

Review

Metal-Loaded ZSM-5 Catalysts for Biomass Pyrolysis Denitrogenation: Nitrogen Migration, Catalyst Deactivation, and Sulfur Resistance

Qing Xu ^{1,2}, Yanxu Chen ¹, Shengxian Xian ^{1,2,*}, Yujian Wu ¹ , Haowei Li ^{1,2}, Zongliang Zhang ¹ and Baokang Chen ¹

¹ College of Ocean Engineering and Energy, Guangdong Ocean University, Zhanjiang 524088, China; xuqing@gdou.edu.cn (Q.X.); chenyanyu2@stu.gdou.edu.cn (Y.C.); yjwu@gdou.edu.cn (Y.W.); lihw@gdou.edu.cn (H.L.); zzl666@stu.gdou.edu.cn (Z.Z.); chenbaokang@stu.gdou.edu.cn (B.C.)

² Guangdong Provincial Key Laboratory of Intelligent Equipment for South China Sea Marine Ranching, Guangdong Ocean University, Zhanjiang 524088, China

* Correspondence: xianshengxian@gdou.edu.cn

Abstract

Thermochemical conversion of nitrogen- and sulfur-rich biomass-derived wastes, such as sewage sludge, algae, and agricultural residues, is a promising route for renewable fuel production and waste valorization. However, fuel-bound nitrogen can be released as NH₃, HCN, and HNCO, while sulfur species such as H₂S, SO₂, and COS accelerate catalyst deactivation and generate NO_x/SO_x precursors. Metal-loaded ZSM-5 catalysts are attractive for clean catalytic pyrolysis because they combine the MFI pore confinement and tunable Brønsted/Lewis acidity of ZSM-5 with the hydrogen transfer, dehydrogenation, cracking, redox, and sulfur-tolerance functions of metal species. This review critically summarizes recent advances in metal-loaded ZSM-5 catalysts for catalytic denitrogenation of biomass-derived solid wastes. The formation and migration of NH₃, HCN, HNCO, tar-N, and char-N are first discussed to clarify the chemical basis of fuel-N conversion. The effects of ZSM-5 pore structure, acid-site distribution, Si/Al ratio, hierarchical porosity, and synergy on adsorption, diffusion, C-N bond cleavage, heterocyclic-N ring-opening, aromatization, and nitrogen redistribution are then analyzed. Catalyst deactivation under realistic pyrolysis atmospheres is also highlighted, including coke deposition, metal sintering, framework dealumination, mineral poisoning, and H₂S/SO₂/COS-induced sulfur poisoning. Finally, future directions are proposed for designing multifunctional ZSM-5-based catalysts integrating denitrogenation activity, sulfur resistance, coke resistance, regenerability, and quantitative nitrogen/sulfur mass balance.

Keywords: biomass pyrolysis; denitrogenation; ZSM-5; nitrogen migration; catalyst deactivation; sulfur resistance



Academic Editor: Helder T. Gomes

Received: 13 June 2026

Revised: 22 July 2026

Accepted: 23 July 2026

Published: 24 July 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

The catalytic pyrolysis of nitrogen-containing organic solid wastes, including sewage sludge, microalgae, fermentation residues, livestock manure, and some agricultural by-products, provides a promising route for waste valorization and renewable fuel/chemical production. However, these feedstocks usually contain abundant protein-N, amino acid-N, inorganic nitrogen, heterocyclic nitrogen, and, in some cases, sulfur-containing species. During pyrolysis, fuel-bound nitrogen can be converted into NH₃, HCN, HNCO, nitriles,

amides, pyrroles, pyridines, indoles, and other nitrogen-containing compounds, while sulfur species can be released as H_2S , SO_2 , COS , thiophenes, sulfides, and sulfones. These nitrogen- and sulfur-containing products not only decrease bio-oil quality but also act as precursors of NO_x/SO_x emissions and cause rapid catalyst deactivation during downstream upgrading [1–7].

As shown in Figure 1, the release of nitrogen-containing gases is closely related to the chemical structure of fuel-bound nitrogen and the temperature-dependent evolution of intermediates. Protein-N and amino acid-N first decompose into amino acids and small nitrogen-containing fragments, which then undergo deamination, dehydration, decarboxylation, condensation, and secondary cracking reactions [2,4,8,9]. Deamination reactions mainly produce NH_3 , especially in the relatively low-temperature region of 400–500 °C, whereas dehydrationcondensation reactions can generate cyclic amide intermediates such as 2,5-diketopiperazine (DKP), which further contributes to the formation of HCN and HNCO [8–11]. At higher temperatures, generally above 500 °C, HCN is preferentially generated through ring-opening and cracking of pyridinic-N, pyrrolic-N, nitrile-N, and other heterocyclic nitrogen species in tar and char [6,10,12–14]. HNCO is usually less stable at elevated temperatures and can be further converted into NH_3 or HCN. Therefore, NH_3 , HCN, and HNCO should not be regarded as isolated products, but as interconnected intermediates within a cascade nitrogen-conversion network.

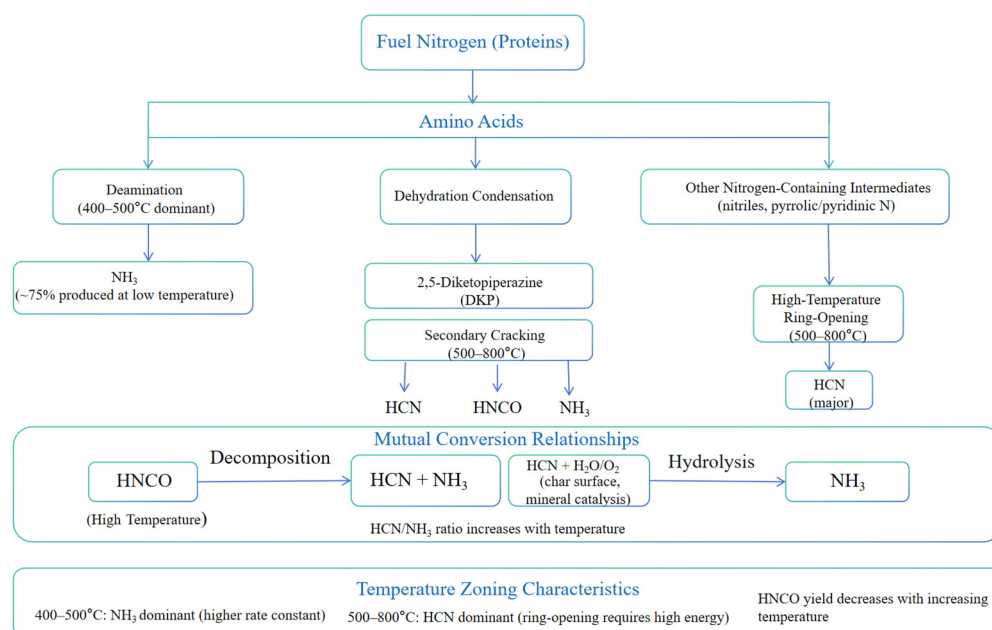


Figure 1. Cascade conversion network of fuel-bound nitrogen and temperature-zoned release characteristics of NH_3 , HCN, and HNCO during biomass pyrolysis.

Nitrogen migration during pyrolysis is also reflected in the partitioning of nitrogen among char, tar, and gas phases. At relatively low temperatures, nitrogen tends to remain in char as protein-N, amide-N, pyridinic-N, or pyrrolic-N. With increasing temperature, more nitrogen is released into tar and gas through devolatilization, cracking, and aromatization reactions. Char-N can be transformed into more stable heterocyclic structures such as pyridinic-N, pyrrolic-N, quaternary-N, and pyridine-N-oxide, while tar-N mainly consists of amides, nitriles, amines, and nitrogen-containing heterocycles [7,15,16]. Catalytic minerals, atmosphere, heating rate, and feedstock composition can further alter this distribution. For example, Fe species may regulate NH_3 and HCN conversion through FeO_x , Fe_xN , or Fe_xC intermediates, alkali and alkaline earth metals can change the energy barriers of deamination and dehydrogenation, and CO_2 or H_2 atmospheres can influence nitrogen

retention and secondary cracking [17–21]. Therefore, catalytic denitrogenation should be evaluated not only by the nitrogen content of bio-oil, but also by the complete nitrogen balance among char-N, tar-N, NH_3 , HCN, HNCO, and N_2 .

Among various catalytic systems, ZSM-5 has been widely used for catalytic pyrolysis because of its MFI topology, intersecting 10-membered-ring channels, tunable Brønsted/Lewis acidity, shape-selective pore confinement, and relatively high hydrothermal stability [22–25]. Brønsted acid sites originate from bridging hydroxyl groups associated with framework Al, while Lewis acid sites are mainly related to extra-framework Al species, framework defects, or introduced metal species. These acid sites can adsorb and activate amino groups, amides, nitriles, and nitrogen-containing heterocycles through hydrogen bonding, protonation, coordination, and acid-catalyzed cracking, thereby regulating the conversion of nitrogen-containing intermediates [26–29]. However, pristine HZSM-5 usually suffers from limited denitrogenation selectivity, insufficient accessibility for bulky nitrogen-containing compounds, excessive coke formation, and rapid deactivation. In many cases, HZSM-5 mainly redistributes nitrogen from tar and char into gaseous nitrogen-containing products rather than achieving deep nitrogen removal.

The catalytic performance of ZSM-5 is strongly governed by the balance among pore accessibility, acid strength, acid density, and acid-site distribution. A lower Si/Al ratio generally increases acid-site density, which can enhance cracking and ring-opening reactions, but excessive strong acidity may accelerate oligomerization, polyaromatization, and coke deposition. Hierarchical ZSM-5, hollow ZSM-5, ZSM-5 nanosheets, and matrix-supported ZSM-5 can introduce mesoporosity or secondary pores, improving the diffusion of bulky nitrogen-containing intermediates such as indoles, pyrroles, pyridines, amides, nitriles, and protein-derived fragments [30–37]. Therefore, ZSM-5 modification should not simply aim to increase acidity; instead, it should optimize the spatial coupling between accessible pores and suitable Brønsted/Lewis acid sites.

As illustrated in Figure 2, ZSM-5 denitrogenation is controlled by the coupling of MFI pore confinement and Brønsted/Lewis acid sites. The ~ 0.55 nm channels favor the diffusion and adsorption of small N-heterocycles, while partly excluding bulky N-compounds. Brønsted sites promote protonation, cracking, deamination, and aromatization, whereas Lewis or metal sites enhance adsorption, polarization, and C–N activation. Thus, effective denitrogenation requires matching pore accessibility, acid-site distribution, and the size/reactivity of N-containing intermediates while avoiding excessive cracking and coke formation.

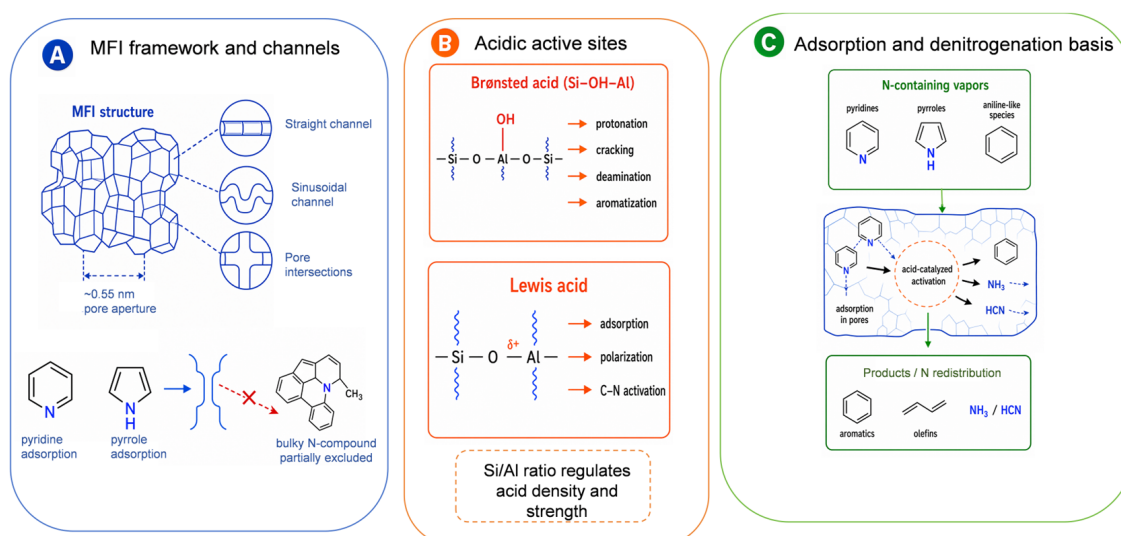


Figure 2. Structure acidity denitrogenation relationship of ZSM-5 during catalytic pyrolysis.

The textural properties of ZSM-5 provide the physical basis for molecular transport and shape-selective catalysis. The BET surface area reflects the overall accessibility of the catalyst, whereas the micropore volume and pore-size distribution determine whether nitrogen-containing intermediates can reach the internal acid and metal sites. The approximately 0.55 nm MFI channels are suitable for small nitrogen-containing molecules, but bulky compounds such as indoles, substituted pyrroles, amides, and protein-derived fragments may experience severe diffusion limitations. Introducing secondary mesopores can shorten diffusion paths, improve active-site accessibility, and facilitate the release of upgraded products. However, excessive loss of microporosity or blockage of the channel entrances by metal particles can weaken shape selectivity, increase the residence time of reactive intermediates, and promote secondary condensation and coke formation. Therefore, BET surface area, micropore and mesopore volumes, and pore-size distribution should be considered together with acidity and metal dispersion when evaluating catalytic pyrolysis performance [22,29,35,36].

More broadly, studies of multi-source solid-waste-derived ceramic foams have similarly demonstrated that pore morphology, pore-size distribution, and pore connectivity are critical structural property descriptors. Although these materials are not direct denitrogenation catalysts, their interconnected three-dimensional pore networks, high specific surface area, and favorable thermal and chemical stability provide broader guidance for designing diffusion-accessible and structurally stable porous materials for harsh biomass-conversion environments [38].

Metal loading is an effective strategy for constructing bifunctional ZSM-5 catalysts, hereafter referred to as metal@ZSM-5. Transition metals such as Fe, Ni, Co, Cu, Zn, and Ga can introduce hydrogenation/dehydrogenation, cracking, reforming, redox, and aromatization functions, while alkali and alkaline earth metals such as K, Na, Ca, and Mg can regulate acid base properties and modify the decomposition pathways of nitrogen-containing intermediates [23,39–44]. The interaction between metal sites and ZSM-5 acid sites can promote C–N bond cleavage, ring-opening of nitrogen heterocycles, nitrogen redistribution, and bio-oil upgrading. Ni and Co species are usually associated with hydrogen-transfer-assisted ring-opening of nitrogen heterocycles; Fe species are promising for redox-mediated nitrogen transformation through nitride/carbide intermediates; Zn and Ga species mainly promote aromatization-driven denitrogenation; and Ca- or alkali-assisted systems can enhance nitrogen retention in char or regulate NH₃/HCN release. Therefore, metal@ZSM-5 provides a more flexible platform than pristine ZSM-5 for catalytic denitrogenation.

Despite these advantages, the practical application of metal@ZSM-5 catalysts remains limited by catalyst deactivation. Coke deposition can block micropores and cover acid or metal active sites, while metal sintering and framework dealumination reduce the number and accessibility of catalytic centers [45,46]. More importantly, sulfur-containing species released from nitrogen- and sulfur-containing organic solid wastes, especially H₂S, SO₂, and COS, can react with metal species to form metal sulfides or sulfates, leading to irreversible or partially reversible loss of active sites [47–50]. In realistic pyrolysis atmospheres, nitrogen-containing compounds, sulfur-containing species, tar vapors, steam, minerals, and coke precursors coexist, resulting in coupled nitrogen/sulfur poisoning and sulfur-carbon deactivation that are more complex than conventional coke deposition alone. Although sulfur poisoning has been widely studied in NH₃-SCR, flue-gas denitration, and methane oxidation systems, the H₂S/COS-dominated sulfur poisoning behavior, sulfur tolerance thresholds, and regeneration strategies of metal@ZSM-5 catalysts under organic solid waste pyrolysis conditions remain insufficiently understood [51,52].

Pristine HZSM-5 has intrinsic limitations in biomass catalytic pyrolysis, including restricted micropore diffusion, excessive strong acidity, insufficient accessibility for bulky

nitrogen-containing intermediates, and rapid deactivation by coke deposition. Therefore, ZSM-5 modification is necessary to improve denitrogenation activity, product selectivity, and catalyst lifetime. Current modification strategies can be grouped into three categories: acidity regulation, hierarchical pore construction, and metal loading. These strategies do not act independently; instead, they jointly determine the accessibility of nitrogen-containing intermediates, the strength of acid-catalyzed cracking, the degree of synergy, and resistance to deactivation.

Acidity regulation is mainly achieved through dealumination, realumination, acid/base treatment or heteroatom incorporation. Liu et al. [33] developed a one-step dealumination realumination method using AlF_3 in an $\text{HF}/\text{NH}_4\text{F}$ buffer solution. Under optimized conditions, the zeolite maintained high crystallinity and acidity, while its mesopore volume increased from 23% to 41% of the total pore volume. Cai et al. [34] used an ethanol triethylamine water buffer solution for mild slow-release alkali treatment of highly acidic ZSM-5. This treatment reduced the strong acid content, increased medium and weak acid sites, enlarged the pore structure, and improved catalyst stability over repeated cycles. These results show that acidity optimization should avoid simply increasing strong acid density; instead, a balanced distribution of medium and strong acid sites is more favorable for cracking nitrogen-containing intermediates while suppressing coke formation.

