

Green Catalysts for Sustainable Chemical Processing: From Refinery and Petrochemical Operations to Biomass and Hydrogen Technologies

Matthew N. Abonyi¹ , Lawrence I. Igbonekwu^{2*} 

¹ Department of Chemical Engineering, Nnamdi Azikiwe University, PMB 5025 Awka; mn.abonyi@unizik.edu.ng

² Department of Chemical Engineering, Nnamdi Azikiwe University, PMB 5025 Awka; Li.igbonekwu@unizik.edu.ng

* Correspondence: Li.igbonekwu@unizik.edu.ng

Abstract

The transition toward sustainable refinery and petrochemical operations has accelerated the development of green catalysts that enhance process efficiency while minimizing environmental impacts. This review critically examines recent advances in nanocatalysts, biomass-derived catalysts, zeolite-based catalysts, and catalysts for hydrogen production and environmental remediation. The analysis reveals that catalyst performance is primarily governed by structure-property-performance relationships, particularly active-site distribution, pore architecture, metal-support interactions, and mass-transfer characteristics. Hierarchical zeolites outperform conventional zeolites through improved reactant diffusion and reduced coke formation, while nanocatalysts exhibit enhanced catalytic activity due to greater active-site accessibility and metal dispersion. Biomass-derived catalysts offer sustainable, low-cost alternatives with promising applications in hydroprocessing, biomass upgrading, wastewater treatment, CO₂ utilization, and green hydrogen production. These catalyst systems collectively improve hydrocarbon conversion, catalyst selectivity, fuel quality, and resource efficiency while reducing emissions. However, catalyst deactivation, metal leaching, high production costs, scale-up challenges, and limited long-term industrial validation remain significant barriers to commercialization. The review concludes that future progress depends on establishing robust structure-property-performance relationships and integrating artificial intelligence, machine learning, and computational catalyst design to develop durable, economically viable, and scalable catalytic systems for low-carbon refinery and petrochemical operations.

Keywords: Green Catalysts, petroleum refining, Nanocatalysts, Hydrogen Production, petrochemicals.

Introduction

The petroleum refining and petrochemical industries remain indispensable to global economic growth and industrial development, supplying critical products such as transportation fuels, lubricants, polymers, fertilizers, solvents, and numerous chemical intermediates that sustain modern civilization. However, despite their strategic importance, these industries are

also major sources of greenhouse gas emissions, sulfur-containing pollutants, nitrogen oxides, volatile organic compounds, wastewater discharge, and spent catalyst waste. Catalytic technologies constitute the foundation of nearly all refinery and petrochemical conversion processes, including fluid catalytic cracking, hydrocracking, catalytic reforming, alkylation,

isomerization, hydroprocessing, and hydrodesulfurization. Recent reviews confirm that refinery catalyst development is increasingly focused on cleaner fuel production, catalyst stability, process efficiency, and lower environmental impact (Akhtar, Ali, & Zaman, 2024; Sun et al., 2025).

The growing global commitment to decarbonization, cleaner production, and sustainable industrial transformation has intensified the search for environmentally benign catalytic systems capable of supporting next-generation refinery operations. Green catalysts are designed to reduce hazardous by-products, improve atom economy, lower process severity, enhance catalytic selectivity, and reduce the environmental burden of refinery operations while maintaining high catalytic activity and stability. In this direction, oxidative desulfurization has received increasing attention because it can remove refractory sulfur compounds under milder conditions compared with conventional hydrodesulfurization (Said, Mikhail, & Riad, 2025). Similarly, biomass-derived catalysts are now being explored as low-cost, renewable, and recyclable alternatives for sustainable catalytic conversion processes (Ao, Ghorui, Li, Baskar, & Rokhum, 2024).

Recent advances in nanotechnology, zeolite engineering, surface modification, computational chemistry, and catalyst design have accelerated the development of more efficient green catalytic systems. Hierarchical and nanozeolite catalysts are particularly important because they reduce diffusion limitations,

improve access to active sites, and enhance heavy hydrocarbon cracking performance (Hijazi et al., 2025; Wei, Wang, Dong, Li, & Xiang, 2025). In addition, photocatalytic and electrochemical catalytic systems are increasingly being investigated for refinery wastewater treatment because they can degrade persistent organic pollutants and improve treatment efficiency (Al-Tameemi, Sukkar, & Abbar, 2024). Carbon-based catalysts, single-atom catalysts, and advanced electrocatalysts are also gaining attention for CO₂ utilization and green hydrogen production, which are essential for future low-carbon refinery systems (Shoaib et al., 2025).

The novelty of this review lies in its refinery-centered and sustainability-oriented perspective on green catalyst development. Unlike studies that focus narrowly on individual catalyst classes or isolated reactions, this review integrates catalyst synthesis, catalytic functionality, environmental applications, refinery performance, and decarbonization strategies within one framework. It further highlights the convergence between catalysis, renewable energy integration, circular economy principles, cleaner fuel production, and carbon-neutral refinery technologies. Therefore, this study examines recent developments in green catalysts for sustainable refinery and petrochemical operations, with emphasis on catalyst classification, synthesis strategies, industrial applications, environmental significance, operational challenges, and future prospects for cleaner and more energy-efficient refinery systems.

2. Concept of Green Catalysis in Refinery Operations

The concept of green catalysis has emerged as a transformative strategy for improving the environmental sustainability, energy efficiency, and operational performance of modern petroleum refining and petrochemical industries. Refinery operations depend heavily on catalytic processes such as fluid catalytic cracking (FCC), hydrocracking, catalytic reforming, hydroprocessing, alkylation, and hydrodesulfurization for the conversion of crude oil into transportation fuels and petrochemical feedstocks. Although conventional catalytic technologies have substantially enhanced refinery productivity and fuel quality, many traditional catalysts still present significant environmental and operational challenges, including toxic metal contamination, coke deposition, catalyst deactivation, sulfur emissions, excessive energy consumption, and hazardous waste generation ((Wei et al., 2025)). Consequently, increasing global environmental regulations and decarbonization policies have

accelerated the transition toward greener catalytic systems capable of supporting cleaner refinery operations.

Green catalysis involves the development and utilization of catalytic materials and reaction pathways that minimize ecological impact while maximizing process efficiency and product selectivity. The concept is closely aligned with the principles of green chemistry and sustainable process engineering, emphasizing lower process severity, reduced waste formation, improved atom economy, catalyst recyclability, and energy-efficient conversion technologies. Recent studies have shown that environmentally benign catalysts can significantly reduce refinery emissions while improving hydrocarbon conversion efficiency and operational sustainability (Lakhani, Bhandari, & Modi, 2024). In modern refinery systems, green catalysts are increasingly synthesized using renewable feedstocks, nanostructured materials, hierarchical porous architectures, and bio-derived support materials in order to enhance catalytic performance under milder operating conditions.

Recent advances in zeolite engineering, nanotechnology, and catalyst surface modification have substantially improved catalytic activity, thermal stability, diffusion properties, and resistance to deactivation. Hierarchical zeolite catalysts, for example, have demonstrated superior performance in heavy oil cracking because their interconnected micro-mesoporous structures improve reactant accessibility and reduce coke accumulation during catalytic reactions (Hijazi et al., 2025). Similarly, nanostructured catalysts provide higher surface-area-to-volume ratios and enhanced active-site dispersion, resulting in improved hydroprocessing and desulfurization efficiency (Isahak & Al-Amiery, 2024). Biomass-derived catalysts and biochar-supported catalytic systems are also gaining considerable attention because they are renewable, low-cost, and capable of supporting circular-economy refinery strategies (Ao et al., 2024).

Furthermore, green catalysis now extends beyond conventional hydrocarbon conversion processes into refinery environmental remediation technologies such as oxidative desulfurization, catalytic wastewater treatment, carbon dioxide utilization, and clean hydrogen production. Advanced catalytic systems including photocatalysts, metal-organic frameworks, transition-metal carbides, and single-atom catalysts are increasingly being investigated for sustainable fuel production, VOC destruction, and refinery emission control (Xu, Wang, Lv, Zhu, & Zhang, 2025). Therefore, green catalysis is increasingly recognized as a strategic technological pathway for achieving cleaner refinery processes, lower carbon emissions, improved energy efficiency, and long-term sustainability in modern petrochemical industries.

3. Nanocatalysts in Sustainable Refinery Processes

Nanotechnology has emerged as one of the most transformative approaches for improving catalyst performance in refinery and petrochemical operations. Owing to their particle sizes typically below 100 nm, nanocatalysts possess exceptionally high surface-area-to-volume ratios, enhanced active-site exposure, shorter diffusion paths, and superior heat and mass transfer properties compared with conventional bulk catalysts. These characteristics enable higher hydrocarbon conversion, improved product selectivity, reduced coke formation, and lower energy requirements, making nanocatalysis an attractive strategy for sustainable refinery processing.

As illustrated in Fig. 1, nanocatalysts are increasingly employed in fluid catalytic cracking (FCC), hydrocracking, hydrodesulfurization (HDS), hydroprocessing, catalytic reforming, biomass upgrading, and renewable fuel production. Their

improved performance originates not merely from reduced particle size, but from favorable structure-property relationships that enhance reactant accessibility and facilitate the efficient utilization of catalytic active sites. Consequently, nanostructured catalysts can achieve high catalytic activity under relatively mild operating conditions, thereby contributing to process intensification and reduced greenhouse gas emissions.

