J Ther Eng, Vol. 11, No. 5, pp. 1552−1584, September, 2025

Journal of Thermal Engineering
Web page info: https://jten.yildiz.edu.tr
DOI: 10.14744/thermal.0000993

Review Article

Novel approaches to zeolite deactivation mitigation and regeneration in biomass gasification

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ARTICLE INFO

Article history
Received 18 February 2024
Revised: 24 June 2024
Accepted 24 September 2024

Keywords:
Biomass Gasification; Catalyst Regeneration; Deactivation Mechanisms; A Mitigation; Environmental Applications; Zeolite Catalys

ABSTRACT

The comprehensive study delves into the intricate realm of zeolite catalyst deactivation within the context of biomass gasification, aiming to provide a thorough understanding of deactivation mechanisms, innovative strategies for mitigation and regeneration, and potential applications for deactivated zeolites. Key findings reveal reversible and irreversible deactivation processes, heavily influenced by physical and chemical interactions with contaminants such as nitrogen, sulfur, and heavy metals. Empirical data-driven mitigation strategies showcase the effectiveness of metal modifiers like nickel and cobalt in reducing coke yield, alongside novel approaches such as core-shell zeolite structures and the integration of redox metal oxides to maintain catalyst basicity and stability. Moreover, successful regeneration methods including thermal regeneration, chemical washing, and steaming demonstrate the restoration of catalytic activity post-deactivation. Despite reduced efficiency, deactivated zeolites exhibit promises in environmental remediation, achieving heavy metal removal efficiencies surpassing 90%, and enhancing durability while reducing permeability in construction materials and concrete additives. Furthermore, the review emphasizes the necessity for refined strategies adaptable to diverse conditions, promoting sustainable catalyst utilization in biomass gasification and beyond. Key contributions highlighted include the identification of deactivation processes, recognition of pivotal factors affecting zeolite catalysts, validation of data-driven mitigation strategies, demonstration of novel approaches, successful application of regeneration methods, and exploration of potential applications for deactivated zeolites. These findings signify significant progress in addressing zeolite catalyst deactivation mitigation and regeneration challenges and enhancing efficiency and sustainability in biomass gasification technologies.

Cite this article as: Rosyadi I, Suyitno, Arifin Z, Sutardi T. Novel approaches to zeolite deactivation mitigation and regeneration in biomass gasification. J Ther Eng 2025;11(5):1552−1584.

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This paper was recommended for publication in revised form by Editor-in-Chief Ahmet Selim Dalkılıç

Published by Yıldız Technical University Press, İstanbul, Turkey

INTRODUCTION

The catalysts, which actively participates in accelerating reactions without being consumed, play a fundamental role in the chemical industry by enabling efficient production of various chemicals and fuels [1–3]. Among these, zeolite catalysts have gained prominence due to their unique micro-porous structure and tunable acidity, which facilitate versatile applications by reducing activation energy and allowing more particles to engage in effective reactions [4–6]. The micro-porous structure, consisting of uniformly sized and shaped pores, allows for the selective adsorption and interaction with specific molecules, thereby facilitating targeted catalytic reactions [7]. The concept of activation energy (Ea), which denotes the minimum energy necessary to initiate a chemical reaction, is pivotal in this context. Zeolites facilitate the reduction of activation energy by strategically orienting reacting particles to enhance the probability of collisions and by forming intermediate compounds with reactants that necessitate lower energy for the production of desired products [8]. Additionally, the acidity of zeolite catalysts is adjustable, a property known as 'tunable acidity,' which allows for the optimization of catalytic activity and selectivity. This tunability is achieved by modifying the concentration and strength of acidic sites through synthesis and post-synthesis treatments [9]. Zeolites contain both Brønsted and Lewis acid sites, which act as catalyst centers. The strength of Brønsted acid sites is influenced by the Si/Al ratio of the zeolite, and achieving the optimal ratio can reduce catalyst deactivation [10]. Effective methods for adjusting the Si/Al ratio, such as dealumination and desilication, optimize zeolite properties and enhance catalytic performance in various chemical reactions [11–16].

As a result, the catalyzed reactions surpass normal reactions and benefit from lower activation energy requirements. However, the long-term performance of zeolite catalysts is often hampered by deactivation, which leads to a decline in their catalytic activity and selectivity. The motivation behind this work lies in addressing the critical challenges associated with zeolite catalyst deactivation in biomass gasification processes. These challenges include the need to prolong catalyst lifespan, reduce operational costs, and maintain high conversion efficiency. By comprehensively understanding deactivation mechanisms and developing innovative mitigation and regeneration strategies, the aim is to enhance the sustainability and efficiency of biomass gasification technologies. Moreover, exploring potential applications for deactivated zeolites underscores the broader goal of sustainable catalyst utilization, not only in biomass gasification but also in various environmental and construction-related applications.

The choice of the catalyst support material significantly affects zeolite catalyst deactivation in biomass conversion processes [17]. Studies indicate that catalysts supported by metal oxides such as CeO_2, MgO, TiO_2, ZrO_2, Al_2O_3, and others exhibit distinct reactivities [18]. However, stability of the support material is crucial. For example, Al_2O_3, an economical support, is prone to deactivation, particularly when Ni is used as the active metal [19,20]. Dolomite or $MgCO_3{\cdot}CaCO_3$ is a cost-effective support that effectively reduces tar content in syngas during biomass gasification, showing promising results [21]. Zeolites, whether natural or synthetic, possess great potential as metal carriers in biomass conversion and hydrocarbon reforming because of their high acidity, large surface area, thermal stability, and remarkable ability to crack macromolecules [22–25]. However, zeolite catalysts are also susceptible to deactivation. Understanding the mechanisms of zeolite catalyst deactivation and selecting appropriate support materials, such as stable metal oxides or dolomite, are crucial for enhancing catalyst performance and stability during biomass conversion processes.

In recent studies, zeolite catalyst deactivation challenges within the realm of biomass gasification have been extensively addressed. Mei et al. (2023) explored the use of zeolites for alkali recovery from catalytic gasification ash (CGA), successfully transforming CGA into zeolite through hydrothermal processing [26]. However, the specific mechanisms and factors leading to zeolite deactivation in this process require further exploration. Similarly, Porawati et al. (2021) investigated the impact of temperature on zeolite-catalyzed biomass gasification, offering valuable insights into gasifier optimization, yet overlooking a thorough examination of zeolite deactivation at different temperatures [27]. The temperature-dependent mechanisms influencing zeolite deactivation are crucial for designing resilient catalysts across diverse operating conditions. Furthermore, State et al.'s (2019) review on zeolite catalysts in microwave-assisted gasification recognized deactivation challenges [28] but lacked a comprehensive understanding of the specific deactivation conditions or mechanisms. Exploring the intricacies of zeolite deactivation in microwave-assisted processes is vital for advancing catalyst design and ensuring prolonged stability. Lastly, Zhang et al. (2018) delved into Ni-based catalysts for biomass tar reforming, highlighting challenges related to deactivation [29]. However, the study missed exploring innovative strategies to overcome these deactivation hurdles, leaving a gap in identifying modifications for enhancing the resistance of Ni-based catalysts to ensure prolonged catalytic activity.

To examine the research trends in the deactivation of natural zeolite catalysts in the last decade (2013-2023), searches were conducted on various research platforms such as Google Scholar and www.sciencedirect.com. Selecting both sources for reviews involves justifying their use due to broad coverage and multidisciplinary content. Both platforms offer extensive academic literature access, including curated databases and freely accessible search engines, ensuring a comprehensive overview. Their widespread use and Google Scholar's open access enhance accessibility, aiding researchers without institutional database access. Several keywords, including deactivation, zeolite, natural zeolite, gasification, pyrolysis, syngas, and biofuel, were used. As shown in Table 1, searches were performed using these keywords in all fields of articles and all titles of articles on Google Scholar. Meanwhile, in ScienceDirect, the search encompassed all articles, titles, abstracts, and keywords. Table 1 provides an overview of the research trend in articles related to zeolite deactivation in biomass gasification over the last decade (2013-2023). The data, sourced from Google Scholar and ScienceDirect, presents the number of articles across various keywords and platforms.

Zeolite Gasification has garnered significant attention with 17,200 articles in Google Scholar and 6,332 in ScienceDirect. This indicates a substantial interest in the utilization of zeolites in the gasification process. Similarly, Zeolite Pyrolysis and Zeolite Biofuel exhibit substantial numbers, showcasing the diverse applications of zeolites in these domains. Moreover, the focus on Zeolite Deactivation is evident with 17,700 articles in Google Scholar and 13,304 in ScienceDirect. This highlights the recognition of challenges associated with zeolite deactivation in both gasification and pyrolysis processes. Interestingly, while Zeolite Deactivation Pyrolysis has a significant presence in Google Scholar, it is relatively lower in ScienceDirect, indicating a potential gap or variation in the coverage of the topic between the platforms.

Natural Zeolite categories also demonstrate considerable interest, with Natural Zeolite Gasification and Natural Zeolite Pyrolysis leading in article count. The emphasis on Natural Zeolite Deactivation further underscores the significance of understanding deactivation challenges in the context of natural zeolites. It is apparent that while there is a substantial volume of research on zeolite applications in gasification, pyrolysis, and biofuel production, the specific focus on zeolite deactivation is comparably limited. This suggests an avenue for more targeted research on the challenges and mitigation strategies associated with zeolite deactivation in the context of biomass gasification.

Therefore, the current investigation aims to comprehensively explore the complexities associated with zeolite catalyst deactivation within the framework of biomass gasification. The primary objectives of this study encompass deciphering the underlying mechanisms and pivotal factors that contribute to zeolite deactivation during biomass gasification, formulating innovative strategies to mitigate deactivation and regeneration issues, and identifying potential applications for deactivated zeolites. The pressing need to pursue these research goals is underscored by existing knowledge gaps that hinder the optimal utilization of zeolite catalysts in biomass gasification processes. Effectively addressing these challenges is not only imperative for enhancing the effectiveness and sustainability of biomass conversion technologies but also presents an opportunity to contribute to the principles of a circular economy.