Hierarchical pore construction is another effective strategy for improving mass transfer and acid-site accessibility. Hollow ZSM-5, desilicated ZSM-5, and matrix-supported ZSM-5 can reduce diffusion limitations for bulky oxygen- and nitrogen-containing intermediates. Zhao et al. [35] prepared hollow HZSM-5 with controllable acidity through protective desilication and external surface modification. Crespo et al. [36] embedded HZSM-5 into a $\gamma\text{-Al}_2\text{O}_3/\alpha\text{-Al}_2\text{O}_3$ matrix and significantly improved catalytic stability during bio-oil cracking. The weakly acidic mesoporous alumina matrix promoted pre-cracking and deoxygenation of large molecules, trapped coke precursors, and delayed micropore blockage. Souza et al. [37] also confirmed that secondary porosity can increase acid-site accessibility and reduce diffusion limitations. For denitrogenation, hierarchical porosity is particularly important because many nitrogen-containing intermediates, such as indoles, pyrroles, pyridines, amides, and protein-derived fragments, are too bulky to diffuse efficiently within purely microporous ZSM-5.

Metal loading provides additional catalytic functions beyond acidity regulation. Fe-modified HZSM-5 has shown dual deoxygenation and denitrogenation effects in microalgae catalytic fast pyrolysis; at an Fe loading of 8 wt% and 500 °C, the aromatics content reached 42.5%, while nitrogen-containing compounds, acids, aldehydes/ketones, and furans decreased markedly [53]. Ga-modified hollow ZSM-5 enhanced aromatization and coke resistance during cassava residue pyrolysis, achieving a high aromatics content and maintaining activity after repeated cycles [54]. Bimetallic Fe-Ni hierarchical zeolites further optimized acid distribution and improved monocyclic aromatic hydrocarbon selectivity while suppressing polycyclic aromatic hydrocarbon formation [43]. Cu-modified HZSM-5 also enhanced decarboxylation and aromatization during co-pyrolysis and maintained stable performance after regeneration. These examples suggest that metal species should be selected according to their specific functions: Fe and Ni are useful for dehydrogenation, cracking, and denitrogenation; Ga and Zn are effective for aromatization; Cu contributes to decarboxylation and aromatic formation; Ce can tune Brønsted acidity and improve catalytic stability.

Overall, the optimization of ZSM-5 for denitrogenation requires the simultaneous regulation of pore structure, acid properties, and metal functions. A suitable catalyst should provide accessible mesopores for bulky nitrogen-containing intermediates, sufficient medium/strong acid sites for C-N bond activation, and dispersed metal species for

hydrogen transfer, redox transformation, or deep nitrogen conversion. Excessive metal loading or overly strong acidity may decrease surface area, block pores, and accelerate coke deposition. Therefore, the design of metal-loaded ZSM-5 should focus on balancing denitrogenation activity, aromatization selectivity, and long-term stability rather than maximizing any single structural parameter. Based on the above considerations, this review summarizes recent advances in metal@ZSM-5 catalysts for catalytic denitrogenation during the pyrolysis of nitrogen-containing organic solid wastes. The review focuses on three key aspects. First, the synergistic mechanisms of single-metal, bimetallic, and tandem metal@ZSM-5 systems are discussed, with emphasis on C-N bond activation, nitrogen heterocycle ring-opening, NH_3 /HCN regulation, aromatization, and nitrogen redistribution. Second, the effects of active-site architecture, preparation methods, process conditions, and reaction/regeneration cycles on denitrogenation performance and catalyst stability are analyzed. Third, sulfur poisoning mechanisms and sulfur-resistance strategies are critically summarized, including metal-site sulfidation/sulfation, acid-site poisoning, pore blockage, sulfur carbon coupled deactivation, upstream sulfur capture, protective coatings, sulfur-tolerant metal design, and regeneration protocols. This review aims to provide guidance for the rational design of multifunctional metal@ZSM-5 catalysts that integrate denitrogenation activity, sulfur resistance, coke resistance, and regenerability under realistic tar-, steam-, mineral-, and sulfur-containing pyrolysis atmospheres.

2. Denitrogenation Mechanisms over Metal-Loaded ZSM-5 Composite Catalysts

2.1. Influence of Single-Metal Loading on Denitrogenation Performance

Single-metal loading is the most direct and widely used strategy for modifying the denitrogenation behavior of ZSM-5. Depending on their physicochemical properties and catalytic functions, loaded metals can be broadly divided into alkali/alkaline earth metals and transition metals. Alkali and alkaline earth metals mainly regulate nitrogen migration by changing the acid base environment, stabilizing nitrogen-containing intermediates, promoting char formation, and modifying the energy barriers of deamination, dehydrogenation, and 2,5-diketopiperazine (DKP) decomposition. In contrast, transition metals introduce hydrogenation/dehydrogenation, cracking, reforming, redox, and coordination functions, which can cooperate with the Brønsted and Lewis acid sites of ZSM-5 to promote C-N bond cleavage, ring-opening of nitrogen-containing heterocycles, aromatization of hydrocarbon fragments, and redistribution of nitrogen among gas, tar, char and oil phases [22,28,29,41,42,55].

For biomass pyrolysis denitrogenation, single-metal modification should not be evaluated only by the apparent decrease in nitrogen-containing compounds in bio-oil. A catalyst that transfers nitrogen from liquid products into NH_3 , HCN, or HNCO may improve bio-oil quality but simultaneously increase NO_x precursor emissions. Therefore, the catalytic effect of a metal-loaded ZSM-5 catalyst should be discussed from three levels: nitrogen removal from bio-oil, suppression of gaseous NO_x precursors, and deep conversion of nitrogen species into N_2 or stable char-N. This distinction is particularly important for nitrogen-rich feedstocks such as sewage sludge, microalgae, fermentation residues, and protein-rich agricultural wastes.

2.1.1. Regulatory Effects of Alkali and Alkaline Earth Metals

Alkali and alkaline earth metals (AAEMs), such as K, Na, Ca, and Mg, are naturally present in biomass and can also be introduced as catalyst modifiers. Their effects on nitrogen migration are complex because they can simultaneously influence char formation, intermediate stability, and nitrogenous gas release. Wei et al. [20] investigated the effects

of K, Ca, Na, and Mg chlorides on glutamic acid pyrolysis and found that these metals generally inhibited the total release of nitrogen-containing gases while promoting char formation. Among them, Na showed the strongest suppression of NH_3 , HCN, and HNCO, whereas Ca and Mg broadened the release temperature window of nitrogen-containing gases, resulting in a more gradual evolution process.

The regulation of NH_3 and HCN by AAEMs is not always in the same direction. Wang et al. [19] reported that AAEMs inhibited NH_3 formation by increasing the energy barrier of deamination, with the inhibitory strength following the order $\text{Na} > \text{Ca} > \text{K} > \text{Mg}$. However, they could simultaneously promote HCN formation by lowering the dehydrogenation barrier, with the promotional strength following the order $\text{Mg} > \text{Ca} > \text{Na} > \text{K}$. This indicates that AAEMs may reduce one NO_x precursor while enhancing another, depending on the dominant reaction pathway. Therefore, their denitrogenation effect should be evaluated according to the overall distribution of NH_3 , HCN, HNCO, char-N, and tar-N rather than by a single gas product.

The effect of AAEMs also depends strongly on feedstock composition and reaction temperature. In amino-acid model systems, AAEMs mainly regulate the formation and decomposition of DKP and amide/nitrile intermediates. In real biomass or sewage sludge systems, inorganic nitrogen, protein-N, heterocyclic-N, ash minerals, sulfur species, and oxygen-containing compounds coexist, leading to more complicated interactions. For example, CaO can promote HCN hydrolysis to NH_3 under some conditions, but it may also inhibit HCN release by suppressing DKP ring-opening or by enhancing nitrogen retention in char. In two-step microalgae pyrolysis, CaO-assisted in-bed catalysis retained part of the feedstock nitrogen in char and reduced the release of NH_3 and HCN before downstream upgrading over Ni-ZSM-5/bentonite [56]. These results suggest that AAEMs are more suitable for directional nitrogen migration regulation than for universal deep denitrogenation.

From a catalyst-design perspective, AAEMs can be used in three ways. First, they can act as basic modifiers to neutralize excessive strong acidity of ZSM-5, thereby suppressing over-cracking and coke formation. Second, they can serve as nitrogen-fixation promoters by stabilizing nitrogen-containing fragments in char or heavy tar. Third, they can be arranged as an upstream bed in tandem catalytic systems to capture acidic gases, sulfur species, or mineral vapors before the vapors reach metal-loaded ZSM-5. However, excessive AAEM loading may neutralize Brønsted acid sites, reduce aromatic selectivity, and weaken the acid-catalyzed activation of nitrogen-containing intermediates. Therefore, AAEMs should be used as auxiliary regulators rather than as the sole active phase for denitrogenation.

2.1.2. Differentiated Regulation by Transition Metals

Compared with AAEMs, transition metals loaded onto ZSM-5 usually show stronger synergistic effects. Ni, Co, Fe, Zn, Cu, and Ce can provide additional active sites for hydrogen transfer, dehydrogenation, redox reactions, cracking, and coordination with nitrogen-containing compounds. These functions are particularly important for the conversion of stable nitrogen heterocycles, which are difficult to completely denitrogenate over pristine HZSM-5 [35,41,42].

Ni and Co are representative metals for promoting hydrogen transfer and ring-opening of nitrogen-containing heterocycles. Niu et al. [22] compared Ni- and Co-modified ZSM-5 catalysts in the catalytic fast pyrolysis of defatted microalgae. At a Ni loading of 0.5 wt%, the relative yield of aromatics increased by 10.9 times compared with non-catalytic pyrolysis, while Co gave a lower increase. The improved performance of Ni/HZSM-5 was attributed to the generation of H radicals and enhanced cracking of nitrogen heterocycles. However, excessive metal loading can substantially decrease the specific surface area and micropore volume of ZSM-5. For example, increasing the Ni loading to 2 wt% decreased the BET

surface area from 459.9 to 381.0 m²g^{−1} and the micropore volume from 0.18 to 0.14 cm³g^{−1}, corresponding to reductions of 17.2% and 22.2%, respectively. For 2 wt% Co/HZSM-5, the BET surface area and micropore volume decreased by 4.4% and 11.1%, respectively [22]. These decreases were attributed to surface coverage and partial micropore blockage by the introduced metal species, which can impair reactant diffusion. Therefore, a relatively low metal loading range, typically 0.5–1 wt% for Ni- or Co-modified HZSM-5, is more suitable for balancing synergy and pore preservation.

Ni loading must be carefully controlled. Yung et al. [57] showed that Ni/ZSM-5 performance depends strongly on Ni loading and pretreatment state. Moderate Ni loading can improve deoxygenation and hydrocarbon formation, whereas excessive Ni may block micropores, cover acid sites, and accelerate coke deposition. Stanton et al. [55] also demonstrated that hydrogen-activating metals such as Ni, Co, Cu, Ga, and Pt influence catalytic fast pyrolysis differently under inert and hydrogen atmospheres. In a hydrogen-containing atmosphere, metal sites may enhance hydrogen transfer and reduce coke formation, but they may also alter the nitrogen migration pathway by promoting hydrogenation, hydrodenitrogenation-like reactions, or conversion of tar-N into NH₃. Therefore, Ni- and Co-loaded ZSM-5 catalysts should be optimized by balancing hydrogen transfer, C-N cleavage, aromatic selectivity, and NO_x precursor suppression.

Zn, Cu, Ce, Ag, and Mo show more differentiated functions. Hong et al. [41] systematically compared several transition metal-loaded HZSM-5 catalysts during the fast pyrolysis of penicillin fermentation residue. Zn/HZSM-5 showed the strongest denitrogenation effect, reducing the nitrogen content of bio-oil from 10.09 wt% to 6.98 wt%. Co/HZSM-5, Cu/HZSM-5, and Ce/HZSM-5 also reduced the nitrogen content, but their effects were slightly weaker. In contrast, Ag/HZSM-5 and Mo/HZSM-5 were more favorable for deoxygenation than for denitrogenation. Cu also contributed to decarboxylation and aromatization, while Ce showed moderate deoxygenation/denitrogenation ability and relatively stable CeO₂ species. These results indicate that different metals should not be evaluated using only one performance index; their functions may favor denitrogenation, deoxygenation, aromatization, coke suppression, or catalyst stability to different extents.

Fe species may participate in redox-mediated nitrogen conversion during the pyrolysis of nitrogen-rich biomass. In an Fe₂O₃-assisted sludge-protein pyrolysis system, XRD analysis showed that Fe₃O₄ was the predominant Fe-containing phase below 763 K, whereas Fe_xN_y and Fe₃C were detected at 1023 K. Thermodynamic analysis further supported a temperature-dependent evolution sequence of Fe₂O₃ → Fe₃O₄ → Fe_xN_y → Fe₃C [17]. These phases were associated with the consumption of NH₃ and HCN and enhanced nitrogen retention in the solid phase. However, this evidence was obtained in an Fe₂O₃ sludge-protein system without ZSM-5 and should therefore be regarded as a mechanistically relevant Fe-phase evolution pathway rather than direct proof of identical phase evolution on Fe-loaded ZSM-5. Fe-modified HZSM-5 has independently been shown to decrease nitrogen-containing compounds during microalgae pyrolysis [53], but the identity and evolution of the active Fe species on the zeolite require further confirmation by in situ or operando characterization.

2.1.3. Targeted Effects of Different Metals on NH₃, HCN, and tar-N Conversion

The effects of metal species on nitrogen conversion should be interpreted according to the nitrogen product directly measured in each study. Alkali and alkaline earth metals do not exhibit a single universal effect on biomass nitrogen conversion. In amino-acid model studies, K, Na, Ca, and Mg altered the energy barriers and reaction pathways of deamination, dehydrogenation, and 2,5-diketopiperazine formation or decomposition, thereby changing the release of NH₃, HCN, and HNCO [19,20]. The direction and magni-

tude of these effects depended on metal identity, temperature, and feedstock composition. Therefore, AAEMs are more appropriately described as regulators of nitrogen migration and nitrogenous-gas evolution than as catalysts for deep denitrogenation.

Direct evidence for transition-metal-loaded ZSM-5 is metal- and feedstock-dependent. Ni- and Co-modified HZSM-5 promoted the cleavage and ring-opening of nitrogen-containing heterocycles during the catalytic pyrolysis of protein-rich microalgae, with Ni/HZSM-5 showing stronger deoxygenation and denitrogenation performance than Co/HZSM-5 [22]. Zn/HZSM-5 decreased the nitrogen content of penicillin-fermentation-residue bio-oil from 10.09 to 6.98 wt%, whereas Co-, Cu-, and Ce-modified HZSM-5 produced smaller reductions under the same conditions [41]. Fe-modified HZSM-5 also decreased nitrogen-containing compounds during microalgae pyrolysis, although the specific Fe phase responsible for this effect was not identified [53].

The available evidence for Ga-modified ZSM-5 should be interpreted differently. Ga/ZSM-5 has been directly shown to enhance dehydrogenation, aromatization, hydrocarbon production, and catalyst stability during the upgrading of lignocellulosic biomass pyrolysis vapors [54,55]. However, these studies did not directly quantify bio-oil nitrogen removal, NH_3 /HCN formation, or the overall nitrogen balance. Ga-modified ZSM-5 should therefore be regarded as an aromatization and vapor-upgrading catalyst rather than as a directly validated biomass-denitrogenation catalyst.

Accordingly, catalyst selection should begin with a clearly defined nitrogen-conversion target. Direct evidence for decreasing nitrogen-containing compounds or bio-oil nitrogen is currently available for Zn-, Ni-, Co-, and Fe-modified ZSM-5 under specific feedstock and reaction conditions [22,41,53]. If the objective is to suppress NO_x precursors, NH_3 , HCN, and HNCO must be directly quantified rather than inferred from a decrease in liquid-phase nitrogen [19,20,28]. If the objective is primarily aromatization and hydrocarbon production, Ga- or Zn-modified ZSM-5 may be useful, but increased aromatic formation should not be considered equivalent to denitrogenation without a complete nitrogen balance [41,54,55].

As shown in Table 1, alkali and alkaline earth metals mainly regulate nitrogen migration by modifying deamination, dehydrogenation, and char formation, whereas transition metals introduce additional hydrogen-transfer, redox, cracking, and aromatization functions. However, the effects on NH_3 and HCN are strongly dependent on metal identity, loading, feedstock composition, and reaction conditions. Therefore, an increase or decrease in a single gaseous nitrogen product should not be interpreted independently of the overall nitrogen balance.

Table 1. Qualitative comparison of the regulatory effects of alkali/alkaline earth metals and transition metals on NH_3 and HCN yields during biomass pyrolysis.

Metal Category	Metal	Effect on NH_3	Effect on HCN	Main Mechanism	Feedstock/Model Compound	Key Implication	Ref.
Alkali metal	K	↓	↑	Raises the deamination barrier and lowers the DKP decomposition temperature	Glycine	May suppress NH_3 but promote HCN release	[19]
Alkali metal	Na	↓↓	-	Strongly inhibits nitrogenous gas release and stabilizes DKP/amide intermediates	Glutamic acid	Effective for suppressing volatile nitrogen formation	[20]
Alkaline earth metal	Ca	↓ or ↑	↑ or ↓	Regulates DKP decomposition and may catalyze HCN hydrolysis to NH_3	Sewage sludge/amino acid systems	Effect depends strongly on feedstock and temperature	[19]
Alkaline earth metal	Mg	↓	↑↑	Lowers the dehydrogenation barrier and promotes HCN formation	Glycine	Can enhance HCN formation despite NH_3 suppression	

Table 1. Cont.