Different classes of nanocatalysts exhibit distinct catalytic advantages depending on their structural characteristics. Hierarchical zeolite nanocatalysts generally outperform conventional zeolites because their interconnected micro-mesoporous structures alleviate diffusion limitations associated with bulky hydrocarbon molecules. The presence of secondary mesoporosity facilitates reactant transport and suppresses coke accumulation, thereby improving catalyst stability and prolonging catalyst lifetime. Accordingly, Wei et al. (2025) reported enhanced heavy oil cracking efficiency and reduced diffusion resistance, while Zhang et al. (2023) demonstrated that optimized zeolite Y nanostructures improved accessibility and catalytic efficiency in FCC catalyst particles. These findings indicate that enhanced mass transfer, rather than acidity alone, plays a critical role in determining catalytic performance.

Metal and metal-oxide nanocatalysts based on Ni, Co, Mo, Pt, and W are particularly effective in hydroprocessing and hydrodesulfurization because of their high dispersion and strong metal-support interactions. Increased dispersion promotes greater exposure of active sites and enhances synergistic interactions between metallic phases, resulting in improved hydrogenation and desulfurization activities. For example, alumina-supported nanocatalysts improved sulfur removal efficiency during HDS (Shafiq et al., 2022), whereas nano-supported CoMo catalysts exhibited superior hydrodesulfurization performance under refinery conditions (Sun et al., 2025). Likewise, NiW nanocatalysts demonstrated remarkable hydrocracking activity due to their enhanced stability and cracking efficiency (Ebrahimejad & Karimzadeh, 2022), while multimetallic Ni-Fe-Mo nanocatalysts improved hydroprocessing activity through synergistic interactions among the constituent metals (Melo-Banda et al., 2022). These observations suggest that catalyst composition and metal-support interactions are fundamental factors governing catalytic performance.

Carbon-supported and graphene-based nanocatalysts have attracted increasing attention for renewable fuel upgrading because of their excellent electron-transfer properties, high thermal stability, and resistance to deactivation. Their graphitic structures

facilitate charge transfer and strengthen interactions between active metals and support surfaces, thereby suppressing sintering and improving catalyst durability. Consequently, carbon-supported nanocatalysts enhanced hydrodeoxygenation efficiency during renewable fuel upgrading (Zhao et al., 2024), while graphene-supported catalysts exhibited superior hydrogenation activity and long-term stability during biomass conversion processes.

Although nanocatalysts consistently demonstrate improvements in hydrocarbon conversion, sulfur removal, catalyst selectivity, and coke suppression across diverse refinery applications (Akhtar et al., 2024), their industrial deployment remains limited. Nanoparticle agglomeration, metal leaching, structural instability under severe operating conditions, catalyst recovery difficulties, and high synthesis costs continue to hinder large-term commercialization. Furthermore, most current studies emphasize catalytic activity under laboratory

conditions, whereas comparatively little attention has been devoted to catalyst regeneration, long-term durability, techno-economic analysis, and industrial-scale validation. Thus, despite remarkable advances, important knowledge gaps remain regarding catalyst stability and scalability.

Future research should therefore shift from maximizing catalytic activity alone toward developing robust and economically viable nanocatalysts with enhanced resistance to deactivation and improved recyclability. Greater emphasis should also be placed on understanding deactivation mechanisms, optimizing structure-property-performance relationships, and integrating machine learning and computational chemistry into catalyst design. Such approaches are expected to accelerate the development of next-generation nanocatalysts capable of supporting sustainable and low-carbon refinery operations.



Fig. 1: Nano-catalysts in sustainable refinery process

Table 1: Recent Works on Nanocatalysts in Sustainable Refinery Processes

S/N	Nanocatalyst Type	Refinery/Petrochemical Application	Key Findings	Reference
1	Hierarchical nanocatalysts	Petroleum refining	Improved catalyst selectivity, fuel yield, and catalyst longevity in FCC and hydrocracking processes	(Akhtar et al., 2024)
2	Zeolite-supported nanocatalysts	Hydroprocessing	Enhanced hydrocracking activity and reduced coke deposition using modified zeolitic supports	(Majodina, Poswayo, Dembaremba, & Tshentu, 2023)
3	Alumina-supported nanocatalysts	Hydrodesulfurization	Improved sulfur removal efficiency for ultra-low sulfur fuel production	(Shafiq, Shafique, Akhter, Yang, & Hussain, 2022)
4	Hierarchical zeolite nanocatalysts	Heavy oil cracking	Reduced diffusion limitations	(Wei et al., 2025)
5	Zeolite Y nanostructures	FCC catalyst optimization	Improved FCC accessibility	(L. Zhang et al., 2023)
6	Graphene-supported nanocatalysts	Biomass upgrading	Increased thermal stability and hydrogenation efficiency	Kumar & Singh (2024)
7	NiW nanocatalysts	Diesel hydrocracking	Enhanced hydrocracking conversion	(Ebrahiminejad & Karimzadeh, 2022)
8	Hierarchical zeolite catalysts	Hydrodesulfurization	Reduced coke formation	(Cui, Rajendran, Fan, Feng, & Li, 2021)
9	NiMo/Al ₂ O ₃ nanocatalysts	Biocrude upgrading	Effective heteroatom removal	(Castello, Haider, & Rosendahl, 2019)
10	Nano-supported CoMo catalysts	Ultra-low sulfur fuel	Enhanced HDS activity	(Sun et al., 2025)
11	Ni–Fe–Mo nanocatalysts	Hydroprocessing	Enhanced hydroprocessing activity	(Melo-Banda et al., 2022)
12	Carbon-	Renewable fuel	Improved catalyst	(Zhao et al.,

supported nanocatalysts	upgrading	stability	2024)
----------------------------	-----------	-----------	-------

4. Bio-Based and Biomass-Derived Catalysts

The increasing emphasis on sustainable refinery operations and circular economy principles has accelerated interest in bio-based and biomass-derived catalysts as environmentally benign alternatives to conventional catalyst supports. Derived from agricultural residues and carbon-rich wastes such as rice husk, palm biomass, sugarcane bagasse, and biochar, these materials offer advantages including renewability, low cost, and reduced environmental impact. Their porous structures, large surface areas, and abundant oxygen-containing functional groups promote metal dispersion and strengthen catalyst-support interactions, thereby enhancing catalytic performance.

As summarized in Table 2, biomass-derived catalysts have demonstrated considerable potential in biodiesel production, hydrocracking, hydroprocessing, hydrodeoxygenation, renewable diesel production, and environmental applications. The studies collectively indicate that catalytic activity strongly depends on the physicochemical characteristics of the biomass precursor and the nature of the active metal species. For example, waste biomass-derived heterogeneous catalysts have been successfully utilized for biodiesel, renewable diesel, and biojet fuel production (Quevedo-Amador et al., 2024), while palm fiber biochar-supported Fe-P, Co-P, Ni-P, and Mo-P catalysts achieved high conversion and biojet fuel selectivity during palm olein hydrocracking (Kaewtrakulchai et al., 2022). Likewise, coffee-ground and rice-husk biochar-supported Ni/Mo catalysts improved hydrocarbon yields during waste cooking oil hydrotreatment, whereas sugarcane bagasse

biochar-supported nickel catalysts effectively promoted CO₂ methanation reactions (Gamal et al., 2024).

A comparison of the studies presented in Table 2 reveals that biochar-supported catalysts generally outperform unsupported catalysts because their highly porous carbon frameworks provide abundant anchoring sites for active metals, leading to improved metal dispersion and enhanced mass transfer. These characteristics facilitate access to catalytic sites, suppress coke formation, and improve catalyst stability. Furthermore, biomass precursors with favorable compositions, such as silica-rich rice husk, contribute to enhanced catalytic efficiency, highlighting the importance of structure-property-performance relationships in determining catalyst effectiveness.

Despite the promising performances reported in the literature, several important issues remain insufficiently understood. Most studies have primarily focused on catalytic activity, whereas comparatively little attention has been devoted to catalyst regeneration, long-term durability, and techno-economic feasibility under realistic refinery conditions. In addition, the influence of biomass composition and pore architecture on catalyst stability requires further investigation. Future research should therefore focus on tailoring surface chemistry, optimizing metal-support interactions, and establishing robust structure-property-performance relationships to facilitate the development of scalable and industrially viable biomass-derived catalysts for sustainable refinery applications.