ROLE OF ZEOLITES IN BIOMASS GASIFICATION

Natural and Synthetic Zeolites

Natural zeolites are minerals that form over geological timescales through the interaction of volcanic ash and groundwater [30]. They are often found in deposits around volcanic regions. In contrast, industrial or synthetic zeolites are typically synthesized in laboratories or manufacturing facilities using various techniques, such as hydrothermal synthesis and alkali fusion, to achieve specific compositions and structures [31, 32]. Natural zeolites and synthetic zeolites represent distinct categories of crystalline materials,

Table 1. The research trend on articles concerning zeolite deactivation in the last decade (2013-2023)

No	Keywords	Google scholar	Google scholar	ScienceDirect	ScienceDirect
		All fields	Filtered by Titles	All fields	Filtered by Titles
1	Zeolite Gasification	17,200	31	6,332	10
2	Zeolite Pyrolysis	22,000	380	13,787	7
3	Zeolite Biofuel	16,900	54	218	4
4	Zeolite Deactivation	17,700	120	13,304	10
5	Zeolite Deactivation Pyrolysis	16,000	10	3,862	7
6	Zeolite Deactivation gasification	10,800	0	2,351	10
7	Zeolite Deactivation Biofuel	13,600	0	2,331	4
8	Natural Zeolite Gasification	17,100	3	4,326	11
9	Natural Zeolite Pyrolysis	18,100	35	7,869	5
10	Natural Zeolite Biofuel	16,600	5	4,024	2
11	Natural Zeolite Deactivation	17,300	0	5,642	6
12	Natural Zeolite Deactivation Pyrolysis	15,700	0	2,035	5
13	Natural Zeolite Deactivation gasification	10,600	0	1,577	6
14	Natural Zeolite Deactivation Biofuel	15,500	0	1,341	2

each with unique characteristics and applications. Natural zeolites, such as clinoptilolite, mordenite, heulandite, analcime, chabazite, natrolite, phillipsite, and stilbite originate from geological processes involving volcanic ash and groundwater [33, 34]. Their compositions can vary significantly, introducing heterogeneity in terms of structure and impurities. In contrast, synthetic zeolites like Zeolite A, Zeolite X, Zeolite Y, Beta Zeolite, Faujasite zeolite and ZSM-5 are intentionally manufactured through controlled laboratory processes, offering precise control over composition and structure [35–37].

One key difference lies in their origins and compositions. Natural zeolites are minerals formed over geological timescales, exhibiting inherent variability and impurities. Industrial applications of natural zeolites often face challenges due to this variability. On the other hand, synthetic zeolites are precisely engineered in laboratories, resulting in consistent compositions and structures. This controlled synthesis allows for tailoring zeolites to specific applications, such as catalysis and adsorption. Catalytic performance is another distinguishing factor. While natural zeolites may possess inherent catalytic activity, it is often less predictable compared to their synthetic counterparts. Synthetic zeolites, designed with specific catalytic properties, offer more reliability and consistency in performance. Additionally, the limitations of natural zeolites, including impurity variability and a lack of control over composition, make them less suitable for applications demanding precision.

Background on Biomass Gasification

Biomass gasification is a thermochemical process that transforms biomass feedstock into gaseous products by undergoing a series of chemical reactions with a limited supply of air [38–40, 41]. The process occurs under high temperatures and limited oxygen conditions, resulting in the production of syngas, consisting of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and other trace components. Syngas is a valuable intermediate that can be further processed into various energy carriers, such as hydrogen or synthetic fuels [41, 42]. Catalysts play a crucial role in biomass gasification by enhancing reaction rates, improving selectivity, and mitigating undesired byproducts [17]. Zeolite catalysts have shown promise for biomass gasification owing to their high surface area, uniform pore structure, and tunable acidity [43]. Zeolites are crystalline microporous materials composed of aluminum, silicon, and oxygen atoms arranged in a regular framework. During biomass gasification, zeolites promote the conversion of complex biomass molecules into smaller and more reactive intermediates [27]. These intermediates undergo further reactions to produce the desired syngas components. The key chemical reactions involved in biomass gasification are as follows:

- Drying and devolatilization. Biomass is first dried to remove moisture, followed by devolatilization, where high temperatures cause the release of volatile compounds (hydrocarbons and tar) from the biomass.
- Pyrolysis. Pyrolysis is the thermal decomposition of biomass in the absence of oxygen. This leads to the production of gases, such as methane (CH_4), carbon monoxide (CO), hydrogen (H_2), and small amounts of higher hydrocarbons. The general equation for pyrolysis is as follows:

$$\text{Biomass} \rightarrow \text{Volatiles} + \text{Char} + \text{Tar} \tag{1}$$

- Gasification. Gasification occurs in the presence of a gasifying agent, typically steam (H_2O) or a mixture of steam and oxygen (O_2). The primary reactions during gasification are as follows:

a. Water-Gas Shift Reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{2}$$

This reaction involves the conversion of carbon monoxide (CO) and water vapor (H_2O) into carbon dioxide (CO_2) and hydrogen (H_2). The water-gas shift reaction helps increase the hydrogen content in the syngas.

b. Boudouard Reaction:

$$2CO \rightleftharpoons CO_2 + C \tag{3}$$

The Boudouard reaction is an equilibrium reaction in carbon monoxide (CO) reacts to produce carbon dioxide (CO_2) and additional carbon. This reaction leads to the formation of solid carbon (char) during gasification.

c. Methanation:

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \tag{4}$$

Methanation is the reaction in which carbon monoxide (CO) and hydrogen (H_2) combine to form methane (CH_4) and water (H_2O). Methanation is desirable for biomass gasification to increase the methane content of syngas.

- Tar Cracking. The tar compounds produced during gasification can be problematic and lead to fouling and corrosion [40]. Tar cracking involves the thermal decomposition, catalytic cracking, plasma cracking, and physical separation of tar molecules into smaller and less complex compounds [44].

In biomass gasification with zeolite as a catalyst, the process initiates with pyrolysis, breaking down biomass into volatile compounds and char. Zeolites, whether of natural or synthetic origin and functioning as catalysts, play a role in promoting the cracking of tar, transforming undesired tar The natural zeolite displayed enhanced tars conversion, peaking at 79% at 900 °C, and facilitated a catalytic tar conversion with a lower activation energy (62.1 kJ/mol) compared to the thermal cracking counterpart (85.0 kJ/mol), showcasing the catalytic benefits of the natural zeolite while concurrently lowering activation energies and revealing distinct frequency factors [45]. During steam gasification of char, zeolites enhance the production of hydrogen and carbon monoxide. Further, zeolites catalyze methane reforming, contributing to the synthesis of carbon monoxide and hydrogen. The water-gas shift reaction (equation 2), facilitated by zeolites, increases hydrogen production by reacting carbon monoxide with water vapor. Additionally, zeolites play a crucial role in adsorption and desorption processes, aiding in the purification and separation of gas components.

It cannot be definitively stated that the gasification reaction mechanisms between natural zeolite and synthetic zeolite are fundamentally identical. While both can act as catalysts in biomass gasification, substantial differences in structure, composition, and catalytic properties can lead to notable variations in their reaction pathways. For example, in the case of natural zeolite, an aluminosilicate mineral with inherent heterogeneity, consider the steam gasification of char (Char + H_2O (steam) → CO + H_2). The varied surface sites of natural zeolite may influence the adsorption and desorption of water vapor, affecting the overall gasification process. Conversely, synthetic zeolite, engineered with controlled structures, may exhibit enhanced catalytic activity in methane reforming (CH_4 + Zeolite → C + $2H_2$), due to its precisely tuned acidic sites. Therefore, while certain aspects of the reaction mechanisms may share similarities, the differences could manifest in the kinetics and selectivity of specific reactions.

Significance of Catalysts in Biomass Gasification

In biomass gasification, catalysts play a significant role in enhancing process parameters and improving the overall efficiency of the gasification process. Zeolites are crystalline aluminosilicate materials with porous structures, and their unique properties make them suitable for various catalytic applications, including biomass gasification [46]. Figure 1 illustrates the role of zeolite catalysts in biomass gasification. The figure was compiled using data and illustrations adapted from references [47–55], and presents a schematic overview of key processes, including tar cracking, reforming reactions, catalytic layer stability, selectivity control, and enhanced hydrogen production.

Biomass gasification holds immense promise for sustainable energy production, and the integration of zeolite-based catalysts enhances the efficiency and effectiveness of this technology. Various biomass feedstocks, including palm kernel shell (PKS), sugarcane bagasse (SB), and Casuarina wood chips, have been subjected to gasification with different zeolite catalysts, showcasing diverse applications and outcomes [27, 56–59] as shown in Table 2.

The application of modified mordenite-zeolite with acid in PKS gasification demonstrated a remarkable reduction in tar content by up to 98%, resulting in a hydrogen-rich syngas [56]. Similarly, natural zeolites in Sugarcane Bagasse gasification substantially increased combustible gas ratios, improving key gas concentrations [27]. Various Ni-based catalysts in Maize gasification exhibited temperature-dependent effects on syngas composition, emphasizing the importance of catalyst selection [60]. By effectively cracking tar and reforming complex organic compounds, zeolites contribute to improved gas quality by reducing tar concentrations in the syngas [53, 54]. The catalytic activity of zeolites in reforming reactions, such as steam reforming and carbon gasification, enables the conversion of biomass components into valuable syngas components such as CO and H_2. In biomass tar reforming, the catalyst with Ni supported on ZSM-5 and a Si/Al ratio of 80 demonstrated the highest level of activity at a temperature of 650 °C [50]. The introduction of steam into the system resulted in a syngas yield of up to 80.5 mmol/g. However, achieving a Si/Al ratio of 80 in natural zeolites remains challenging [50]. Nevertheless, the porous structure of zeolites further enhances their conversion efficiency by providing a large surface area for efficient catalytic reactions. The optimal catalytic performance for syngas production and tar elimination from rice straw gasification was achieved at a catalytic temperature of 250 °C with the prepared Ni-based zeolite catalyst, yielding 5.92 MJ/kg a lower heating value (LHV) and 73.9% tar removal efficiency [55].

Moreover, the studies on rice straw, heavy metal-contaminated biomass (HMCB), poplar wood, and wood chips further contribute to our understanding of zeolite catalysts' versatility in different contexts [55, [61–67]. Zeolite 13X in Casuarina wood chips gasification generated high-purity hydrogen, highlighting its potential for clean energy applications [59]. Clinoptilolite natural zeolite in lignocellulosic biomass gasification significantly decreased tar and CO_2 concentration, leading to higher inflammable gas content [68]. The varying operating conditions and catalyst compositions explored in these studies emphasize the nuanced nature of biomass gasification and the need for tailored solutions. These findings collectively underscore the pivotal role of zeolite-based catalysts in optimizing biomass gasification processes.

