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AMMONIUM-MODIFIED NATURAL ZEOLITE: A PROMISING CATALYST FOR RENEWABLE DIESEL PRODUCTION – A REVIEW

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Abstract

The global shift toward sustainable energy has intensified research into renewable diesel production, owing to its superior fuel properties and environmental benefits. Catalysts play a crucial role in the hydrodeoxygenation of vegetable oils and biomass-derived feedstocks to produce green diesel. Natural zeolites, valued for their high thermal stability and tunable acidity, have emerged as cost-effective catalytic alternatives. This review explored recent advancements in the application of ammonium-modified natural zeolites as catalysts in green diesel production. Characterization techniques, including FT-IR (Fourier Transform Infrared Spectroscopy), XRD (X-ray Diffraction), SEM (Scanning Electron Microscopy), TG-DTG (Thermogravimetric Analysis), nitrogen adsorption isotherms, and NH_3*-TPD (Temperature-Programmed Desorption of Ammonia), were employed to analyze* NH_4^+*-zeolites. Results demonstrate that ammonium modification enhanced the acidity, porosity, and catalytic efficiency of natural zeolites, leading to improved deoxygenation selectivity and increased green diesel yields. The* NH_4^+*-modified zeolite achieved a* C_{15} *hydrocarbon selectivity of 70%, compared to 54% for the unmodified variant. Furthermore, introducing ammonium ions helped regulate acidity by mitigating excessive Brønsted acidity, ultimately reducing coke formation and improving catalyst stability. This review discusses the physicochemical properties and catalytic performance of ammonium-modified natural zeolites in green diesel production. It also addresses the challenges and future directions for scaling up their application in renewable fuel technologies.*

Keywords: *ammonium-modified natural zeolite; catalyst; green diesel; hydrodeoxygenation; renewable fuel*

Introduction

The depletion of non-renewable energy resources and the escalating ecological challenges have intensified the search for sustainable and renewable energy alternatives. Among them, green diesel produced via the hydrodeoxygenation (HDO) of vegetable oils has gained significant attention due to its compatibility with conventional diesel engines, high cetane number, and absence of oxygen-containing compounds (Mahdia et al., 2021). However, the HDO process requires a substantial amount of hydrogen (e.g., 35–420 mol/kg), rendering it economically impractical for large-scale industrial applications (Wijayapala et al., 2017). To address this challenge, developing highly efficient catalysts is crucial for optimizing conversion rates, selectivity, and yield, thereby reducing hydrogen consumption and improving the overall feasibility of the process. Catalysts used in HDO reactions have demonstrated excellent performance and specificity for producing diesel-range hydrocarbon fractions (Nugraha et al., 2022). Moreover, the support material for these catalysts plays a vital role in enhancing activity and selectivity. The design of catalyst supports is especially critical in obtaining high-quality diesel-range hydrocarbon fuels. For effective HDO processes, the support material must exhibit high catalytic efficiency and strong selectivity for hydrocarbon fractions within the diesel range (C_{15}-C_{18}).

A wide range of catalyst supports has been investigated for HDO reactions, including activated carbon (Ruangudomsakul et al., 2021), multi-walled carbon nanotubes (MWCNTs) (Aliana-Nasharuddin et al., 2019), carbon nanofibers (CNFs) (Muñoz-Arjona et al., 2025), mesoporous TiO_2 (Phan & Ko, 2017), ZrO_2, Al_2O_3, SiO_2 (Papageridis et al., 2020), $CaCO_3$ (Dwiatmoko et al., 2019), Al-MCM-41 (Nugraha et al., 2021), SBA-15 (Oh et al., 2020), MIL-96 (Aisyah et al., 2023), and natural zeolite (Yan et al., 2023). Among these, aluminosilicate-based supports, especially natural zeolites, have emerged as highly promising candidates for HDO applications. Their favorable properties include a high density of acid sites, strong ion exchange capacity, uniform porosity, and interconnected pore structures (Hakim et al., 2024; Lestari et al., 2018; Yan et al., 2021b). One of the primary challenges in HDO catalysis is the selection of an appropriate catalyst. Natural zeolites show great potential for enhancing the quality of biocrude oil due to their inherent abundance of iron species, which are essential for C–O bond cleavage (Putra et al., 2018; Zhang et al., 2022). Consequently, natural zeolite-supported catalysts are anticipated to be highly efficient in various applications, including chemical manufacturing, environmental protection, and biomass conversion.

Natural zeolites possess a distinctive porous framework, large surface area, and tunable acidity, making them attractive candidates for catalytic processes (Prihadiyono et al., 2022; Putra et al., 2018; Yan et al., 2021b). However, their performance in HDO reactions remains limited due to their predominantly microporous nature, which poses diffusion constraints for bulky oxygenated bio-oil molecules (Yan et al., 2021b, 2021a). Moreover, the strong Brønsted acid sites in natural zeolites can accelerate coke formation, leading to rapid catalyst deactivation. To mitigate these limitations, ammonium (NH_4^+)-modified natural zeolites have been proposed as acidity moderators to reduce excessive acidity. Given the central role of acid sites in acid-catalyzed hydrocarbon reactions, examining and quantifying their characteristics, such as origin, type, quantity, and strength, is of scientific and practical importance. Recent research (post-2023) has investigated the role of NH_4^+-modified SAPO-34 zeolite in the selective oxidation of cyclohexane (Liu et al., 2024). These studies demonstrated that NH_4^+ incorporation could modulate Brønsted acidity and significantly enhance catalytic performance.