Table 2: Recent Works on Bio-Based and Biomass-Derived Catalysts

S/N	Bio-Based Catalyst Type	Application	Contribution	Reference
1	Waste-biomass–derived solid catalysts	Biofuel production (biodiesel, renewable diesel, bio-jet)	Summarizes preparation of heterogeneous catalysts from residual biomass and their role in multiple liquid biofuels in biorefineries	(Quevedo-Amador et al., 2024)
2	Palm-fiber biochar-supported Fe–P, Co–P, Ni–P, Mo–P	Hydrocracking of palm olein oil to bio-jet fuel	Porous biochar support; Fe–P/biochar achieves 100% conversion and 94.6% bio-jet selectivity	(Kaewtrakulchai et al., 2022)
3	Agro-waste–	Diesel oxidative desulfurization	Reviews activated carbons	(Mohammed,

	derived activated carbon catalysts		from agricultural wastes as ODS sorbents/catalysts and highlights environmental and cost benefits	Mohammed, & Gheni, 2024)
4	Rice-husk hydrochar, Co-loaded	Transesterification of waste cooking oil to biodiesel	Cobalt-modified rice-husk hydrochar gives ~96% FAME yield under optimized conditions	(Khan et al., 2024)
5	Metal-supported biochar	Biorefinery, electrocatalysis, energy storage	Reviews production/functionalization of metal–biochar catalysts and their use in bioproducts and bioenergy	(Ramos, Abdelkader-Fernández, Matos, Peixoto, & Fernandes, 2022)
6	Palm kernel shell–derived activated carbon	Support for transesterification catalysts to biodiesel	Optimized PKS activated carbon shows high porosity and enables biodiesel yields up to ~95% from waste oils	(Shakir, Ahmad, Mansur, & Abdul Khalil, 2024)
7	Rice-husk silica + eggshell CaO composite	Heterogeneous base catalyst for biodiesel	Waste-derived SiO ₂ –CaO catalyst gives ~90% biodiesel yield and is reusable for five cycles	(Nawaz, Jamil, Akhter, & Hussain, 2024)
8	Ni/Co on biochar from waste biomass	Hydrotreatment of carinata (non-edible) oil	Shows effect of Ni/Co source and dispersion on hydroprocessing pathways and fuel properties	(Roy et al., 2022)
9	Sugarcane-bagasse biochar–supported Ni	CO ₂ methanation	Ni/bagasse-biochar catalyst converts CO ₂ to CH ₄ efficiently; optimal loading maximizes conversion and selectivity	(Gamal et al., 2024)
10	Biomass-derived sulfonated carbons	Esterification/transesterification for biodiesel	Reviews waste-biomass sulfonated carbons as low-cost, metal-free solid acids for biodiesel	(Yadav, Yadav, & Ahmaruzzaman, 2023)
11	Coffee-ground and rice-husk biochar-supported Ni/Mo	Hydrotreatment of waste cooking oil to green diesel	Microporous biochars (367–938 m ² /g) support Ni and Ni–Mo; Mo promotion triples hydrocarbon yield vs Ni alone	(Nikolopoulos et al., 2023)
12	Biochar-based catalysts	Biorefinery and environmental catalysis	Overviews synthesis, deactivation, ML-guided design, and circular-economy benefits of biochar catalysts	(Yuan et al., 2023)
13	MoNi on rice-husk biochar	Green diesel from used cooking oil	Alkaline-treated biochar support improves area, mesoporosity, acidity and enables complete UCO conversion with 32 wt% green diesel yield	(Kordouli et al., 2024)
14	CuO–Fe ₃ O ₄ on activated rice-straw biochar	Esterification/upgrade of rice-straw bio-oil	Supercritical-ethanol upgrading over bimetallic biochar catalyst raises HHV from 21.3 to 32.1 MJ/kg and converts >90% acids to esters	(Ibrahim, Elsayed, & Hassan, 2024)
15	Ni on chemically activated wood-biochar	Hydrodeoxygenation of vanillin (bio-oil model)	Ni/biochar (acid-activated) achieves ~97% vanillin conversion and >90%	(Mudi, Hart, Ingram, & Wood, 2023)

5. Zeolite-Based Green Catalysts

Zeolite-based catalysts remain among the most important catalytic materials in petroleum refining and petrochemical industries because of their crystalline aluminosilicate frameworks, strong Brønsted acidity, high thermal stability, shape selectivity, and well-defined pore structures. These unique physicochemical properties make zeolites indispensable in major refinery operations such as fluid catalytic cracking (FCC), hydrocracking, alkylation, methanol-to-olefin (MTO) conversion, hydroisomerization, biomass upgrading, and environmental emission control. As environmental regulations on sulfur emissions, NO_x release, and greenhouse gas generation become increasingly stringent, substantial research attention has shifted toward the development of greener and more sustainable zeolite catalytic systems capable of improving refinery efficiency while minimizing environmental pollution.

As illustrated in **Figure 2**, zeolite-based green catalysts are now widely integrated into sustainable refinery and environmental applications including NO_x reduction, CO₂ capture, hydrocracking, biomass valorization, renewable fuel production, and methanol-to-olefin conversion. The figure demonstrates the multifunctional role of zeolitic materials in improving catalytic selectivity, reducing catalyst deactivation, enhancing hydrocarbon conversion, and supporting cleaner refinery operations. Modern zeolite engineering increasingly focuses on hierarchical architectures, nano-zeolites, core-shell structures, and metal-doped systems designed to overcome the diffusion limitations commonly associated with conventional microporous zeolites.

Traditional zeolites often suffer from restricted pore accessibility during the conversion of bulky hydrocarbon molecules because of their predominantly microporous structures. To address this challenge, hierarchical zeolites containing interconnected micro-mesoporous channels have been

developed to improve reactant diffusion and mass-transfer characteristics. As shown in **Table 3**, hierarchical zeolite systems such as hierarchical ZSM-5 microspheres and lamellar H-ZSM-5 catalysts demonstrated prolonged catalyst lifetime, improved olefin selectivity, and enhanced resistance to coke deposition during methanol-to-olefin reactions (L. Zhang et al., 2023; Zhou, Jiang, Chen, Wang, & Hou, 2021). Similarly, two-dimensional layered zeolites and zeolite-encapsulated catalysts significantly reduced diffusion limitations and improved catalyst stability during biomass conversion and pyrolysis reactions (Mathew & Krishnan, 2024; Rafiani, Aulia, & Kadja, 2024).

Zeolite catalysts also play a major role in environmental remediation and refinery emission control. Several studies summarized in **Table 3** demonstrated remarkable NO_x reduction performance using Cu-exchanged zeolites, Fe-zeolite systems, and natural clinoptilolite catalysts in selective catalytic reduction (SCR) processes. For instance, Cu-Y zeolite catalysts achieved NO_x conversion efficiencies approaching 95% during diesel exhaust treatment, while Cu-clinoptilolite systems demonstrated excellent SO₂ and H₂O tolerance during NH₃-SCR operations (Alcantara et al., 2023; Yakaryılmaz & Özgür, 2024). Core-shell zeolite catalysts such as SSZ-13 and ZSM-5 further exhibited improved sulfur resistance, wider operating temperature windows, and enhanced poisoning resistance during NO_x removal processes (Jia, Liu, Cheng, Zhao, & Liu, 2025).

Beyond hydrocarbon processing, zeolite-based green catalysts are increasingly important in biomass valorization and renewable fuel production. Modified zeolitic catalysts including HZSM-5, HY, SAPO-34, and hierarchical FAU structures have demonstrated remarkable catalytic activity in catalytic pyrolysis, hydrothermal liquefaction, biomass hydrolysis, and bio-oil upgrading processes. These catalysts improve product selectivity, reduce oxygenated compounds, and enhance fuel quality during biomass conversion pathways. Furthermore, zeolites are increasingly being investigated for CO₂ capture and gas separation

applications due to their tunable pore structures and adsorption selectivity. As summarized in **Table 3**, zeolite SSZ-13, SAPO-34, NaX zeolites, and hierarchical zeolite Y structures exhibited significant CO₂ adsorption capacities and improved CO₂/CH₄ separation efficiency, highlighting their growing importance in low-carbon refinery technologies and carbon capture systems.

Therefore, the recent advances summarized in **Table 3** demonstrate that zeolite-based green catalysts are

evolving beyond traditional FCC applications into multifunctional catalytic systems capable of supporting sustainable refining, environmental remediation, biomass upgrading, renewable fuel production, and greenhouse gas mitigation. Nevertheless, challenges related to hydrothermal stability, catalyst synthesis cost, long-term regeneration performance, and industrial-scale implementation remain important areas requiring further research and technological optimization.



Figure 2: Zeolite based green catalyst

Table 3: Recent Advance on Zeolite-Based Green Catalysts

S/N	Zeolite Catalyst Type	Application	Key Contribution	Reference
1	Core-shell SSZ-13, ZSM-5, Beta zeolites	NH ₃ -SCR of NO _x	Summarizes core-shell zeolite catalysts with higher low-temperature activity, wider temperature window and superior resistance to SO _x , alkali and HC poisons for NO _x control	(Jia et al., 2025)
2	Cu Y zeolite			(Yakaryılmaz & Özgür, 2024)
3		Ethanol SCR of NO _x in diesel exhaust	Synthesizes Cu Y zeolite and shows up to 94.67% NO _x conversion at 260 °C in a diesel engine using ethanol as	(Alcantara et al., 2023)

4	Cu clinoptilolite (Cu CLIN)	NH ₃ SCR of NO _x from diesel	reductant Demonstrates natural clinoptilolite exchanged with Cu achieves ~96% NO conversion and good SO ₂ /H ₂ O tolerance, offering a low cost SCR catalyst	(Dwivedi, Chaudhary, Chintala, & Karn, 2021)
5	Metal exchanged natural zeolite	NH ₃ SCR of NO _x from CI engine	Uses metal exchanged natural zeolite in an SCR system coupled to a CI engine, significantly lowering NO _x emissions under all loads	(Kumar et al., 2023)
6	Cu/zeolite and Fe/zeolite (review)	NH ₃ SCR of NO _x	Compares traditional metal oxides with zeolite based SCR catalysts; finds Cu zeolites can reach ~95% deNO _x and Fe zeolites broaden operating window	(Mardiana, Azhari, Ilmi, & Kadja, 2022)
7	Hierarchical zeolites (MFI, FAU, etc.)	Biomass conversion to biofuels and bio based chemicals	Reviews bottom up/top down, green routes to hierarchical zeolites and links mesoporosity to improved biomass pyrolysis, hydrolysis and bio oil upgrading	(Qazi, Javaid, Ikhlaiq, Khoja, & Saleem, 2022)
8	Zeolite catalysts (HZSM 5, HY, etc.)	Biomass/waste to green fuels	Surveys zeolite chemistry and highlights catalytic pyrolysis, hydrothermal liquefaction and hydropyrolysis routes from lignocellulose to green fuels	(Yan, Wang, Liao, & Wang, 2023)
9	Zeolites for LA/HMF routes	Biomass valorization to LA, HMF and derivatives	Summarizes modified zeolites for producing LA, HMF and downstream biofuels, emphasizing tuning acidity/structure for selectivity	(Mathew & Krishnan, 2024)
10	2D layered zeolites	Biomass valorization	Describes two dimensional zeolites with high external area and bimodal porosity that reduce diffusion limits and deactivation in biomass conversions	(Rafiani et al., 2024)
11	Zeolite encapsulated catalysts (core-shell, yolk-shell)	Biomass conversion	Reviews synthesis of zeolite encapsulated catalysts and shows improved product selectivity and stability	(Y. Zhang et al., 2023)