Furthermore, zeolite thermal stability and resistance to coke deposition are highly beneficial in biomass gasification processes because coke formation on catalyst surfaces can diminish their activity and lifespan. The robust nature of zeolites allows them to maintain their catalytic activity over an extended period, ensuring the stability and longevity of the gasification process. Thermodynamic modelling has revealed that factors such as cation abundance, silica activity, and temperature influence zeolite stability during gasification [69]. Siliceous zeolites, such as clinoptilolite, mordenite, and erionite, are favored in environments with elevated silica activity, whereas aluminous zeolites such as natrolite, mesolite, scolecite, and thomsonite are favored in reduced silica environments [69]. Gasification conditions, including temperature and aqueous composition, further impact stability [70, 71]. By leveraging zeolite stability, gasification processes can be optimized to improve the efficiency and high-quality syngas production.

Moreover, zeolites provide the ability to control selectivity, allowing the production of specific syngas components

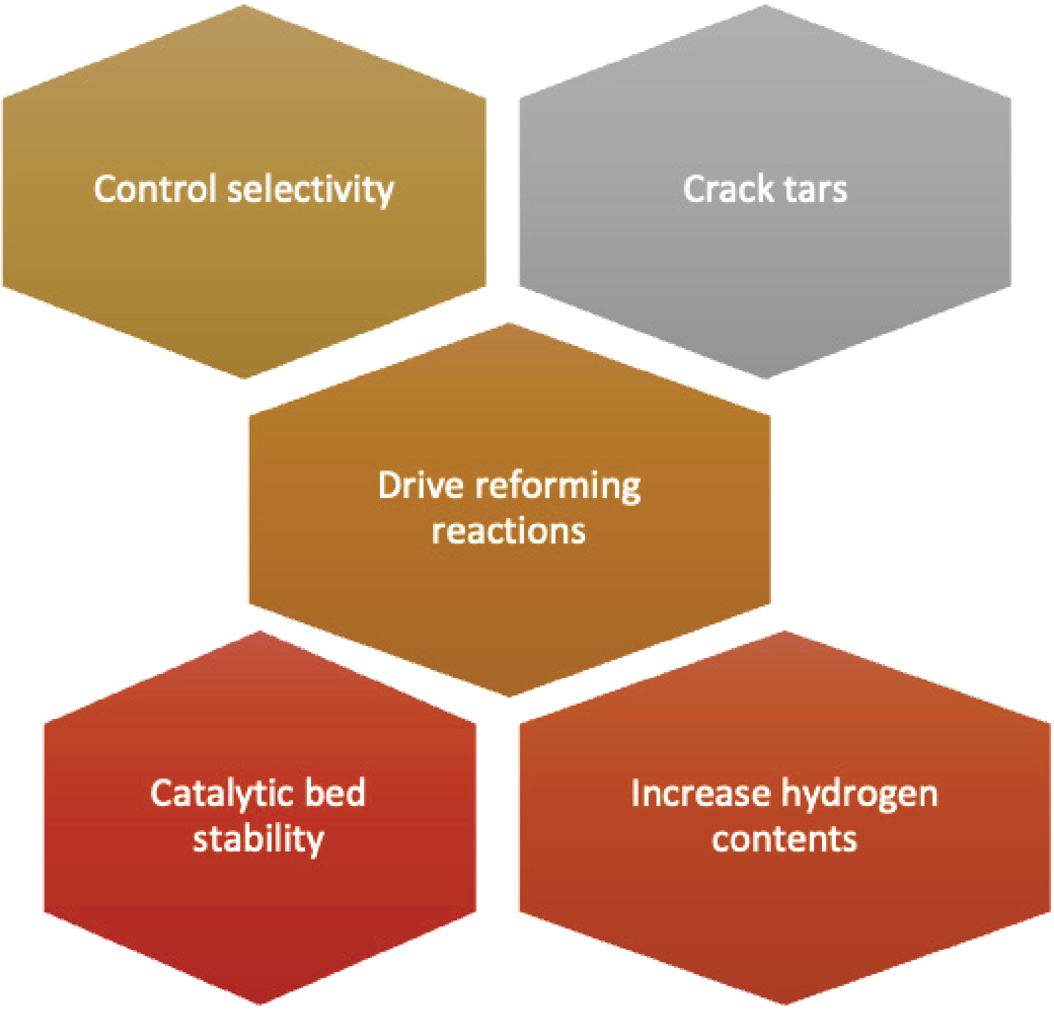


Figure 1. General role of zeolite catalysts in biomass gasification.

as desired [52]. By selectively choosing zeolite catalysts with tailored properties, the gasification process can be optimized to achieve the desired syngas composition for various applications. This versatility opens up new possibilities for power generation, biofuel production, and chemical synthesis. Moreover, the catalyst design principle of the oxide-zeolite-based composite (OXZEO) allows for the direct conversion of syngas into mixed light olefins, achieving an impressive 80% selectivity among hydrocarbons [51].

Challenges of Zeolites in Biomass Gasification

Natural zeolites can exhibit variations in their composition, Si/Al ratio, crystal properties, acidity, and coke deposition depending on their type as shown in Table 3. The challenges associated with using natural zeolite catalysts in biomass gasification include variability in composition, catalyst deactivation, pore size limitations, pore blockage, coke formation, tar deposition, dealumination, thermal stability, and advances in natural zeolite development as shown in Table 4. These variations can affect the performance and consistency of the catalysts in biomass gasification processes. The differing compositions may affect the ability of the catalyst to precisely control the reaction conditions and product quality, making it challenging to achieve consistent results.

Moreover, biomass feedstocks often contain impurities, such as ash, sulfur, and alkali metals [74, 75]. These impurities can accumulate on the catalyst surface during gasification resulting in catalyst deactivation [45, 76]. Ash deposits can block active sites and reduce catalytic activity, whereas sulfur compounds and alkali metals can poison the catalyst. Moreover, biomass gasification involves complex reactions and harsh operating conditions, that can lead to catalyst deactivation over time. Although natural zeolites are relatively stable, they can still undergo deactivation due to factors such as coke deposition, sintering, and poisoning by impurities present in biomass feedstocks. Additionally, different biomass feedstocks have different chemical compositions and molecular sizes. Natural zeolites may have limitations in terms of their pore size and shape, which can

Table 2. Summary of Catalysts and Operating Conditions for Biomass Gasification to Syngas using Zeolite-Based Catalysts

Feedstocks	Catalysts	Operating Conditions	Findings	Ref
Biomass: Palm Kernel Shell	- Modified mordenite-zeolite with acid	- Steam Gasification. - Temperature varying between 750 and 850 °C. - The ratio of steam to biomass ranged from 0 to 2.25.	- The syngas hydrogen content ranged from 52-64%. - Acid washing of natural zeolites reduced specific impurities, thus improve efficacy. - Introducing a zeolite catalyst at 750°C with a steam-to-biomass ratio of 2.25 decreased tar content by up to 98%, achieving 0.7 g/Nm^3.	[56]
Biomass: Sugarcane bagasse	- Natural zeolites	- Air/steam gasification - Temperature varying between 300 and 500 °C. - The ratio of steam to biomass ranged from 0 to 2.25.	- At 500°C, adding 20 mL/minute of water led to notable increases in CO (38.25 mol%), H_2 (4.01 mol%), and CH_4 (10.17 mol%). - Zeolite catalysis was pivotal in elevating the combustible gas ratio, with the inclusion of water further enhancing it significantly.	[27]
Biomass: bagasse	- Natural zeolites	-	- The syngas composition: 9.294% for CO, 1.348% for CH_4, and 2.773% for H_2.	[57]
Biomass	- Synthetic zeolites: Ni/HZSM-5 and Ni–Ca–Co/HZSM-5	- water scrubber and zeolite catalyst as a filter. - downdraft gasifier. - air as gasifying agent.	- The Ni-based catalyst (Ni/HZSM–C-Co5) exhibited strong efficacy in VOC degradation. - Test of various VOCs including toluene, phenol, furan, acetic acid, and cyclohexane revealed notable catalytic activity. - Heating the model compounds to 800°C significantly enhanced their conversion into gases, with over 90% of each compound undergoing transformation, yielding gases such as H_2 and CH_4. - Toluene and cyclohexane decomposition resulted in 93% and 98% conversion into H_2 and CH_4, respectively, at 800°C.	[58]
Biomass	- Natural Jordanian zeolite	- Temperatures: 700 °C, 800 °C, and 900 °C.	- Zeolite surpassed thermal cracking, attaining 79% toluene conversion at 900°C with an activation energy of 62.1 kJ/mol. - Notably, the zeolite catalyst lowered the overall activation energy, exhibiting a significant frequency factor of 3.1754×10^3 s^{-1} at 800°C.	[45]
Casuarina wood chips	- Zeolite 13X	- Feed streams: oxy-steam and air gasification of casuarina wood chips. - Adsorption pressure: varied. - Feed flow rate: varied. - Gas contaminant analysis: conducted for precise optimization. ion	- A recovery range of 40.7–74.4% for purity >98 mol% (ISO grade A and above). - With a feed of 100 Nm^3/h, fuel cell compliant hydrogen was generated with an average recovery of 68.4 ± 3.5%.	[59]
Maize	- Ni/ZSM-5 - Ni/CaO - Ni/Al_2O_3 - Ni/Clinoptilolite	- Temperature Range: - 1st Reactor Zone: 200–800 °C - 2nd Reactor Zone: 500–700 °C - Regeneration: 800 °C	- Optimal temperatures for the 1st and 2nd reactor zones: 400 °C and 700 °C respectively; regeneration: 800 °C. - Ni/ZSM-5: increased lighter hydrocarbons, decreased CO and CO_2; Ni/CaO: declining CO_2 till 3rd cycle, reduced CO and H_2 till 10th cycle. - Ni/Al_2O_3: significant CO_2 and CO reductions each cycle; Ni/Clinoptilolite: decreased H_2 and CO_2, increased CO, enhanced syngas yield. - Ni/Clinoptilolite enhanced syngas and captured CO_2 even at low pyrolysis temps.	[60]

Table 2. Summary of Catalysts and Operating Conditions for Biomass Gasification to Syngas using Zeolite-Based Catalysts (continued)