The NH_4^+-modified natural zeolite effectively reduces dependence on expensive and less sustainable metals (Graça & Chadwick, 2020). Functionalization with ammonium ions has been shown to provide better acidity control than H-form zeolites (e.g., H-ZSM-5, H-Beta, H-Y) (Graça & Chadwick, 2020) and to enhance the metal dispersion stability of catalysts used in green diesel production (Putra et al., 2022). This review aimed to highlight the potential of ammonium-modified natural zeolites as catalyst supports by analyzing their physical and chemical characteristics, as well as their performance in HDO processes. The discussion began with a concise overview of the composition, structure, and properties of NH_4^+-zeolites, emphasizing their role as solid catalysts. The core of the review focused on various catalytic processes employed in HDO for green diesel production. Finally, the review presents perspectives on future developments in the field, particularly the design of more efficient NH_4^+-zeolites and the prospects of biofuel co-processing.

Methodology

This study employed a literature review (LR) approach to gather information on NH_4^+-zeolite as a catalyst. Research articles from the past decade were sourced from reputable databases, including Web of Science, Springer, Taylor & Francis, and ScienceDirect. The search strategy utilized keywords such as "NH_4^+-zeolite," "ammonium-zeolite catalyst," and "zeolite catalyst for green diesel production." The review process comprised several stages: (1) selecting the review topic, (2) identifying and selecting relevant publications, (3) analyzing the selected articles, and (4) organizing the manuscript review.

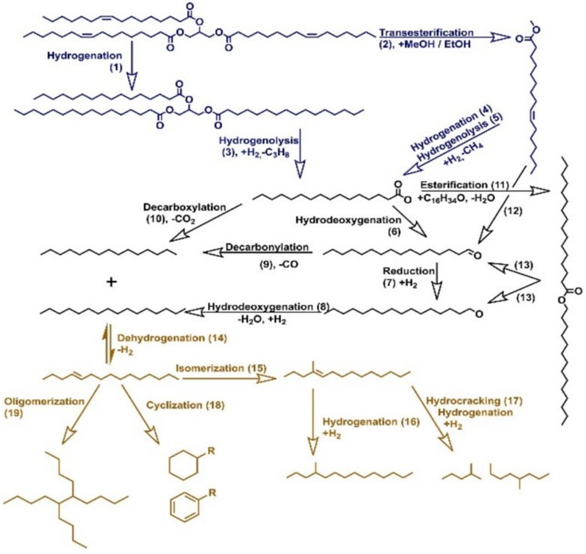

Figure 1. Proposed full hydrotreatment pathway for triglycerides derived from biomass (Žula et al., 2022)

Studies were included if they met the following criteria: peer-reviewed, focused on NH_4^+-exchanged natural or synthetic zeolites, and provided experimental data or comprehensive reviews concerning physicochemical characterization and catalytic performance in HDO reactions. Studies were excluded if they lacked a focus on NH_4^+-modified zeolites, were not peer-reviewed, or addressed applications unrelated to catalytic performance. The literature was thematically organized into five categories: (1) structural characteristics of NH_4^+-modified zeolites, (2) physicochemical characterization, (3) mechanistic insights into hydrodeoxygenation pathways, (4) catalytic activity and selectivity, and (5) industrial challenges and future directions. This structured framework enabled a comprehensive and coherent synthesis of existing knowledge while identifying research gaps for future exploration of ammonium-modified natural zeolite catalysts.

Results and Discussion

Overview of renewable diesel production

Renewable diesel, often referred to as green diesel, comprises diesel-like hydrocarbons produced via the deoxygenation of triglycerides derived from vegetable oil feedstocks. These processes include hydrodeoxygenation (HDO) and/or decarboxylation (DCO_2)/decarbonylation (DCO), as summarized in Table 1 (Farooqui et al., 2022; Long et al., 2021). The HDO reaction yields paraffinic hydrocarbons and water (H_2O) (Pattanaik & Misra, 2017). The mechanism of fatty acid transformation via HDO involves the formation of branched and cracked alkanes, as illustrated in Figure 1 (Žula et al., 2022). Additionally, gases such as CH_4, H_2, CO_2, and H_2O are produced through methanation and the water-gas shift reaction in the gas phase.

Table 1. Comparison of deoxygenation pathways in green diesel production

Mechanism	By-Product	H_2 Requirement	Carbon Efficiency	Favorable Catalysts
HDO	H_2O	High	High	Metals and strong acids
DCO_2	CO_2	Low-Moderate	Moderate	NH_4^+-modified zeolites
DCO	CO	Low	Low	Mild or weak acid catalysts

HDO is a catalytic process that removes oxygen-containing compounds using catalysts such as nickel supported on zeolites (Kordulis et al., 2016; Zamani & Saidi, 2024). Hydrogen plays a critical role by facilitating the cleavage of carbon-carbon and carbon-heteroatom bonds. Typically, water is generated through the direct HDO pathway, wherein the C=O double bond is first cleaved to form an alcohol, followed by the hydrogenation of the C–O bond to produce alkanes (Arun et al., 2015).

$$R - COOH + 3\,H_2 \rightarrow R - CH_3 + 2H_2O \quad (1)$$

Bio-oil feedstock can also undergo decarboxylation, wherein oxygen is removed as carbon dioxide (CO_2), leading to the formation of saturated hydrocarbons through direct C–C bond cleavage (Mohammad et al., 2013). In this pathway, the carboxyl group is eliminated without the need for hydrogen (Hongloi et al., 2021).

