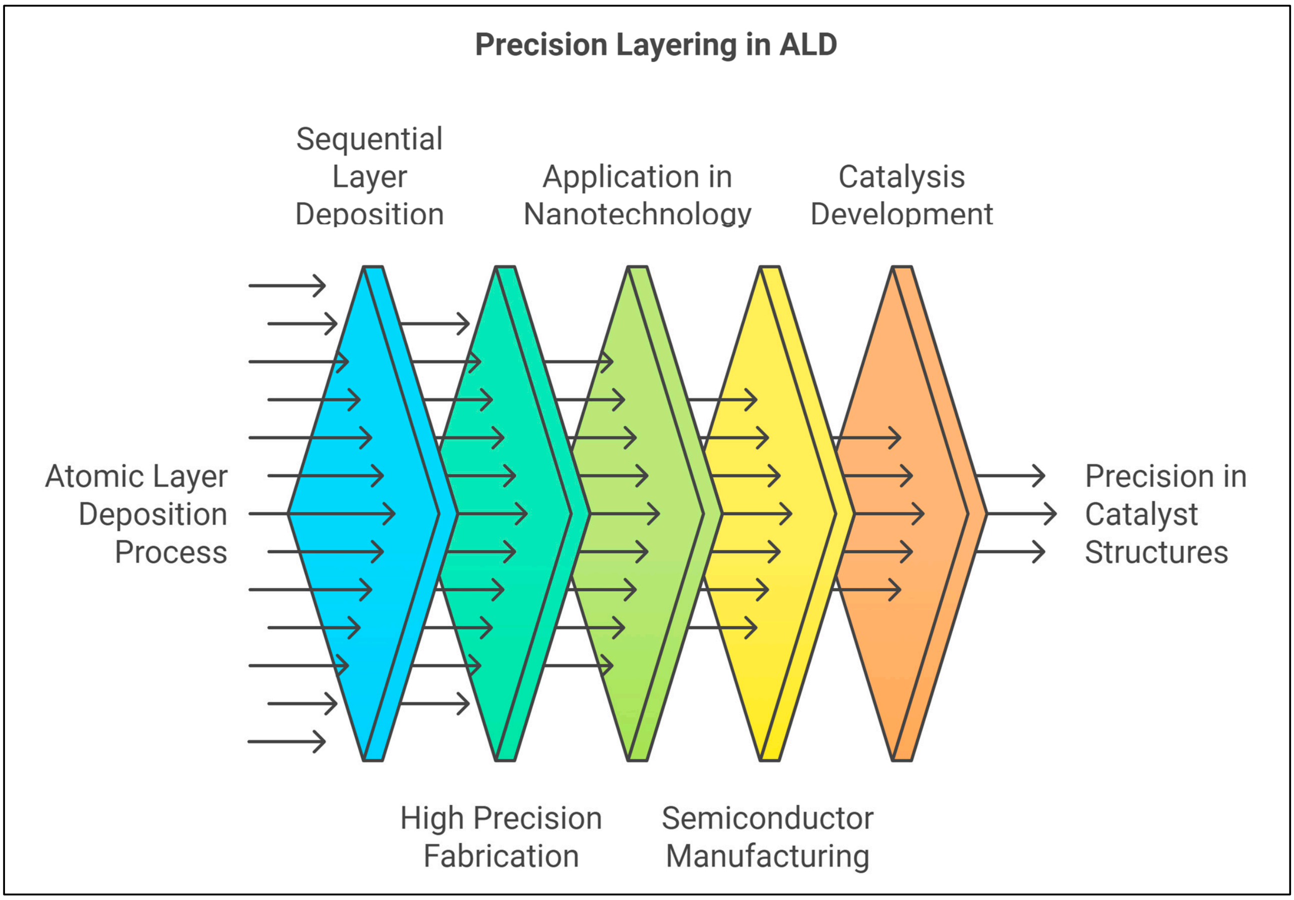

Figure 3. Diagram of the atomic layer deposition (ALD) process, showing the sequential deposition of layers to achieve a highly precise catalyst structure.

Advancements in catalytic materials and synthesis methods have led to significant improvements in the performance and sustainability of petroleum refining systems (Table 2). These technologies facilitate the development of more efficient, selective, and durable catalysts, thus allowing for the processing of complex feedstocks, reducing environmental impacts, and producing cleaner, higher-quality fuels.