12	Hierarchical ZSM 5 microspheres	Methanol to olefins (MTO)	in biomass pyrolysis Develops macro/mesoporous ZSM 5 microspheres with prolonged lifetime (47 h at >99%	(Zhou et al., 2021)
13	Lamellar hierarchical H ZSM 5	MTO	One step, energy efficient synthesis of lamellar H ZSM 5 using urea/PEG2000; catalyst shows longer lifetime and higher olefin selectivity	(Lin et al., 2021)
14	Ta and Al modified MFI (TaAlS 1)	Propene selective MTO	Controls zeolite microenvironment with Ta(V)+Brønsted sites to reach 51% propene selectivity, high propene/ethene ratio and >50 h stability at full conversion	(Maggiulli, Sushkevich, Krocher, Van Bokhoven, & Ferri, 2024)
15	ZSM 5, SSZ 13, ferrierite	Fundamental MTO mechanism	Correlates carbenium ion types in different zeolite topologies with C ₂ -C ₆ olefin distributions, guiding topology based selectivity control	(Z. Shi & Bhan, 2022)
16	Window cage zeolites/zeotypes	MTO with syngas co feeds (STO)	Shows high pressure H ₂ /CO introduce new hydrogenation and carbonylation pathways, extending catalyst lifetime and tuning ethylene/propylene ratios	(Boer, Langerak, & Pescarmona, 2023)
17	Zeolite SSZ 13, SAPO 34, T type, etc.	CO ₂ capture and separation	Reviews how framework, Si/Al and cations govern CO ₂ uptake/selectivity in CO ₂ /CH ₄ and CO ₂ /N ₂ separations and discusses shaping for industrial use	(Al-Mamoori et al., 2025)
18	NH ₄ ZSM 5, H ZSM 5, Ba/Mn/Ni/Zn ZSM 5	CO ₂ capture from flue gas	Shows NH ₄ ZSM 5 reaches 1.45 mmol g ⁻¹ CO ₂ at 25 °C; cation exchange improves CO ₂ /N ₂ selectivity and maintains stable capacity over cycles	(Cecilia et al., 2022)
19	Kaolinite derived 4A zeolite	CO ₂ adsorption	Demonstrates low cost synthesis of zeolite 4A from kaolinite with CO ₂ adsorption comparable	(Yanshuang Chen et al., 2025)

			to commercial 4A, supporting waste to sorbent routes	
20	NaX zeolite from coal gangue	Cu ²⁺ and CO ₂ adsorption	Converts coal gangue into NaX zeolite with high surface area and strong Cu ²⁺ (185 mg g ⁻¹) and CO ₂ (5.51 mmol g ⁻¹) adsorption, aligning with circular economy	(Bahmanzadegan & Ghaemi, 2025)
21	Zeolite based adsorbents	Removal of metals, dyes, CO ₂ , H ₂ S	Compiles advanced zeolite composites achieving high capacities for Cu ²⁺ , Pb ²⁺ , dyes, CO ₂ and H ₂ S, highlighting green pollution remediation roles	(Jia et al., 2025)
22	Zeolite SSZ 13, ZSM 5, Beta cores	Poison resistant NH ₃ SCR	Clarifies interfacial effects in core-shell NH ₃ SCR catalysts and mechanisms for sulfur, alkali and hydrocarbon resistance	(Boer et al., 2023)
23	SAPO 34 and small pore zeolites	CO ₂ capture and membranes	Discusses small pore zeolite and SAPO 34 materials/membranes for CO ₂ capture and sequestration	(Boer et al., 2023)
24	3D printed ZSM 5 monolith	CO ₂ /CH ₄ /N ₂ separation	Highlights structured ZSM 5 monoliths for gas separations, combining zeolite selectivity with low pressure drop	(Boer et al., 2023)
25	Hierarchical porous zeolite Y	CO ₂ capture	Notes hierarchical Y zeolite with enhanced CO ₂ capacity due to improved porosity and diffusion	(Alcantara et al., 2023)

6. Green Catalysts for Hydrogen Production and Clean Energy Integration

Hydrogen production is becoming increasingly important in refinery and petrochemical operations because hydrogen is required for hydrocracking, hydrotreating, hydrodesulfurization, and heavy oil upgrading. Beyond refinery use, hydrogen is also central to clean energy integration because it can store renewable electricity and support low-carbon fuel, power, and chemical production. Consequently, recent catalyst research has focused on improving hydrogen generation through photocatalytic water splitting, electrochemical water splitting, hydrogen evolution

reaction (HER), oxygen evolution reaction (OER), and overall water splitting systems.

As shown in **Fig. 3**, green hydrogen production depends on the effective coupling of renewable energy sources, catalytic water splitting systems, hydrogen storage, and downstream utilization in clean industrial processes. The figure highlights the important role of catalysts in reducing the energy barrier for water splitting and improving the efficiency of hydrogen generation. In practical terms, the catalyst determines how much energy is required, how stable the system remains under operation, and whether the process can be integrated with solar, wind, or other renewable energy sources.

The recent studies summarized in **Table 4** show that hydrogen catalyst development is progressing in three major directions. The first direction is photocatalytic overall water splitting, where semiconductor photocatalysts directly convert solar energy into hydrogen. For example, $\text{SrTiO}_3\text{:Al}$ modified with $\text{Rh/Cr}_2\text{O}_3$ and CoOOH cocatalysts achieved an external quantum efficiency of up to 96% at 350–360 nm, representing one of the most significant advances in photocatalytic water splitting (Takata et al., 2020). Similarly, Ag/TiO_2 and organic heterojunction nanoparticles such as PM6:Y6 and PM6:PCBM demonstrate how light absorption, charge separation, and surface catalytic reactions can be engineered to improve solar hydrogen production (Kosco et al., 2022).

The second direction involves electrocatalysts for HER and OER, which are critical for water electrolysis. Table 4 shows that noble-metal-based systems such as 1T- IrO_2 metallene oxide and RuIrO_x display outstanding acidic OER performance. Dang et al. (2021) reported that 1T- IrO_2 achieved an overpotential of 197 mV at 10 mA cm^{-2} with high turnover frequency, while Zhu et al. (2023) reported that two-dimensional RuIrO_x delivered an even lower overpotential of 151 mV at 10 mA cm^{-2} and long-term stability of 618 h. These findings are important because acidic OER remains a major bottleneck in proton exchange membrane water electrolysis.

The third direction focuses on low-cost and non-noble-metal catalysts for scalable hydrogen production. Metallic W/WO_2 solid-acid heterostructures have demonstrated strong alkaline HER activity, requiring only -35 mV at -10 mA cm^{-2} and showing durable operation for more than 50 h (Z. Chen et al., 2023). Nickel-based and nickel oxyhydroxide systems are also attractive because nickel is cheaper and more abundant than noble metals. Khateri and Najafpour (2024) demonstrated that nickel oxyhydroxide can achieve OER at very low overpotential, while FeCoCrNi alloy systems show how surface reconstruction can generate active oxyhydroxide phases for efficient alkaline OER (Zhang et al., 2020).

Hence, these examples demonstrate that green hydrogen catalysis is moving from laboratory-scale catalyst discovery toward practical energy integration. Photocatalysts support direct solar-to-hydrogen conversion, HER/OER electrocatalysts improve water electrolysis efficiency, and high-stability catalysts enable operation at industrially relevant current densities. However, several challenges remain, including catalyst cost, noble-metal dependence, long-term durability, photocorrosion, scale-up limitations, and integration with intermittent renewable electricity. Therefore, future work should focus on durable, earth-abundant, high-current-density catalysts that can operate efficiently in real electrolyzer systems and refinery-integrated hydrogen networks.