$$R - COOH \rightarrow R - H + CO_2 \quad (2)$$

In the decarbonylation process, the hydroxyl group of the acid reacts with hydrogen to form water, and the remaining oxygen is released as carbon monoxide (CO), resulting in either alkanes or unsaturated hydrocarbons (Hermida et al., 2015).

$$R - COOH + H_2 \rightarrow R - H + CO + H_2O \quad (3)$$

Additionally, hydrogenation reactions can saturate the unsaturated bonds in fatty acids in the presence of hydrogen (Hermida et al., 2015). Conversely, dehydrogenation reactions can yield H_2 via the cracking process or by generating unsaturated hydrocarbons:

Hydrogenation

$$R - COOH + H_2 \rightarrow R' - COOH \quad (4)$$

Dehydrogenation

$$R' - COOH \rightarrow R - COOH + H_2 \quad (5)$$

R = unsaturated hydrocarbon
R′ = saturated hydrocarbon

Influence of catalysts on renewable diesel production

The design of catalysts with enhanced activity, selectivity, stability, and reusability is critical for their application in the HDO of vegetable oils. Catalysts play a vital role in accelerating reaction kinetics, improving product selectivity, and reducing overall energy consumption during the process (Yan et al., 2025; Zhang et al., 2021). Their significance in HDO arises from several key attributes, including high catalytic efficiency, elevated turnover rates, robust chemical stability, and the ability to achieve effective catalysis with minimal catalyst loading (Nugraha et al., 2022). In recent years, various catalyst formulations and modifications have been developed to optimize catalytic performance and specificity in HDO reactions. These reactions have traditionally utilized moderately to highly acidic support materials such as alumina, silica, and zirconia, all exhibiting strong ionic potentials (Arun et al., 2015).

Based on their composition, HDO catalysts are commonly classified into three categories: (1) metal/metal oxide catalysts, (2) metal/metal oxide-supported catalysts, and (3) support materials (Nugraha et al., 2022). The use of metal/metal oxide and metal/metal oxide-supported catalysts has been extensively explored to enhance HDO efficiency (Ameen et al., 2020; Deo & Janik, 2021). A wide range of metals and metal oxides have been employed in HDO reactions, including Pd, Pt, Rh, Fe, Ni, Mo, Cu, Co, W, Sn, Ni-Cu, Ni-Co, Pt-Sn, NiMo, WO_3, Fe_2O_3, NiO, ZnO, CaO, ZrO_2, and La_2O_3. Support materials used in HDO catalysis include porous structures such as SiO_2, Al_2O_3, SiO_2-Al_2O_3, activated carbon (AC), multi-walled carbon nanotubes (MWCNTs), MCM-2, MCM-41, SAPO-11, SBA-15, and ITQ-2 (Kubička et al., 2014; Kubičková & Kubička, 2010). Furthermore, zeolite-based supports, such as zeolite beta, USY, ZSM-5, zeolite NaX, and metal-organic frameworks (MOFs), have also been employed (Aisyah et al., 2023; Phan et al., 2023; Zamani & Saidi, 2024).

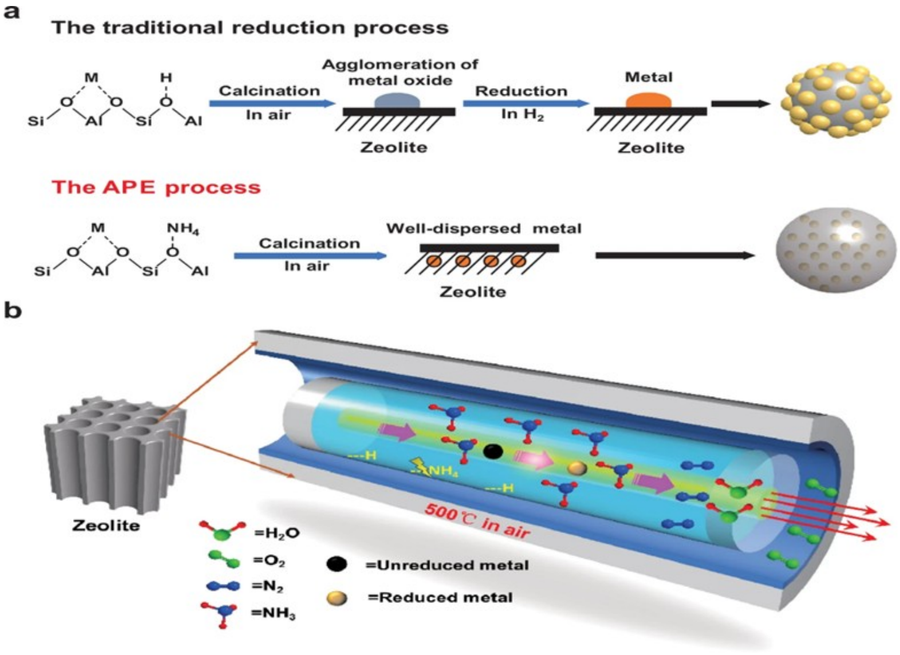

Figure 2. (a) Differences in reaction mechanisms; (b) Diagrammatic representation of the APE process (Yao et al., 2022)