Table 2. Summary of synthesis techniques for refining catalysts and their impact on catalyst properties.

Synthesis Technique	Impact on Catalyst Properties	References
Sol-gel	Precise control over particle size and pore structure, resulting in a high surface area and uniform porosity.	[86]
Microwave-assisted	Rapid synthesis with improved crystallinity and smaller particle sizes due to uniform heating, resulting in more uniform active site distribution.	[87]
ALD	Atomic-level control over thin-film deposition leads to highly uniform catalysts with enhanced stability and performance.	[88]

3.3. Enhancements in Catalyst Performance

The development of catalysts that can improve selectivity and yield is a primary focus of refining technology. Modifying the catalyst composition, pore structure, and/or surface area has been demonstrated to improve catalytic performance. For example, in a large-scale hydrodesulfurization unit, cobalt-molybdenum (Co-Mo/Al_2O_3) catalysts demonstrated a sulfur removal efficiency exceeding 95%, leading to a substantial reduction in SOx emissions [89]. This illustrates the practical effectiveness of mixed metal-oxide catalysts in meeting stringent sulfur content regulations for fuels. However, catalyst deactivation and the need for regular regeneration hinder the long-term operational efficiency of large-scale applications [90].

Stability and longevity are essential attributes of refinery catalysts because harsh operating conditions can degrade the catalyst structure over time [91]. Additionally, new approaches such as doping catalysts with isolated cobalt atoms to enhance hydrodeoxygenation stability have shown promise, allowing for operations at lower temperatures and minimizing sulfur loss and deactivation [92]. Organic additives, such as maleic acid, have also proven effective in reactivating CoMo/Al_2O_3 catalysts after regeneration, restoring performance to levels that are closer to the initial activity [93].

3.3.1. Improvement in Selectivity and Yield

Improving the selectivity and yield of catalysts enhances the production of desired products while minimizing waste and byproducts. One useful method for achieving this is by modifying the composition of the catalyst. In particular, researchers can significantly improve catalytic activity and selectivity by adjusting the type and quantity of active metals or promoters [94]. In hydrocracking operations, the incorporation of specific metal promoters such as platinum or palladium can enhance hydrogenation activity, leading to a higher output of light hydrocarbons such as diesel and gasoline. Similarly, the utilization of particular metal oxides in FCC catalysts can enhance the selectivity for olefins, which are vital feedstocks for petrochemical manufacturing. These modifications are carefully tuned to ensure that the characteristics of the catalyst align with the specific requirements of the refining process, resulting in optimal performance (Figure 4).

Controlling the pore structure and surface area of the catalyst enhances the selectivity and yield. The internal architecture of the catalyst, especially the size and distribution of pores, significantly influences the interaction of reactants with active sites. Engineering catalysts with specific pore sizes and morphologies can enhance the diffusion of reactants and products, prevent the formation of coke, and improve the overall reaction efficiency [25,30]. For example, hierarchically structured catalysts with micro-, meso-, and macropores create an optimal environment for processing large hydrocarbon molecules in FCC units, leading to improved product dispersion and higher yields [95]. The precise control of the pore morphology and surface area is a valuable tool for improving catalyst performance in refining operations.

Figure 4 presents the performance of standard catalysts, nanocatalysts, and supported metal catalysts in terms of their conversion efficiency, selectivity, and reaction rate. Significant improvements in catalytic performance have been achieved by reducing particle sizes and using strong metal–support interactions (SMSIs) in supported metal catalysts. Traditional catalysts (composed of nickel or platinum on Al_2O_3 or SiO_2 supports, typically used in CO oxidation reactions) typically have a conversion efficiency of about 60% and a selectivity of around 50%. These catalysts often require higher temperatures and pressures to achieve moderate reaction rates [96]. Nanocatalysts (metal nanoparticles such as platinum and gold dispersed on high-surface-area supports such as carbon nanotubes, optimized for CO_2 hydrogenation), due to their smaller particle size and larger surface area, demonstrate enhanced performance, with a conversion efficiency reaching 85% and a selectivity of up to 70%. Nanocatalysts also operate at lower temperatures, further boosting their reaction rates [97]. Supported metal catalysts (metals such as palladium or rhodium on reducible oxide supports, including TiO_2 and CeO_2), which use SMSIs for selective hydrogenation reactions, such as acetylene to ethylene, represent the most advanced type of catalyst, with a conversion efficiency up to 90% and a selectivity as high as 80%. These catalysts benefit from SMSIs, which enhance both activity and durability, resulting in the highest reaction rates even under mild conditions [98].