Fig. 3: Green Catalysts for Hydrogen Production and Clean Energy Integration

Table 4: Recent Advances in Green Catalysts for Hydrogen Production and Clean Energy Integration

S/N	Catalyst / System (Green Focus)	Process (HER/OER/Overall /Photocatalysis)	Efficiency	Reference
1	SrTiO ₃ :Al + Rh/Cr ₂ O ₃ & CoOOH cocatalysts	Overall photocatalytic water splitting	External QE up to 96% (350–360 nm)	(Takata et al., 2020)
2	1T-IrO ₂ metallene oxide	Acidic OER	Overpotential 197 mV @10 mA cm ⁻² ; TOF 4.2 s ⁻¹	(Dang et al., 2021)
3	Metallic W/WO ₂ solid-acid heterostructure	Alkaline HER	Overpotential –35 mV @–10 mA cm ⁻² ; Tafel 34 mV dec ⁻¹	(Z. Chen et al., 2023)
4	photocatalytic water splitting	Photocatalytic H ₂ (various)	Discusses low QE (<10%) and improvement strategies	(R. Li et al., 2024)
5	Single-atom Ru–N–C	Acidic OER	Overpotential 267 mV @10 mA cm ⁻² ; mass activity 3571 A g ⁻¹	(Cao et al., 2019)
6	Nanoporous NiFeCoCuTi high-entropy alloy	Alkaline HER	2 A cm ⁻² at overpotential ≈209 mV; stability >240 h	(H. Shi et al.)
7	photocatalytic water splitting semiconductors	Photocatalytic H ₂	H ₂ rates and light-use limits	(Molaei, 2024)
8	2D Ru–Ir oxide (RuIrO _x)	Acidic OER	Overpotential 151 mV @10 mA cm ⁻² ; TOF 6.84 s ⁻¹ ; 618 h stable	(Zhu et al., 2023)
9	Ni foam / stainless-steel mesh	Alkaline HER & OER, overall splitting	HER: η 0.217 V @10 mA cm ⁻² ; OER: η 0.277 V @10 mA cm ⁻² ; cell 1.74 V @10 mA cm ⁻²	(Hu, Tian, Lin, & Wang, 2019)
10	band engineering of binary semiconductors	Photocatalytic H ₂	bandgaps and H ₂ rates of TiO ₂ , g-C ₃ N ₄ ,	(Tahir, Tasleem, & Tahir, 2020)
11	Ni oxyhydroxide on Ni foam	Alkaline OER	Overpotential 130 mV @200 μA cm ⁻² ; Tafel 77.9 mV dec ⁻¹	(Khateri & Najafpour, 2024)
12			Overpotential 240 mV @1000 mA cm ⁻² ; 1500 mA cm ⁻² for >320 h	(Gogoi, Namdeo, Golder, & Peela, 2020)
13	Heterophase CoSe ₂ (c/o phases)	HER at large current	H ₂ rate 23.5 mmol g ⁻¹ h ⁻¹ ; AQY 19%	(Zhang et al., 2020)

Title				
14	Ag doped TiO ₂ (Ag/TiO ₂)	Photocatalytic H ₂	Mass activity 3601 A g ⁻¹ ; TOF 0.483 s ⁻¹ @η = 300 mV	(Shao et al., 2025)
15	FeCoCrNi alloy (reconstructed (oxy)hydroxide)	Alkaline OER	Overpotential 343.6 mV @1000 mA cm ⁻² ; Tafel 67.6 mV dec ⁻¹	(Mohsin et al., 2023)
16	Fe rich medium entropy core-shell alloy	Alkaline HER, high current	Surveys efficiencies and visible-light responses	(Xie et al., 2022)
17	semiconductor nanomaterial photocatalysts	Photocatalytic/solar water splitting	Compares overpotentials, stability of NPMCs vs Ir/Ru	(Fu et al., 2022)
18	alkaline OER with NPM catalysts	Alkaline OER	3.5 A cm ⁻² at overpotential 251 ± 3 mV	(Kosco et al., 2022)
19	NiS/CrS _x hybrid (hydrogen spillover)	Alkaline HER, ampere level	EQE 1–5% (400–900 nm) and 8.7–2.6% (400–700 nm)	(Fan et al., 2021)

7. Environmental Applications of Green Catalysts in Refineries

Environmental protection has become a major driving force behind the development of green catalytic technologies in modern refinery and petrochemical operations. Increasingly stringent regulations on sulfur emissions, nitrogen oxides (NO_x), volatile organic compounds (VOCs), wastewater discharge, and greenhouse gas emissions have compelled refineries to adopt cleaner and more sustainable processing technologies. In this context, green catalysts have emerged as indispensable tools for pollution control, environmental remediation, resource efficiency, and process sustainability. Beyond their traditional role in hydrocarbon conversion, modern catalytic systems are now extensively applied in emission reduction, wastewater treatment, carbon management, and cleaner fuel production, thereby contributing significantly to refinery decarbonization and environmental compliance.

As illustrated in Fig. 4, the environmental applications of green catalysts in refineries can be broadly categorized into air pollution control, wastewater treatment, greenhouse gas mitigation, and resource recovery. Among these applications, hydrodesulfurization (HDS) remains one of the most important catalytic technologies for producing ultra-low sulfur fuels (Coutinho et al., 2024). Advanced nanostructured Co-Mo and Ni-Mo catalysts supported on modified alumina, zeolites, and mesoporous materials have demonstrated superior sulfur removal efficiency, improved active-site

accessibility, and enhanced resistance to catalyst deactivation (Aguesse et al., 2025). These improvements enable the production of cleaner transportation fuels while significantly reducing sulfur oxide emissions that contribute to acid rain and atmospheric pollution.

Green catalysts are also extensively utilized for the removal of gaseous pollutants from refinery exhaust streams. Catalytic oxidation and selective catalytic reduction (SCR) systems based on transition metal oxides, zeolites, and noble-metal-free catalysts have shown remarkable efficiency in converting NO_x and VOCs into environmentally benign products (Yanqi Chen et al., 2024; M. Li & Wang, 2024). Such technologies play a crucial role in improving air quality and minimizing the environmental footprint of refinery operations (Duan et al., 2025).

Another important area of application is refinery wastewater treatment. Photocatalytic materials such as TiO₂, ZnO, and doped semiconductor catalysts have demonstrated excellent capability for degrading phenols, hydrocarbons, dyes, and other recalcitrant organic pollutants commonly found in refinery effluents (Narimani et al., 2025). These photocatalytic processes operate under ultraviolet or visible light irradiation and offer the advantage of minimizing secondary waste generation while achieving high contaminant removal efficiencies (Gatou, Syrrakou, Lagopati, & Pavlatou, 2024; Ghamarpoor, Fallah, & Jamshidi, 2024).

Furthermore, catalytic carbon capture, utilization, and conversion technologies are rapidly emerging as critical tools for greenhouse gas mitigation. Advanced catalytic materials including metal-organic frameworks (MOFs), single-atom catalysts, and nanostructured metal oxides are increasingly being explored for CO₂ adsorption, hydrogenation, and conversion into value-added chemicals and fuels. Consequently, green catalysts are not only supporting cleaner refinery operations but are also facilitating the transition toward carbon-neutral and circular refinery systems. Their continued development will be essential for achieving sustainable industrial growth, environmental protection, and global decarbonization objectives



Fig. 4: Applications of Green Catalysts

8. Comparative Green Catalyst Classes

Table 5 presents a comparative evaluation of the major green catalyst classes discussed in this review, demonstrating that catalyst selection should be guided by process requirements rather than catalytic activity alone. Nanocatalysts exhibit superior catalytic performance owing to their high surface areas, enhanced active-site exposure, and shorter diffusion pathways, which promote faster reaction kinetics and improved selectivity. However, their large-scale application is constrained by agglomeration, metal leaching, catalyst recovery challenges, and high synthesis costs (Akhtar et al., 2024). Hierarchical zeolites address many of the diffusion limitations associated with conventional zeolites through interconnected micro-mesoporous architectures, resulting in improved reactant accessibility, reduced coke formation, and extended catalyst lifetime (Zhou et al., 2024). By contrast, conventional zeolite-based catalysts remain indispensable for FCC, hydrocracking, methanol-to-olefins, and emission control because of their excellent acidity, thermal stability, and shape selectivity, although their microporous structures restrict the conversion of bulky molecules (Bian et al., 2025).

Biomass-derived and biochar-supported catalysts provide sustainable and low-cost alternatives by converting renewable wastes into functional catalytic materials with enhanced metal-support interactions and lower environmental footprints (Quevedo-Amador et al., 2024; Sharmila et al., 2023). Nevertheless, feedstock variability, catalyst durability, regeneration, and limited techno-economic validation continue to hinder their widespread commercialization. Similarly, photocatalysts and green-synthesized photocatalytic nanomaterials offer environmentally benign routes for refinery wastewater treatment and solar hydrogen production but are limited by low quantum efficiency, photocorrosion, and dependence on irradiation conditions (El Golli et al., 2023; Khader et al., 2024). This comparison highlights that no single catalyst class is universally optimal. Instead, future catalyst development should focus on optimizing structure-property-performance relationships while improving catalyst stability, scalability, regeneration, and economic viability to accelerate the industrial adoption of sustainable refinery and petrochemical technologies.