Structure and properties of natural zeolites

Zeolites are porous crystalline aluminosilicates composed of TO_4 tetrahedral units, where the central T-atoms are either Si^{4+} or Al^{3+}, each surrounded by four oxygen atoms. These TO_4 units share corners with adjacent units, resulting in a three-dimensional framework that forms cavities, channels, and voids commonly referred to as micropores. Zeolites have shown promise as alternative catalysts due to their cost-effectiveness, thermal stability, and tunable acidity (Primo & Garcia, 2014). Natural, untreated zeolites, which are more readily available and less expensive than synthetic zeolites (such as MFI, ZSM-5, BEA), are rarely used in HDO reactions (Yan et al., 2021b). However, natural zeolites also present as crystalline hydrated aluminosilicates with framework structures such as mordenite and clinoptilolite (Putra et al., 2018). Today, desilicated and activated natural zeolites are widely utilized due to their strong acidity, which facilitates the cracking of C=O bonds in feed oils and enables high green diesel selectivity (92.74% in C_{15}–C_{18} range) via DCO and DCO_2

pathways (Aziz et al., 2023).

Natural zeolites are often referred to as "solid acids" because their microporous structure enables internal protons to act as Brønsted acid sites in heterogeneous catalysis. These Brønsted acid sites originate from bridging hydroxyl groups [≡Al–(OH)–Si≡] that connect aluminum and silicon tetrahedra. In contrast, Lewis acid sites are typically attributed to the presence of extra-framework aluminum (EFAL) within the zeolite structure (Busca, 2017; Primo & Garcia, 2014). These strong acid sites are generally the result of dealumination and structural degradation. Yao et al. (2022) discovered a unique property of zeolites used as catalyst supports: their pore channels exhibit a self-reducing behavior in NH_4^+-zeolites, known as the Ammonia Pool Effect (APE). Metal-zeolite catalysts synthesized via the APE method demonstrate enhanced catalytic efficiency and specificity compared to those prepared through conventional reduction techniques (see Figure 2). These findings confirm that the APE method can be effectively applied across various zeolite types and under diverse reaction conditions. In terms of acidity, NH_4^+-zeolites are gaining increased attention due to their moderate acidity, as well as their favorable surface area and pore diameter, which accommodate the processing of complex, larger-molecule feedstocks (Lanzafame et al., 2017; Lanzafame et al., 2019).

Modification of natural zeolite with ammonium

Natural zeolite is generally considered catalytically inactive, and the catalytic performance of its NH_4^+-form has rarely been explored. Although this form lacks stability in high-temperature gas-phase reactions, it can exhibit catalytic activity in acid-catalyzed reactions in the liquid phase, particularly those involved in biomass transformation processes (Lanzafame et al., 2020). The substitution of H^+ ions with NH_4^+, which can reversibly dissociate into NH_3 and H^+ ions, introduces a unique active site type (Brønsted/Lewis pair), offering a promising strategy to fine-tune the acidity of Al-containing zeolites (Lanzafame et al., 2017). This modification enhances the electrostatic field, as NH_4^+ exhibits properties similar to pseudo-alkali metals (Whiteside et al., 2011).

Despite increasing interest, studies focusing on the catalytic performance of NH_4^+-zeolites remain limited. Existing research can generally be categorized into two modification approaches (Table 2): 1) Ion exchange, where alkali metal ions (e.g., Na^+, K^+) are replaced with NH_4^+ to enhance Brønsted acidity; 2) Thermal treatment, involving controlled calcination to decompose NH_4^+ into H^+, thereby generating protonic sites that contribute to catalytic activity.

Wu and Weitz (2014) explored potential bonding configurations of NH_4^+ within zeolite structures, identifying interactions involving three NH groups that form hydrogen bonds with the zeolite framework. These configurations can be free, monodentate, bidentate, or tridentate (see Figure 3). As illustrated, NH_4^+ interacts with Brønsted acid sites, acting as a hydrogen bridge that anchors NH_4^+ ions to oxygen atoms on the zeolite surface. Liu et al. (2024) and Zecchina et al. (1997) noted that NH_4^+ ions can adopt bidentate and tridentate configurations with various local symmetries, depending on the specific positioning of the third hydrogen atom. Barbera et al. (2016) and Bonelli et al. (2010) corroborated these findings, identifying tridentate structures with C_{3v} or C_s symmetry. Additionally, unbound NH groups were observed to extend into the channels and cavities of the zeolite, remaining relatively uninfluenced by interactions with opposing pore walls (Barbera et al., 2016). Nonetheless, the precise nature and stability of NH_4^+ species in zeolites are still subjects of ongoing debate in the literature.

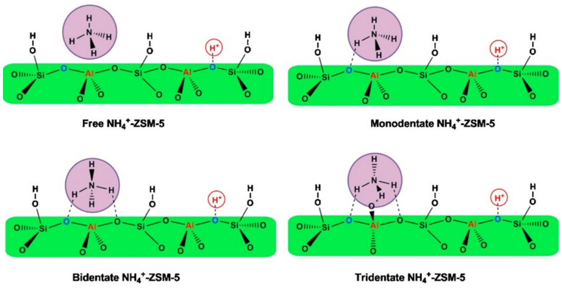

Figure 3. Possible configurations of NH_4-zeolite bonding (Wu & Weitz, 2014)