Feedstocks	Catalysts	Operating Conditions	Findings	Ref
Lignocellulosic biomass	- Clinoptilolite natural zeolite	- Utilization of Mg/Al-layered double hydroxides clinoptilolite (Mg/Al-LDH@ clinoptilolite) - Incorporation of zeolite-layered double hydroxides impregnated with clinoptilolite and Mg/Al-layered double hydroxide into conventional water scrubbers	- Mg/Al-LDH@clinoptilolite was designed to enhance tar removal in lignocellulosic biomass gasification. - Water scrubbers with Zeolite-layered double hydroxides, including clinoptilolite and Mg/Al-LDH, were employed to boost tar removal and improve syngas quality. - A significant decrease in tar and CO_2 concentration, leading to a higher content of inflammable gas. - These findings propose a practical method to enhance power efficiency and durability in lignocellulosic biomass gasification.	[68]
Biomass	- zeolite	- Gasifier Conditions: - Contact Time: 240 minutes - Column Height: 30 cm - Temperature: 450 °C	- Biomass gasification holds promise for renewable energy, but improving yield percentages poses a challenge. - Effective strategies include optimizing gasifier design, employing active catalysts, and understanding decomposition pathways. - At a 240-minute contact time at 450 °C, yielding promising syngas concentrations.	[27]
Rice straw	- Zeolite - Ni-based catalysts	- Hot Gas Temperature Range: 250 °C to 400 °C - Use of Zeolite and Prepared Ni-based Catalysts	- Increasing hot gas temperature and using zeolite or Ni-based catalysts improves energy yield efficiency in rice straw gasification. - Adjusting zeolite catalyst and temperature (250 °C to 400 °C) moderately increases H_2 and CO concentrations, with 70% to 90% tar removal efficiency. - Substituting zeolite with Ni-based catalysts at 250 °C significantly boosts H_2 content, reducing tar and methane. - At 400 °C, deactivated Ni-based catalyst hinders syngas and tar reduction. - Ni-based catalysts at 250 °C exhibit higher stability, activity, and less coke decomposition, achieving optimal performance with 5.92 MJ/kg LHV and 73.9% tar removal efficiency.	[55]
Heavy metal-contaminated biomass (HMCB)	- Zeolite, - Tincal, and - Potassium Carbonate	- Pyrolysis and Gasification Processes - Highest Temperatures: 700 and 900 °C - Heating Rates: 30 and 5 °C/min - Use of Zeolite, Tincal, and Potassium Carbonate Catalysts	- Ionic liquid (IL) pretreatment of HMCB reduced syngas yield and altered composition in pyrolysis. - Tincal and zeolite additives improved syngas yield and H_2 concentration during catalytic pyrolysis of IL-treated HMCB but didn't exceed raw biomass pyrolysis. - Combining IL pretreatment with catalytic gasification led to significantly higher syngas yield and H_2/CO ratio compared to noncatalytic gasification. - Catalytic gasification of IL-treated HMCB produced five times more syngas (with higher H_2 content and lower CO_2) compared to tincal catalytic pyrolysis.	[61]

Table 2. Summary of Catalysts and Operating Conditions for Biomass Gasification to Syngas using Zeolite-Based Catalysts (continued)

Feedstocks	Catalysts	Operating Conditions	Findings	Ref
Wood	- Comparison between zeolite and fire clay chips as catalysts	- Catalytic gasification of wood - Variation in the content of the heat-carrying agent - Introduction of K_2CO_3 as an additive	- Zeolite's lower combustion temperature than fire clay may cause incomplete oxygen reaction and unburned carbon in gasification products. - Zeolite in wood pyrolysis generates fewer liquid products than fire clay. - Lowering the heat-carrying agent content reduces the difference in liquid product yields between zeolite and fire clay. - K_2CO_3 alters gaseous product composition during wood gasification.	[62]
Biomass gasification tar	- zeolite	- Thermal cracking - Catalytic cracking in the presence of zeolite, magnesium oxide, and aluminum oxide catalysts	- Biomass gasification tar underwent thermal and catalytic cracking to yield biodiesel, with zeolite, magnesium oxide, and aluminum oxide catalysts producing biodiesel in the ranges of 62-75 wt.%, 55-66 wt.%, and 67-71 wt.%, respectively. - The resulting bio-oil closely resembled conventional diesel but had slightly higher viscosity and acidic value.	[63]
Poplar wood	- ZSM-5	- Biomass gasification produces syngas rich in hydrogen and carbon monoxide, which is purified before being used to synthesize methanol and convert it into gasoline using catalysts like copper/zinc oxide/alumina and ZSM-5, respectively.	- The economic assessment analyzes biomass-derived syngas for gasoline production, covering gasification, syngas cleanup, methanol synthesis, and gasoline conversion with a ZSM-5 zeolite catalyst. - Estimated at 2007 U.S. dollars, the plant gate price for gasoline and LPG was \$15.73/GJ (\$16.60/MMBtu), with unit prices of \$0.52/L (\$1.95/gal) for gasoline and \$0.40/L (\$1.53/gal) for LPG. - Yields were 229.9 L of gasoline and 38.8 L of LPG per metric tons of dry biomass.	[64]
Biomass	- ZY - ZSM5 - ZY-5.2 - ZY-80 - Ni-supported ZY-30 - Ni-supported ZY-80 - Ni-supported ZY-5.2 - SiO_2/Al_2O_3 - Chabazite	- Investigation of catalytic activity for tar removal - Use of zeolites with varying pore sizes and acidity - Impregnation of nickel on zeolites - Long-term catalytic activity tests over a 97-hour period -	- Efficient biomass gasification relies on effective tar removal, with ZY showing superior catalytic activity over ZSM5. - ZY-5.2 exhibits higher acidity and better tar conversions than ZY-80. - Ni impregnation significantly boosts catalytic activity, particularly in ZY-30 and ZY-80, maintaining optimal tar conversions over time. - Reduced activity in some cases is attributed to coke deposition and reduced catalyst surface area.	[65]
Rice straw	- Natural zeolite	- Fixed-bed setup with temperature: 350°C - H_2S absorption using $Zn(NH_3)_6(OH)_2$ solution in impingers	- At 350 °C, the adsorption capacity for H_2S is 2.22.	[66]
Wood chips	- Natural zeolite - Calcined natural zeolite	- Wood chips (0.4-2.0 mm, 15 mg) are heated at 800 °C with N_2 gas flow. - Catalysts: natural zeolite and calcined natural zeolite, with surface areas of 25.1 and 6.91 g/m^2, respectively.	- Equivalence ratio: 0.1595, air separation ratio: 0.325. - Achieved efficiencies: CGE 62.33%, CCE 80.90%, feedstock conversion 94.15%. - Syngas tar concentration: 3.64 g/Nm^3, tar yield: 5.21 g/kg. - Syngas lower heating value: 7.34 MJ/Nm^3.	[67]

Table 3. Properties of Natural Zeolites

Type of natural zeolites	Formula	Si/Al	BET m^2/g	Smicro m^2/g	V cm^3/g	Vmicro cm^3/g	Dav, nm	Acidity μmol/g	Coke deposition wt%	Ref
Clinoptilolite-fresh	$(Na,K,Ca)_2$–$3Al_3(Al,Si)_2 Si_{13}O_{36}\bullet 12H_2O$	4.9	18	5	0.0972	0.0022	18.4	1953	-	[60]
Clinoptilolite-after the 10th cycle		4.52	14	0.9	0.0003	0.1028	21.3	-	2.33	[60]
Mordenite	$(Ca, Na_2, K_2) Al_2Si_{10}O_{24}\cdot 7H_2O$	4.88	25.28	16.75	0.05	0.0087	-	1190	-	[72]
Mordenite-synthetic-6.5		6.5	338.2	320.6	0.221	0.159	-	-	-	[73]
Mordenite synthetic-9.2		9.2	384.1	354.6	0.306	0.198	-	-	-	[73]
Mordenite synthetic-10.2		10.2	307.7	289.5	0.217	0.157	-	-	-	[73]
Chabazite-fresh	$(Ca,K_2,Na_2,Mg) Al_2Si_4O_{12}\bullet 6H_2O$	4.0	283	-	-	-	-	-	-	[65]
Chabazite-spent		-	2.25	-	-	-	-	-	0.4	[65]

affect their ability to accommodate and effectively catalyze all biomass components. Some larger molecules may not fit into the zeolite pores, limiting their effectiveness for certain reactions. Nevertheless, most medium and large pore zeolites in the range 5.2–5.9 Å can accommodate the majority of aromatic products and reactants within their pores [77].

In addition, natural zeolite catalysts face inherent limitations related to their structure and properties, including pore blockage, coke formation, dealumination, and thermal stability. Zeolites have a specific pore structure, and during the course of a reaction, products or byproducts can accumulate within the pores, leading to blockages. This pore blockage restricts reactant access to the

Table 4. Challenges of natural zeolite in biomass gasification

Challenges	Impact and Limitations	Ref
Variability in Composition	- Natural zeolites show variations in composition and catalytic properties, impacting performance consistency. - Composition variations impact reaction control and product quality.	[78]
Catalyst Deactivation	- Impurities from biomass (ash, Sulfur, alkali metals) lead to catalyst deactivation. - Ash deposits block active sites, reducing catalytic activity. - Sulfur compounds and alkali metals poison the catalyst. - Complex reactions and harsh conditions cause catalyst deactivation over time.	[79, 80]
Pore Size Limitations	- Biomass components may not fit zeolite pores. - Limitations in pore size affect effectiveness for certain reactions.	[81–83]
Pore Blockage	- Products or byproducts accumulate within pores, leading to blockage. - Reactant access to active sites is restricted, reducing catalytic activity.	
Coke Formation	- Carbonaceous species deposition occurs, blocking active sites and reducing surface area for catalysis. - Removal of coke is challenging, leading to irreversible deactivation.	[84, 85]
Tar Deposition	- Tar deposition hampers catalyst activity. - Reactants' accessibility to active sites is reduced, promoting catalyst deactivation.	[47, 86]
Dealumination	- Removal of aluminum atoms under harsh conditions leads to active site destruction and structure changes. - Catalytic performance is reduced due to dealumination.	[87]
Thermal Stability	- Natural zeolites have lower thermal stability compared to synthetic counterparts. - High-temperature reactions cause structural rearrangements and loss of catalytic activity.	[88, 89]
Advances in Natural Zeolite Development	- Enhance catalytic performance, stability, and selectivity. - Advancements contribute to the efficiency and viability of biomass gasification as a sustainable process.	[79, 90]

active sites and reduces catalytic activity. Furthermore, larger molecules may not fit into the zeolite pores, limiting their effectiveness for certain reactions. Coke refers to the deposition of carbonaceous species on the catalyst surface, which can occur owing to cracking or polymerization of the reactants. Coke deposition can block the active sites and reduce the overall surface area available for catalysis, leading to decreased activity and selectivity. Furthermore, coke removal is often challenging and result in irreversible deactivation. Additionally, during biomass gasification, tar compounds can condense and deposit on the catalyst surface, inhibiting catalytic activity. Tar deposition reduces the accessibility of reactants to the active sites and promotes catalyst deactivation.