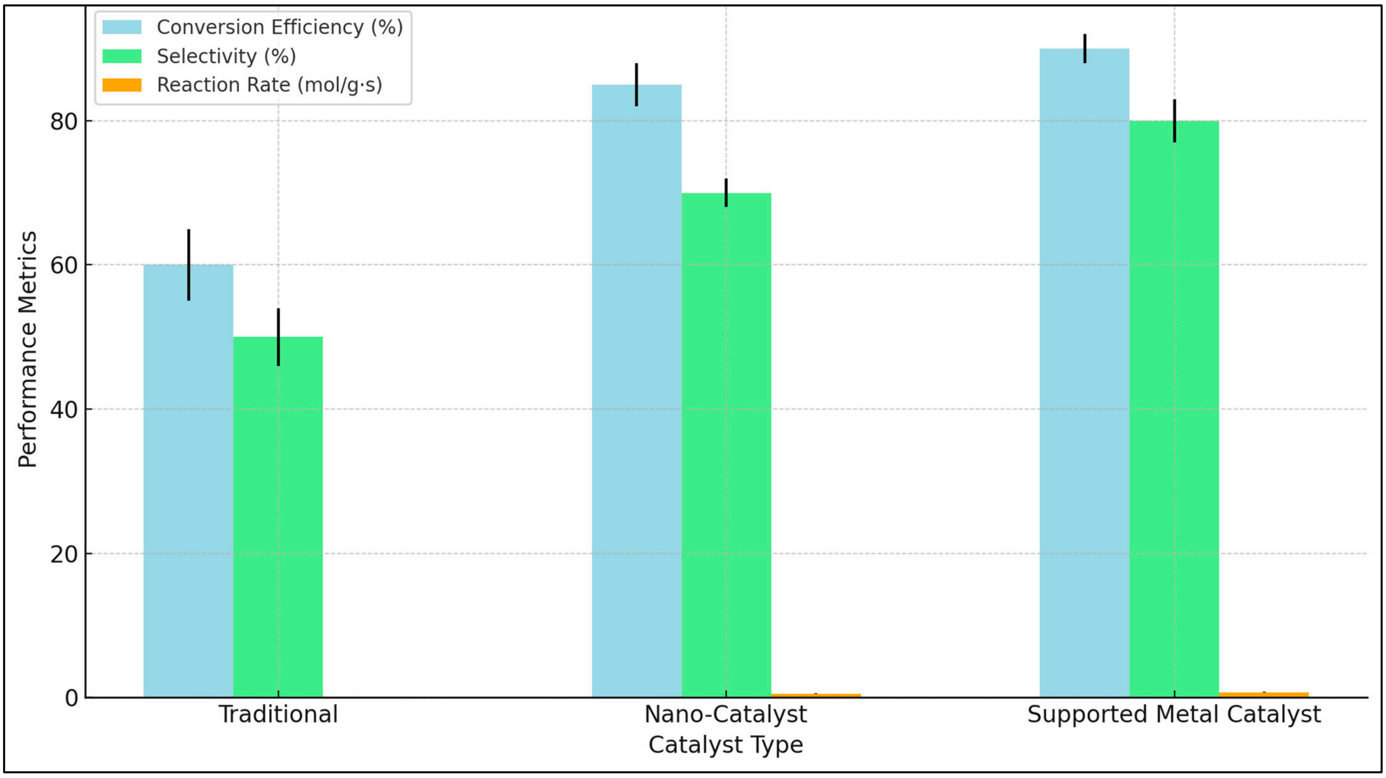

Figure 4. Comparative performance of catalysts before and after modifications.