Table 2. Summary of studies on NH_4^+-zeolites with varying catalyst properties

Catalyst	Method	Parameter	Reference
NH_4^+-SAPO-34 zeolite	Thermal treatment	550°C, 4 h	(Liu et al., 2024)
NH_4^+-ZSM-5	Thermal treatment	663 K, 2 h	(Bonelli et al., 2010)
NH_4^+-ZSM-5	Thermal treatment	570°C, 10 h	(Liang et al., 2015)
NH_4^+/ZSM-5	Thermal treatment	723 K, 1.5 h	(Takeuchi et al., 2015)
NH_4^+-ZSM-5	Thermal treatment	390°C, 16 h	(Rostami et al., 2021)
NH_4^+-Silicalite-1	Thermal treatment	170°C, 24 h	(Lanzafame et al., 2017)
NH_4^+-BEA zeolite	Thermal treatment	500°C, 5 h	(Barbera et al., 2016)
NH_4^+-ZSM-5	Ion-exchange	90°C, 4 h	(Kitaev et al., 2014)
NH_4^+-MOR	Ion-exchange	120°C, 12 h	(Yao et al., 2022)
NH_4^+-Beta zeolite	Ion-exchange	65°C, 30 min	(Lanzafame et al., 2019)
NH_4^+-ZSM-5	Ion-exchange	Room temperature, 4 h	(Graça & Chadwick, 2020)
NH_4^+-ZSM-5	Ion-exchange	120°C, 3 h	(Wu & Weitz, 2014)
NH_4^+-Natural chabazite	Ion-exchange	75°C, 2 weeks	(Gualtieri & Passaglia, 2006)
NH_4^+-Indonesian zeolite	Ion-exchange	130°C, 3 h	(Putra et al., 2022)

Physicochemical characterization

The NH_4^+ species on various zeolites exhibit similar FTIR profiles, indicating the presence of bi- and tri-dentate coordination modes (Barbera et al., 2016; Lanzafame et al., 2019). Specifically, distinct absorption bands in the 1550–1350 cm^{-1} range are attributed to different types of hydrogen-bonded NH_4^+ complexes, including monodentate, bidentate, and tridentate configurations (Bonelli et al., 2010). Lanzafame et al. (2019), investigating NH_4^+-Beta zeolites, reported IR bands in the 3850–3500 cm^{-1} region corresponding to O-H stretching vibrations. Additionally, a band near 3675 cm^{-1} was assigned to partially EFAL species. Liu et al. (2024) observed that the FTIR profile of NH_4^+-SAPO-34 revealed the formation of bidentate and tridentate NH_4^+ structures stabilized within the cages and channels of the H-SAPO-34 framework. A new peak appearing at approximately 1400 cm^{-1} corresponded to the bending vibration of NH_4^+ at Brønsted acid sites.

A comparable pattern was identified by Suzuki et al. (2007), who reported absorption bands near 1450 and 1484 cm^{-1} associated with N-H bending modes of NH_4^+ species with differing bonding interactions. Wu and Weitz (2014) further corroborated these findings in their analysis of NH_4^+-ZSM-5, where broad absorption bands between 2400 and 3300 cm^{-1} were attributed to N-H stretching of hydrogen-bonded NH_4^+ ions, while a sharper band at 3375 cm^{-1} was linked to the N-H stretching of non-hydrogen-bonded (free) ammonium ions. This is consistent with the spectrum presented in Figure 4, which shows absorption bands near ~3300 cm^{-1} and ~1400 cm^{-1} corresponding to the stretching and bending vibrations of N-H bonds in NH_4^+-modified natural zeolites (Putra et al., 2022; Zecchina et al., 1997). The NH_4^+ ions interact with Brønsted acid sites, acting as hydrogen bridges that connect ammonium species to oxygen atoms on the zeolite surfaces (Barbera et al., 2016; Lanzafame et al., 2017; Lanzafame et al., 2019). The application of zeolites in their NH_4^+ form has been shown to be an effective strategy for moderating acidity. However, performance is strongly affected by the material's ability to undergo controlled and reversible NH_4^+ dissociation (Lanzafame et al., 2020).

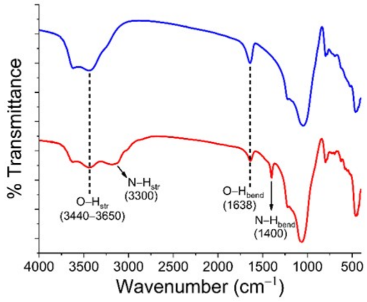

Figure 4. FTIR spectra of natural zeolite (blue) and NH_4^+-Indonesian zeolite (red) (Putra et al., 2022)

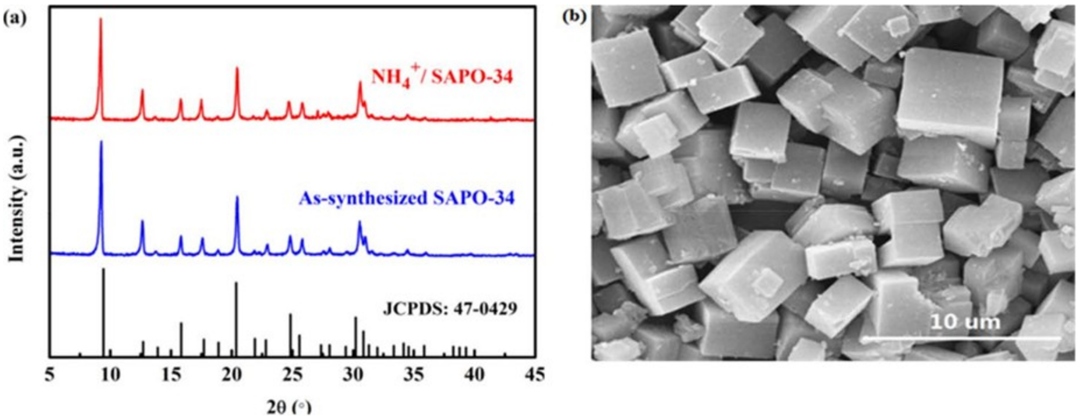

Figure 5. (a) XRD patterns and (b) SEM image of NH_4^+-SAPO-34 zeolite (Liu et al., 2019)