Moreover, dealumination involves the removal of aluminum atoms from the zeolite framework [91]. This phenomenon can occur under harsh reaction conditions, such as high temperatures or strong acid/base environments. Dealumination leads to the destruction of active sites and changes in zeolite structure, resulting in reduced catalytic performance. Furthermore, natural zeolites, compared to their synthetic counterparts, tend to have lower thermal stability [92]. High-temperature reactions can cause structural rearrangements, collapse of the zeolite framework, and formation of amorphous phases, leading to a loss of catalytic activity. To address these challenges and limitations, researchers are actively developing advanced natural zeolites. These advancements aim to enhance the catalytic performance, stability, and selectivity, contributing to the efficiency and viability of biomass gasification as a sustainable energy conversion process.

The Mechanisms of Zeolites Deactivation

Zeolites deactivation refers to the loss of catalytic activity over time due to various processes occurring during the course of a chemical reaction. This phenomenon can significantly impact the performance and efficiency of the catalysts, leading to reduced reaction rates, selectivity, and overall productivity. Deactivation mechanisms can be broadly categorized into two types: reversible and irreversible. Reversible deactivation involves processes that can be reversed under appropriate conditions, such as desorption or poisoning. Irreversible deactivation, on the other hand, involves permanent changes in the catalyst structure or active sites, rendering them less effective or completely inactive. Specific deactivation mechanisms depend on the nature of the catalyst, reaction conditions, and reactants involved.

Deactivation primarily occurs through two mechanisms as shown in Figure 2: physical and chemical interactions with detrimental components present in the feed or reaction environment [102]. Physical deactivation involves the obstruction or damage of active sites by the deposition of coke, tar, or carbonaceous species, which hinders reactant molecule access and compromises the structural integrity of zeolite catalysts. Chemical deactivation, on the other hand, involves chemical reactions between the catalyst and certain components in the feed, leading to the formation of species that block or chemically modify the active sites,

Table 5. Zeolite catalyst deactivation in industrial process

Industrial application	Reaction conditions	Zeolite used	Deactivation process	Impact of deactivation	Catalyst lifetime	Ref
Methyl Mercaptan Conversion	Temperature range: 573-823 K, N_2, CH_4, H_2O present	H-ZSM-5, H-SAPO-34, H-MOR, H-Y, H-Ferrierite, H-BEA	Coke formation	CH_3SH conversion drops from >99% to 87% over 6 hours on stream	Short to Moderate term, approximately 6-17 h	[93]
MTO (Methanol-To-Olefins)	Temperature: 450 °C Pressure: 4.0 MPa. H_2/MEOH/H_2O/N_2 = 3/1/2.67/2.66	SAPO-34	Coke deposition	In H_2 atmosphere, coke amount was 74.2%, while with H_2 and H_2O, deposition rate decreased to 2.0 mg/(g·h), with 19.7% coke.	- In N_2: Short lifetime. - In H_2O: 15 h. - In H_2: 75 h - In H_2 and H_2O coexisting: 118 h	[94]
Benzene from CH_2	T = 993 K, P = 1 atm, SV = 1500 mL/g*h, CO_2 = 2%	MCM-22	Coke deposition	Coke deposition reduced micropore and external surface areas by 60% and 10% respectively	100 h	[95]
Methanol Conversion	T = 723 K, P = 1 bar, WHSV = 9.5 g methanol/g zeolite/h	Z50-H1	Alkaline treatment with TPA+	Conventional zeolites accumulate nearly 100% internal coke within 15 h, while hierarchical zeolites show less than 20% coke deposition.	24 h (sharp deactivation)	[96]

Table 5. Zeolite catalyst deactivation in industrial process (continued)

Industrial application	Reaction conditions	Zeolite used	Deactivation process	Impact of deactivation	Catalyst lifetime	Ref
2-methyl-2-butene (2M2B) cracking	T = 773 K, P = 1 bar, WHSV = 12 g 2M2B h^{-1}	OH-M	Coke deposition ranging from -0.701% to -0.028% min^{-1}. OH-N: Coke deposited = 6.6 wt%. OH-N-H: Coke deposited = 22.6 wt%. F-N: Coke deposited = 5.8 wt%. F-N-H: Coke deposited = 15.5 wt% -	The rates of deactivation exhibited a range spanning from -0.701 to -0.028% per minute.	15 h	[97]
		OH-M-H			63 h	[97]
		OH-N			39 h	[97]
		OH-N-H			347 h	[97]
		F-M			15 h	[97]
		F-N			39 h	[97]
		F-N-H			190 h	[97]
		OH-M			15 h	[97]
		OH-M-H			63 h	[97]
Methanol-to-olefins (MTO)	Inlet methanol partial pressure: 22 kPa at 623 K	HSSZ-13	Coke deposition	At 22 kPa methanol partial pressure and 623 K using HSSZ-13 catalyst (Si/Al = 8.4), methanol conversion stopped after about 102 s.	~102 s (for certain conditions)	[98]
Methanol-to-Olefins (MTO) Process	T = 723 K, WHSV = 6.6 g MeOH g cat. h^{-1}. Steam Cracking: T = 953 K, WHSV = 2.6 g Steam g cat. h^{-1}	SAPO-34	Transformation of coke to naphthalene through steam cracking	-	~25 minutes (pilot plant)	[99]
Methanol-to-Aromatics	MTA at 450°C, 0.15 MPa, WHSV = 1.5 h^{-1}	HZSM-5	Steam and Alkaline Treatment	The average coking rates range from Z having the highest rate (0.391%) to SAZ0.2 with the lowest (0.149%)	212 h for SAZ0.2, 125 h longer than AZ0.2, 63 h longer than SAZ0.3, 154 h longer than untreated HZSM-5	[13]
Methanol to Olefins	Room Conditions	Nano-SAPO-34	Exposure to Moisture	Optimizing catalysts like SAPO-34 and ZSM-5 by reducing crystal size, improving humidity stability, and boosting mesoporosity extends lifespan and enhances selectivity in methanol-to-olefins conversion.	14 d	[100]
Methanol to Olefins	Room Conditions	Standard-SAPO-34	Exposure to Moisture		Higher stability compared to nano-SAPO-34, slower changes after exposure to moisture	[100]
Aromatics production from syngas	-	Z15, Z25, Z140, ZN50 (microcrystalline and nanocrystalline ZSM-5 zeolites)	Acid site poisoning by heavy hydrocarbons (coke)	CO conversion increased from 79% to over 90% indicating mitigation of pore blockage and maintenance of active sites by zeolite acid sites.	15–17 h	[101]

thereby reducing their activity and selectivity. For instance, carbon monoxide (CO) or sulfur compounds in the feed can react with active sites, forming inactive species such as carbonates or sulfides, whereas reactions with oxygen-containing species can degrade the zeolite framework.

The deactivation mechanisms of zeolites exhibit variability across different industrial processes as outlined in Table 5. In the conversion of methyl mercaptan, the formation of coke on catalysts such as H-ZSM-5, H-SAPO-34, and other zeolites resulted in a decline in CH_3SH conversion from >99% to 87% over a period of 6 hours, accompanied by a catalyst lifespan of short to moderate duration. Methanol-to-olefins (MTO) reactions employing SAPO-34 demonstrated diminished rates of coke deposition under conditions involving H_2 and H_2O, leading to an extension of catalyst lifetimes up to 118 hours. MCM-22 zeolites utilized in benzene production exhibited reductions in micropore and external surface areas by 60% and 10%, respectively, over a timeframe of 100 hours due to coke deposition. Alkaline-treated hierarchical zeolites exhibited coke deposition levels of less than 20% during methanol conversion, thereby prolonging the catalyst lifespan to 24 hours. Furthermore, variations in coke deposition during 2-methyl-2-butene cracking were observed across different zeolite types, resulting in lifetimes ranging from 15 to 347 hours. In the contexts of methanol-to-olefins and aromatics production, the detrimental effects of coke deposition and acid site poisoning were mitigated through the optimization of catalysts such as SAPO-34 and ZSM-5, leading to lifespans extended up to 14 days and 212 hours, respectively.

Factors Contributing to Zeolites Deactivation

Zeolites deactivation in industrial processes is influenced by various factors that affect the catalyst performance and longevity [103]. Understanding these factors is crucial for developing effective strategies to mitigate the deactivation effects. Key factors include contaminants, abrasion, structural changes in the zeolite framework, pore blockage, sintering and agglomeration of active sites, and poisoning of the active sites, as shown in Figure 2.

Contaminants such as nitrogen, Sulfur, and heavy metals chemically react with active sites of zeolite catalysts, deactivating or poisoning them [105]. Contaminants like nitrogen and nitrogen compounds present significant challenges to the catalytic activity of natural zeolites, contributing to deactivation or poisoning through multifaceted mechanisms. Nitrogen compounds pose a substantial threat by obstructing acid centers within zeolite catalysts and serving as precursors for coke formation. The significant molecular size of nitrogen often results in obstructing access to active sites within zeolite structures, thereby potentially poisoning acid sites and reducing catalytic activity [106–108]. Additionally, they promote coke formation, block pores in catalysts, reduce conversion rates, lower reaction rate constants, and alter selectivity [106–108].