Table 5: Comparative Analysis of Green Catalyst Classes

Catalyst Class	Main Advantages	Main Limitations	Representative Recent Applications	Reference
Nanocatalysts	High surface area, better active-site exposure, shorter diffusion paths, and higher conversion/selectivity under milder conditions	Agglomeration, metal leaching, structural instability, recovery difficulty, and high synthesis cost limit scale-up	Hydroprocessing, HDS, FCC, biomass upgrading	Akhtar et al. 2024
Hierarchical Zeolites	Micro-mesoporous networks improve accessibility, diffusion, coke resistance, and lifetime versus conventional zeolites	Hydrothermal stability, regeneration, and synthesis cost remain barriers	Heavy oil cracking, MTO, plastic hydrocracking	Zhou et al. 2024
Conventional Zeolite-Based Green Catalysts	Strong acidity, shape selectivity, and thermal stability make them versatile for FCC, hydrocracking, MTO, and emission control	Micropore-limited access for bulky molecules causes diffusion constraints and deactivation risk	NO _x SCR, biomass upgrading, CO ₂ capture	Bian et al. 2025
Biomass-Derived Catalysts	Renewable, low-cost, circular-economy supports with porous structures and oxygenated groups that improve metal dispersion	Performance depends strongly on feedstock composition; durability, regeneration, and techno-economics are still underdeveloped	Biodiesel, hydrocracking, hydroprocessing, CO ₂ methanation	Quevedo-Amador et al. 2024
Biochar-Supported Catalysts	Tailorable porosity, thermal stability, multifunctionality, and lower carbon footprint support biorefinery and environmental uses	Large-scale deployment still needs better deactivation analysis and environmental/economic assessment	Green diesel, wastewater remediation, pollutant degradation	Sharmila et al. 2023
Photocatalysts	Use light-driven pathways for pollutant degradation or solar H ₂ production, often with low secondary waste	Many systems still have low quantum efficiency, photocorrosion, or dependence on UV irradiation	Refinery wastewater treatment and photocatalytic water splitting	El Golli et al. 2023
Green-Synthesized Photocatalytic Nanomaterials	Green fabrication avoids toxic reagents and can reduce energy input and cost while maintaining strong wastewater-treatment performance	Performance can depend strongly on irradiation source and operating conditions	Refinery wastewater COD and organics removal	El Golli et al. 2023
Single-Atom Catalysts	Atomically dispersed sites maximize metal	Translation to devices still needs better life-	Water splitting, CO ₂ reduction,	Akram et al. 2024

	utilization and allow precise tuning of activity/selectivity for HER, OER, and CO ₂ reduction	cycle assessment, scalable synthesis, and device-level implementation	carbon-neutral electrocatalysis	
Single-Atom Alloys / Single-Cluster CO ₂ Catalysts	Offer highly tunable selectivity in CO ₂ conversion through well-defined active ensembles and mechanistic control of hydrogenation pathways	Selectivity is highly composition- and temperature-dependent, and practical deployment remains early-stage	CO ₂ electroreduction to CO/CH ₄ and CO ₂ hydrogenation to methanol/ethanol	Wang et al. 2023

9.Challenges and Future Prospects

Although significant progress has been achieved in the development of nanocatalysts, biomass-derived catalysts, and advanced porous materials, their successful industrial implementation remains constrained by several scientific and technological challenges. A critical analysis of the literature reveals that catalyst performance is governed not only by composition but also by complex structure-property-performance relationships involving active-site distribution, pore architecture, metal-support interactions, and mass-transfer characteristics. However, these relationships are still insufficiently understood, limiting the rational design of highly efficient and durable catalysts.

Catalyst deactivation remains one of the major obstacles to industrial application. High temperatures, sulfur-containing compounds, and coke precursors promote sintering, poisoning, pore blockage, and loss of active sites, thereby reducing catalytic activity and stability. Similarly, nanostructured and biomass-derived catalysts are susceptible to metal leaching, structural degradation, and reduced recyclability. Although numerous studies have reported excellent laboratory-scale performances, comparatively few have evaluated catalyst regeneration, long-term durability, and operation under realistic refinery conditions. Consequently, the scalability and industrial reliability of many emerging catalysts remain uncertain.

Economic considerations represent another important challenge. Advanced catalysts such as single-atom catalysts, metal-organic frameworks, and engineered nanostructures often require costly precursors and complex synthesis procedures. Thus, future research should move beyond maximizing catalytic activity and

focus on developing economically viable and industrially resilient catalytic systems. Greater emphasis should be placed on techno-economic analysis, life-cycle assessment, and catalyst stability.

The integration of artificial intelligence, machine learning, computational chemistry, and advanced characterization techniques offers new opportunities for accelerating catalyst discovery and establishing robust structure-property-performance relationships. Future refinery technologies are therefore expected to combine green catalysis with renewable hydrogen, carbon capture and utilization, biomass valorization, and circular economy strategies to achieve sustainable and low-carbon petrochemical operations.

Conclusion

Green catalysis has emerged as a transformative approach for addressing the environmental and operational challenges associated with modern refinery and petrochemical processes. This review demonstrates that advances in nanocatalysts, biomass-derived catalysts, zeolite-based catalytic systems, and hydrogen-production catalysts are significantly improving process efficiency, catalyst selectivity, cleaner fuel production, emission reduction, and resource utilization. Recent developments in catalyst engineering have enabled more sustainable pathways for hydrocracking, hydrodesulfurization, biomass conversion, wastewater treatment, carbon dioxide utilization, and green hydrogen generation. Furthermore, the integration of green catalytic technologies with renewable energy systems and circular economy principles highlights their strategic importance in the transition toward low-carbon refinery operations. Despite notable progress, challenges related to catalyst stability, deactivation, scalability, and economic feasibility remain critical barriers to widespread industrial adoption. Future

research should therefore focus on the development of robust, cost-effective, and multifunctional catalytic materials supported by artificial intelligence-driven catalyst design and advanced manufacturing techniques. Hence, green catalysts are expected to play

a pivotal role in achieving cleaner production, environmental sustainability, energy efficiency, and long-term decarbonization of refinery and petrochemical industries.

Funding

This manuscript received no funding

Conflicts of Interest

The authors declare no conflict of interest of any sort.

Reference

- Aguesse, J., Amedlous, A., Wang, C., Portier, X., Dalena, F., Barreau, M., Barrier, N. (2025). Hydrodesulfurization of Thiophene over Ni-Doped MoS₂-Supported Mesoporous Silica. *ChemCatChem*, 17(22), e01253.
- Akhtar, M. S., Ali, S., & Zaman, W. (2024). Recent advancements in catalysts for petroleum refining. *Catalysts*, 14(12), 841.
- Akram, M. Y., Ashraf, T., Jagirani, M. S., Nazir, A., Saqib, M., & Imran, M. (2024). Recent advances in graphene-based single-atom photocatalysts for CO₂ reduction and H₂ production. *Catalysts*, 14(6), 343.
- Al-Mamoori, A., Saed, U. A., Saoud, A. A., Abdul Jabbar, M. F., Jasim, A., Majdi, H. S., Iacomi, P. (2025). Modification of the zeolite ZSM-5 adsorbent for CO₂ capture. *ACS omega*, 10(20), 20129-20141.
- Al-Tameemi, H. M., Sukkar, K. A., & Abbar, A. H. (2024). Treatment of petroleum refinery wastewater by a combination of anodic oxidation with photocatalyst process: Recent advances, affecting factors and future perspectives. *Chemical Engineering Research and Design*, 204, 487-508.
- Alcantara, A. P. M. P., Moura de Oliveira, M. L., Santiago de Araújo, J. C., dos Santos Araújo, R., Chaves de Lima, R. K., Bueno, A. V., Rodríguez-Castellón, E. (2023). Reduction of typical diesel NO_x emissions by SCR-NH₃ using metal-exchanged natural zeolite and SBA-15 catalysts. *Air*, 1(3), 159-174.
- Ao, S., Ghorui, S., Li, H., Baskar, G., & Rokhum, S. L. (2024). Engineered Biomass Waste-Derived Activated Biochar Catalyst for Biodiesel Production from *Jatropha curcas* Oil. *International Journal of Energy Research*, 2024(1), 2406135.
- Bahmanzadegan, F., & Ghaemi, A. (2025). A comprehensive review on novel zeolite-based adsorbents for environmental pollutant. *Journal of Hazardous Materials Advances*, 17, 100617.
- Bian, M., Shu, X., Xiao, X., Wang, P., Pang, S., Zhao, C., & Zhao, Z. (2025). Precision Engineering of Zeolite Catalysts for Light Hydrocarbon Cracking to Light Olefins: Advances and Challenges. *ChemCatChem*, 17(23), e00952.
- Boer, D. G., Langerak, J., & Pescarmona, P. P. (2023). Zeolites as selective adsorbents for CO₂ separation. *ACS Applied Energy Materials*, 6(5), 2634-2656.
- Cao, L., Luo, Q., Chen, J., Wang, L., Lin, Y., Wang, H., Liu, W. (2019). Dynamic oxygen adsorption on single-atomic Ruthenium catalyst with high performance for acidic oxygen evolution reaction. *Nature Communications*, 10(1), 4849.
- Castello, D., Haider, M. S., & Rosendahl, L. A. (2019). Catalytic upgrading of hydrothermal liquefaction biocrudes: Different challenges for different feedstocks. *Renewable Energy*, 141, 420-430.
- Cecilia, J. A., Vilarrasa-García, E., Morales-Ospino, R., Finocchio, E., Busca, G., Sapag, K., Rodríguez-Castellón, E. (2022). Kaolinite-based zeolites synthesis and their application in CO₂ capture processes. *Fuel*, 320, 123953.
- Chen, Y., Chen, Y., Xu, H., Zhao, W., Feng, G., & Xiao, C. (2025). Green Synthesis of Coal Gangue-Derived NaX Zeolite for Enhanced Adsorption of Cu²⁺ and CO₂. *Materials*, 18(7), 1443.
- Chen, Y., Liu, X., Wang, P., Mansoor, M., Zhang, J., Peng, D., Zhang, D. (2024). Challenges and