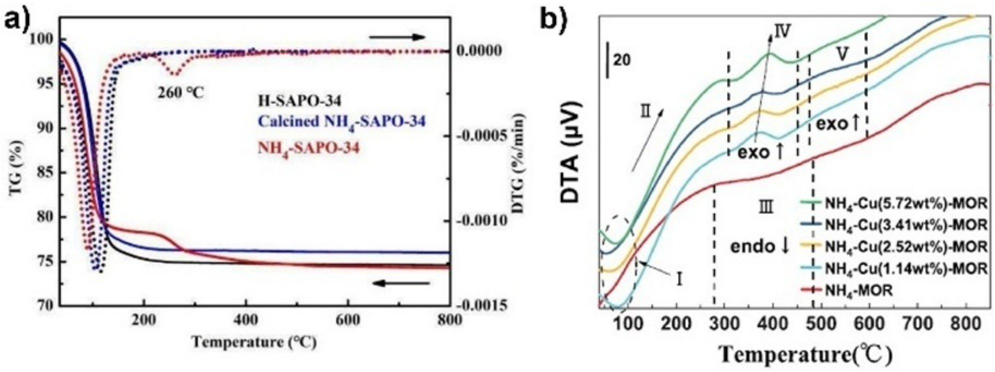

Figure 6. (a) TG-DTG curves of NH_4^+-SAPO-34 zeolite (Liu et al., 2024) and (b) DTA results of NH_4^+-MOR (Yao et al., 2022)

Liu et al. (2019, 2024) reported that XRD and SEM analyses (see Figure 5) revealed no significant alterations in the crystal structure or morphology of the NH_4^+-SAPO-34 framework following ion-exchange treatment. The SEM image in Figure 5 confirms that the cubic morphology of NH_4^+-SAPO-34 was preserved. Similarly, Lanzafame et al. (2019) found that the diffraction patterns of NH_4^+-Beta zeolites closely resemble those of their parent counterparts, indicating that long-range structural order remains intact after modification. These findings suggest that ion exchange does not significantly disrupt the framework, as evidenced by the relatively stable diffraction peak intensities (Graça & Chadwick, 2020). However, XRD data indicate a decrease in the relative crystallinity of NH_4^+-Indonesian zeolite to 74.1% following modification, compared to the natural zeolite's reference crystallinity of 100% (Putra et al., 2022).

Thermogravimetric-derivative

Thermogravimetric (TG-DTG) analyses confirmed that the zeolite frameworks remain structurally stable post-modification, reflecting their high thermal stability. As shown in Figure 6(a), NH_4^+-SAPO-34 exhibits a mass loss at ~260 °C, marking the onset of NH_4^+ decomposition within the SAPO-34 matrix. This finding aligns with studies of NH_4^+-natural zeolites based on chabazite (Gualtieri & Passaglia, 2006). Liu et al. (2024) concluded that this temperature signifies the beginning of NH_4^+ degradation. Furthermore, Figure 6(b) illustrates that NH_4^+-MOR zeolites show a broad endothermic peak in the 275–490 °C range on the DTA curve, corresponding to NH_4^+ decomposition into NH_3 and H^+ (Yao et al., 2022).

Several studies have indicated that increased surface area and porosity enhance reactant accessibility. Liu et al. (2019) investigated the surface area and pore structure of NH_4^+/SAPO-34 zeolite, revealing that the sample exhibited a high surface area and significant porosity, with an S_{BET} of 378.97 m²/g and a pore volume of 0.071 cm^3/g. Furthermore, research by Rathouský and Thommes (2007) confirmed that the adsorption isotherm observed in beta zeolite corresponds to type I, which is characteristic of predominantly microporous materials. Conversely, the N_2 adsorption isotherm of NH_4^+-Beta zeolite exhibits reversible pore condensation in larger mesopores at high relative pressures (P/P_0 = 0.6–1), with an S_{BET} of 601 m²/g. This phenomenon is accompanied by hysteresis, resulting in a characteristic type IV isotherm shape defined by the IUPAC classification (Lanzafame et al., 2019). A similar observation was reported by Putra et al. (2022), where hysteresis in the isotherm indicates enhanced mesoporosity in NH_4^+-Indonesian zeolite, as shown in Figure 7. The presence of hysteresis also confirms the existence of mesopores in NH_4^+-Indonesian zeolite at relatively high pressures (P/P_0 = 0.5–0.95), associated with capillary condensation. As noted by Kadja et al. (2020), when crystals are closely packed, the gaps between them can act as intercrystalline mesopores, causing nitrogen capillary condensation and resulting in hysteresis at elevated relative pressures.

Catalyst acidity is a key factor influencing catalytic performance, as zeolites are widely recognized in refining applications (Primo & Garcia, 2014). The acid site strength in zeolite-based catalysts has been explored through theoretical and experimental approaches (Haw, 2002; Wu & Weitz, 2014). Among the various methods, Temperature-Programmed Desorption (TPD), particularly NH_3-TPD, is one of the most commonly employed techniques. According to findings by Yao et al. (2022), the NH_4^+-MOR zeolite profiles can primarily be divided into two regions (see Figure 8).