Furthermore, different nitrogen compounds interact distinctively with the acid centers of zeolites. Nitrogen compounds like ammonia (NH_3) acts as a base and undergoes reactions with the acid centers, potentially altering their chemical properties [109]. Such alterations can substantially diminish the catalytic activity of the zeolite, hindering its ability to facilitate reactions, particularly evident in processes like biomass gasification [109]. Meanwhile, examining the interaction between the natural zeolite clinoptilolite and ammonium ions (NH^{4+}), a common nitrogen compound, provides insights into the mechanisms involved. Clinoptilolite, characterized by a framework structure composed of $[SiO_4]$ and $[AlO_4]$ tetrahedra, forms a three-dimensional network of interconnected channels and cavities [109]. The channels in clinoptilolite are sufficiently large to

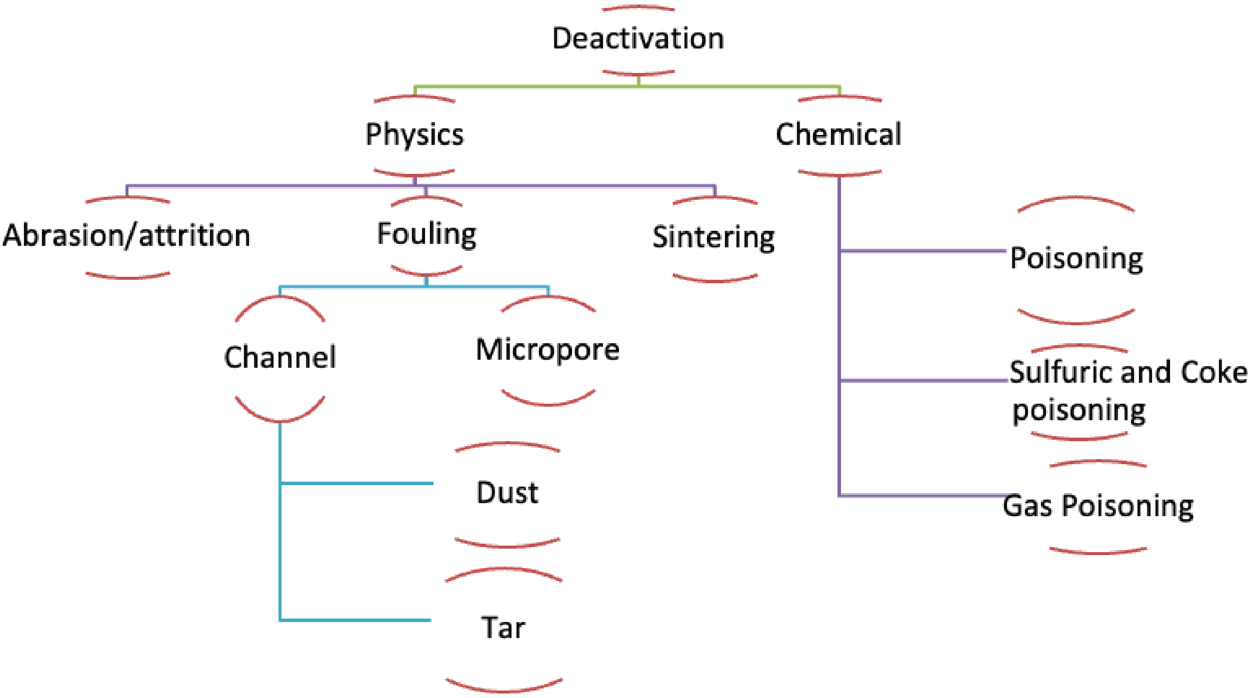
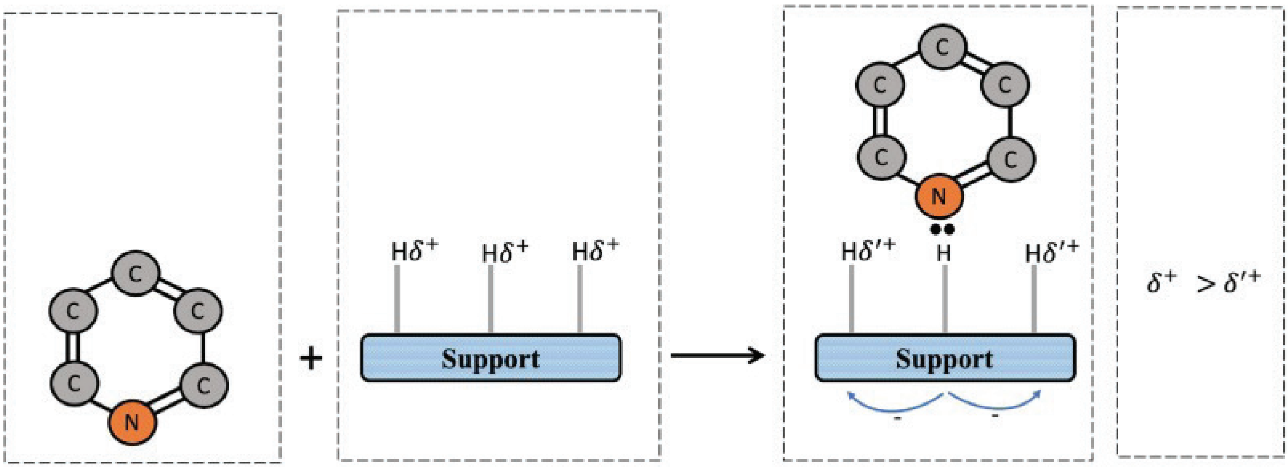


Figure 2. The various mechanisms of catalyst deactivation categorized by type.



Pyridine

Catalysts support showing Brønsted active sites

Reduction in the activity of Catalysts on Brønsted active sites

Decreased activity of Brønsted active sites

Figure 3. The mechanisms involved in the inhibitory effects of basic nitrogen compounds on the Brønsted acid centers. [From Adanenche et al. [104], with permission from Elsevier (Number: RLNK505682204/3002296642).

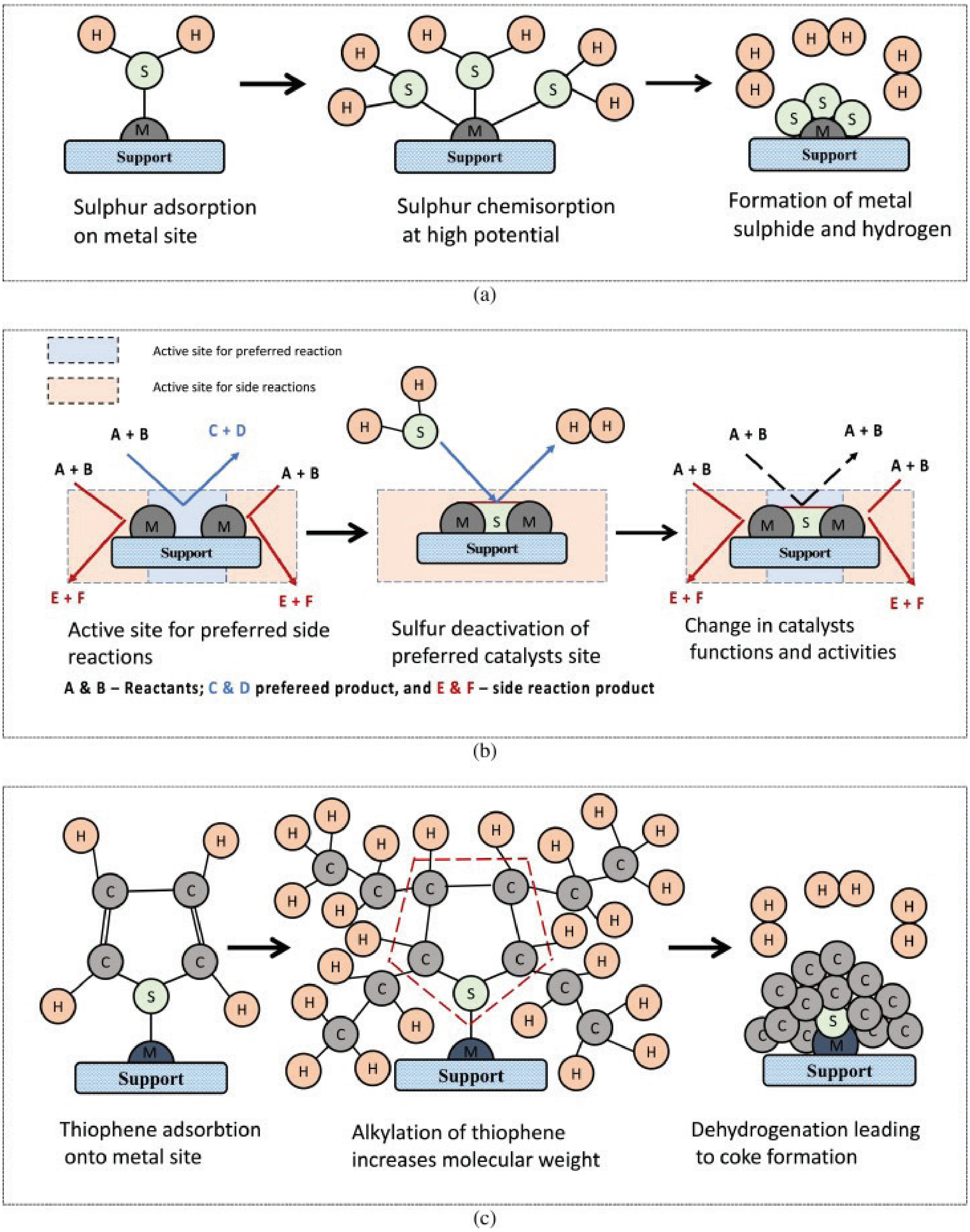
permit the passage of ammonium ions, which can interact with the zeolite through a process known as ion exchange [109]. In this exchange, ammonium ions in a solution can displace original cations (e.g., sodium, potassium, calcium, or magnesium ions) within the zeolite framework due to their attraction to the negatively charged framework [109]. Thus, nitrogen and nitrogen compounds adversely affect the catalytic activity of natural zeolites through mechanisms such as obstruction of acid centers, promotion of coke formation, and alteration of chemical properties. Understanding these mechanisms as shown in Figure 3 is critical for developing strategies to mitigate zeolite catalyst deactivation effectively [104].

A comprehensive understanding of these mechanisms is essential for optimizing catalytic performance in processes such as biomass conversion. Sulfidation stands out as a primary mechanism by which sulfur compounds impact zeolite catalyst deactivation as shown in Figure 4. Upon exposure to sulfur-containing compounds such as hydrogen sulfide (H_2S) or sulfur-containing organic compounds, zeolite active sites undergo interaction, forming metal-sulfur species. These species effectively compete for active sites, thereby reducing the availability of sites crucial for catalytic reactions [110, 111]. Consequently, the catalytic activity of zeolites diminishes, culminating in deactivation. Furthermore, sulfur compounds induce alterations in the structure and functionality of zeolites. The presence of sulfur can trigger chemical modifications or surface perturbations in zeolites, thereby influencing their catalytic prowess. This alteration further contributes to the decline in catalytic activity [110, 111]. Additionally, sulfur compounds exacerbate coke formation on the zeolite catalyst surface. Coke, a carbonaceous deposit, forms when undesirable side reactions are promoted or when active sites are blocked by sulfur compounds. This phenomenon accelerates catalyst deactivation [110, 111].