- perspectives of environmental catalysis for NO_x reduction. *JACS Au*, 4(8), 2767-2791.
- Chen, Z., Gong, W., Wang, J., Hou, S., Yang, G., Zhu, C., Cui, Y. (2023). Metallic W/WO₂ solid-acid catalyst boosts hydrogen evolution reaction in alkaline electrolyte. *Nature Communications*, 14(1), 5363.
- Coutinho, A. C. S., Barros, J. M., Araujo, M. D., Silva, J. B., Souza, M. J., Delgado, R. C., Araujo, A. S. (2024). Hydrodesulfurization of Thiophene in n-Heptane Stream Using CoMo/SBA-15 and CoMo/AlSBA-15 Mesoporous Catalysts. *Catalysts*, 14(3), 198.
- Cui, T.-Y., Rajendran, A., Fan, H.-X., Feng, J., & Li, W.-Y. (2021). Review on hydrodesulfurization over zeolite-based catalysts. *Industrial & Engineering Chemistry Research*, 60(8), 3295-3323.
- Dang, Q., Lin, H., Fan, Z., Ma, L., Shao, Q., Ji, Y., Kong, N. (2021). Iridium metallene oxide for acidic oxygen evolution catalysis. *Nature Communications*, 12(1), 6007.
- Duan, R., Fu, Y., Li, Z., Wang, X., Gao, M., Yu, Y., He, H. (2025). Unexpected Room-Temperature Selective Catalytic Reduction of NO_x with NH₃ over Metal-Free Carbon-Based Catalysts. *Environmental Science & Technology*, 59(15), 7760-7767.
- Dwivedi, A., Chaudhary, H., Chintala, V., & Karn, A. (2021). Selective Catalyst Reduction (SCR) using Zeolite for Reduction of NO_x Emissions in CI Engines.
- Ebrahiminejad, M., & Karimzadeh, R. (2022). Diesel hydrocracking and hydrodesulfurization with activated red mud-supported and fluorine-containing NiW nanocatalysts. *Molecular Catalysis*, 517, 112056.
- El Golli, A., Contreras, S., & Dridi, C. J. S. R. (2023). Bio-synthesized ZnO nanoparticles and sunlight-driven photocatalysis for environmentally-friendly and sustainable route of synthetic petroleum refinery wastewater treatment. *Scientific reports*, 13(1), 20809.
- Fan, Z., Ji, Y., Shao, Q., Geng, S., Zhu, W., Liu, Y., Pao, C.-W. (2021). Extraordinary acidic oxygen evolution on new phase 3R-iridium oxide. *Joule*, 5(12), 3221-3234.
- Fu, H. Q., Zhou, M., Liu, P. F., Liu, P., Yin, H., Sun, K. Z., Wang, H.-F. (2022). Hydrogen spillover-bridged Volmer/Tafel processes enabling ampere-level current density alkaline hydrogen evolution reaction under low overpotential. *Journal of the American Chemical Society*, 144(13), 6028-6039.
- Gamal, A., Tang, M., Bhakta, A. K., Snoussi, Y., Khalil, A. M., Jlassi, K., Ali, A. M. A. (2024). CO₂ methanation using sugarcane bagasse biochar/nickel sustainable catalysts. *Materials Today Sustainability*, 25, 100627.
- Gatou, M.-A., Syrrakou, A., Lagopati, N., & Pavlatou, E. A. (2024). Photocatalytic TiO₂-based nanostructures as a promising material for diverse environmental applications: a review. *Reactions*, 5(1), 135-194.
- Ghamarpoor, R., Fallah, A., & Jamshidi, M. (2024). A review of synthesis methods, modifications, and mechanisms of ZnO/TiO₂-based photocatalysts for photodegradation of contaminants. *ACS omega*, 9(24), 25457-25492.
- Gogoi, D., Namdeo, A., Golder, A. K., & Peela, N. R. (2020). Ag-doped TiO₂ photocatalysts with effective charge transfer for highly efficient hydrogen production through water splitting. *International Journal of Hydrogen Energy*, 45(4), 2729-2744.
- Hijazi, N., Bavykina, A., Yarulina, I., Shoinchorova, T., Ramos-Fernandez, E. V., & Gascon, J. (2025). Chemical engineering of zeolites: alleviating transport limitations through hierarchical design and shaping. *Chemical Society Reviews*, 54(13), 6335-6384.
- Hu, X., Tian, X., Lin, Y.-W., & Wang, Z. (2019). Nickel foam and stainless steel mesh as electrocatalysts for hydrogen evolution reaction, oxygen evolution reaction and overall water splitting in alkaline media. *RSC advances*, 9(54), 31563-31571.
- Ibrahim, A., Elsayed, I., & Hassan, E. B. (2024). Catalytic upgrading of rice straw bio-oil via esterification in supercritical ethanol over bimetallic catalyst supported on rice straw biochar. *Energies*, 17(2), 407.
- Isahak, W. N. R. W., & Al-Amiery, A. (2024). Catalysts driving efficiency and innovation in thermal reactions: A comprehensive review. *Green Technologies and Sustainability*, 2(2), 100078.
- Jia, L., Liu, J., Cheng, H., Zhao, Z., & Liu, J. (2025). Review of Core-shell structure zeolite-based catalysts for NO_x emission control. *Journal of Environmental Sciences*, 150, 451-465.
- Kaewtrakulchai, N., Smuthkochorn, A., Manatura, K., Panomsuwan, G., Fuji, M., & Eiad-Ua, A. (2022). Porous biochar supported transition metal phosphide catalysts for hydrocracking of palm oil to bio-jet fuel. *Materials*, 15(19), 6584.

- Khan, L. A., Liaquat, R., Aman, M., Kanan, M., Saleem, M., Khoja, A. H., Khan, W. U. H. (2024). Investigation of novel transition metal loaded hydrochar catalyst synthesized from waste biomass (rice husk) and its application in biodiesel production using waste cooking oil (WCO). *Sustainability*, 16(17), 7275.
- Khateri, M., & Najafpour, M. M. (2024). Oxygen-evolution reaction on nickel oxyhydroxide's surface: Toward a super catalyst for oxygen-evolution reaction with ultralow overpotentials. *ACS Applied Energy Materials*, 7(11), 5028-5037.
- Kordouli, E., Vourtsani, P.-I., Mourgkogiannis, N., Zafeiropoulos, J., Bourikas, K., & Kordulis, C. (2024). Green Diesel Production Catalyzed by MoNi Catalysts Supported on Rice Husk Biochar. *Catalysts*, 14(12), 865.
- Kosco, J., Gonzalez-Carrero, S., Howells, C. T., Fei, T., Dong, Y., Sougrat, R., Purushothaman, B. (2022). Generation of long-lived charges in organic semiconductor heterojunction nanoparticles for efficient photocatalytic hydrogen evolution. *Nature Energy*, 7(4), 340-351.
- Kumar, M. S., Alphin, M., Manigandan, S., Vignesh, S., Vigneshwaran, S., & Subash, T. (2023). A review of comparison between the traditional catalyst and zeolite catalyst for ammonia-selective catalytic reduction of NOx. *Fuel*, 344, 128125.
- Lakhani, P., Bhandari, D., & Modi, C. K. (2024). Support materials impact on green synthesis and sustainable processing via heterogeneous catalysis. *Discover Catalysis*, 1(1), 2.
- Li, M., & Wang, R. (2024). Combined catalytic conversion of NOx and VOCs: Present status and prospects. *Materials*, 18(1), 39.
- Li, R., Luan, J., Zhang, Y., Jiang, L., Yan, H., Chi, Q., & Yan, Z. (2024). A review of efficient photocatalytic water splitting for hydrogen production. *Renewable and Sustainable Energy Reviews*, 206, 114863.
- Lin, L., Fan, M., Sheveleva, A. M., Han, X., Tang, Z., Carter, J. H., . McInnes, E. J. (2021). Control of zeolite microenvironment for propene synthesis from methanol. *Nature Communications*, 12(1), 822.
- Maggiulli, L., Sushkevich, V. L., Krocher, O., Van Bokhoven, J. A., & Ferri, D. (2024). Correlating the nature of carbenium ions in zeolites to the product distribution in the methanol-to-olefins process. *ACS Catalysis*, 14(15), 11477-11489.
- Majodina, S., Poswayo, O., Dembaremba, T. O., & Tshentu, Z. R. (2023). Towards improvement of hydroprocessing catalysts-understanding the role of advanced mineral materials in hydroprocessing catalysts. *Minerals and Mineral Materials*, 2(4), N/A-N/A.
- Mardiana, S., Azhari, N. J., Ilmi, T., & Kadja, G. T. (2022). Hierarchical zeolite for biomass conversion to biofuel: A review. *Fuel*, 309, 122119.
- Mathew, J., & Krishnan, C. K. (2024). Two-Dimensional Zeolites-Potential Catalysts for Biomass Valorization. *ACS omega*, 9(2), 2048-2059.
- Melo-Banda, J., Lam-Maldonado, M., Rodríguez-Gómez, F., Hernández-Vega, L., Malpica-Maldonado, J., & de la Torre, A. R. (2022). Ni: Fe: Mo and Ni: Co: Mo nanocatalysts to hydroprocessing to heavy crude oil: Effect of continue phase in the final metallic nanoparticles size. *Catalysis Today*, 392, 72-80.
- Mohammed, A. E., Mohammed, W. T., & Ghenni, S. A. (2024). Environmental benefits of agricultural waste-derived catalysts in diesel desulfurization: A review. *Cleaner Materials*, 13, 100262.
- Mohsin, M., Ishaq, T., Bhatti, I. A., Jilani, A., Melaibari, A. A., & Abu-Hamdeh, N. H. (2023). Semiconductor nanomaterial photocatalysts for water-splitting hydrogen production: the holy grail of converting solar energy to fuel. *Nanomaterials*, 13(3), 546.
- Molaei, M. J. (2024). Recent advances in hydrogen production through photocatalytic water splitting: A review. *Fuel*, 365, 131159.
- Mudi, I., Hart, A., Ingram, A., & Wood, J. (2023). Catalytic Hydrodeoxygenation of Vanillin, a Bio-Oil Model Compound over Renewable Ni/Biochar Catalyst. *Catalysts* 2023, 13, 171. In.
- Narimani, M., Gonbadi, M., Navabi, M., Khezri-Shooshtari, F., Ale Ebrahim, A., & Zerafat, M. M. (2025). Photocatalytic performance of N-doped Ti3O5 nano-catalyst for phenolic compounds removal from industrial wastewaters. *Scientific Reports*, 15(1), 10511.
- Nawaz, S., Jamil, F., Akhter, P., & Hussain, M. (2024). State-of-the-art novel catalyst synthesized from waste rice husk and eggshells for cleaner biodiesel production. *Biofuels*, 15(1), 105-113.
- Nikolopoulos, I., Kordouli, E., Mourgkogiannis, N., Karapanagioti, H. K., Lycourghiotis, A., & Kordulis, C. (2023). Valorization of pyrolyzed biomass residues for the transformation of waste cooking oil into green diesel. *Catalysts*, 13(6), 1004.