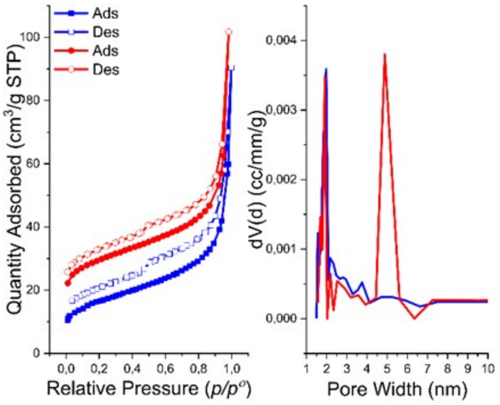

Figure 5. N_2 isotherms at 77 K and BJH analysis of natural zeolite (blue) and NH_4^+-Indonesian zeolite (red) (Putra et al., 2022)

The peak around 200 °C corresponds to the physical adsorption of NH_3 molecules and weak interactions with low-strength acid sites. The peak at temperatures above 400 °C primarily arises from NH_3 molecules adsorbed on Brønsted acid or strong acid sites (Aziz et al., 2023).

TPD analysis of NH_4^+-Indonesian zeolite indicates the presence of hydrogen bonding between NH_3 molecules and NH_4^+ species. The NH_4^+ cations can reversibly dissociate into NH_3 and H^+ (Putra et al., 2022). The high-temperature desorption peak corresponds to the release of ammonia from stronger Brønsted and Lewis acid sites (Beheshti et al., 2020). However, TPD alone cannot inherently distinguish between Brønsted and Lewis acid sites. While ammonia interacts with Brønsted acid sites, it can partially dissociate during catalytic reactions, leaving these sites available for further catalysis (Lanzafame et al., 2017). This indicates an irreversible reduction in NH_4^+ ions interacting with Brønsted acidic centers (Barbera et al., 2016). The resulting increase in acidity and enhancement of catalytic sites may improve performance relative to the protonic form. This phenomenon has been demonstrated in the etherification of hydroxymethylfurfural (HMF) with ethanol, a reaction of industrial significance for biodiesel additive production (Barbera et al., 2016).

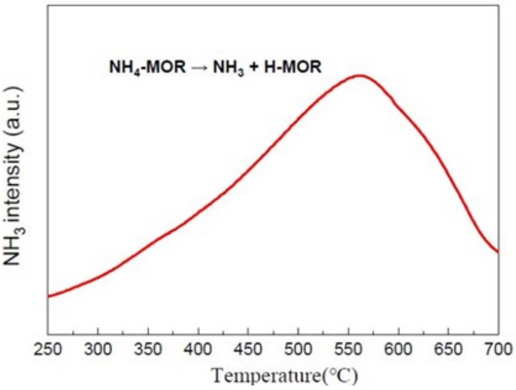

Figure 6. TPD signal of NH_4^+-MOR zeolite (Yao et al., 2022)

Hydrodeoxygenation efficiency

Recent research suggests that ammonium-modified natural zeolites exhibit high selectivity toward C_{15}-C_{18} hydrocarbons, which are key components in the production of green diesel (Putra et al., 2022). Incorporating NH_4^+ ions into the catalyst enhances the direct deoxygenation of fatty acids. It modulates the acidity of the zeolite, thereby influencing its catalytic performance, particularly in terms of selectivity. According to Putra et al. (2022), the structural modification of Indonesian zeolite into its NH_4^+ form significantly improved catalytic efficiency in the HDO of palm oil. Their findings indicated that the NH_4^+-modified zeolite achieved a higher selectivity toward C_{15} diesel, reaching 70% via the DCO/DCO_2 pathway, compared to 54% selectivity observed with the unmodified zeolite. In addition, hydrogen consumption increased to 90% v/v with the NH_4^+-modified catalyst, compared to 64% without it. While this enhancement in selectivity underscores the advantages of NH_4^+ modification, the substantial rise in hydrogen consumption suggests the occurrence of side reactions, such as excessive hydrogenation, which could compromise hydrogen utilization efficiency. Thus, although the modification improves reaction selectivity and accelerates deoxygenation, further optimization is necessary to enhance hydrogen efficiency.

Additional catalyst optimization is recommended to improve hydrogen utilization while maintaining high selectivity. Modifying the catalyst to favor selective deoxygenation pathways while minimizing redundant hydrogenation could yield better results. Moreover, adjusting reaction parameters such as temperature, pressure, and hydrogen flow rate may help optimize H_2 use. Exploring alternative deoxygenation mechanisms that require less hydrogen while effectively removing oxygen could also prove beneficial. Furthermore, the study revealed a significant reduction in coke formation, contributing to improved catalyst stability. Figure 9 illustrates the reaction mechanism, which involves the adsorption of carboxylic compounds onto the NH_4^+-Indonesian zeolite, followed by hydrogen interaction with the carboxylic-zeolite complex through the DCO mechanism. This interaction leads to the production of deoxygenated compounds and water via cleavage of the C-O bond. Notably, the C-O bond, with a bond dissociation energy of 351 kJ/mol, breaks more readily than the C=O bond, which has a dissociation energy of 745 kJ/mol, thereby facilitating deoxygenation.