Metal Category	Metal	Effect on NH ₃	Effect on HCN	Main Mechanism	Feedstock/Model Compound	Key Implication	Ref.
Transition metal	Fe	↓	↓	Forms Fe ₃ O ₄ , Fe _x N, and Fe _x C intermediates; promotes redox conversion and cracking	Sludge protein/biomass-derived nitrogen	Promising for deeper nitrogen conversion and N ₂ formation	[17,58]
Transition metal	Ni	↓↓	↓	Generates H radicals and promotes ring-opening of nitrogen heterocycles	Defatted microalgae	Strong metal–acid synergy, but loading must be controlled	[22]
Transition metal	Co	↓	↓	Promotes conversion of polycyclic N-heterocycles to amines/amides and aromatics	Defatted microalgae	Moderate denitrogenation activity	
Transition metal	Zn	↓↓	-	Highly dispersed Zn species promote aromatization and bio-oil denitrogenation	Penicillin fermentation residue	Shows strong bio-oil denitrogenation performance	[41]
Transition metal	Cu	↓	-	Promotes decarboxylation, aromatization, and partial denitrogenation	Penicillin fermentation residue	Useful for combined deoxygenation and denitrogenation	
Transition metal	Ag	-	-	Mainly improves deoxygenation; limited denitrogenation contribution	Penicillin fermentation residue	Not a primary denitrogenation metal	
Rare earth metal	Ce	↓	-	Provides moderate deoxygenation/denitrogenation and stable CeO ₂ species	Penicillin fermentation residue	Useful as a promoter for stability and redox regulation	

(Note: ↑ indicates promotion, ↓ indicates inhibition, ↑↑ indicates strong promotion, ↓↓ indicates strong inhibition, and “-” indicates no clear or limited effect. The number of arrows reflects the relative strength of the effect. Because the reported trends depend on feedstock, temperature, atmosphere, and catalyst preparation method, these symbols should be interpreted qualitatively rather than as universal rules).

To further illustrate the metal-specific regulation pathways, the major catalytic functions of representative metals in nitrogen conversion are schematically summarized in Figure 3.

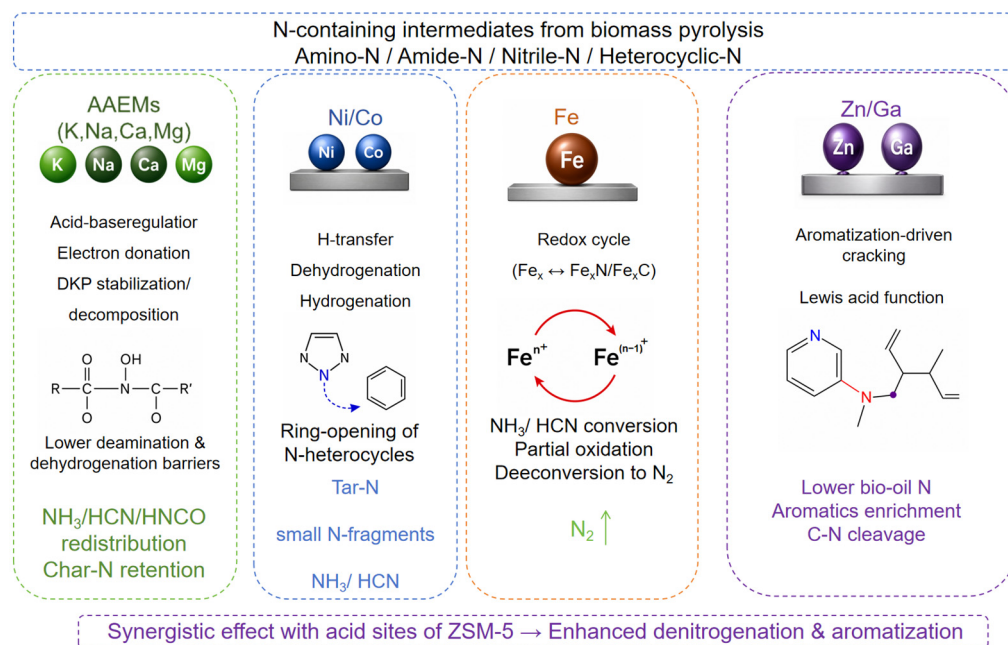


Figure 3. Metal-specific regulation pathways of nitrogen conversion over metal-loaded ZSM-5.

As summarized in Figure 3, the reported functions of metal modifiers should be distinguished according to the level of direct evidence. K, Na, Ca, and Mg directly regulate NH₃, HCN, and HNCO evolution by changing amino-acid and DKP reaction pathways [19,20].

Ni- and Co-modified HZSM-5 promote the cleavage of nitrogen-containing heterocycles, while Zn/HZSM-5 directly decreases bio-oil nitrogen under the reported fermentation-residue conditions [22,41]. Fe/HZSM-5 has been shown to decrease nitrogen-containing compounds during microalgae pyrolysis, although the active Fe phase and its evolution under reaction conditions remain unresolved [53]. Ga-modified ZSM-5 directly enhances dehydrogenation and aromatization, but its effect on nitrogen removal has not yet been quantitatively established [54,55]. Therefore, metal-specific functions should be assigned only to the nitrogen or hydrocarbon products directly measured in the cited study.

2.2. Multi-Metal Synergistic Catalysis and Underlying Mechanisms

Although single-metal loading can regulate specific nitrogen conversion pathways, one type of active site is often insufficient to simultaneously achieve denitrogenation, deoxygenation, aromatization, coke suppression, sulfur resistance, and regenerability. Multi-metal and tandem catalytic systems have therefore been developed to combine complementary functions. Synergy can arise from spatial separation of acid/base sites, electronic interaction between different metals, interfacial redox cycles, hydrogen spillover, and coupling between hierarchical pores and active-site distribution. According to the location and interaction mode of different components, multi-metal systems can be divided into tandem catalytic systems and bimetallic/multimetallic co-loaded ZSM-5 catalysts.

2.2.1. Multi-Component Tandem Synergistic Catalysis

Tandem catalysis separates different catalytic functions into different beds or spatial regions, thereby avoiding direct neutralization between incompatible active sites. This strategy is particularly useful for biomass pyrolysis because nitrogen-containing vapors usually coexist with oxygenates, hydrocarbons, steam, and coke precursors. Basic catalysts can first promote deoxygenation, decarboxylation, nitrogen fixation, or tar cracking, while acidic ZSM-5-based catalysts can subsequently promote aromatization, cracking, and further vapor upgrading.

Niu et al. [56] developed a two-step catalytic strategy for nitrogen-rich microalgae. CaO was first mixed with microalgae during pyrolysis, and the generated vapors were then upgraded over Ni-ZSM-5/bentonite. In this NG-CaO-Ni mode, 41.1% of feedstock nitrogen was retained in char, while the heavy bio-oil fraction achieved a deoxygenation degree of 89.4% and a denitrogenation degree of 38.9%. CaO acted both as a reactant and as a catalyst, promoting dehydration, decarboxylation, ring-opening, and cracking reactions while reducing the release of NH₃ and HCN. This example shows that tandem catalysis can balance two objectives that are difficult to achieve simultaneously in a single catalyst: nitrogen fixation in char and vapor-phase upgrading.

Other tandem systems mainly emphasize deoxygenation and aromatization but still provide useful guidance for denitrogenation catalyst design. Sun et al. [59] reported that HZSM-5/CuMgAl tandem catalysis increased tar aromatics to 76.88 wt% during coal-biomass co-pyrolysis through acid base synergy. CuMgAl first cracked macromolecular intermediates, which then diffused into HZSM-5 channels for cyclization and aromatization. Zhang et al. [60] showed that a CaO-Ca₁₂Al₁₃O₂₃/Zn-ZSM-5 tandem catalyst enhanced BTX formation and suppressed polycyclic aromatic hydrocarbons. Hernando et al. [61] also demonstrated that sequential acidic and basic zeolite beds can reduce oxygen content while avoiding acid–base neutralization. For denitrogenation, these studies suggest that spatially separated acid–base catalysis may be used to first stabilize or capture nitrogen species and then upgrade the remaining vapors over metal-loaded ZSM-5.

The key advantage of tandem catalysis is functional separation. However, its effectiveness depends on catalyst-bed sequence, residence time, vapor transfer, and the stability

of each component. If the basic bed excessively cracks nitrogen-containing compounds into NH_3 or HCN before downstream conversion, NO_x precursor release may increase. Therefore, future tandem systems should be designed with explicit nitrogen balances, including char-N, tar-N, NH_3 , HCN, HNCO, and N_2 selectivity.

2.2.2. Bimetallic and Multimetallic Chemical Synergy

Unlike tandem catalysis, bimetallic and multimetallic ZSM-5 catalysts integrate different active metals on the same support. Their synergy can originate from electronic interactions, alloy or oxide interface formation, redistribution of acid sites, improved hydrogen transfer, and enhanced resistance to coke deposition. This strategy is especially useful when one metal mainly promotes cracking or hydrogen transfer while another metal promotes aromatization, redox conversion, or nitrogen fixation.

Fe-Ni/ZSM-5 is a representative bimetallic system. Li et al. [45] investigated the deactivation and regeneration behavior of Fe-Ni/ZSM-5 during poplar wood catalytic pyrolysis. The incorporation of Fe and Ni improved deoxygenation activity and hydrocarbon yield, but coke deposition became the dominant cause of deactivation when the cumulative biomass-to-catalyst ratio increased. Importantly, the bimetallic catalyst could recover activity through oxidative regeneration and showed better regeneration stability than the corresponding monometallic catalysts. This indicates that bimetallic design can improve not only catalytic activity but also regeneration behavior.

Ga-Ni and Zn-Ni systems further demonstrate the importance of coupling metal function with hierarchical pore structure. Tian et al. [62] prepared an M@3Ga-8Ni/AZ catalyst by combining alkali-treated ZSM-5, Ga-Ni loading, and an MCM-41 shell. The monocyclic aromatic hydrocarbon yield increased from 40.35% over alkali-treated HZSM-5 to 69.48% over 3Ga-8Ni/AZ, and further to 83.61% after introducing the MCM-41 coating. The Ga-Ni synergy suppressed excessive aromatization and PAH polymerization, while the mesoporous shell improved mass transfer. Similarly, Zn-Ni bimetallic catalysts improved MAH and BTX yields, and the MCM-41 structure further enhanced mass transfer and coke resistance. For nitrogen-rich vapors, this type of design is valuable because bulky nitrogen-containing intermediates require accessible pores before they can undergo C-N cleavage or ring-opening.

Fe-Ca composite catalysts provide a more direct example of nitrogen-specific synergy. Cheng et al. [40] used proline as a nitrogen-rich biomass model compound and found that a Fe:Ca mass ratio of 1:3 produced the strongest inhibition of nitrogenous gas release, reducing NH_3 by 38.7% and HCN by 53.6%. Fe promoted proline ring-opening and amine-N formation, while Ca immobilized nitrogen in char and tar through basic sites. This shows that bimetallic synergy does not always aim to increase aromatics; it can also be designed to suppress gaseous NO_x precursors by coupling ring-opening with nitrogen fixation.

Overall, multi-metal catalysts provide more flexible regulation than monometallic systems. Their main advantage lies in combining complementary functions, such as Fe-mediated redox conversion, Ni-assisted hydrogen transfer, Zn/Ga-promoted aromatization, Ca-induced nitrogen fixation, and mesoporous-shell-assisted diffusion. However, excessive complexity can also introduce new problems, including unclear active-site attribution, competitive adsorption, pore blockage, and more difficult regeneration. Therefore, future studies should combine isotopic tracing, in situ spectroscopy, and quantitative nitrogen balance to clarify whether multi-metal synergy truly promotes deep denitrogenation or only redistributes nitrogen among products.

2.3. Preparation Methods and Active-Site Architecture

The preparation method determines how metal species are introduced onto or into ZSM-5, thereby governing metal dispersion, metal support interaction, acid-site distribution, particle size, oxidation state, and catalytic stability. For metal-loaded ZSM-5 catalysts used in biomass pyrolysis denitrogenation, preparation is not only a synthetic step but also a key factor controlling the architecture of active sites. A suitable preparation method should provide highly dispersed metal species, preserve the pore structure of ZSM-5, maintain an appropriate Brønsted/Lewis acid balance, and avoid excessive pore blockage or metal aggregation. The most commonly used methods include impregnation, ion exchange, and deposition precipitation, each of which generates different types of metal sites and metal support interactions.

2.3.1. Impregnation Method

Impregnation is the most widely used method for preparing metal-loaded ZSM-5 catalysts because of its simplicity, low cost, and broad applicability. In this method, ZSM-5 is contacted with a solution containing metal precursors, followed by drying, calcination, and sometimes reduction. Depending on the solution volume, impregnation can be performed as excess-solution impregnation or incipient-wetness impregnation. This method is particularly suitable for rapid screening of different metals, metal loadings, and catalyst formulations.

Bhuyan et al. [63] prepared Co/ZSM-5 and Ni/ZSM-5 catalysts by impregnation and applied them to the catalytic pyrolysis of invasive plant species in a fixed-bed reactor. Characterization results confirmed successful metal incorporation while largely preserving the zeolite microstructure. The modified catalysts reduced the oxygen content of bio-oil, increased its carbon content and heating value, and lowered the activation energy compared with non-catalytic pyrolysis. Shafaghat et al. [64] used incipient-wetness impregnation to prepare Fe-, Cu-, Zn-, Mo-, and Ni-modified HZSM-5 catalysts and found that 1 wt% Ni/HZSM-5 exhibited the highest hydrocarbon yield under methane co-feeding conditions. Iliopoulou et al. [65] also demonstrated the applicability of impregnation-prepared Co-ZSM-5 in larger scale catalytic pyrolysis systems. Stanton et al. [55] also prepared Ga-, Ni-, Cu-, Co-, and Pt-modified ZSM-5 catalysts and demonstrated that metal modification strongly changed product selectivity and coke behavior under inert and hydrogen atmospheres.

However, impregnation has intrinsic limitations. During drying and calcination, metal precursors can migrate and aggregate on the external surface of ZSM-5, producing relatively large oxide particles and partially blocking micropores. As a result, impregnation-prepared catalysts often exhibit moderate metal support interactions and less uniform metal dispersion than ion-exchanged catalysts. For denitrogenation, this may reduce the accessibility of nitrogen-containing intermediates to acid and metal sites. Therefore, impregnation is useful for preliminary catalyst screening, but further optimization of drying, calcination, reduction, and metal loading is required when high dispersion and long-term stability are needed.

2.3.2. Ion-Exchange Method

Ion exchange introduces metal cations by replacing protons or charge-balancing cations associated with framework Al sites in ZSM-5. Compared with impregnation, ion exchange can generate stronger metal-support interactions and more highly dispersed or even isolated metal species. Because exchanged metal ions are closely associated with framework Al, this method is particularly effective for regulating Brønsted/Lewis acidity and constructing well-defined metal-acid bifunctional sites.

Mullen et al. [66] prepared Fe-HZSM-5 catalysts with different Fe loadings by partial ion exchange of NH_4 -ZSM-5 and evaluated their performance in catalytic fast pyrolysis of cellulose, cellobiose, lignin, and switchgrass. The introduction of Fe changed the chemoselectivity of aromatic products and demonstrated that ion-exchanged Fe species can strongly influence acid-catalyzed vapor upgrading. Ávila et al. [67] introduced Na^+ , K^+ , and Mg^{2+} into H-ZSM-5 and H-Beta through ion exchange and found that these cations promoted decarboxylation and decarbonylation while suppressing coke formation, especially for Mg^{2+} -exchanged ZSM-5. Fu et al. [68] further showed that ion-exchanged Ag-, Mo-, Ni-, and Ce-modified ZSM-5 nanosheets could tune acid strength and preserve the channel structure when the metal loading was properly controlled.

The use of an ion-exchange procedure alone does not necessarily demonstrate that all introduced metal species occupy exchange positions. Successful ion exchange should be supported by combined compositional, structural, and spectroscopic evidence. ICP-OES can determine the actual metal loading and metal/Al ratio, while analysis of the residual exchange solution can provide the ion-exchange efficiency. A decrease in Brønsted acid-site density, together with a corresponding increase in Lewis acidity, is consistent with the replacement of framework-associated protons by metal cations, although this change alone does not prove successful ion exchange. XPS, UV vis spectroscopy, electron paramagnetic resonance, or X-ray absorption spectroscopy can identify the predominantly cationic state and local coordination of the exchanged metal. In addition, the absence of crystalline metal oxide peaks in XRD and the absence of large external particles in TEM or STEM-EDS support high dispersion. Therefore, ion exchange should be distinguished from simple surface deposition using several complementary techniques rather than a single characterization result.

For denitrogenation, ion exchange is attractive because isolated or highly dispersed metal cations can work together with nearby acid sites to promote C-N bond cleavage, ring-opening of nitrogen heterocycles, and hydrogen-transfer reactions. Nevertheless, the method is limited by the ion-exchange capacity of the zeolite and the accessibility of exchangeable sites. Excessive metal exchange may neutralize Brønsted acid sites and reduce cracking activity, while insufficient exchange may not provide enough metal sites for deep nitrogen conversion. Therefore, ion exchange is most suitable when precise control of metal location and acid metal proximity is required.

2.3.3. Deposition Precipitation Method

Deposition precipitation involves the controlled hydrolysis and precipitation of metal precursors in a suspension containing the zeolite support. Metal species are deposited as hydroxides or oxides on the support surface and are then converted into active phases by calcination or reduction. Compared with impregnation, deposition precipitation can achieve higher metal loading while maintaining better dispersion and reducing metal migration during drying.

Barton et al. [69] prepared Ni/HZSM-5 catalysts by deposition precipitation and systematically investigated the effects of Ni loading, precipitation time, and calcination temperature. The 15 wt% Ni/HZSM-5 catalyst prepared with a long deposition precipitation time of 16 h and a low calcination temperature of 673 K exhibited a small particle size of approximately 5 nm and a Ni dispersion of 7%. Further studies showed that deposition-precipitation-prepared Ni/HZSM-5 had higher hydrodeoxygenation activity and lower coke deposition than impregnation-prepared catalysts [70]. Yu et al. [71] used deposition-precipitation followed by electroless plating and phosphidation to prepare highly dispersed Ni_3P /HZSM-5, where Ni_3P nanoparticles with a size of approximately 4–6 nm showed high activity and selectivity in hydrodeoxygenation.

Although many deposition precipitation studies focus on deoxygenation rather than denitrogenation, their implications for denitrogenation are clear. Highly dispersed metal nanoparticles can provide more accessible hydrogenation/dehydrogenation and redox sites, while reduced coke formation helps maintain access to ZSM-5 acid sites. For nitrogen-rich biomass pyrolysis, deposition precipitation may therefore be useful for preparing catalysts that require relatively high metal loading, such as Ni-, Fe-, or Ni-Fe-based systems, while still preserving dispersion and stability.