3.3.2. Stability and Longevity of Catalysts

The stability and lifespan of catalysts strongly influence the economic viability of refining processes. Catalysts that maintain their functionality over extended periods require less frequent replacement, thus reducing operating costs and minimizing downtime. Enhancing the thermal stability of catalysts is primarily achieved through the development of materials capable of withstanding the high temperatures typical of refining processes [99]. For example, the catalysts used in catalytic reforming and FCC must operate effectively at temperatures exceeding 500 °C. To improve the thermal stability of these catalysts, researchers have focused on incorporating stabilizing agents, modifying support materials, and optimizing synthesis methods to produce more resilient structures [100]. These advancements ensure that catalysts retain their activity and structural integrity in demanding conditions, extending their operational life.

Coke resistance can increase the longevity of catalysts [101]. Coke formation is a significant restriction in many refining processes, particularly in FCC and hydrocracking, which involve the conversion of heavy hydrocarbons to lighter products [3]. Coke deposits on the catalyst surface can obstruct active sites, weakening catalyst performance and necessitating frequent regeneration or replacement. Recent advancements have focused on enhancing coke resistance in catalysts by modifying their surface characteristics or incorporating elements that inhibit coke formation. For example, the use of zeolites with specific pore structures has been employed to restrict the access of coke precursors to active sites, while the addition of metal oxides, such as lanthanum, can help prevent coke deposition [102]. These innovations enhance coke resistance, leading to longer catalyst lifespans, more stable operation, and lower maintenance costs in refining processes.

4. Environmental Considerations in Catalyst Development

The petroleum refining industry is increasingly focused on minimizing its environmental impact by developing catalysts that improve process efficiency, reduce harmful emissions, and support sustainability [103]. With stricter global emissions regulations, the industry is seeking innovative catalytic technologies to address environmental problems. This includes reducing pollutants such as sulfur oxides (SOx) and nitrogen oxides (NOx) through enhanced catalyst performance and the development of green catalysis technologies, demonstrating a commitment to reducing its environmental footprint.

4.1. Reduction of Harmful Emissions

In petroleum refining, a key environmental concern is the need to decrease harmful emissions such as SOx and NOx, which contribute to air pollution and acid rain. Catalysts are essential for managing these emissions because they improve the effectiveness of processes that eliminate or transform these pollutants into less harmful compounds [104,105]. In terms of environmental performance, various catalysts, including HDS, hydrotreating, and catalytic reforming catalysts, have demonstrated significant potential in reducing SOx, NOx, and CO_2 emissions (Table 3). The development of green bio-based and recyclable catalysts also highlights the industry's commitment to sustainability and emission reduction efforts.

Table 3. Environmental performance of various catalysts.

Catalyst Type	Emission Reductions	References
HDS	Significant reduction in SOx emissions by removing sulfur from crude oil fractions.	[106]
Hydrotreating	Effective in reducing both SOx and NOx emissions by removing sulfur and nitrogen compounds.	[6]
Catalytic Reforming	Reduces CO_2, emissions by improving hydrogen efficiency and limiting aromatic compound formation.	[107]
Bio-based/Recyclable	Potential for an overall reduction in CO_2, footprint and waste production through sustainable materials.	[108]

4.1.1. Sulfur Removal Efficiency

To reduce harmful emissions in petroleum refining, the removal of sulfur is required. This is because the sulfur compounds found in crude oil are transformed into sulfur dioxide (SO_2) during combustion, which is a significant contributor to air pollution and acid rain [109]. To address this issue, refiners utilize hydrotreating processes, in which catalysts aid in the removal of sulfur by converting it into hydrogen sulfide (H_2S), which can then be captured and processed. The HDS reaction relies on cobalt-molybdenum or nickel-molybdenum catalysts on an Al_2O_3 support. The high surface area and acidic properties of these catalysts promote the adsorption of sulfur compounds, allowing the active metal sites to break sulfur-carbon bonds and facilitate hydrogenation. These properties are critical for enhancing sulfur removal efficiency, particularly when processing heavy and sour crude oils with high sulfur content [110]. Recent advancements have focused on enhancing the activity and selectivity of HDS catalysts, ensuring that the resulting fuels meet strict ultra-low sulfur standards [111,112]. Improved sulfur removal efficiency not only assists in meeting regulatory requirements but also enhances the overall quality of the refined products.