Challenges in ammonium-modified natural zeolite catalysis

Despite their promising performance, ammonium-modified natural zeolite catalysts encounter several challenges in green diesel production. One key issue is the optimization of acidity, requiring a balanced distribution of Brønsted and Lewis acid sites to enhance deoxygenation selectivity while minimizing undesired side reactions. In addition, ensuring thermal, hydrothermal, and ion-exchange stability under high-temperature HDO conditions is critical for maintaining long-term catalyst durability. Effective synthesis and modification methods must be employed to prevent structural degradation and active site loss. Another major challenge lies in scaling up the application of these catalysts from laboratory settings to industrial processes.

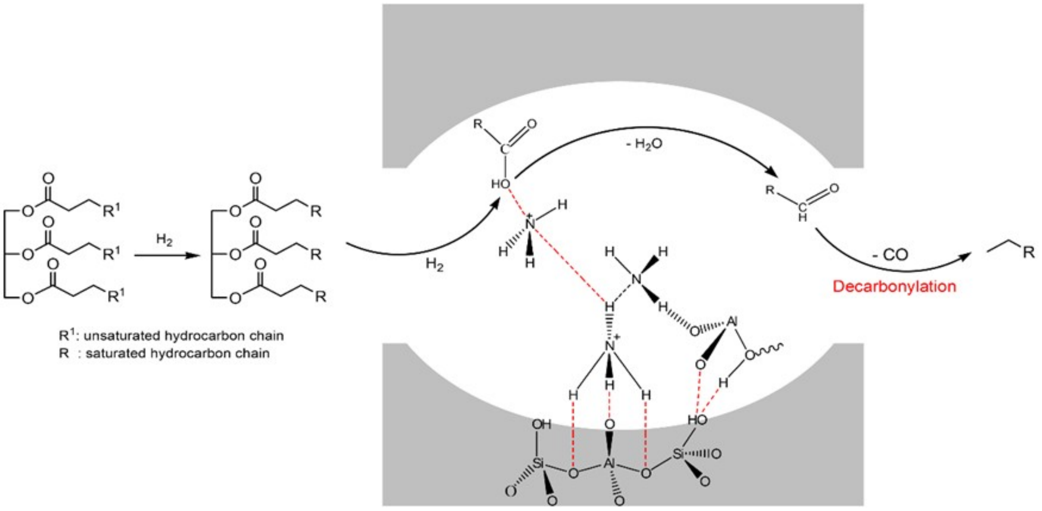

Figure 7. The catalytic process of NH_4^+-Indonesian zeolite in green diesel production through a DCO (decarbonylation) reaction (Putra et al., 2022)

This transition necessitates improvements in catalyst longevity, regeneration strategies, and cost-effective synthesis techniques. Addressing these technical and economic barriers is essential for realizing efficient and commercially viable green diesel production.

Future Directions

Future research on ammonium-modified natural zeolite catalysts should prioritize the development of hybrid catalysts through the integration of transition metals to enhance catalytic performance, selectivity, and stability in HDO reactions. Furthermore, machine learning and AI-driven optimization can refine synthesis parameters, predict catalyst performance, and accelerate the discovery of more efficient catalytic systems. Expanding the use of sustainable feedstocks, such as waste oils, algae, and lignocellulosic biomass, will further improve the feasibility of green diesel production while reducing dependence on conventional fossil resources. These advancements are essential for developing more efficient, durable, and scalable catalysts for industrial applications

Conclusion

Ammonium-modified natural zeolites have emerged as highly promising catalyst support for the HDO process in green diesel production. Their distinct characteristics, including tunable acidity, high surface area, and porous structure, can facilitate the efficient deoxygenation of bio-oils, resulting in high selectivity toward C_{15}-C_{18}

hydrocarbons, which are vital components of renewable diesel. Moreover, modification with ammonium ions mitigates excessive acidity and reduces coke formation, thereby enhancing catalyst stability and longevity. The incorporation of NH_4^+ ions has been shown to improve catalytic performance, with recent studies reporting selectivity toward diesel-range hydrocarbons (C_{15}) of up to 70%. Characterization techniques have confirmed that ammonium modification preserves the structural integrity of zeolites while enhancing their textural and acidic properties. FTIR, XRD, NH_3-TPD, and N_2 adsorption isotherm analyses validate the formation of stable NH_4^+-zeolites. These attributes position NH_4^+-modified natural zeolites as a sustainable and cost-effective alternative to conventional catalysts, supporting the global transition to renewable energy sources.

Despite their promising potential, several challenges remain to be addressed for the effective industrial application of ammonium-modified natural zeolites. Key issues include optimizing the balance between Brønsted and Lewis acid sites to ensure thermal and ion-exchange stability, as well as developing scalable and reproducible synthesis methods. Additionally, improving hydrogen utilization efficiency through tailored catalyst design is crucial for promoting selective deoxygenation with minimal hydrogen consumption. Future efforts should focus on the incorporation of transition metals (e.g., Ni, Fe) into NH_4^+-zeolites to develop bifunctional or hybrid catalysts, the application of machine learning techniques for precise process optimization, and the broader adoption of sustainable raw materials such as waste oils and algae. By addressing these challenges and advancing catalyst design, ammonium-modified natural zeolites can play a pivotal role in developing efficient, robust, and economically viable green diesel production technologies, thereby contributing to a cleaner and more sustainable energy future.

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Conflict of Interest

No potential conflict of interest was reported by the author(s).

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