2.3.4. Metal Dispersion, Preparation Conditions, and Active-Site Stability

Metal dispersion and metal support interaction are central parameters linking preparation method to catalytic performance. Impregnation usually produces a mixture of oxide nanoparticles and partially dispersed cationic species. Ion exchange favors isolated cations anchored near framework Al sites. Deposition precipitation produces supported nanoparticles with tunable particle size and interaction strength. These different active-site structures directly affect C-N bond cleavage, ring-opening of nitrogen-containing heterocycles, aromatization, coke formation, and catalyst regeneration.

Preparation parameters such as metal loading, calcination temperature, reduction temperature, and treatment time must be carefully optimized. Barton et al. [69] showed that extending the deposition precipitation time from 2 to 16 h increased Ni dispersion from 3.5% to 7.0% and reduced the particle size from approximately 15 to 5 nm. However, increasing the calcination temperature from 673 to 823 K caused metal sintering and dispersion loss. Qu et al. [72] found that increasing the reduction temperature from 400 to 600 °C enlarged Ni particles from 21.7 to 30.5 nm, which changed both catalytic activity and deactivation behavior. Niu et al. [22] further showed that for Ni- and Co-modified HZSM-5 in defatted microalgae pyrolysis, the optimal metal loading was 0.5–1 wt%; higher loading reduced specific surface area and pore volume and weakened catalyst performance. Wu et al. [73] demonstrated that single-atom Ga in hollow ZSM-5 can improve mass transfer and suppress coke formation while avoiding conventional metal sintering. Studies of non-zeolitic metal phosphides further illustrate that synthesis history can strongly affect active-phase formation, catalytic stability, and coke deposition. Guo et al. prepared MOF-derived Cu₃P catalysts at different phosphidation temperatures and found that Cu₃P-350 maintained relatively stable conversion during 6 h of CH₄-CO₂ reforming, whereas phosphidation at 400 °C resulted in substantially greater carbon deposition. Although this reaction differs from biomass pyrolysis denitrogenation, the results reinforce the need to correlate preparation conditions and metal-phase evolution with catalytic pathways and deactivation behavior rather than assuming a generic synergistic effect [74].

A more directly relevant HZSM-5 example was recently reported by Hu et al., who coupled NaOH treatment, activation atmosphere, and Ni loading for catalytic toluene cracking. Air activation primarily expanded the mesopore structure and improved mass transfer, whereas CO₂ activation increased the abundance of weak and medium-strength acid sites. Highly dispersed Ni nanoparticles then cooperated with the zeolite acid sites to promote C-H and C-C bond cleavage and aromatic-ring opening, with 7 wt% Ni under CO₂ activation achieving a maximum toluene conversion of 78.92%. Although toluene is a biomass-tar model compound rather than a nitrogen-containing intermediate, this study demonstrates that pore architecture, acidity, metal state, and activation atmosphere should be evaluated as a coupled system during biomass-vapor upgrading [75].

The catalytic function of a loaded metal depends not only on its elemental identity but also on its oxidation and coordination states. Ni and Co may exist as exchanged Ni²⁺/Co²⁺ ions, oxide species, or reduced metallic particles, while Cu may be present as Cu²⁺, Cu⁺, CuO, Cu₂O, or Cu⁰ depending on the preparation and reaction atmosphere. Ag

can occur as exchanged Ag^+ ions or metallic Ag clusters, whereas Ce generally exists as mixed $\text{Ce}^{3+}/\text{Ce}^{4+}$ species associated with CeO_2 . Metallic Ni, Co, and Cu sites generally favor hydrogen activation, hydrogen transfer, and C-N bond cleavage, whereas cationic or oxide species can provide Lewis acidity, coordination sites, and redox functions for the adsorption and transformation of nitrogen-containing intermediates. Mixed oxidation states may further facilitate redox cycling, but excessive reduction can promote particle sintering and pore blockage. Because these species may change dynamically under reducing pyrolysis atmospheres, the active phase should be identified using pre- and post-reaction XPS or X-ray absorption measurements rather than inferred only from the metal precursor or preparation method [41,57,63,76,77].

A reliable comparison of preparation methods requires a consistent characterization workflow. N_2 analysis should be used to determine whether impregnation, ion exchange, or deposition–precipitation changes the BET surface area, micropore volume, mesopore volume, and pore-size distribution. XRD can confirm preservation of the MFI framework and detect sufficiently large crystalline metal or oxide phases, whereas TEM, HAADF-STEM, and elemental mapping provide information on particle size, dispersion, and external-surface deposition. XPS and X-ray absorption spectroscopy identify metal oxidation states and local coordination, while H_2 -TPR evaluates reducibility and metal support interaction. NH_3 -TPD and pyridine-IR should be used to determine changes in acid strength and in the Brønsted/Lewis acid balance. These characterization results should be correlated with catalytic activity to distinguish whether performance changes originate from metal chemistry, acid-site modification, improved diffusion, or pore blockage.

Because no single characterization technique can fully distinguish exchanged cations, surface oxides, metallic nanoparticles, and strongly anchored isolated species, complementary methods are required. The principal characterization techniques and the information expected from each method are summarized in Table 2.

Table 2. Characterization methods for identifying the textural properties, location, dispersion, and chemical state of metals in ZSM-5.

Technique	Main Information	Expected Evidence
BET	Bet surface area, micropore/mesopore volumes, and pore-size distribution	Decreases in surface area or micropore volume indicate possible pore occupation or blockage
XRD	MFI framework retention and crystalline metal/oxide phases	Retention of characteristic ZSM-5 peaks indicates framework preservation; additional peaks may indicate large crystalline metal species
TEM/HAADF-STEM-EDS	Particle size, dispersion, and spatial distribution	Identifies external particles, agglomeration, isolated species, and elemental distribution
XPS/XANES/EXAFS	Metal oxidation state, local coordination, and metal–support interaction	Distinguishes metallic, oxide, and exchanged cationic metal species
H_2 -TPR	Reducibility and strength of metal–support interaction	Reduction temperatures reflect the reducibility and interaction strength of metal species with ZSM-5
ICP-OES	Actual metal loading, metal/Al ratio, and exchange degree	Quantifies metal uptake and supports estimation of ion-exchange efficiency
NH_3 -TPD/Pyridine-IR	Changes in Brønsted/Lewis acidity after metal introduction	Changes indicate proton exchange, acid-site coverage, or generation of Lewis acid sites

These techniques should be used in combination because the absence of metal oxide peaks in XRD alone does not prove successful ion exchange, and a decrease in BET surface area alone cannot distinguish pore blockage from framework damage or metal aggregation. Correlating these characterization results with catalytic performance is therefore essential for identifying the active metal species and clarifying the structure activity relationship.

Overall, the design of active-site architecture should follow a balance principle. Too little metal loading cannot provide sufficient synergy, whereas excessive loading can block micropores, reduce acid-site accessibility, and accelerate sintering. High calcination or reduction temperatures may improve precursor decomposition but can also enlarge metal particles and decrease dispersion. Therefore, future preparation strategies should focus on constructing stable, accessible, and highly dispersed metal sites in close proximity to acid sites, while preserving hierarchical porosity and coke resistance.

2.4. Process Conditions for Catalytic Denitrogenation and Catalyst Stability

Catalytic denitrogenation performance is controlled not only by catalyst structure but also by reaction conditions. Temperature, biomass-to-catalyst ratio, catalyst contact mode, residence time, and regeneration strategy all influence nitrogen migration, product distribution, and catalyst lifetime. Under realistic pyrolysis conditions, catalyst deactivation is unavoidable and mainly arises from coke deposition, metal sintering, mineral poisoning, framework degradation, and active-site loss. Therefore, process optimization should not aim only at high initial denitrogenation activity but also at long-term stability and regenerability.

2.4.1. Effects of Temperature, Biomass-to-Catalyst Ratio, and Contact Mode

Temperature is the primary factor controlling nitrogen conversion pathways. In general, the low-temperature region of 400–500 °C favors deamination of amino acids and proteins, leading mainly to NH₃ formation. The higher temperature region of 500–800 °C promotes ring-opening and cracking of heterocyclic nitrogen species, leading to increased HCN formation. In catalytic pyrolysis, ZSM-5-based catalysts can shift nitrogen from tar and char into the gas phase. For example, Tian et al. [28] showed that H-ZSM-5 increased the proportion of gaseous nitrogen-containing products from 38.54% to 53.95% while reducing tar-N and char-N by 69.22% and 58.07%, respectively. Niu et al. [56] achieved favorable denitrogenation performance in two-step microalgae pyrolysis when both the CaO-assisted pyrolysis stage and the Ni-ZSM-5/bentonite vapor-upgrading stage were operated at 500 °C. In industrial biomass waste pyrolysis, temperatures above 550 °C promoted HCN formation from heterocyclic nitrogen in tar, while NH₃ mainly originated from the hydrogenation of heterocyclic nitrogen in char [78].

The biomass-to-catalyst ratio, often expressed as B/C, determines the balance between conversion efficiency and catalyst lifetime. A low B/C ratio provides sufficient active sites for vapor upgrading but increases catalyst consumption and lowers process throughput. A high B/C ratio improves throughput but accelerates pore blockage and active-site coverage. Li et al. [45] reported that the deoxygenation activity of Fe-Ni/ZSM-5 gradually declined with increasing cumulative B/C ratio during poplar wood pyrolysis, and the catalyst became nearly deactivated at B/C = 4. Sonsupap et al. [79] proposed a partial regeneration strategy in which coke content was controlled at 2–4 wt% under B/C = 10, reducing catalyst demand while maintaining deep bio-oil deoxygenation. Other studies also show that the optimal B/C ratio varies with feedstock and catalyst; for example, Ce/HZSM-5 gave the highest oil yield from sugarcane bagasse at B/C = 2.0, whereas the highest C₆–C₈ hydrocarbon selectivity was obtained at B/C = 1.5 [80]. Therefore, B/C optimization should consider both nitrogen removal and catalyst lifetime, rather than product yield alone.

Catalyst contact mode also strongly affects denitrogenation and deactivation. In-situ catalytic pyrolysis, biomass and catalyst are mixed in the same reactor, allowing immediate contact between pyrolysis intermediates and catalyst sites. This configuration can enhance vapor conversion but exposes the catalyst directly to ash minerals, alkali metals, char particles, and coke precursors. These species may neutralize Brønsted acid sites and accelerate irreversible deactivation. In ex-situ catalytic pyrolysis, pyrolysis and catalytic upgrading occur in separate zones, allowing independent temperature control and reducing direct contact between catalyst and solid ash. Hernando et al. [81] showed that an ex-situ configuration allowed independent control of the pyrolysis and catalytic stages, while Mao et al. [82] observed that ex-situ catalytic fast pyrolysis over bimetallic modified zeolites and clays effectively delayed deactivation. For nitrogen-rich biomass, ex-situ or two-step catalysis is often preferable because nitrogen fixation, mineral capture, and vapor upgrading can be spatially separated.

2.4.2. Catalyst Deactivation and Regeneration

Coke deposition is the most common deactivation pathway for ZSM-5-based catalysts during biomass pyrolysis. Coke can form through oligomerization, polymerization, hydrogen transfer, aromatization, and condensation of oxygenated and nitrogen-containing intermediates. It blocks micropores, covers acid sites, reduces metal-site accessibility, and limits diffusion. However, the severity of deactivation is not determined only by total coke amount. Yao et al. [83] showed that coke morphology and location are more important than coke quantity. Amorphous carbon coating on the zeolite surface or inside micropores caused more severe deactivation than graphitic carbon located mainly on the external surface. Co/ZSM-5 exhibited better resistance to deactivation than Mo/ZSM-5 because Co favored the decomposition of macromolecular compounds and produced less harmful coke structures.

Hierarchical structures can improve coke resistance by controlling where coke forms. Mao et al. [82] showed that after five catalytic runs, parent HZSM-5 retained only 16.24% aromatic selectivity and a catalytic activity index of 45.45%, whereas the M@3Ga-8Ni/AZ catalyst retained 67.46% aromatic selectivity and an activity index of 84.44%. After oxidative regeneration, the activity recovered to 98.46%. This improved stability was attributed to the MCM-41 shell, which protected microporous acid sites and confined coke mainly to the external surface. Such structural design is also valuable for denitrogenation because it maintains access to acid and metal sites required for nitrogen-containing intermediates.

Metal sintering is another important cause of deactivation. Under high-temperature pyrolysis and oxidative regeneration conditions, metal nanoparticles can migrate, aggregate, and undergo Ostwald ripening, resulting in fewer exposed active sites and weaker metal-acid synergy. Wu et al. [73] emphasized that conventional metal-loaded zeolites can deactivate through metal sintering, whereas single-atom Ga anchored in hollow ZSM-5 avoids thermally driven migration and aggregation. Qu et al. [72] also showed that Ni particle size increased from 21.7 to 30.5 nm as the reduction temperature increased, confirming the sensitivity of Ni dispersion to thermal treatment. Therefore, stabilizing metal sites through ion exchange, strong anchoring, encapsulation, or single-atom design is essential for long-term catalytic denitrogenation.

Active-site loss can be reversible or irreversible. Reversible deactivation is mainly caused by coke deposition and can be partially removed by oxidative regeneration. Irreversible deactivation arises from mineral accumulation, framework dealumination, metal sintering, and chemical transformation of active metals. Niu et al. [46] found that repeated reaction/regeneration cycles over HZSM-5/Al₂O₃ led to mineral accumulation from mi-

croalgae ash; the mineral content increased by 2.5 times, the specific surface area decreased by 4.4%, and the Brønsted acid amount dropped by 70.4%. This type of deactivation cannot be fully reversed by coke combustion. Li et al. [45] also showed that regenerated Fe-Ni/ZSM-5 retained most deoxygenation activity, but aromatic yield remained slightly lower than that of the fresh catalyst because of partial irreversible loss of acid sites and pore structure.

Regeneration strategy should be selected according to the deactivation mechanism. Oxidative regeneration at approximately 500–600 °C can remove coke but may also accelerate metal sintering or framework degradation if conditions are too severe. Mild regeneration or partial regeneration may better preserve metal dispersion and acidity. Pretreatment strategies can also reduce irreversible poisoning. For example, CaO pre-mixing before microalgae pyrolysis can capture inorganic minerals and reduce their poisoning effect on downstream Ni-ZSM-5 catalysts [56]. In sulfur-containing atmospheres, however, regeneration becomes more complicated because metal sulfides or sulfates may form, requiring H₂ reduction, thermal treatment, or sulfur-resistant catalyst design. Therefore, coke resistance, mineral tolerance, metal stability, and sulfur resistance should be considered together rather than separately.

Metal-loaded ZSM-5 catalysts can deactivate through coke deposition, metal sintering, mineral poisoning, framework degradation, and sulfur poisoning. Figure 4 summarizes the principal reversible and irreversible pathways associated with coking, metal sintering, and sulfur poisoning. Coke deposition is partly reversible through oxidative regeneration, whereas metal sintering, framework dealumination, and mineral-induced neutralization of Brønsted acid sites are largely irreversible. Sulfur poisoning, involving the formation of metal sulfides, sulfates, or strongly adsorbed sulfur species, is chemically more complex and is therefore discussed separately in the following section.

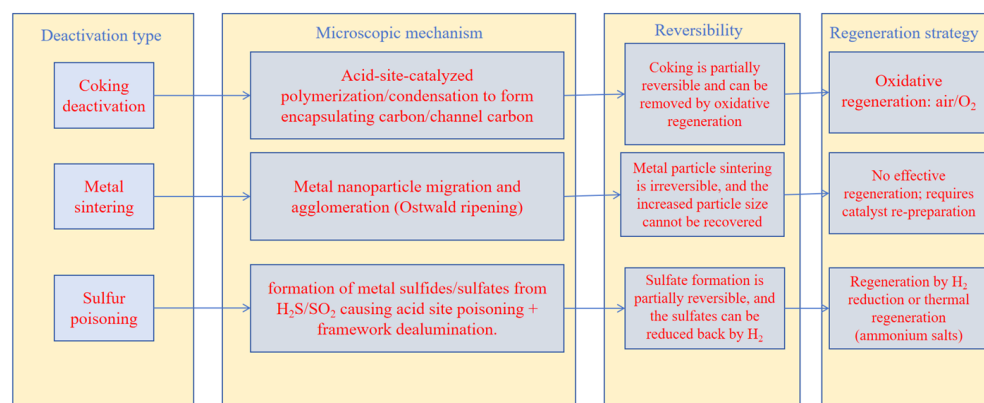


Figure 4. Catalyst deactivation mechanisms and regeneration strategies for metal-loaded ZSM-5 during biomass pyrolysis.

Despite these mechanistic insights, quantitative long-term stability data remain considerably more limited than initial-activity data, and the available cycling studies generally use overall catalytic activity or aromatic selectivity rather than nitrogen-specific conversion as the stability metric. In sequential reuse tests, parent HZSM-5 retained an activity index of only 45.45% after five catalytic runs, whereas the hierarchical M@3Ga-8Ni/AZ catalyst retained 84.44% and recovered to 98.46% of its initial activity after oxidative regeneration [82]. During repeated reaction regeneration cycles of HZSM-5/Al₂O₃ in microalgae pyrolysis, mineral accumulation increased by approximately 2.5-fold, while the specific surface area and Brønsted acid amount decreased by 4.4% and 70.4%, respectively [46]. These results demonstrate that apparent activity recovery after coke combustion does not necessarily indicate complete structural recovery. Nevertheless, most available studies are based on

sequential batch reuse or reaction regeneration cycles rather than prolonged continuous time-on-stream operation. Future continuous tests should report denitrogenation activity, NH_3 and HCN formation, product-N distribution, coke accumulation, and changes in pore structure, metal dispersion, and acidity as functions of time on stream.