4.1.2. Reduction of Nitrogen Oxide (NOx) Formation

Reducing NOx emissions is another important environmental objective for refining systems. NOx, a combination of nitric oxide (NO) and nitrogen dioxide (NO_2), is produced during fuel combustion and contributes to smog and causes respiratory problems [113,114]. Catalytic processes can minimize NOx formation, especially in the treatment of refinery off-gases and fuel combustion. Selective catalytic reduction (SCR) is a widely used method for NOx control, which involves reducing NOx to harmless nitrogen (N_2) and water vapor. This process utilizes catalysts based on vanadium, tungsten, or zeolite materials, which provide a high surface area and the thermal stability necessary for effective NOx reduction [115]. SCR relies on ammonia as a reducing agent, which reacts with NOx at the active sites of the catalyst to form nitrogen and water [116]. Recent advancements in SCR catalysts have focused on optimizing these active sites to operate more efficiently at lower temperatures and prolong catalyst longevity, enhancing both environmental and operational performance [117,118]. Moreover, the development of catalysts capable of removing both sulfur and nitrogen molecules from fuels helps to reduce NOx generation during combustion, leading to lower emissions.

4.2. Green Catalysis

The refining industry has increasingly embraced green catalysis to align with global environmental objectives. Green catalysis involves the development and application of catalysts that mitigate the environmental effects of refining operations by utilizing sustainable materials, minimizing waste, and improving catalyst longevity [119,120]. This strategy thus reduces the ecological impact of the refining industry and promotes more sustainable practices.

4.2.1. Use of Bio-Based Materials

Utilizing bio-based materials in catalyst synthesis is a fundamental approach to green catalysis. These compounds, sourced from renewable biological sources, represent an eco-friendly substitute for conventional catalysts, which often depend on metals that are limited or possess significant environmental costs [121]. In contrast, bio-based catalysts can be produced from natural polymers, plant-derived substances, or waste biomass [122]. Catalysts generated from lignin, a principal component of plant biomass, have demonstrated potential in many refining processes due to their distinctive structure and reactivity. The utilization of bio-based materials reduces the dependence on non-renewable resources and facilitates the development of biodegradable catalysts with a lower environmental impact when they reach the end of their operational life [123].

4.2.2. Recycling and Reusability of Catalysts

The recycling and reusability of catalysts prolong the catalytic lifespan and minimize waste [124]. Conventional refining catalysts, especially those employed in hydrotreating and cracking operations, may experience deactivation over time due to fouling, poisoning, and sintering. This frequently requires their substitution, resulting in considerable waste and ecological consequences [125,126]. Recent improvements in catalyst design have concentrated on enhancing the durability and regenerability of catalysts, enabling their reuse over several cycles with minimal activity loss. For example, the active metal constituents of regenerable supported metal catalysts can be retrieved and redeposited onto the support material, significantly prolonging the catalyst's longevity [127]. Moreover, methods that enable the recycling of exhausted catalysts into new catalytic substances or alternative industrial products are under investigation, reducing the demand for new raw materials and mitigating the overall environmental impact of refining activities [128,129].

The refining industry has recently made efforts to strike a balance between the demand for high-performance catalysts and the requirement to minimize associated environmental impacts [120,130]. By seeking to minimize harmful emissions and develop eco-friendly catalysts, the industry is making substantial progress toward the establishment of more sustainable refining operations, thus contributing to a cleaner and more sustainable energy future. Recent advancements in catalyst technology have also led to significant improvements in refining efficiency and product quality (Figure 5). These real-life examples demonstrate how advanced catalyst developments have been implemented in practical operations, demonstrating the advantages and constraints of these technologies.