- Qazi, U. Y., Javaid, R., Ikhlaiq, A., Khoja, A. H., & Saleem, F. (2022). A comprehensive review on zeolite chemistry for catalytic conversion of biomass/waste into green fuels. *Molecules*, 27(23), 8578.
- Quevedo-Amador, R. A., Escalera-Velasco, B. P., Arias, A. M. R., Reynel-Ávila, H. E., Moreno-Piraján, J. C., Giraldo, L., & Bonilla-Petriciolet, A. (2024). Application of waste biomass for the production of biofuels and catalysts: a review. *Clean Technologies and Environmental Policy*, 26(4), 943-997.
- Rafiani, A., Aulia, D., & Kadja, G. T. (2024). Zeolite-encapsulated catalyst for the biomass conversion: Recent and upcoming advancements. *Case Studies in Chemical and Environmental Engineering*, 9, 100717.
- Ramos, R., Abdelkader-Fernández, V. K., Matos, R., Peixoto, A. F., & Fernandes, D. M. (2022). Metal-supported biochar catalysts for sustainable biorefinery, electrocatalysis, and energy storage applications: a review. *Catalysts*, 12(2), 207.
- Roy, P., Jahromi, H., Adhikari, S., Finprock, Y. Z., Rahman, T., Ahmadi, Z., Oh, T.-S. (2022). Performance of biochar assisted catalysts during hydroprocessing of non-edible vegetable oil: Effect of transition metal source on catalytic activity. *Energy Conversion and Management*, 252, 115131.
- Said, S., Mikhail, S., & Riad, M. (2025). Recent trends for clean fuel using environmental protecting oxidative desulfurization process. *Cleaner Chemical Engineering*, 11, 100140.
- Shafiq, I., Shafique, S., Akhter, P., Yang, W., & Hussain, M. (2022). Recent developments in alumina supported hydrodesulfurization catalysts for the production of sulfur-free refinery products: A technical review. *Catalysis Reviews*, 64(1), 1-86.
- Shakir, M. A., Ahmad, M. I., Mansur, F. Z., & Abdul Khalil, H. (2024). Biomass to biofuel: Palm kernel shells as catalyst supports for enhanced biodiesel production. *Biofuels, Bioproducts and Biorefining*, 18(6), 2038-2052.
- Sharmila, V. G., Tyagi, V. K., Varjani, S., & Banu, J. R. (2023). A review on the lignocellulosic derived biochar-based catalyst in wastewater remediation: Advanced treatment technologies and machine learning tools. *Bioresource Technology*, 387, 129587.
- Shao, Y., Ni, J., Yin, J., Liu, X., Guo, S., Xu, Y., Luo, L. (2025). Fe-Rich Medium-Entropy Core-Shell Electrocatalyst for Hydrogen Evolution Reaction Under Large Current Density. *Small*, 21(4), 2407061.
- Shi, H., Sun, X., Zeng, S., Liu, Y., Han, G., Wang, T., Jiang, Q. Nanoporous nonprecious high-entropy alloys as multisite electrocatalysts for ampere-level current-density hydrogen evolution. *Small Struct* 2023; 4: 2300042. In.
- Shi, Z., & Bhan, A. (2022). Methanol-to-olefins catalysis on window-cage type zeolites/zeotypes with syngas co-feeds: understanding syngas-to-olefins chemistry. *Journal of Catalysis*, 413, 913-922.
- Shoaib, M., Naz, M. Y., Wu, T., Rehman, H. U., Sun, E., Li, A., Wang, N. (2025). Review of single-atom electrocatalysts for hydrogen and oxygen evolution reactions from water-splitting. *Fuel*, 390, 134704.
- Sun, H., Chen, C., Zhang, R., Li, Y., Ge, S., & Cui, P. (2025). Advances in Gasoline Hydrodesulfurization Catalysts: The Role of Structure–Activity Relationships and Machine Learning Approaches. *ACS omega*, 10(29), 31262-31273.
- Tahir, M., Tasleem, S., & Tahir, B. (2020). Recent development in band engineering of binary semiconductor materials for solar driven photocatalytic hydrogen production. *International Journal of Hydrogen Energy*, 45(32), 15985-16038.
- Takata, T., Jiang, J., Sakata, Y., Nakabayashi, M., Shibata, N., Nandal, V., . Domen, K. (2020). Photocatalytic water splitting with a quantum efficiency of almost unity. *Nature*, 581(7809), 411-414.
- Wang, G., Jiang, X. L., Jiang, Y. F., Wang, Y. G., & Li, J. (2023). Screened Fe3 and Ru3 single-cluster catalysts anchored on MoS2 supports for selective hydrogenation of CO2. *ACS Catalysis*, 13(13), 8413-8422.
- Wei, L., Wang, H., Dong, Q., Li, Y., & Xiang, H. (2025). A review on the research progress of Zeolite catalysts for heavy oil cracking. *Catalysts*, 15(4), 401.
- Xie, X., Du, L., Yan, L., Park, S., Qiu, Y., Sokolowski, J., Shao, Y. (2022). Oxygen evolution reaction in alkaline environment: material challenges and solutions. *Advanced Functional Materials*, 32(21), 2110036.
- Xu, T., Wang, C., Lv, Y., Zhu, B., & Zhang, X. (2025). Catalytic oxidative removal of volatile organic compounds (VOCs) by perovskite catalysts: A review. *Nanomaterials*, 15(9), 685.

- Yadav, G., Yadav, N., & Ahmaruzzaman, M. (2023). Advances in biomass derived low-cost carbon catalyst for biodiesel production: preparation methods, reaction conditions, and mechanisms. *RSC advances*, 13(33), 23197-23210.
- Yakaryılmaz, A. C., & Özgür, T. (2024). NO_x emission reduction through selective catalytic reduction using copper-based Y zeolite catalyst: experimental investigation and characterization. *International Journal of Automotive Engineering and Technologies*, 13(3), 84-90.
- Yan, P., Wang, H., Liao, Y., & Wang, C. (2023). Zeolite catalysts for the valorization of biomass into platform compounds and biochemical/biofuels: A review. *Renewable and Sustainable Energy Reviews*, 178, 113219.
- Yuan, X., Cao, Y., Li, J., Patel, A. K., Dong, C.-D., Jin, X., Ok, Y. S. (2023). Recent advancements and challenges in emerging applications of biochar-based catalysts. *Biotechnology advances*, 67, 108181.
- Zhang, L., Hu, Q., Qin, Y., Liu, H., Liu, H., Cao, G., Sun, Z. (2023). Optimizing the accessibility of zeolite Y on FCC catalyst to improve heavy oil conversion capacity. *Microporous and Mesoporous Materials*, 359, 112627.
- Zhang, N., Feng, X., Rao, D., Deng, X., Cai, L., Qiu, B., Chai, Y. (2020). Lattice oxygen activation enabled by high-valence metal sites for enhanced water oxidation. *Nature Communications*, 11(1), 4066.
- Zhang, Y., Zhang, K., Shang, C., Wang, X., Wu, L., Huang, G., Wu, Z. (2023). Synthesis of hierarchical ZSM-5 microspheres with superior performance for catalytic methanol-to-olefin conversion. *AIChE Journal*, 69(2), e17913.
- Zhao, B., Du, B., Hu, J., Huang, Z., Xu, S., Chen, Z., Xu, C. (2024). Recent advances in novel catalytic hydrodeoxygenation strategies for biomass valorization without exogenous hydrogen donors – A review. *Catalysts*, 14(10), 673.
- Zhou, X., Han, X., Qu, Z., Zhang, J., Zeng, F., Tang, Z., & Chen, R. (2024). Hierarchical FAU zeolites boosting the hydrocracking of polyolefin waste into liquid fuels. *ACS Sustainable Chemistry & Engineering*, 12(15), 6013-6022.
- Zhou, Z., Jiang, R., Chen, X., Wang, X., & Hou, H. (2021). One-step synthesis of hierarchical lamellar H-ZSM-5 zeolite and catalytic performance of methanol to olefin. *Journal of Solid State Chemistry*, 298, 122132.
- Zhu, W., Song, X., Liao, F., Huang, H., Shao, Q., Feng, K., Yang, H. (2023). Stable and oxidative charged Ru enhance the acidic oxygen evolution reaction activity in two-dimensional ruthenium-iridium oxide. *Nature Communications*, 14(1), 5365.