2.5. Critical Understanding of “Denitrogenation” over Metal-Loaded ZSM-5

A critical issue in evaluating metal-loaded ZSM-5 catalysts is that “denitrogenation” is not always defined consistently. In many catalytic pyrolysis studies, denitrogenation is evaluated mainly by the decrease in nitrogen-containing compounds in bio-oil. However, a lower nitrogen content in the liquid product does not necessarily indicate complete nitrogen removal from the whole pyrolysis system. Part of the fuel-bound nitrogen may be transferred into NH_3 , HCN, HNCO, char-N, coke-N, or unquantified gas-phase nitrogen species [12,17,28,29,56,84]. Therefore, the apparent denitrogenation performance of metal-loaded ZSM-5 should be interpreted at three different levels: nitrogen redistribution among char, tar, and gas phases; removal of nitrogen from bio-oil; and deep conversion of reactive nitrogen species into harmless N_2 [21,28,56,58]. Based on this critical distinction, a three-level framework is proposed in Figure 5 to differentiate apparent denitrogenation from real denitrogenation.

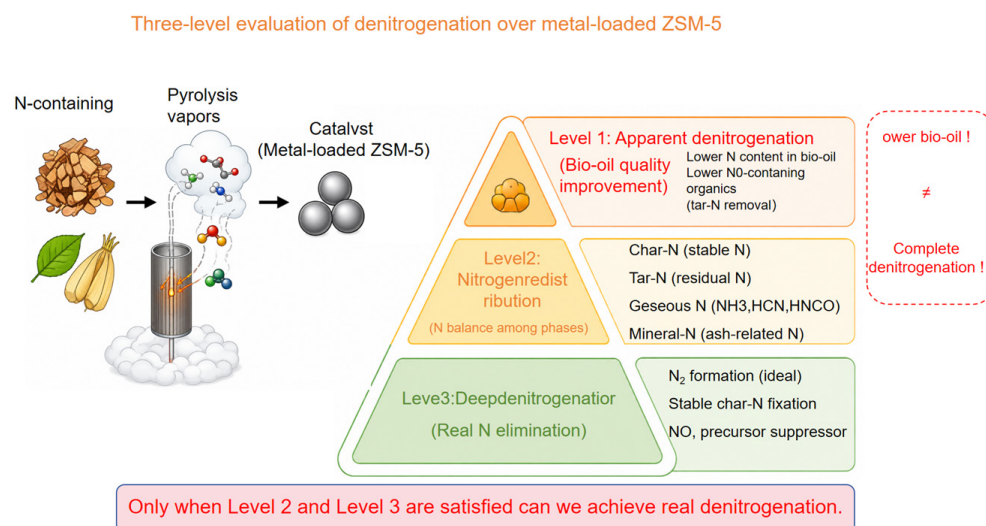


Figure 5. Three-level evaluation of apparent and real denitrogenation.

This distinction is particularly important for ZSM-5-based catalysts. Pristine HZSM-5 can promote the migration of nitrogen from tar and char into the gas phase through acid-catalyzed deamination, cracking, and ring-opening reactions [28,29]. Such behavior may improve bio-oil quality but may also increase the formation of NO_x precursors if NH_3 , HCN, and HNCO are not further converted or captured. Metal loading can partly overcome this limitation by introducing hydrogen-transfer, dehydrogenation, redox, and C-N activation functions [22,53,57]. For example, Ni- and Co-modified ZSM-5 catalysts can enhance the cracking and ring-opening of nitrogen heterocycles through hydrogen-transfer-assisted pathways [22,57,85], whereas Zn/HZSM-5 has been reported to reduce the nitrogen content of penicillin fermentation residue bio-oil from 10.09 wt% to 6.98 wt% [41]. Fe-based systems are more promising for deeper nitrogen conversion because Fe species may participate in redox cycles and form Fe_xN intermediates that further regulate NH_3 /HCN conversion [17,53,58].

As illustrated in Figure 5, the denitrogenation performance of metal-loaded ZSM-5 should be evaluated using a three-level framework rather than by the nitrogen content of

bio-oil alone. The first level is apparent denitrogenation, which is reflected by a decrease in bio-oil nitrogen content or a reduction in nitrogen-containing organic compounds in the liquid phase. This level is directly related to bio-oil quality improvement, but it does not necessarily represent complete nitrogen removal from the whole pyrolysis system.

The second level is nitrogen redistribution among different product phases. During catalytic pyrolysis, fuel-bound nitrogen may migrate among tar-N, char-N, coke-N, gaseous nitrogen species such as NH_3 , HCN, and HNCO, and mineral-associated nitrogen. Therefore, a decrease in bio-oil nitrogen may simply indicate the transfer of nitrogen from the liquid phase to the gas or solid phase. Without a quantitative nitrogen balance, apparent denitrogenation may overestimate the real nitrogen-removal ability of the catalyst.

The third level is deep denitrogenation, which represents the real elimination or stabilization of reactive nitrogen species. Ideally, reactive nitrogen intermediates should be converted into harmless N_2 or immobilized as stable char-N, while the formation of NO_x precursors such as NH_3 , HCN, and HNCO should be suppressed. Accordingly, a reliable evaluation of metal-loaded ZSM-5 catalysts should integrate bio-oil N removal, nitrogen redistribution, NO_x precursor control, and deep nitrogen conversion. Only when nitrogen removal from bio-oil is accompanied by suppression of reactive gaseous nitrogen species or conversion into N_2 /stable char-N can the catalyst be considered to achieve real denitrogenation.

2.6. Structure Function Matching Between Metal Sites and Nitrogen-Containing Intermediates

Different nitrogen-containing intermediates require different catalytic functions. Amines and amides are relatively reactive and can be converted through deamination, dehydration, or cracking over acid sites [4,8,28]. Nitriles may undergo cracking, hydrogenation, or hydrolysis depending on the reaction atmosphere and catalyst composition [4,16,86]. In contrast, pyridines, pyrroles, indoles, carbazoles, and other nitrogen-containing heterocycles are more difficult to denitrogenate because the nitrogen atom is embedded in an aromatic or conjugated ring structure [29,35]. For these stable species, acid sites alone are insufficient; metal-assisted hydrogen transfer, dehydrogenation, redox activation, and C-N bond weakening are usually required [41,57,85].

The catalytic function of the loaded metal should therefore be matched with the dominant nitrogen species in the feedstock. For protein-rich biomass or microalgae, Ni and Co are useful because they promote hydrogen-transfer-assisted cracking and ring-opening of nitrogen heterocycles [22,29,55,57]. For fermentation residues and other nitrogen-rich solid wastes containing complex N/O compounds, Zn, Cu, Ce, and Fe show different advantages in denitrogenation, deoxygenation, aromatization, and coke suppression [41,53,77]. For systems aiming at deeper nitrogen conversion, Fe-based catalysts deserve special attention because Fe oxides can be reduced during pyrolysis and may form metallic Fe, iron carbides, or iron nitrides, thereby participating in the secondary conversion of tar-N, NH_3 , and HCN [17,58,87].

However, increasing metal loading does not always improve denitrogenation. Excessive loading may cover Brønsted acid sites, block micropores, decrease specific surface area, and weaken the shape-selective function of ZSM-5 [22,53,69,72]. Therefore, the key design principle is not simply to maximize the number of metal sites, but to construct accessible and highly dispersed metal species near Brønsted/Lewis acid sites while preserving hierarchical porosity for bulky nitrogen-containing intermediates.

2.7. Evaluation Criteria for Future Metal-Loaded ZSM-5 Denitrogenation Catalysts

In the context of biomass pyrolysis, “denitrogenation” should not be interpreted simply as a decrease in the relative abundance of nitrogen-containing compounds in bio-oil. At least three different outcomes should be distinguished: (i) removal of nitrogen from the

liquid product; (ii) suppression of gaseous NO_x precursors, particularly NH₃, HCN, and HNCO; and (iii) deep conversion of fuel-bound nitrogen into N₂ or environmentally stable char-N. A catalyst may improve bio-oil quality by transferring nitrogen from the liquid phase into NH₃ or HCN, but such redistribution does not necessarily represent environmentally effective denitrogenation. Therefore, both apparent bio-oil denitrogenation and overall nitrogen-conversion performance should be reported.

Future studies should report complete nitrogen balances instead of relying only on the relative content of nitrogen-containing compounds in bio-oil. At minimum, char-N, tar-N, gas-phase NH₃/HCN/HNCO, coke-N, and, where possible, N₂ should be quantified [17,21,28,58]. The decrease in bio-oil-N should be distinguished from the suppression of NO_x precursors. A catalyst that converts bio-oil-N into NH₃ or HCN may improve liquid-fuel quality, but it does not necessarily improve environmental performance [28,29,41]. Therefore, metal-loaded ZSM-5 catalysts should be evaluated using both product-upgrading indicators and emission-control indicators.

Available quantitative results illustrate the difference between nitrogen removal and nitrogen redistribution. During the catalytic upgrading of penicillin fermentation residue, Zn/HZSM-5 decreased the nitrogen content of bio-oil from 10.09 to 6.98 wt%, demonstrating substantial liquid-phase upgrading [41]. In another study, H-ZSM-5 increased the proportion of gaseous nitrogen-containing products from 38.54% to 53.95%, while tar-N and char-N decreased by 69.22% and 58.07%, respectively [28]. The former result demonstrates a decrease in bio-oil nitrogen, whereas the latter indicates that a considerable fraction of nitrogen was redistributed toward the gas phase. These examples show why bio-oil-N, char-N, tar-N, NH₃, HCN, HNCO, coke-N, and N₂ should be quantified simultaneously whenever possible.

In addition, catalyst performance should be compared under realistic pyrolysis conditions. Many studies use model compounds or single feedstocks, but real biomass-derived solid wastes contain proteins, inorganic nitrogen, ash, alkali/alkaline earth metals, sulfur species, steam, and tar precursors. These components may change the reaction pathway, active metal state, acid-site accessibility, and coke formation behavior. Therefore, future evaluation should include nitrogen balance, sulfur balance, coke content, residual metal dispersion, acid-site recovery, pore structure retention, and regeneration efficiency after repeated cycles [45–47,50,56].

3. Sulfur Resistance of Metal-Loaded ZSM-5 Catalysts

3.1. Sulfur Release During Biomass Pyrolysis and Its Threat to Catalyst Stability

During biomass pyrolysis, sulfur in the feedstock can be released into the pyrolysis atmosphere as H₂S, SO₂, COS, mercaptans, thiophenes, sulfides, sulfones, and other sulfur-containing organic vapors. These species pose a serious threat to the activity and stability of downstream catalysts. Unlike coke deposition, which is mainly a physical blockage and can often be removed by oxidative regeneration, sulfur poisoning is primarily chemical deactivation. Sulfur-containing species can react with metal sites, acid sites, or framework species, thereby changing the chemical state, electronic structure, and accessibility of active centers.

Sulfur resistance is particularly important for metal-loaded ZSM-5 catalysts used in biomass pyrolysis denitrogenation because many nitrogen-rich feedstocks are also sulfur-rich. Sewage sludge contains proteins, inorganic sulfates, sulfides, and organic sulfur compounds. Microalgae contain sulfur-containing amino acids and sulfate-containing biomolecules. Herbaceous biomass and cruciferous plants may contain inorganic sulfates or glucosinolate-derived sulfur species [88–90]. During pyrolysis, these sulfur species can

be converted into H_2S , SO_2 , COS , or sulfur-containing organics depending on temperature, atmosphere, mineral composition, and char reactivity [49,50,89].

For metal-loaded ZSM-5, sulfur poisoning can directly destroy the same synergy required for denitrogenation. Ni, Co, Cu, Fe, Zn, Ga, and Ce species may react with H_2S or SO_2 to form sulfides, sulfates, or strongly adsorbed sulfur species. Meanwhile, sulfur species can poison Brønsted or Lewis acid sites and promote coke formation. This is especially problematic under realistic pyrolysis conditions, where tar vapors, steam, NH_3 , HCN , H_2S , COS , alkali metals, and coke precursors coexist. Therefore, sulfur resistance should be treated as a core performance index rather than as a secondary stability issue.

3.2. Microscopic Mechanisms of Sulfur Poisoning

3.2.1. Metal-Site Sulfidation and Sulfation

The first and most direct sulfur-poisoning pathway is the reaction between sulfur-containing gases and metal sites. Under reducing pyrolysis atmospheres, H_2S and COS can react with metal oxides or reduced metal species to form metal sulfides such as NiS , CoS , CuS , FeS , ZnS , or mixed metal sulfides. Under more oxidizing local environments, SO_2 or SO_3 can react with metal oxides to form metal sulfates such as CuSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, or ZnSO_4 . These transformations change the oxidation state, coordination environment, and electronic structure of metal active sites, thereby weakening hydrogen transfer, redox cycling, and C-N bond activation.

Direct identification of metal sulfides or sulfates requires evidence beyond the observed decrease in catalytic activity. S 2p and metal core-level XPS can identify changes in sulfur speciation and metal oxidation state, while XRD can detect sufficiently crystalline sulfide or sulfate phases. XANES/EXAFS, Raman spectroscopy, and STEM-EDS elemental mapping can further determine the local coordination and spatial association of sulfur with metal particles. In the reviewed literature, the formation of NiS on Fe-Ni/biochar and CuSO_4 on Cu-Ir/H-ZSM-5 provides mechanistic evidence for sulfur-induced transformation of active metal sites [47,91]. However, direct operando evidence for sulfide formation on metal-loaded ZSM-5 during actual biomass pyrolysis remains limited. Results obtained from biochar-supported metals, SCR, methane oxidation, or syngas-cleaning systems should therefore be regarded as mechanistically informative but not fully equivalent to H_2S / COS -containing biomass pyrolysis conditions.

Liu et al. [47] showed that sulfur and carbon in pyrolysis volatiles can jointly deactivate Fe-Ni/biochar catalysts. H_2S and COS promoted the formation of NiS from active Ni species, while carbon deposition further covered active sites. Although this study used biochar-supported Fe-Ni rather than ZSM-5, the mechanism is highly relevant to metal-loaded ZSM-5 because Ni, Fe, and other transition metals on ZSM-5 can undergo similar sulfidation. In SO_2 -containing systems, Zhang et al. [51] showed that sulfur poisoning of Rh-ZSM-5 became more severe at lower temperatures and higher SO_2 concentrations. Hua et al. [91] showed that CuSO_4 formation was a key cause of deactivation for Cu-Ir/H-ZSM-5, and H_2 reduction could partially restore activity.

For denitrogenation, metal sulfidation or sulfation has two consequences. First, metal sites lose their ability to promote hydrogen transfer, dehydrogenation, or redox conversion, thereby reducing C-N bond activation and heterocyclic-N ring-opening. Second, sulfur-modified metal sites may change product selectivity, sometimes promoting coke formation or stabilizing undesirable nitrogen-containing intermediates. Therefore, sulfur poisoning affects both catalyst lifetime and nitrogen migration selectivity.

3.2.2. Acid-Site Poisoning and Framework Degradation

The second sulfur-poisoning pathway is the deactivation of ZSM-5 acid sites. Sulfur species can adsorb on Brønsted or Lewis acid sites, reducing their ability to activate amino groups, amides, nitriles, and nitrogen-containing heterocycles. In the presence of steam or acidic sulfur-containing species, framework dealumination may also occur, leading to irreversible loss of Brønsted acidity and changes in pore structure. Because acid sites are required for deamination, cracking, aromatization, and ring-opening reactions, acid-site poisoning directly weakens the denitrogenation function of ZSM-5.

Acid-site poisoning is especially severe when sulfur-containing species and nitrogen-containing species coexist. NH_3 generated during pyrolysis can adsorb strongly on Brønsted acid sites, while H_2S , SO_2 , and COS may compete for metal sites or react with them. This competitive adsorption can change the local acid base environment and suppress the cooperative activation of nitrogen-containing intermediates. If metal sites are sulfided and acid sites are simultaneously neutralized, the bifunctional pathway collapses, and the catalyst may only act as an inert adsorbent or coke surface.

3.2.3. Sulfur Carbon Coupled Deactivation and Pore Blockage

The third pathway is pore blockage caused by sulfate/sulfide deposition and sulfur carbon coupling. Sulfur species can promote coke formation by changing the adsorption and conversion behavior of hydrocarbon and tar intermediates on metal surfaces. Conversely, coke deposits can encapsulate sulfur species and hinder their desorption during regeneration. This positive-feedback cycle of “sulfur promoting carbon deposition and carbon encapsulating sulfur species” makes sulfur carbon coupled deactivation more severe than coke deposition or sulfur poisoning alone. Sulfur-induced pore blockage should also be supported by paired textural characterization of the fresh and spent catalysts. A decrease in BET surface area alone is insufficient because it may originate from coke deposition, mineral accumulation, framework damage, or metal sintering. Changes in micropore volume, mesopore volume, pore-size distribution, and hysteresis should therefore be measured before and after sulfur exposure.

A 4.4% decrease in specific surface area was reported after repeated microalgae-pyrolysis cycles [46]. However, the simultaneous 2.5-fold mineral accumulation and 70.4% decrease in Brønsted acidity indicate that this result reflects multi-factor deactivation and cannot be used as direct evidence of sulfur-induced pore blockage. Direct paired measurements of sulfur speciation and pore-volume changes under realistic $\text{H}_2\text{S}/\text{COS}$ -containing pyrolysis conditions remain scarce. At present, paired sulfur-speciation and pore-volume data for metal-loaded ZSM-5 under actual biomass pyrolysis conditions remain scarce. This limitation should be recognized when pore blockage is proposed as a sulfur-deactivation mechanism.

This issue is particularly important for real biomass pyrolysis. In model SO_2 poisoning experiments, catalysts are usually exposed to low concentrations of SO_2 and simple gas mixtures. In biomass pyrolysis, however, sulfur-containing gases coexist with tar vapors, phenolics, furans, nitrogen heterocycles, steam, CO_2 , and mineral vapors. Therefore, sulfur poisoning under real pyrolysis atmospheres may involve simultaneous sulfidation, sulfation, acid-site poisoning, coke deposition, and mineral accumulation. This complexity explains why sulfur tolerance measured under simple SCR or methane oxidation conditions cannot be directly extrapolated to biomass pyrolysis denitrogenation.