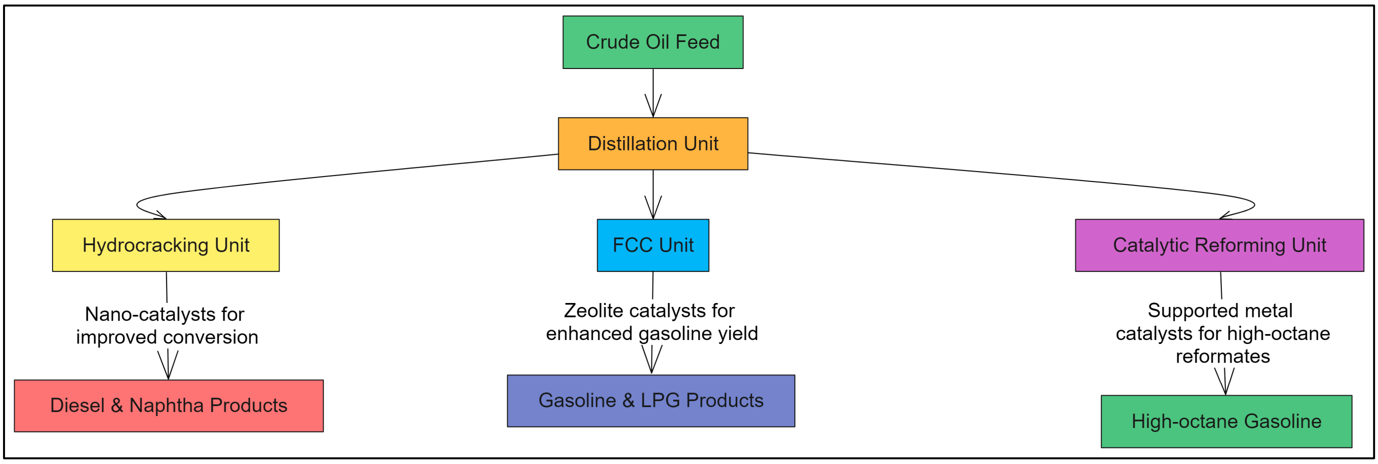

Figure 5. Process flow for a refinery incorporating novel catalysts.

5. Challenges and Future Directions

Significant issues still need to be addressed to fully harness the potential of novel catalytic technologies in the petroleum refining industry. Various initiatives have been introduced for catalyst development with the aim of ensuring that the industry meets the increasing demand for cleaner fuels and more efficient production methods.

5.1. Technical Challenges in Catalyst Development

The development of advanced refining catalysts is a complex endeavor, with several technical issues that need to be overcome to ensure the successful deployment of these technologies on an industrial scale.

5.1.1. Scalability of Novel Materials

The scalability of novel materials is one of the major challenges facing catalyst development. Many advanced catalysts, such as nanocatalysts or hierarchically structured catalysts, are initially developed and tested in laboratory settings. However, scaling these materials from the lab to full-scale industrial production is often difficult. While precise control over material properties is possible when working with small batches, this becomes significantly more challenging when producing the quantities required for industrial use. In particular, issues such as uniformity, reproducibility, and cost-effectiveness are significant concerns during scaling [131]. The synthesis processes for some of these advanced materials can be complex and expensive, raising questions about their economic viability in a competitive market. Thus, improving the scalability of these advanced catalysts can promote their widespread adoption by the refining industry.

5.1.2. Integration with Existing Technologies

Successfully integrating new catalytic materials with existing refining technologies is also an issue that needs to be resolved. Refineries require substantial capital investment, and the viability of any new technology depends on its compatibility with existing infrastructure. This means that new catalysts need to be capable of being physically integrated into current reactors and processing units while also functioning efficiently under identical operating conditions (e.g., temperature and pressure) and with the same feedstocks as conventional catalysts. Furthermore, new catalysts must provide more benefits than existing technologies to justify the costs associated with their implementation [131]. The requirement for seamless integration that does not disrupt current operations or necessitate substantial alterations to existing equipment can thus restrict the adoption of new catalysts in refineries.

5.2. Future Research Directions

Research on catalyst development is currently following several promising directions that aim to address current issues and further optimize petroleum refining systems (Table 4). Addressing specific research gaps can significantly impact the practical application of advanced catalysts in petroleum refining. One major area is reducing the costs associated with novel materials such as nanocatalysts and mixed metal oxides, which can be expensive due to material costs and complex synthesis processes. Reducing these costs can ensure that advanced catalysts are more economically feasible on a large scale.

Table 4. Summary of ongoing research and emerging trends.