In the context of sulfur dioxide (SO_2) exposure, sulfite (SO_3^{-2}) and sulfate (SO_4^{-2}) species emerge. Notably, sulfite can decompose or oxidize into sulfate at temperatures lower than those typical for conventional reactions in hydrocarbon processing (typically 400-600°C) [112, 113]. The generation of heat-stable sulfate species on the zeolite surface emerges as a primary factor in deactivation induced by SO_2 exposure [114, 115]. Moreover, sulfur compounds can influence catalytic cracking activity in metal catalysts, albeit to a lesser extent compared to nitrogen compounds. Sulfur's interaction with metal sites in the catalyst alters the catalytic cracking process, leading to decreased activity [116]. The susceptibility of aluminum-rich zeolites to sulfur uptake is noteworthy, with higher aluminum content correlating with increased sulfation at aluminum sites, consequently leading to decreased catalytic activity [116]. Thus, understanding the compositional characteristics of zeolite catalysts is imperative in evaluating their susceptibility to sulfur poisoning. Thus, sulfur's reactivity with the active sites of natural zeolites involves sulfidation, alteration, and coke formation mechanisms, collectively contributing to catalyst deactivation or poisoning. A profound comprehension of these sulfur-related factors is indispensable for optimizing catalytic performance in diverse industrial processes.

Nickel, another heavy metal contaminant, significantly contributes to the deactivation of zeolite catalysts during biomass gasification by promoting excessive coke formation as shown in Figure 5 [104]. Ni deposition on the catalyst surface leads to pore destruction and undesirable reactions. The conversion of nickel to nickel-oxides decreases the hydrogen generation ability, but caution is needed to prevent reactivation of detrimental metallic nickel. However, unlike other heavy metals, Ni does not play a role in the destruction of zeolite structures [117]. Understanding the impact of nickel is crucial for optimizing catalyst performance in biomass gasification processes. In metal catalysts such as nickel, the primary cause of accelerated catalyst poisoning is the formation and migration of sulfur elements [118].

Heavy metals interact with natural zeolites, causing deactivation of gasification processes primarily by



(a)

(b)

(c)

Figure 4. The three primary mechanisms responsible for the deactivation of catalysts due to Sulfur. These mechanisms include sulfidation, alteration, and coke formation. [From Adanenche et al. [104], with permission from Elsevier (Number: RLNK505682204/3002296642).

poisoning the active sites crucial for catalytic reactions. This interaction involves the binding of alkali and alkaline earth metals to the acid centers of zeolites, essential for adsorbing and activating reactants like ammonia and NOx in the SCR (Selective Catalytic Reduction) process [119]. Alkali metals such as potassium and sodium from coal fly ash or biomass combustion inhibit the adsorption of ammonia and reduce catalytic activity in SCR processes [119]. Additionally, heavy metals like Ni and Pb, immobilized within newly formed zeolite structures during processes like composting, reduce their mobility and environmental impact [120]. The mineralogical properties of coal fly ash in gasification processes can influence zeolite synthesis and properties, affecting their ability to adsorb heavy metals [121]. Experimental studies have shown that phosphates and sulfates can mitigate the poisoning effects of alkali metals on zeolite-based catalysts, preventing interactions with vanadium active sites [119]. Furthermore, alkali metals inhibit surface oxygen transfer crucial for activating adsorbed reactants, affecting zeolite deactivation [119]. Despite efforts to regenerate zeolites, only partial recovery of adsorption capacity is typically achievable, highlighting challenges in reusing zeolites once poisoned by heavy metals [119]. Understanding the intricate mechanisms by which heavy metals interact with natural zeolites is critical for developing strategies to mitigate catalyst deactivation in gasification processes.

Common structural changes in zeolite frameworks during deactivation in the biomass gasification process primarily involve the loss of crystallinity, decrease in acidity, and alterations in the distribution of active sites. One prevalent phenomenon contributing to structural changes is coke formation, where the accumulation of carbonaceous coke on the catalyst surface obstructs the zeolite pores, impeding access to active sites. This coke is derived from heavy hydrocarbons and tars produced during gasification, hindering catalytic activity [122]. Another notable structural change is amorphization, wherein zeolites undergo structural collapse, transitioning from a crystalline to an amorphous state. This transformation is often induced by the harsh conditions encountered during biomass gasification, such as high temperatures and the presence of steam, which can degrade the zeolite framework [123]. Additionally, metal poisoning poses a significant concern, as alkali and alkaline earth metals present in biomass can interact with the zeolite framework, altering its acidity and leading to structural changes that compromise catalytic activity [122]. Furthermore, dealumination, characterized by the removal of aluminum atoms from the zeolite framework, can occur under the elevated temperature conditions of gasification, resulting in a reduction in acidic sites and impacting the zeolite's catalytic properties [122]. Lastly, high temperatures can induce phase transformations in the zeolite, altering its structural and chemical characteristics, further contributing to deactivation [122].

Another key factor that contributes to the deactivation of zeolite catalysts is abrasion. Abrasion significantly influences zeolite catalyst deactivation [17]. Both activated and deactivated catalysts experience mass loss, and the severity of attrition intensifies at higher temperatures and longer operation times. The activated catalysts exhibited improved attrition resistance and durability. Striking the balance between carbon removal and attrition resistance during regeneration ensures overall stability and performance. Moreover, the erosion or breakage of catalysts into

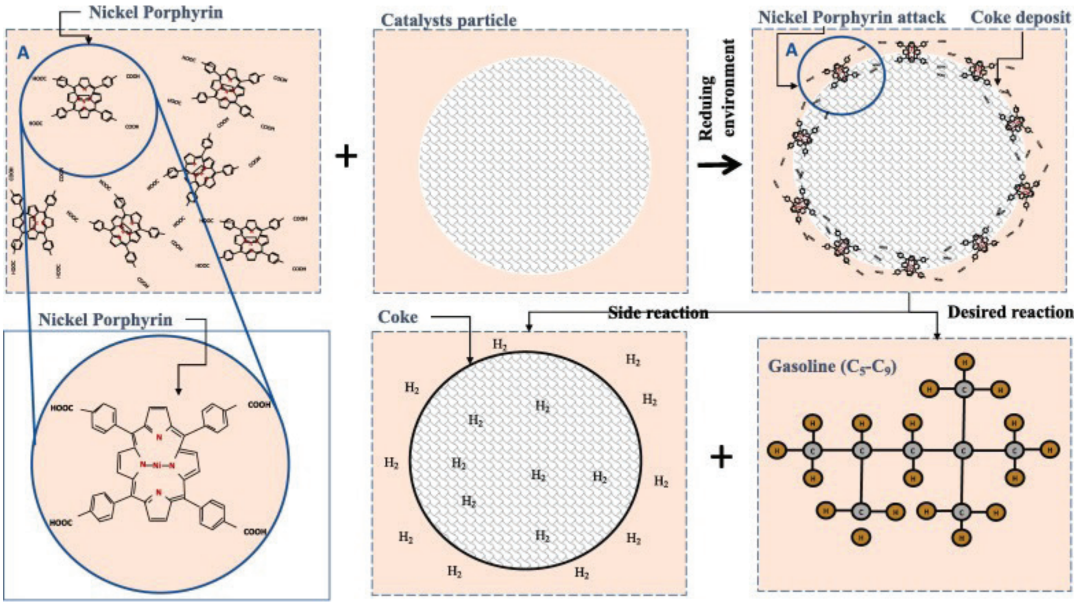


Figure 5. An illustration of the mechanisms involved in the poisoning of catalysts by nickel. [From Adanenche et al. [104], with permission from Elsevier (Number: RLNK505682204/3002296642).

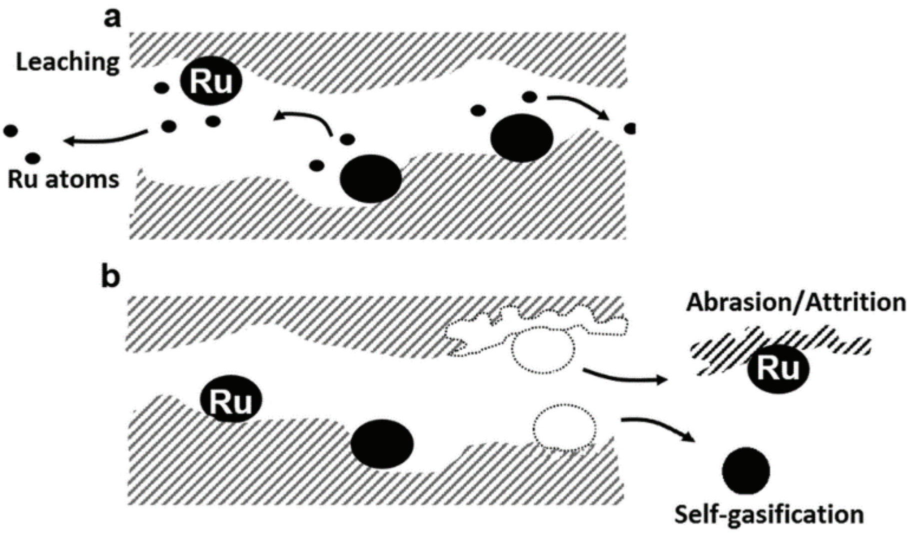


Figure 6. The schematic view of the mechanism for Ru loss from AC-supported catalyst. a) Ru leaching, b) loss of support fragments resulting in the loss of Ru NPs, which can be caused by the gasification process itself or from abrasion/friction between particles in the catalyst. [From Hunston et al. [124], with permission from The Royal Society of Chemistry (RSC) under CC-BY open access lisense.

smaller particles results from chemical reactions and prolonged exposure to high temperatures. However, smaller particles exiting the system can lead to a decline catalytic performance. Abrasion is crucial for designing efficient and durable catalysts. The schematic in Figure 6 depicts the mechanism of Ru abrasion and loss from activated carbon (AC)-AC-supported catalysts, highlighting two primary processes [124]. First, Ru leaching occurs, where Ru nanoparticles (NPs) dissolve and detach from the catalyst support. This leaching process can be influenced by various factors, including the gasification process. Second, the loss of support fragments leads to the detachment and loss of Ru NPs. This phenomenon can result from both the gasification process and abrasion or friction between particles within the catalyst.