3.3. Sulfur-Resistance Strategies for Metal-Loaded ZSM-5 Catalysts

3.3.1. Sulfur-Tolerant Metal Selection and Promoter Modification

Because metal-site sulfidation or sulfation is usually the first step of catalyst poisoning, metal selection is the most direct strategy for improving sulfur resistance. Different metals have different affinities for sulfur. Ni and Co tend to form relatively stable sulfides, whereas Fe and Zn sulfides may show different stability and regeneration behavior depending on temperature and atmosphere. Fe is particularly attractive because it combines denitrogenation, deoxygenation, redox flexibility, and relatively good sulfur tolerance.

Wang et al. [92] compared Fe, Co, Ni, and Cu supported on HZSM-5 under SO₂-containing conditions and found that Fe/HZSM-5 exhibited the highest sulfur resistance among the tested transition metals. Cs modification further improved SO₂ tolerance by suppressing SO₂ adsorption, increasing Fe dispersion, and increasing the proportion of isolated Fe³⁺ and Fe-O-Fe species. These results suggest that Fe can be used as a base metal for sulfur-resistant ZSM-5 catalysts, while alkali-metal promoters can tune surface adsorption and active-site dispersion.

Rare-earth promoters such as Ce can also improve sulfur resistance. In Mn-Fe-Ce/ZSM-5 systems, Ce addition suppressed H₂O adsorption and mitigated SO₂ poisoning. Ce can enhance oxygen storage/release capacity, regulate surface oxygen species, and reduce direct poisoning of active metal centers. However, for biomass pyrolysis, Ce-based sulfur-resistance mechanisms need further validation under H₂S-rich, COS-containing, tar-rich, and reducing atmospheres rather than only SO₂-containing SCR conditions.

3.3.2. Upstream Sulfur Capture and Tandem Protection

Tandem protection is another promising strategy. Instead of requiring the active ZSM-5 catalyst itself to tolerate all sulfur species, an upstream sulfur adsorbent can preferentially capture sulfur-containing compounds before they reach the denitrogenation catalyst. Wang et al. [93] placed a Ce-doped TiO₂ adsorbent upstream of Mn/HZSM-5 with millimeter-scale separation. The adsorbent captured SO₂ as surface sulfates and protected Mn active species, allowing stable operation for 160 h. For biomass pyrolysis, this idea can be extended to upstream CaO, ZnO, Fe oxide, biochar-based adsorbents, dolomite, or alkaline mineral beds to capture H₂S/COS before vapor upgrading over metal-loaded ZSM-5.

ZnO-based sorbents are particularly relevant because ZnO can react with H₂S to form ZnS and is widely used for hot-gas desulfurization. CaO- and Fe₂O₃-based sorbents can also interact with H₂S and NH₃ in biomass gasification producer gas [94]. Although these studies focus on gasification or syngas purification rather than pyrolysis vapor upgrading, they provide useful guidance for designing upstream protection beds in biomass pyrolysis systems. A practical configuration may involve a first bed for mineral/sulfur capture, a second bed for tar pre-cracking, and a final metal-loaded ZSM-5 bed for denitrogenation and aromatization.

3.3.3. Support-Side Protection, Coating, and Hierarchical-Shell Design

Support-side protection can suppress sulfur diffusion and adsorption while maintaining catalytic accessibility. Wu et al. [95] prepared a BaSO₄-coated V/Fe/BS-ZSM-5 catalyst and proposed a dual-protection mechanism. Ba²⁺ first reacts with SO₂ to form a BaSO₄ layer, which then acts as a physical barrier to inhibit further SO₂ adsorption and diffusion, protecting V⁵⁺-Ov-Fe³⁺ interfacial active sites. Similar coating, and hierarchical-shell strategies may be useful for biomass pyrolysis because they can protect active sites while maintaining diffusion channels for pyrolysis vapors.

For metal-loaded ZSM-5, protective layers should meet three requirements. First, the shell must be permeable enough to allow rapid diffusion of target vapors, especially

small nitrogen-containing intermediates and light oxygenates. Second, it should block or capture sulfur species before they reach vulnerable interfaces. Third, it should suppress coke deposition by reducing external strong acid sites or providing mesoporous diffusion pathways. MCM-41 shells, alumina matrices, BaSO₄ coatings, and oxide-modified hierarchical shells may all be explored, but their stability under tar-rich pyrolysis atmospheres must be verified.

3.4. Regeneration of Sulfur-Poisoned Catalysts

The regeneration of sulfur-poisoned catalysts is more difficult than the regeneration of coke-deactivated catalysts. Coke can usually be removed by oxidative regeneration at 500–600 °C, but metal sulfides and sulfates often require higher decomposition temperatures or reducing treatments. Harsh regeneration conditions may cause secondary damage, including metal sintering, framework dealumination, and loss of acid sites. Therefore, regeneration strategy must be designed according to the chemical form of sulfur species on the catalyst.

H₂ reduction is effective for regenerating sulfate-poisoned catalysts. For Cu-Ir/H-ZSM-5, H₂ reduction at 500 °C reduced surface CuSO₄ and restored catalytic activity to 95% of the fresh catalyst [91]. Li et al. [96] showed that sulfur-deactivated Ni-based biomass syngas cleaning catalysts could be regenerated, but regeneration efficiency depended on sulfur species, treatment temperature, and gas atmosphere. Chein et al. [97] further showed that H₂S poisoning of Ni-based catalysts depends on reaction temperature and exposure time, and low-temperature sulfur poisoning may be difficult to fully reverse. These findings suggest that regeneration of sulfur-poisoned metal-loaded ZSM-5 catalysts should avoid severe thermal treatment and should combine controlled oxidation, reduction, and sulfur capture.

For sulfidation-dominated poisoning caused by H₂S, regeneration may be more challenging because stable metal sulfides can persist. A possible regeneration sequence is mild oxidation to convert sulfides into oxides or sulfates, followed by controlled reduction to restore active metal states. However, this sequence may release SO₂ or induce metal sintering. Therefore, regeneration should be evaluated by both catalytic activity recovery and structural recovery. XPS, XRD, NH₃-TPD, BET, TEM, and sulfur mass balance should be used to determine residual sulfur species, acid-site recovery, pore reopening, and metal dispersion after regeneration. Based on the above analysis, the sulfur resistance of metal-loaded ZSM-5 catalysts is governed by the coupling of sulfur adsorption, metal-site transformation, acid-site preservation, pore accessibility, coke suppression, and regeneration behavior. Table 3 summarizes representative strategies for improving sulfur resistance and regenerability of metal-loaded ZSM-5 catalysts. These strategies include sulfur-tolerant active-metal selection, promoter-assisted modification, upstream sulfur-capture beds, protective coating or structures, and controlled regeneration of sulfur-poisoned catalysts. Each strategy targets a different stage of catalyst deactivation, including suppression of sulfur adsorption, inhibition of metal sulfidation/sulfation, protection of Brønsted/Lewis acid sites, mitigation of sulfur–carbon coupled pore blockage, or restoration of active sites after poisoning. This comparison indicates that effective sulfur resistance cannot be achieved by a single modification alone, but requires the integrated design of active metals, zeolite acidity, pore architecture, sulfur-capture components, and regeneration protocols under realistic biomass pyrolysis atmospheres.

Table 3. Summary of sulfur-resistance and regeneration strategies for metal-loaded ZSM-5 catalysts.

Strategy	Representative System	Main Sulfur-Resistance Mechanism	Key Advantage	Key Limitation	Ref.
Feedstock pretreatment	Hydrothermal pretreatment of corncob residue	Transfers sulfur into the aqueous phase and reduces volatile sulfur release	Reduces catalyst poisoning at the source	Requires additional pretreatment step	[49]
Organic acid pretreatment	Microwave-assisted citric acid pretreatment of star anise	Reduces organic sulfur content before pyrolysis	Mitigates downstream metal sulfidation	Feedstock-specific effectiveness	[47]
Sulfur-tolerant metal selection	Fe/HZSM-5	Fe shows higher SO ₂ tolerance than Co, Ni, and Cu	Combines denitrogenation and sulfur resistance	Single Fe may have limited low-temperature activity	[92]
Alkali-metal promotion	Cs-Fe-HZSM-5	Cs suppresses SO ₂ adsorption and improves Fe dispersion	Improves sulfur tolerance of Fe-based catalysts	Potential neutralization of acid sites at excessive loading	
Rare-earth promotion	Mn-Fe-Ce/ZSM-5	Ce enhances oxygen storage/release and mitigates SO ₂ /H ₂ O poisoning	Improves resistance to SO ₂ and steam	Needs validation under H ₂ S-rich pyrolysis atmospheres	
Tandem adsorbent protection	Ce-TiO ₂ adsorbent + Mn/HZSM-5	Upstream adsorbent captures SO ₂ before it reaches ZSM-5	Protects active metal sites for long-term operation	Increases reactor complexity	
Multimetallic synergy	Cu-Mn-Fe/ZSM-5	Multiple redox centers improve SO ₂ /H ₂ O tolerance	Improves activity and stability	Active-site attribution becomes complex	[76]
Protective coating	BaSO ₄ -coated V/Fe/BS-ZSM-5	BaSO ₄ layer acts as sacrificial and diffusion barrier	Physically protects interfacial active sites	May introduce diffusion limitation	[95]
H ₂ reduction regeneration	Cu-Ir/H-ZSM-5	Reduces surface CuSO ₄ and restores active sites	High activity recovery	Consumes H ₂ and may induce sintering	[91]

3.5. Evaluation Criteria for Sulfur Resistance Under Realistic Pyrolysis Conditions

Future studies should establish standardized sulfur-resistance evaluation protocols for metal-loaded ZSM-5 catalysts. First, sulfur tolerance should be tested under H₂S/COS/tar/steam-containing atmospheres rather than only SO₂-containing model gases. Second, nitrogen and sulfur mass balances should be measured simultaneously because denitrogenation and sulfur poisoning are coupled. Third, catalyst stability should be evaluated through repeated reaction regeneration cycles instead of only short-time activity tests. Fourth, the location and chemical state of sulfur should be characterized, distinguishing sulfur on metal sites, acid sites, coke deposits, and inorganic mineral residues.

A practical sulfur-resistance index should include initial denitrogenation activity, nitrogen-containing compound removal from bio-oil, NH₃/HCN/HNCO suppression, N₂ selectivity, sulfur uptake capacity, activity retention time, coke content, residual sulfur after regeneration, and acid-site recovery. Only with such multi-dimensional evaluation can the real applicability of metal-loaded ZSM-5 catalysts be assessed for nitrogen- and sulfur-rich biomass pyrolysis.

As shown in Figure 6, sulfur poisoning of metal-loaded ZSM-5 catalysts follows a cascade pathway involving metal-site sulfidation/sulfation, acid-site poisoning, framework damage, pore blockage, and sulfur-carbon coupled deactivation. Effective sulfur-resistance strategies include sulfur-tolerant metal selection, Fe- or Ce- based active-site design, alkali or rare-earth promotion, upstream ZnO/CaO/Fe oxide sulfur capture, protective coatings, hierarchical-shell structures, and controlled regeneration. These strategies should be integrated with denitrogenation catalyst design rather than treated as an independent problem.

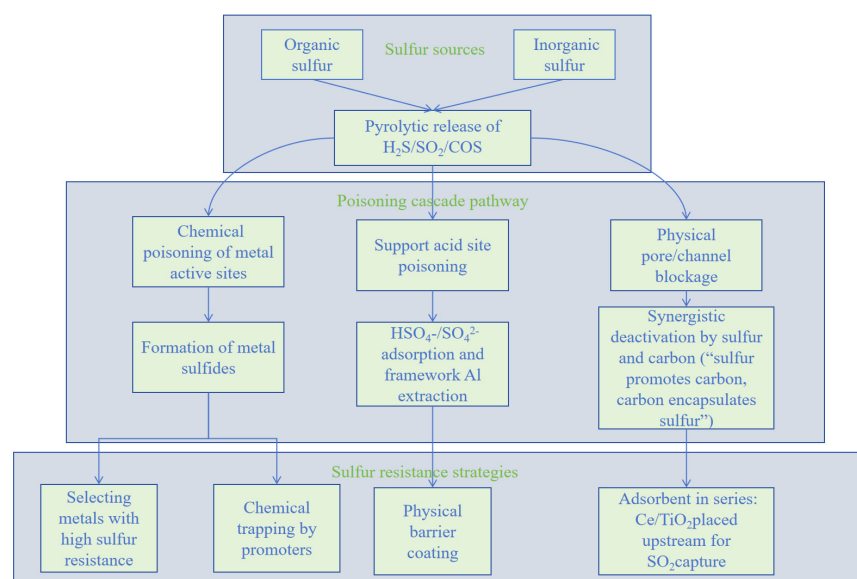


Figure 6. Microscopic mechanisms of sulfur poisoning and sulfur-resistance strategies for metal-loaded ZSM-5 catalysts.

4. Challenges and Future Prospects

Representative high-performing ZSM-5-based systems have demonstrated different advantages, although direct comparison remains difficult because of variations in feedstocks, reaction conditions, and evaluation methods. For example, Zn/HZSM-5 showed effective bio-oil denitrogenation, while the CaO-Ni-ZSM-5/bentonite tandem system combined nitrogen retention in char with downstream vapor upgrading [41,56]. Hierarchical catalysts such as M@3Ga-8Ni/AZ exhibited improved coke resistance and showed an activity recovery of 98.46% after oxidative regeneration [82]. Fe-based ZSM-5 catalysts also showed comparatively favorable sulfur tolerance under SO₂-containing model conditions, which could be further improved through promoter modification [92]. However, no reported catalyst has yet been systematically demonstrated to simultaneously achieve high denitrogenation activity, sulfur resistance, coke resistance, and regenerability under the same realistic biomass pyrolysis conditions.

Future studies should therefore move beyond optimization of a single performance parameter toward the integrated regulation of metal sites, acidity, pore architecture, and catalyst stability. Related non-zeolitic multifunctional systems provide useful design analogies. A Cr-ZIFs-8/ZnCo-LDH composite integrated Lewis-acid and basic sites, achieved a maximum biodiesel yield of 96.32%, and maintained catalytic applicability over four consecutive reuse cycles [98]. Although esterification and transesterification differ from biomass pyrolysis denitrogenation, this example demonstrates how spatially coupled complementary functions can improve catalytic activity and recyclability. For metal-loaded ZSM-5, analogous multifunctional design should integrate metal, Brønsted-acid, Lewis-acid, and, where appropriate, basic functions while preserving MFI pore confinement and shape selectivity.

Beyond conventional regulation of metal loading and porosity, local strain and defect engineering may offer additional strategies for tuning catalytic activity. A ligand-engineered Cu-containing MOF demonstrated a “pre-strain and release” mechanism, in which torsional distortion stored in the framework was released during the transition state, lowering the activation barrier and increasing the turnover frequency by up to 4.7-fold [99]. Although this mechanism was established for epoxide ring-opening, it highlights the potential of controlling local structural distortion, metal coordination, and framework flexibility in future metal-loaded ZSM-5 catalysts. Molecular catalysts with structurally

well-defined active centers provide a complementary mechanistic reference. A tetranuclear Th-containing antimonotungstate achieved a 93% yield and a turnover frequency of 3720 h^{-1} in Knoevenagel condensation, where Lewis-acidic Th centers activated benzaldehyde and the SbW_9 units promoted proton abstraction [100]. Although this molecular system is not directly comparable with biomass pyrolysis, its clearly separated catalytic functions emphasize the value of constructing identifiable and spatially cooperative active centers. These cross-system examples are presented as transferable catalyst-design analogies rather than direct performance benchmarks for biomass pyrolysis denitrogenation.

Future catalyst design should therefore combine hierarchical porosity and moderated acidity with stable Fe-, Ni-, Zn-, or multimetallic active sites, together with upstream sulfur-capture components, protective shells, or controlled regeneration strategies. Catalyst performance should be evaluated through complete nitrogen and sulfur balances, coke deposition, sulfur speciation, acid-site and pore-structure retention, metal dispersion, and repeated reaction regeneration cycles. Testing under realistic atmospheres containing H_2S , COS, tar, steam, mineral vapors, and nitrogen-containing intermediates will be essential for developing multifunctional metal-loaded ZSM-5 catalysts with high denitrogenation activity, sulfur resistance, coke resistance, and regenerability.

5. Conclusions

This review summarizes recent advances in metal-loaded ZSM-5 catalysts for biomass pyrolysis denitrogenation, focusing on nitrogen migration, synergy, catalyst deactivation, and sulfur resistance. Fuel-bound nitrogen is converted through a cascade network involving amino acid decomposition, DKP-type intermediates, heterocyclic-N cracking, and secondary reactions that generate NH_3 , HCN, and HNCO. Therefore, denitrogenation should be understood as regulation of the whole nitrogen migration network rather than suppression of a single product. ZSM-5 provides MFI pore confinement, shape selectivity, and tunable Brønsted/Lewis acidity, but pristine HZSM-5 is limited by micropore diffusion, excessive acidity, and rapid coking. Hierarchical pores, acidity regulation, and metal loading are therefore required to improve access to bulky N-containing intermediates, balance cracking and aromatization, and enhance catalyst lifetime. Metal loading introduces functions that cannot be provided by acidity alone. AAEMs mainly regulate acid base properties and nitrogen retention, while Ni/Co promote hydrogen-transfer-assisted ring-opening, Fe enables redox-mediated nitrogen conversion, and Zn/Ga favor aromatization-driven denitrogenation. Bimetallic and tandem systems further combine complementary functions, but their real benefit must be verified by complete nitrogen balances rather than bio-oil N reduction alone. Catalyst deactivation remains a central barrier. Coke deposition, metal sintering, mineral accumulation, framework dealumination, and sulfur poisoning jointly reduce active-site accessibility. For N/S-rich feedstocks, H_2S , SO_2 , COS, steam, tar vapors, minerals, and nitrogenous intermediates coexist, leading to coupled nitrogen sulfur carbon deactivation. Sulfur-tolerant metals, Fe/Ce-type redox systems, upstream sulfur capture, protective coatings, and controlled regeneration are promising, but they still require validation under realistic pyrolysis atmospheres.