Research Focus	Emerging Trends	Key Challenges	References
Exploration of MOFs	MOFs offer tunable porosity and a large surface area, thus they have the potential for selective catalysis and gas separation.	Scalability of MOF synthesis for industrial applications and maintaining stability under refining conditions.	[132]
Development of Perovskite-based Catalysts	Perovskites are gaining attention due to their thermal stability and potential to replace noble metals in catalytic reactions.	Integration of perovskites with existing technologies and addressing deactivation over time.	[133]
Multi-functional Catalysts	Multi-functional catalysts have been designed to perform multiple reactions simultaneously, improving efficiency and reducing process complexity.	Balancing activity, selectivity, and stability for complex industrial processes.	[134]
Catalyst Regeneration and Recycling Techniques	Efforts are underway to enhance the catalyst lifespan via improved regeneration and recycling methods, reducing waste and operating costs.	Ensuring cost-effective regeneration techniques without performance loss and addressing environmental impacts.	[135]

Another critical area is the scalability and integration of multi-functional catalysts. These catalysts, designed to perform multiple reactions in a single stage, have the potential to simplify refining processes, reduce energy consumption, and improve operational efficiency. However, balancing activity, selectivity, and stability for these versatile catalysts is difficult, especially when scaling from laboratory conditions to full-scale refinery applications.

Enhancing catalyst stability under the harsh conditions associated with industrial refining also remains a priority. Current catalysts, such as Co-Mo and Ni-Mo, are subject to deactivation due to impurities such as sulfur and nitrogen, necessitating costly regeneration processes. Developing sulfur-tolerant formulations and optimizing regeneration techniques could extend catalyst lifespans and lower operational costs. By focusing on these areas, namely, cost reduction, scalability, and stability, future research can provide a roadmap for the development of advanced refining catalysts that align with the industry's dual goals of increasing efficiency and sustainability.

5.2.1. Exploration of New Catalytic Materials

Investigating novel catalytic materials is a key focus of future research in refining technologies. This involves analyzing unconventional materials in refining, such as metal–organic frameworks (MOFs), perovskites, and two-dimensional materials such as graphene. These materials possess unique characteristics, including adjustable porosity, a higher surface area, and novel electronic structures, which have the potential to significantly enhance catalytic activity, selectivity, and stability [136,137]. Researchers are also exploring catalysts derived from sustainable and renewable materials, reflecting the growing emphasis on green chemistry and sustainability within the refining sector. Developing these new materials requires a comprehensive understanding of the fundamental chemistry and physics underlying catalytic processes, as well as innovative synthesis techniques capable of large-scale production. This pursuit aims to drive advancements in refining technologies and contribute to environmentally friendly practices within the industry.

5.2.2. Development of Multi-Functional Catalysts

The development of multifunctional catalysts is an exciting and unique area for future research. These catalysts are designed to simultaneously carry out various catalytic functions, thus simplifying the refining process and reducing the need for multiple catalytic stages. For example, a multifunctional catalyst can be employed for both hydrocracking and desulfurization, allowing for the direct conversion of heavy crude fractions into light, sulfur-free products in a single reactor. This would not only streamline the refining process but also reduce operational costs and energy consumption. However, it remains difficult to develop materials that can maintain high performance across a variety of reactions without compromising selectivity or stability. Nevertheless, this field has the potential to revolutionize refining by improving the efficiency and environmental sustainability of refining processes, leading to significant economic benefits (Figure 6).