Future work should establish quantitative N/S mass balances, distinguish apparent bio-oil denitrogenation from deep conversion to N_2 or stable char-N, and test catalysts under real tar-, steam-, mineral-, and sulfur-containing conditions. Advanced in situ characterization, isotope tracing, online MS, XAFS/DRIFTS, and theoretical modeling should be combined to identify active sites and intermediates. This integrated approach will support the design of multifunctional metal-loaded ZSM-5 catalysts with denitrogenation activity, sulfur resistance, coke resistance, regenerability, and practical environmental value.

Author Contributions: Q.X.: Writing—review editing, Investigation, Formal analysis, Data curation, Conceptualization. Y.C.: Writing—review editing, Writing—original draft, Methodology, Formal analysis. S.X.: Writing—review editing, Formal analysis, Data curation. Y.W.: Writing—review editing, Methodology, Investigation. H.L.: Writing—review editing, Methodology, Investigation. Z.Z.: Writing—review editing, Methodology, Investigation., B.C.: Writing—review editing, Methodology, Investigation. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (No.52476190), the National Natural Science Foundation of China (No.52376171), Joint Training Demonstration Base Project for Graduate Students of “Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences” in Guangdong Province, Guangdong Basic and Applied Basic Research Foundation (2023A1515110541), Guangdong Basic and Applied Basic Research Foundation (2025A1515010722), Characteristic and Innovative Projects of General Institutions of Higher Education in Guangdong Province (2025KTSCX044), Youth S&T Talent Support Programme of Guangdong Provincial Association for Science and Technology (SKXRC2025404), Zhanjiang Non-Funded Science and Technology Research Program Projects (2025B01054), Guangdong Basic and Applied Basic Research Foundation (2024A1515010637), Zhanjiang Marine Youth Talent Innovation Project (Grant No. 2024R3002).

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Acknowledgments: The authors used ChatGPT5.5 to assist with scientific language refinement, the generation of selected graphical elements, and the visual optimization of selected schematic elements in Figures 2, 3 and 5. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Bridgwater, A.V. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy* **2012**, *38*, 68–94. [CrossRef]
2. Duan, C.; Yan, X.; Zhang, W.; Zhang, Y.; Ji, X.; Huang, Z.; Chu, H. A review on nitrogen transformation mechanism during biomass pyrolysis. *J. Anal. Appl. Pyrolysis* **2024**, *184*, 106863. [CrossRef]
3. Kan, T.; Strezov, V.; Evans, T.J. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. *Renew. Sustain. Energy Rev.* **2016**, *57*, 1126–1140. [CrossRef]
4. Chen, H.; Si, Y.; Chen, Y.; Yang, H.; Chen, D.; Chen, W. NO_x precursors from biomass pyrolysis: Distribution of amino acids in biomass and Tar-N during devolatilization using model compounds. *Fuel* **2017**, *187*, 367–375. [CrossRef]
5. Ren, Q.; Zhao, C. NO_x and N₂O precursors (NH₃ and HCN) from biomass pyrolysis: Interaction between amino acid and mineral matter. *Appl. Energy* **2013**, *112*, 170–174. [CrossRef]
6. Tian, F.-J.; Yu, J.-L.; McKenzie, L.J.; Hayashi, J.-i.; Chiba, T.; Li, C.-Z. Formation of NO_x precursors during the pyrolysis of coal and biomass. Part VII. Pyrolysis and gasification of cane trash with steam. *Fuel* **2005**, *84*, 371–376. [CrossRef]
7. Cheng, S.; Qiao, Y.; Huang, J.; Wang, W.; Wang, Z.; Yu, Y.; Xu, M. Effects of Ca and Na acetates on nitrogen transformation during sewage sludge pyrolysis. *Proc. Combust. Inst.* **2019**, *37*, 2715–2722. [CrossRef]
8. Hansson, K.-M.; Samuelsson, J.; Tullin, C.; Åmand, L.-E. Formation of HNCO, HCN, and NH₃ from the pyrolysis of bark and nitrogen-containing model compounds. *Combust. Flame* **2004**, *137*, 265–277. [CrossRef]
9. Meng, J.; Yang, B.; Ren, L.; Yang, F.; Li, J.; Wang, J. Amino acid structure-oriented pyrolysis nitrogen evolution mechanism: Multi-scale experiment and DFT simulation. *Chem. Eng. J.* **2025**, *519*, 165372. [CrossRef]
10. Hansson, K.-M.; Samuelsson, J.; Åmand, L.-E.; Tullin, C. The temperature’s influence on the selectivity between HNCO and HCN from pyrolysis of 2,5-diketopiperazine and 2-pyridone. *Fuel* **2003**, *82*, 2163–2172. [CrossRef]
11. Liu, J.; Zhao, W.; Yang, S.W.; Hu, B.; Xu, M.X.; Ma, S.W.; Lu, Q. Formation mechanism of NO(x) precursors during the pyrolysis of 2,5-diketopiperazine based on experimental and theoretical study. *Sci. Total Environ.* **2021**, *801*, 149663. [CrossRef] [PubMed]
12. Liu, L.; Zheng, Y.; Huang, S.; Xiao, T.; Tian, H.; Qing, M. Review of nitrogen migration and transformation during biomass pyrolysis. *Trans. Chin. Soc. Agric. Eng.* **2022**, *38*, 227–236.
13. Lv, W.; Cui, Y.; Ding, W.; Zhang, D.; Li, X.; Liu, J. Study On Migration And Transformation Of Nitrogen During Pyrolysis Process Of Agricultural And Forestry Biomass. *Acta Energiæ Solaris Sin.* **2024**, *45*, 452–459.

14. Liu, J.; Zhao, W.; Yang, S.-w.; Hu, B.; Xia, Y.-g.; Wu, Y.-w.; Xie, W.-l.; Lu, Q. Mechanistic insight into the effects of alkali metal ions on the formation of NO_x precursors during the pyrolysis of 2,5-diketopiperazine. *Fuel* **2023**, *334*, 126773. [\[CrossRef\]](#)
15. Xiong, J.; Zhang, S.; Ke, L.; Wu, Q.; Zhang, Q.; Cui, X.; Dai, A.; Xu, C.; Cobb, K.; Liu, Y.; et al. Research progress on pyrolysis of nitrogen-containing biomass for fuels, materials, and chemicals production. *Sci. Total Environ.* **2023**, *872*, 162214. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Tian, K.; Liu, W.-J.; Qian, T.-T.; Jiang, H.; Yu, H.-Q. Investigation on the Evolution of N-Containing Organic Compounds during Pyrolysis of Sewage Sludge. *Environ. Sci. Technol.* **2014**, *48*, 10888–10896. [\[CrossRef\]](#) [\[PubMed\]](#)
17. Meng, J.; Wang, J.; Yang, F.; Cheng, F. Unveiling the complex effect of Fe₂O₃ on NO_x precursors evolution mechanism during sludge protein pyrolysis based on product characteristics. *Fuel* **2024**, *358*, 130105. [\[CrossRef\]](#)
18. Xu, P.; Wang, P.; Shen, L. Fast Pyrolysis of Tea Waste under a Hydrogen-Rich Atmosphere: A Study on Nitrogen Evolution and Green Ammonia Production. *Energy Fuels* **2022**, *36*, 14304–14314. [\[CrossRef\]](#)
19. Wang, Y.; Ye, L.; Yang, B.; Chen, Y.; Li, J. The influence of alkali and alkaline earth metals on the generation of NO_x precursors during sewage sludge pyrolysis: An experimental & theoretical. *J. Environ. Manag.* **2025**, *394*, 127393. [\[CrossRef\]](#)
20. Wei, Y.; Tian, H.; Liu, L.; Cheng, S.; Qing, M.; Chen, Y.; Yang, H.; Yang, Y. The effects of alkali metals and alkaline earth metals on the mechanism of N-containing gases production during glutamic acid pyrolysis. *J. Anal. Appl. Pyrolysis* **2022**, *168*, 105787. [\[CrossRef\]](#)
21. Chen, Z.; Lei, C.; Yao, L.; Mo, Y.; Li, J.; Qu, H.; Zhou, Z.; Luo, W. Synergistic pyrolysis of rice and chili straw under N₂/CO₂ atmosphere: Nutritional elements (N/P/K) migration and transformation from straw to pyrolysis products. *Energy* **2025**, *316*, 134636. [\[CrossRef\]](#)
22. Niu, Q.; Du, X.; Li, K.; Lu, Q.; Prins, W.; Ronsse, F. Effects of porosity and acidity on deoxygenation and denitrogenation in catalytic pyrolysis of protein-rich microalgae with metal-doped zeolites. *J. Anal. Appl. Pyrolysis* **2024**, *183*, 106780. [\[CrossRef\]](#)
23. Balasundram, V.; Ibrahim, N.; Kasmani, R.M.; Isha, R.; Hamid, M.K.A.; Hasbullah, H. Catalytic upgrading of biomass-derived pyrolysis vapour over metal-modified HZSM-5 into BTX: A comprehensive review. *Biomass Convers. Biorefinery* **2022**, *12*, 1911–1938.
24. Nastase, S.A.F.; Cavallo, L. Role of Acid Site Density and Pore Type on the Brønsted Acid Strength of Zeolite H-ZSM-5. *Catal. Lett.* **2025**, *155*, 155. [\[CrossRef\]](#)
25. Li, Z.; Dai, W.; Liu, X.; Wang, F.; Li, R. Insight into structure and reactivity of ZSM-5. *Chem. Ind. Eng. Prog.* **2025**, *44*, 788–808.
26. Yi, F.; Xu, D.; Tao, Z.; Hu, C.; Bai, Y.; Zhao, G.; Chen, H.; Cao, J.-P.; Yang, Y. Correlation of Brønsted acid sites and Al distribution in ZSM-5 zeolites and their effects on butenes conversion. *Fuel* **2022**, *320*, 123729. [\[CrossRef\]](#)
27. Jin, F.; Zhang, P.; Wu, G. Fundamental kinetics model of acidity-activity relation for ethylene oligomerization and aromatization over ZSM-5 zeolites. *Chem. Eng. Sci.* **2021**, *229*, 116144. [\[CrossRef\]](#)
28. Tian, H.; Wei, Y.; Huang, Z.; Chen, Y.; Tursunov, O.; Cheng, S.; Yang, H.; Yang, Y. The nitrogen transformation and controlling mechanism of NH₃ and HCN conversion during the catalytic pyrolysis of amino acid. *Fuel* **2023**, *333*, 126215. [\[CrossRef\]](#)
29. Niu, Q.; Du, X.; Li, K.; Lu, Q.; Ronsse, F. Role of catalyst porosity and acidity in nitrogen transformation during catalytic fast pyrolysis of microalgae: Study on extracted protein and model amino acids. *Energy Convers. Manag.* **2024**, *322*, 119210. [\[CrossRef\]](#)
30. Chai, M.; Liu, R. Effect of Ga, Zn modified ZSM-5 catalysts on the biomass catalyticpyrolysis for MAHs production. *Energy Environ. Prot.* **2024**, *38*, 123–135.
31. Al-Nahari, S.; Dib, E.; Cammarano, C.; Saint-Germes, E.; Massiot, D.; Sarou-Kanian, V.; Alonso, B. Impact of Mineralizing Agents on Aluminum Distribution and Acidity of ZSM-5 Zeolites. *Angew. Chem. Int. Ed.* **2023**, *62*, e202217992. [\[CrossRef\]](#)
32. Wei, Y.; Tian, H.; Cheng, S.; Leng, E.; Liu, L.; Chen, Y.; Yang, Y. The impact of H-ZSM-5 catalyst on the mechanism of fuel-N conversion during glutamic acid pyrolysis. *J. Anal. Appl. Pyrolysis* **2023**, *176*, 106269. [\[CrossRef\]](#)
33. Liu, T.; Ning, F.; Li, Q.; Li, Z.; Feng, X.; Zhao, X. Post-Synthesis of HZSM-5 by Aluminum Fluoride in an Acidic Fluoride Solution for Enhanced Reforming of Lignite Pyrolytic Volatiles into Light Aromatics. *Energy Fuels* **2023**, *37*, 10929–10938. [\[CrossRef\]](#)
34. Cai, S.-J.; Cao, J.-P.; Yao, N.-Y.; Zhao, J.-P.; Pang, X.-B.; Xu, M.; Lu, Y.; Zhao, X.-Y.; Bold, T. Modification of highly acid ZSM-5 composed of nanocrystal stacks for reforming of lignite pyrolysis volatiles to light aromatics. *J. Anal. Appl. Pyrolysis* **2025**, *187*, 107009. [\[CrossRef\]](#)
35. Zhao, J.-P.; Cao, J.-P.; Wei, F.; Chen, F.; Yao, N.-Y.; Pang, X.-B.; Cai, S.-J.; Yi, F.-J.; Feng, X.-B.; Zhao, X.-Y. Acidity-controlled hollow HZSM-5 for lignite pyrolysis volatiles valorization to light aromatics. *Chem. Eng. Sci.* **2024**, *292*, 120003. [\[CrossRef\]](#)
36. Crespo, I.; Hertzog, J.; Carré, V.; Aubriet, F.; Valle, B. Alumina-embedded HZSM-5 with enhanced behavior for the catalytic cracking of biomass pyrolysis bio-oil: Insights into the role of mesoporous matrix in the deactivation by coke. *J. Anal. Appl. Pyrolysis* **2023**, *172*, 106009. [\[CrossRef\]](#)
37. Souza, J.C.; Mello, M.I.S.; Barbosa, F.F.; Souza, I.M.S.; Sachse, A.; Pergher, S.B.C. Influence of Secondary Porosity Introduction via Top-Down Methods on MOR, ZSM-5, and Y Zeolites on Their Cumene Cracking Performance. *Catalysts* **2025**, *15*, 146. [\[CrossRef\]](#)
38. Li, T.; He, G.; Jiang, Z.; Duan, Y.; Liu, M. Research advances and new insights into multi-source solid waste-derived ceramic foams. *Sustain. Mater. Technol.* **2025**, *45*, e01535. [\[CrossRef\]](#)

39. Liu, H.; Chen, Z.; Wang, H.; You, C. Active centers response to SO₂ and H₂O poisoning over Fe-W-Ni exchanged zeolite for high-temperature NH₃-SCR: Experimental and DFT studies. *Appl. Surf. Sci.* **2021**, *570*, 151105. [\[CrossRef\]](#)
40. Cheng, S.; Yao, K.; Tian, H.; Yang, T.; Chen, L. Synergistic Catalytic Effects on Nitrogen Transformation during Biomass Pyrolysis: A Focus on Proline as a Model Compound. *Molecules* **2024**, *29*, 3118. [\[CrossRef\]](#) [\[PubMed\]](#)
41. Hong, C.; Li, Y.; Si, Y.; Li, Z.; Xing, Y.; Chang, X.; Zheng, Z.; Hu, J.; Zhao, X. Catalytic upgrading of penicillin fermentation residue bio-oil by metal-supported HZSM-5. *Sci. Total Environ.* **2021**, *767*, 144977. [\[CrossRef\]](#) [\[PubMed\]](#)
42. Gu, B.; Cao, J.-P.; Wei, F.; Zhao, X.-Y.; Ren, X.-Y.; Zhu, C.; Guo, Z.-X.; Bai, J.; Shen, W.-Z.; Wei, X.-Y. Nitrogen migration mechanism and formation of aromatics during catalytic fast pyrolysis of sewage sludge over metal-loaded HZSM-5. *Fuel* **2019**, *244*, 151–158. [\[CrossRef\]](#)
43. Mao, H.; Chen, Z.; Tian, H.; Cheng, S.; Liu, L.; Xuan, Y.; Yin, Y. Fast pyrolysis of baked wheat straw catalyzed by Fe-Ni modified composite porous molecular sieves for the preparation of aromatics. *J. Anal. Appl. Pyrolysis* **2025**, *189*, 107088. [\[CrossRef\]](#)
44. Chen, B.; Tian, H.; Zhou, Z.; Xuan, Y.; Wang, Z.; Liu, S. Catalytic study of metal-modified HZSM-5 core-shell molecular sieves on pyrolysis products of wheat straw after acid washing and torrefaction. *Fuel* **2026**, *405*, 136639. [\[CrossRef\]](#)
45. Li, Y.; Nishu; Yellezuome, D.; Li, C.; Liu, R. Deactivation mechanism and regeneration effect of bi-metallic Fe-Ni/ZSM-5 catalyst during biomass catalytic pyrolysis. *Fuel* **2022**, *312*, 122924. [\[CrossRef\]](#)
46. Niu, Q.; Du, X.; Li, K.; Ghysels, S.; Lu, Q.; Prins, W.; Ronsse, F. Coke formation and mineral accumulation on HZSM-5/Al₂O₃ catalysts during in-situ catalytic fast pyrolysis of microalgae over multiple regeneration cycles. *J. Anal. Appl. Pyrolysis* **2024**, *182*, 106701. [\[CrossRef\]](#)
47. Liu, J.; Zhang, T.; Den, J.; Lu, Q.; Zhao, Y.; Yuan, S. Effect of sulfur and carbon in the pyrolysis volatiles on the activity of Fe-Ni/biochar. *Fuel Process. Technol.* **2023**, *244*, 107720. [\[CrossRef\]](#)
48. Kwoczynski, Z.; Čmelík, J. Characterization of hazardous gases evolved from various biomass wastes during biochar production using TGA-MS. *Int. J. Environ. Sci. Technol.* **2021**, *18*, 73–88.
49. Zhang, X.; Zhan, L.; Yang, Y.; Wu, Y.; Song, X.; Li, R. Investigation on hydrothermal-pyrolysis process to eliminate S-pollution from corn cob residue utilization: Experiment and life cycle assessment. *Fuel* **2024**, *362*, 130810. [\[CrossRef\]](#)
50. Xu, L.; Cheng, J.-H.; Ma, X.-Q.; Shen, J.-Y.; Xu, Z.-X.; Duan, P.-G. Transformation of the Sulfur Element during Pyrolysis of Sewage Sludge at Low Temperatures. *Energy Fuels* **2021**, *35*, 501–509. [\[CrossRef\]](#)
51. Zhang, Y.; Glarborg, P.; Andersson, M.P.; Johansen, K.; Torp, T.K.; Jensen, A.D.; Christensen, J.M. Sulfur poisoning and regeneration of Rh-ZSM-5 catalysts for total oxidation of methane. *Appl. Catal. B Environ.* **2020**, *277*, 119176. [\[CrossRef\]](#)
52. He, Z.; Wang, Y.; Liu, Y.; Lian, L.; Kong, D.; Zhao, Y. Recent advances in sulfur poisoning of selective catalytic reduction (SCR) denitration catalysts. *Fuel* **2024**, *365*, 131126. [\[CrossRef\]](#)
53. Wang, X.; Li, C.; Yang, J.; Liu, Y.; Hei, J.; Huang, S.; Gao, D. Production of aromatic hydrocarbons from catalytic fast pyrolysis of microalgae over Fe-modified HZSM-5 catalysts. *RSC Adv.* **2024**, *14*, 36970–36979. [\[CrossRef\]](#) [\[PubMed\]](#)
54. Liu, H.; Zhang, J.; Shan, R.; Yuan, H.; Chen, Y. Mechanistic insights into Ga-modified hollow ZSM-5 catalyzed fast pyrolysis of cassava residue. *Energy* **2024**, *295*, 131068. [\[CrossRef\]](#)
55. Stanton, A.R.; Iisa, K.; Yung, M.M.; Magrini, K.A. Catalytic fast pyrolysis with metal-modified ZSM-5 catalysts in inert and hydrogen atmospheres. *J. Anal. Appl. Pyrolysis* **2018**, *135*, 199–208. [\[CrossRef\]](#)
56. Niu, Q.; Du, X.; Xing, P.; Ghysels, S.; Li, K.; Li, J.; Lu, Q.; Prins, W.; Ronsse, F. Two-step catalytic pyrolysis of microalgae combining in-bed CaO with vapour phase upgrading over Ni-ZSM-5/bentonite extrudates. *Green Chem.* **2025**, *27*, 13667–13681. [\[CrossRef\]](#)
57. Yung, M.M.; Starace, A.K.; Mukarakate, C.; Crow, A.M.; Leshnov, M.A.; Magrini, K.A. Biomass Catalytic Pyrolysis on Ni/ZSM-5: Effects of Nickel Pretreatment and Loading. *Energy Fuels* **2016**, *30*, 5259–5268. [\[CrossRef\]](#)
58. Liu, Y.; Yang, S.; Liu, S.; Shangguan, J.; Yu, Z. Nitrogen migration and transformation during the pyrolysis of corn straw with iron-based catalyst. *J. Anal. Appl. Pyrolysis* **2024**, *182*, 106696. [\[CrossRef\]](#)
59. Sun, D.; Xiao, C.; Liu, Q.; Bai, X.; Xie, X.; Zhang, W.; Li, J.; Zhang, X.; Dai, Z. Catalytic upgrading of NaoMaohu and biomass co-pyrolysis over HZSM-5/CuMgAl. *New J. Chem.* **2025**, *49*, 13376–13388. [\[CrossRef\]](#)
60. Zhang, J.; Huang, Y.; Sekyere, D.T.; Wang, W.; Tian, Y. Catalytic fast pyrolysis of waste pine sawdust over solid base, acid and base-acid tandem catalysts. *Bioresour. Technol.* **2024**, *394*, 130294. [\[CrossRef\]](#) [\[PubMed\]](#)
61. Hernando, H.; Puértolas, B.; Pizarro, P.; Feroso, J.; Pérez-Ramírez, J.; Serrano, D.P. Cascade Deoxygenation Process Integrating Acid and Base Catalysts for the Efficient Production of Second-Generation Biofuels. *ACS Sustain. Chem. Eng.* **2019**, *7*, 18027–18037. [\[CrossRef\]](#)
62. Tian, H.; Mao, H.; Wang, J.; Cheng, Y. Ga-Ni modified MCM-41@HZSM-5 core-shell zeolite for catalytic fast pyrolysis of wheat straw to produce monocyclic aromatics. *Chem. Eng. J.* **2025**, *510*, 161707. [\[CrossRef\]](#)
63. Bhuyan, N.; Bora, N.; Boruah, K.; Choudhury, N.D.; Saikia, N.; Kataki, R. Effect of Co and Ni impregnated ZSM-5 catalyst on pyrolysis products of *Tithonia diversifolia*: Kinetic study and thermodynamics. *Process Saf. Environ. Prot.* **2024**, *185*, 807–816. [\[CrossRef\]](#)

64. Shafaghat, H.; Jae, J.; Jung, S.-C.; Jeon, J.-K.; Ko, C.H.; Park, Y.-K. Effect of methane co-feeding on product selectivity of catalytic pyrolysis of biomass. *Catal. Today* **2018**, *303*, 200–206. [\[CrossRef\]](#)
65. Iliopoulou, E.F.; Stefanidis, S.; Kalogiannis, K.; Psarras, A.C.; Delimitis, A.; Triantafyllidis, K.S.; Lappas, A.A. Pilot-scale validation of Co-ZSM-5 catalyst performance in the catalytic upgrading of biomass pyrolysis vapours. *Green Chem.* **2014**, *16*, 662–674. [\[CrossRef\]](#)
66. Mullen, C.A.; Boateng, A.A. Production of Aromatic Hydrocarbons via Catalytic Pyrolysis of Biomass over Fe-Modified HZSM-5 Zeolites. *ACS Sustain. Chem. Eng.* **2015**, *3*, 1623–1631. [\[CrossRef\]](#)
67. Ávila, M.I.; Alonso-Doncel, M.M.; Briones, L.; Gómez-Pozuelo, G.; Escola, J.M.; Serrano, D.P.; Peral, A.; Botas, J.A. Catalytic upgrading of lignin-derived bio-oils over ion-exchanged H-ZSM-5 and H-beta zeolites. *Catal. Today* **2024**, *427*, 114419. [\[CrossRef\]](#)
68. Fu, Z.; Pan, Y.; Wang, R.; Suo, S.; Wang, Z.; Peng, X.; Fang, P. The Use of Metal/ZSM-5 Nanosheet for Efficient Catalytic Cracking of Cross-Linked Polyethylene for High-Voltage Cable Insulation. *Materials* **2025**, *18*, 4675. [\[CrossRef\]](#) [\[PubMed\]](#)
69. Barton, R.R.; Carrier, M.; Segura, C.; Fierro, J.L.G.; Escalona, N.; Peretti, S.W. Ni/HZSM-5 catalyst preparation by deposition-precipitation. Part 1. Effect of nickel loading and preparation conditions on catalyst properties. *Appl. Catal. A Gen.* **2017**, *540*, 7–20. [\[CrossRef\]](#)
70. Barton, R.R.; Carrier, M.; Segura, C.; Fierro, J.L.G.; Park, S.; Lamb, H.H.; Escalona, N.; Peretti, S.W. Ni/HZSM-5 catalyst preparation by deposition-precipitation. Part 2. Catalytic hydrodeoxygenation reactions of lignin model compounds in organic and aqueous systems. *Appl. Catal. A Gen.* **2018**, *562*, 294–309. [\[CrossRef\]](#)
71. Yu, Z.; Wang, Y.; Zhang, G.; Sun, Z.; Liu, Y.-Y.; Shi, C.; Wang, W.; Wang, A. A highly dispersed Ni₃P/HZSM-5 catalyst for hydrodeoxygenation of phenolic compounds to cycloalkanes. *J. Catal.* **2022**, *410*, 294–306. [\[CrossRef\]](#)
72. Qu, B.; Wang, T.; Ji, X.; Qin, T.; Zhang, Y.S.; Ji, G. Effect of reduction temperatures of Ni-modified zeolites on the product distribution, catalyst deactivation, and reaction mechanism during polypropylene pyrolysis. *Fuel* **2025**, *384*, 133947. [\[CrossRef\]](#)
73. Wu, L.; Xin, J.; Wang, Y.; Zhang, K.; Zhang, J.; Sun, J.; Zou, R.; Liang, J. Hollow ZSM-5 encapsulated with single Ga-atoms for the catalytic fast pyrolysis of biomass waste. *J. Energy Chem.* **2023**, *84*, 363–373. [\[CrossRef\]](#)
74. Guo, L.; Chen, W.; Wang, C.; Dong, B. Application of electrochemically assisted synthesis of MOFs-derived phosphides as catalyst for CH₄-CO₂ reforming. *Int. J. Electrochem. Sci.* **2023**, *18*, 26–32. [\[CrossRef\]](#)
75. Hu, Q.; Lou, H.; Niu, Z.; Zhang, J.; Wang, X.; Jin, H.; Bu, Z.; Li, G.; Tang, Y.; Ye, C. A combined experimental and simulation study on toluene cracking: Synergistic strategy of Ni loading, alkali treatment, and atmosphere activation on HZSM-5 zeolite. *J. Energy Inst.* **2026**, *125*, 102467. [\[CrossRef\]](#)
76. Qiao, Y.; Guan, Z.; Zhang, M.; Chen, G.; Zhou, S.; Liu, H.; Wu, J.; Guo, R.; Pan, W.; Li, F.; et al. Promoting effect of Cu and Mn doping on the Fe/ZSM-5 catalyst for selective catalytic reduction of NO with NH₃. *Fuel* **2024**, *357*, 129947. [\[CrossRef\]](#)
77. Zhu, Y.; Shi, J.; Xia, Y.; Wang, J.; Xing, E.; Zhang, Y.; Wang, D.; Luo, Y.; Gong, J.; Cheng, X.; et al. In situ synergistic catalysis by Nano-CeO₂ oil dispersoid concerted with ZSM-5: Enhanced catalytic cracking for light olefins. *Microporous Mesoporous Mater.* **2025**, *398*, 113833. [\[CrossRef\]](#)
78. Zhan, H.; Yin, X.; Huang, Y.; Yuan, H.; Wu, C. NO_x precursors evolving during rapid pyrolysis of lignocellulosic industrial biomass wastes. *Fuel* **2017**, *207*, 438–448. [\[CrossRef\]](#)
79. Sonsupap, S.; Pattiya, A. Effect of partial catalyst regeneration on the production of deeply deoxygenated bio-oil by catalytic fast pyrolysis of biomass using HZSM-5 in a bench-scale fluidized-bed reactor. *Fuel* **2026**, *405*, 136467. [\[CrossRef\]](#)
80. Balasundram, V.; Ibrahim, N.; Kasmani, R.M.; Isha, R.; Hamid, M.K.A.; Hasbullah, H.; Ali, R.R. Catalytic upgrading of sugarcane bagasse pyrolysis vapours over rare earth metal (Ce) loaded HZSM-5: Effect of catalyst to biomass ratio on the organic compounds in pyrolysis oil. *Appl. Energy* **2018**, *220*, 787–799. [\[CrossRef\]](#)
81. Hernando, H.; Ochoa-Hernández, C.; Shamzhy, M.; Moreno, I.; Fierro, J.; Pizarro, P.; Coronado, J.M.; Čejka, J.; Serrano, D.P. The crucial role of clay binders in the performance of ZSM-5 based materials for biomass catalytic pyrolysis. *Catal. Sci. Technol.* **2019**, *9*, 789–802. [\[CrossRef\]](#)
82. Mao, H.; Tian, H.; Lv, D.; Xuan, Y.; Cheng, S.; Liu, L. Deactivation mechanism and regeneration performance of Ga-Ni modified HZSM-5@MCM-41 Core-Shell catalyst during catalytic fast pyrolysis of wheat straw. *J. Energy Inst.* **2025**, *122*, 102220. [\[CrossRef\]](#)
83. Yao, N.-Y.; Cao, J.-P.; Zhao, X.-Y.; Pang, X.-B.; Zhao, J.-P.; Chen, C.-X.; Cai, S.-J.; Feng, X.-B.; Dung Le, D. Coke formation on different metal-modified (Co, Mo and Zr) ZSM-5 in the catalytic pyrolysis of cellulose to light aromatics. *J. Anal. Appl. Pyrolysis* **2024**, *179*, 106516. [\[CrossRef\]](#)
84. Liu, X.; Song, H.; Chen, Y.; Wang, X.; Li, P.; Xue, J.; Yang, H.; Fodah, A.E.M.; Tang, Z.; Chen, H. Microwave-assisted catalytic pyrolysis of microalgae over a composite catalyst of HZSM-5/BC for nitrogen-containing chemicals. *Renew. Energy* **2026**, *256*, 124650. [\[CrossRef\]](#)
85. Ding, Y.-L.; Wang, H.-Q.; Xiang, M.; Yu, P.; Li, R.-Q.; Ke, Q.-P. The Effect of Ni-ZSM-5 Catalysts on Catalytic Pyrolysis and Hydro-Pyrolysis of Biomass. *Front. Chem.* **2020**, *8*, 790. [\[CrossRef\]](#) [\[PubMed\]](#)
86. Zhan, H.; Zhuang, X.; Song, Y.; Yin, X.; Wu, C. Insights into the evolution of fuel-N to NO_x precursors during pyrolysis of N-rich nonlignocellulosic biomass. *Appl. Energy* **2018**, *219*, 20–33. [\[CrossRef\]](#)

87. Ma, J.; Ye, Z.; Zhou, J.; Hu, Z.-T.; Wang, Q.; Wang, J.; Pan, Z.; Hu, M. Co-pyrolysis of soybean straw and spirulina platensis for N-containing chemicals and N-doped carbon materials production: Unraveling the nitrogen migration mechanism and involved chemical reactions. *J. Anal. Appl. Pyrolysis* **2024**, *181*, 106641. [\[CrossRef\]](#)
88. Demirbas, A. Combustion characteristics of different biomass fuels. *Prog. Energy Combust. Sci.* **2004**, *30*, 219–230. [\[CrossRef\]](#)
89. Cheah, S.; Malone, S.C.; Feik, C.J. Speciation of Sulfur in Biochar Produced from Pyrolysis and Gasification of Oak and Corn Stover. *Environ. Sci. Technol.* **2014**, *48*, 8474–8480. [\[CrossRef\]](#) [\[PubMed\]](#)
90. Halkier, B.A.; Gershenzon, J. Biology and biochemistry of glucosinolates. *Annu. Rev. Plant Biol.* **2006**, *57*, 303–333. [\[CrossRef\]](#) [\[PubMed\]](#)
91. Pan, H.; Jin, Y.F.; Gao, Y.H.; Chen, N.N.; He, C. Regeneration of sulfur poisoning Cu-Ir/H-ZSM-5 catalyst in catalytic reduction of NO_x with propane by H₂ reduction. *China Environ. Sci.* **2016**, *36*, 1360–1365.
92. Wang, F.; Liu, P.; Guo, J.; Xu, K.; Zhang, Y.; Yi, Y.; Zhu, Y.; Wang, L. Enhanced SO₂ Resistance of Cs-Modified Fe-HZSM-5 for NO Decomposition. *Catalysts* **2022**, *12*, 1579. [\[CrossRef\]](#)
93. Wang, J.; He, N.; Zhang, Y.; Chang, Y.; Liu, C.; Jiang, X.; Xie, H.; Chen, S.; Liu, J.; Gao, J.; et al. Enhancing the sulfur resistance of Mn/HZSM-5 catalyst for selective catalytic reduction of NO_x by coupling the adsorbent. *Fuel* **2024**, *375*, 132594. [\[CrossRef\]](#)
94. Dashtestani, F.; Nusheh, M.; Siri Wongrungson, V.; Hongrapipat, J.; Materic, V.; Pang, S. Effect of H₂S and NH₃ in biomass gasification producer gas on CO₂ capture performance of an innovative CaO and Fe₂O₃ based sorbent. *Fuel* **2021**, *295*, 120586. [\[CrossRef\]](#)
95. Wu, Y.; Li, J.; Zhang, J. BaSO₄-Coated V/Fe/Barium Slag ZSM-5 Catalysts for Improved SO₂ Tolerance in SCR: Insights into a Dual-Protection Mechanism. *Langmuir ACS J. Surf. Colloids* **2026**, *42*, 12176–12189. [\[CrossRef\]](#)
96. Li, L.; Howard, C.; King, D.L.; Gerber, M.; Dagle, R.; Stevens, D. Regeneration of Sulfur Deactivated Ni-Based Biomass Syngas Cleaning Catalysts. *Ind. Eng. Chem. Res.* **2010**, *49*, 10144–10148. [\[CrossRef\]](#)
97. Chein, R.-Y.; Chen, Y.-C.; Chen, W.-H. Experimental Study on Sulfur Deactivation and Regeneration of Ni-Based Catalyst in Dry Reforming of Biogas. *Catalysts* **2021**, *11*, 777. [\[CrossRef\]](#)
98. Duan, X.; Yan, S.; Li, Y.; Fang, S.; Tie, X.; Wang, H.; Liu, J.; Zou, C.; Wang, T.; Feng, W. Preparation of chromium-doped ZIFs-8/ZnCo-LDH composite as a acid-base bifunctional catalyst for biodiesel production. *Renew. Energy* **2025**, *238*, 121940. [\[CrossRef\]](#)
99. Ou, J.; Yu, S.; Xie, Y.; Jiang, H.; Lyu, C.; Xia, G.; Chen, K.; Liu, K.; Liu, J. Pre-strain and release in MOF catalysts: Ligand-engineered strain storage for enhanced catalytic activity. *J. Colloid Interface Sci.* **2025**, *700*, 138325. [\[CrossRef\]](#) [\[PubMed\]](#)
100. Xiong, M.; Wang, X.; Ji, S.; Liu, Y.; Zhao, H.; Gong, Z.; Wang, H.H.; Niu, J.; Zhang, D. A Tetranuclear Thorium-Containing Hexameric Antimonotungstate: Synthesis, Structure, and Catalysis of the Knoevenagel Condensation. *Inorg. Chem.* **2026**, *65*, 6802–6810. [\[CrossRef\]](#) [\[PubMed\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.