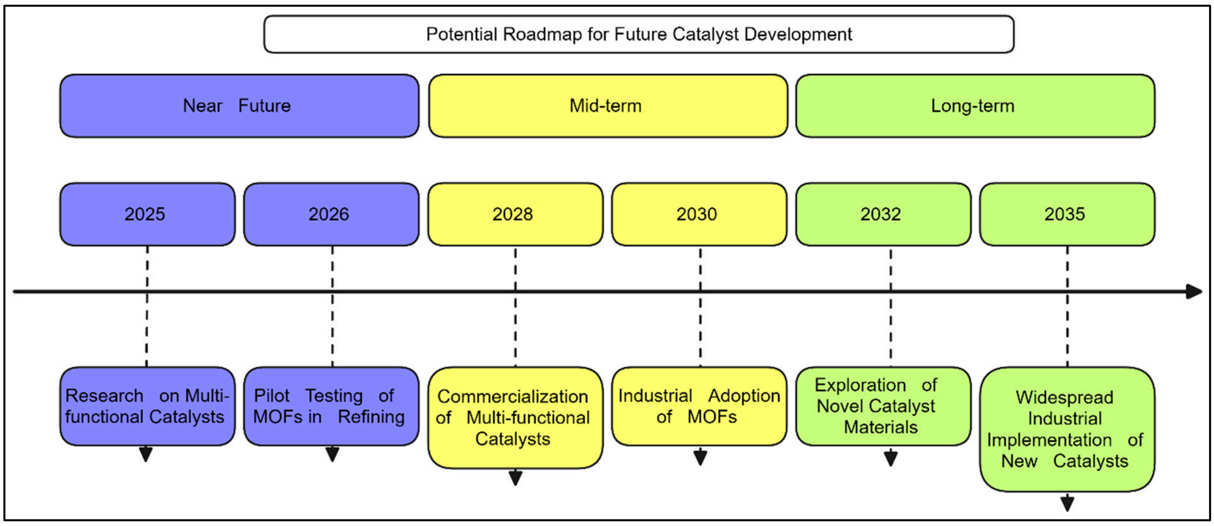

Figure 6. Potential roadmap for future catalyst development.

6. Conclusions

This review highlights recent advancements in petroleum refining catalysts, with a focus on novel catalytic materials such as nano-catalysts, hierarchically structured catalysts, and mixed metal oxide catalysts. These innovations have shown substantial improvements in refining processes, with nano-catalysts demonstrating high surface area-to-volume ratios that enhance reaction rates, and hierarchically structured catalysts facilitating improved mass transport, which is crucial in handling heavier crude fractions. Mixed metal oxide catalysts, particularly those incorporating cobalt-molybdenum or nickel-molybdenum, offer effective sulfur removal capabilities, thus aligning with stringent environmental standards for cleaner fuels. The review identifies several challenges that remain critical for future research. For instance, while synthesis methods like atomic layer deposition (ALD) enable precise control over catalyst structure, scalability, and cost-effectiveness need further optimization to make these catalysts feasible on an industrial scale. Additionally, catalyst deactivation, especially in sulfur-rich and nitrogen-rich feeds, poses a limitation that necessitates continued exploration of sulfur-tolerant materials and regeneration techniques to extend catalyst lifespan and reduce operational costs. Looking forward, the integration of multi-functional catalysts capable of performing multiple refining tasks simultaneously presents a transformative potential for simplifying refinery operations and reducing energy consumption. The environmental advantages of bio-based and recyclable catalysts also provide a pathway to sustainable practices in refining, addressing both regulatory demands and corporate sustainability goals.

In summary, this review underscores the crucial role of innovative catalyst design in meeting the dual objectives of operational efficiency and environmental compliance in petroleum refining. By outlining the specific advancements, ongoing challenges, and strategic research priorities, this review provides a roadmap for researchers and industry stakeholders to drive continued progress in refining catalysis.

7. Theoretical and Managerial Implications

This review offers important theoretical contributions by providing a comprehensive synthesis of recent advancements in petroleum refining catalysts. From a theoretical standpoint, the review consolidates knowledge of the properties, synthesis methods, and performance of cutting-edge catalysts, including nanocatalysts and mixed metal oxides. By contextualizing these advancements in relation to current research challenges, the review establishes a foundation for future studies to build on, particularly in addressing stability, cost, and scalability issues.

From a managerial perspective, the insights presented here have strategic implications for the petroleum refining industry. The focus on multi-functional and sulfur-resistant catalysts is particularly relevant in light of increasingly strict environmental regulations because these catalysts enable companies to achieve compliance more rapidly. Overall, this review serves as a strategic guide for stakeholders in the refining industry to make informed decisions about catalyst development, acquisition, and implementation.

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Appendix A

As this review article synthesizes existing literature on advancements in petroleum refining catalysts, no experimental procedures were conducted. Instead, this review was based on a comprehensive analysis of peer-reviewed journal articles, case studies, and industry reports. The selection criteria for the literature focused on recent developments in catalyst materials, synthesis techniques, environmental impacts, and industrial applications. Sources were identified through academic databases such as Google Scholar, ScienceDirect, MDPI, Wiley, and Springer, emphasizing high-impact, relevant publications.

Furthermore, the figures included in this review were created using the following tools:

- Whimsical Diagrams and Napkin.ai for diagram generation.
- Flowcharts and Mindmaps for flowcharts and mind maps.

These tools were used to create visual representations that aid in explaining key concepts in the review. All figures were carefully reviewed to ensure they accurately represent the content discussed.

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