To mitigate the impact of abrasion on zeolite catalyst activation, several strategies have been employed, each tailored to address specific challenges and operational requirements. One approach involves catalyst coating, where zeolite catalysts are encased in a protective layer during the synthesis of fine chemicals. This coating serves to shield the catalysts from abrasion, thereby preserving their activity over prolonged durations [9, 122]. Additionally, pelletizing, a technique commonly utilized in fluid catalytic cracking (FCC) processes in the petrochemical industry, has proven effective in enhancing the mechanical strength of zeolite catalysts, thus rendering them more resistant to abrasion [125, 126]. Furthermore, the addition of binders to zeolite catalysts in biomass conversion processes has been implemented to bolster their resistance to abrasion and extend their operational lifespan [9, 122]. Optimal reactor design also plays a crucial role in mitigating abrasion-induced deactivation, with designs engineered to minimize high-impact points and turbulence, particularly in CO_2 utilization processes. Such designs aim to reduce wear on zeolite catalysts, thereby preserving their activity [9, 122]. Moreover, the implementation of regular regeneration cycles has proven effective in various industrial processes to restore the activity of zeolite catalysts following abrasion-related deactivation [9, 122]. Finally, the utilization of mesoporous zeolites represents a promising avenue for mitigating abrasion. By introducing mesopores into zeolite structures, diffusion limitations can be alleviated, and more active sites can be exposed, rendering the catalysts less susceptible to abrasion in catalytic applications [9, 122]. These diverse strategies collectively contribute to enhancing the durability and longevity of zeolite catalysts in the face of abrasion-related challenges.

Coke formation significantly affects zeolite catalyst deactivation by causing pore blockage and hindering the diffusion of reactants and products, leading to reduced catalytic activity [127, 128]. Understanding the characteristics and mechanisms of coke is vital for optimizing catalytic processes and mitigating catalyst deactivation, providing valuable insights from extensive studies on biomass gasification. The formation of coke is a complex process influenced by various factors, including operating conditions, catalyst composition, and feed properties [102, 129].

During biomass gasification, coke deposits can block pores and active sites, reducing catalytic activity, whereas contaminants such as alkali metals, sulfur, and chlorine further contribute to catalyst deactivation by chemically poisoning the catalyst and promoting coke formation. The increased presence of steam and/or oxygen supports the gasification and/or combustion of coke precursors. The aromatic properties of the feed undergoing reforming can promote coke deposition via polymerization reactions. Therefore, addressing coke-related challenges and managing catalyst deactivation are crucial for enhancing the efficiency and effectiveness of biomass gasification.

Another influential factor in zeolite catalyst deactivation is the reduction in catalytic activity and selectivity due to sintering and agglomeration of active sites. The sintering and agglomeration of active sites play a crucial role in zeolite catalyst deactivation, leading to larger and fewer active sites. This process occurs at elevated temperatures and reduces the overall activity and selectivity of the catalyst. Factors such as high temperature, metal mobility, and the presence of reactive species can accelerate sintering, while the nature of the support material and metal influence the process [130]. Coke deposits on the catalyst surface promote sintering by acting as bridges between the metal particles, facilitating their migration and coalescence. In turn, sintering modifies the catalyst surface structure, influencing the adsorption and polymerization reactions that lead to coke formation during fouling or coking.

In the realm of natural zeolites, extensive research has been conducted to unravel the intricacies of deactivation, particularly in several types of natural zeolites such as clinoptilolite, chabazite, and mordenite. Deactivation in natural zeolites is driven by both surface and emboli mechanisms, exerting a profound impact on their sustained efficacy over time [131]. Detailed investigations into natural zeolites such as clinoptilolite, mordenite, and chabazite underscore distinctive deactivation processes influenced by factors such as metal poisoning, calcination procedures, and modifications.

The deactivation induced by thiophene in Ni/Clinoptilolite underscores the crucial role of the iron-nickel interaction in conferring sulfur resistance [132]. A more robust iron-nickel interaction is directly proportional to higher sulfur resistance, a critical factor for the catalyst's endurance. Furthermore, calcination before Ni impregnation in the ethylbenzene hydrogenation process enhances the interaction strength and sulfur resistance [133]. While clinoptilolite demonstrates promise in hydrogen sulfide removal through adsorption capacity of approximately 0.03 g S/g, its susceptibility to deactivation is evident in the oxidative removal of dissolved iron, especially in the presence of Mn^{2+} cations [134, 135].

Meanwhile, mordenite catalysts manifest diverse deactivation mechanisms contingent on specific catalytic processes. The significance of redox treatment and dealumination in influencing catalytic activity and stability is underscored [136]. Furthermore, chabazite zeolites exhibit diverse deactivation profiles in different catalytic scenarios. The incorporation of small platinum crystallites in Pt/H-chabazites and Pt/H-Y zeolite enhances deactivation profiles during n-butane conversion [137]. Ga+-chabazite zeolites emerge as highly selective catalysts for nonoxidative propane dehydrogenation, boasting a remarkable 96% propylene selectivity [138]. These findings underscore the intricate interplay between zeolite structure, metal incorporation, and reactant species in determining deactivation behaviors in various catalytic processes.

In the realm of catalyst deactivation, both synthetic and natural zeolites encounter shared and distinctive factors influencing their performance over time. Common culprits include contaminants like nitrogen, sulfur, and heavy metals, which chemically react with active sites, inducing deactivation or poisoning in both zeolite types [105]. Additionally, coke formation stands out as a major contributor, impeding reactant and product diffusion, leading to pore blockage and reduced catalytic activity [127, 128]. Abrasion, characterized by mass loss and attrition, also plays a role, with its severity escalating at higher temperatures and extended operation times [17, 139]. Moreover, the sintering and agglomeration of active sites contribute to the reduction in catalytic activity, affecting both synthetic and natural zeolites [130, 140].

Natural zeolites, exemplified by clinoptilolite, mordenite, and chabazite, introduce unique dimensions to the deactivation narrative. These zeolites exhibit distinctive metal interactions, as seen in clinoptilolite's sensitivity to the iron-nickel interaction influencing sulfur resistance [132, 133]. Each natural zeolite showcases specific deactivation mechanisms; for instance, clinoptilolite displays notable potential for reactivation through nitrous oxide treatment and susceptibility to oxidative removal of dissolved iron [135, 141]. Mordenite experiences irreversible deactivation due to dealumination and pore blockage [142, 143]. Chabazite zeolites present trial-dependent deactivation patterns and demonstrate highly selective catalytic activity [138, 144].

Quantitative insights, encompassing sulfur resistance, adsorption capacity, and catalytic activity, serve as crucial metrics for understanding and comparing zeolite performance in both synthetic and natural contexts [104, 117]. Hence, a thorough understanding of these common and unique deactivation mechanisms, along with quantitative data, is essential for devising efficient strategies to alleviate deactivation consequences and improve the overall catalytic efficiency across various industrial applications.

Understanding the Mechanisms of Zeolites Deactivation in Biomass Gasification

The mechanisms of zeolite catalyst deactivation are crucial for developing strategies to mitigate their effects and improve catalyst performance. Several key factors contribute to catalyst deactivation, including the adsorption and diffusion of reactants and intermediates, reaction-induced structural changes, role of surface acidity and basicity, impact of contaminants, and use of modelling and simulation approaches. Surface acidity and basicity are integral factors influencing zeolite deactivation, particularly in the realm of catalyst performance within biomass gasification applications. Zeolite structures, characterized by interconnected silica and alumina tetrahedra, engender Brønsted acid sites pivotal for catalytic reactions essential in biomass gasification, such as cracking and hydrocracking of petro-fractions [122]. However, the presence of these robust acid sites can hasten zeolite deactivation by fostering the accumulation of carbonaceous coke on the catalyst surface. Furthermore, acid sites are vulnerable to poisoning by basic nitrogen compounds and ions like Ca^{2+} or K^+ [125].

Conversely, surface basicity offers promise in bolstering catalytic stability by impeding carbon deposition on the catalyst surface during biomass gasification [145]. Basic sites facilitate the activation of acidic molecules, such as CO_2, thereby potentially enhancing catalyst stability. Nevertheless, the generation of basic sites often mandates severe pre-treatment temperatures, necessitating careful control to avert adverse effects on catalyst performance [145]. Moreover, modifications to the acid-base characteristics of zeolite surfaces, achieved through techniques such as dealumination or metal incorporation, can alter catalyst activity, selectivity, and stability across various processes, including CO_2-mediated dehydrogenation of propane [146, 147]. Additionally, the distribution of acidic and basic sites within zeolite structures influences catalyst resistance to deactivation by modulating the rate of carbon species production and oxidation [148].

Furthermore, the adoption of strategies such as core–shell structures in zeolites holds potential for enhancing catalyst performance by furnishing shape selectivity and resistance to sintering, particularly advantageous in biomass conversion and CO_2 conversion processes [149]. Additionally, the fine-tuning of physicochemical properties of catalyst supports, encompassing acidity and basicity, offers a feasible avenue to mitigate carbon deposition and enhance CO_2 activation, thereby augmenting catalyst stability and curtailing deactivation [148]. The adsorption and diffusion of reactants and intermediates on zeolite catalyst surfaces are prevalent mechanisms contributing to deactivation. These phenomena entail the blocking of active sites and consequent reduction in catalytic activity. Investigations have indicated that the adsorption of phenol on zeolite catalysts employed in biomass gasification can lead to a substantial decline in catalytic activity, reaching up to 50%, attributable to the obstruction of active sites [65, 150, 151]. Diffusion limitations of bulky reactant molecules within the zeolite framework can also affect the catalytic performance [152].

Furthermore, the high temperatures and reactive conditions prevalent in biomass gasification can induce structural modifications in zeolite catalysts, leading to deactivation. Thermal aging during biomass gasification can result in the collapse of the zeolite framework, reducing surface area and pore volume. Studies have indicated that zeolite catalysts' surface area may decrease by approximately 25-30% after thermal aging at 800°C for 24 h [153]. Additionally, contaminants like alkali metals and sulfur compounds in biomass feedstocks can interact with zeolite catalysts, contributing to their deactivation. For example, alkali metals such as potassium and sodium can react with zeolite catalysts, diminishing their catalytic activity. Research findings suggest that the presence of 1 wt% potassium on zeolite catalyst surfaces can lead to a reduction in biomass gasification conversion rates by up to 40% [154]. Similarly, sulfur compounds can poison zeolite catalysts, leading to decreased activity and selectivity [155].

In the realm of gasification processes, the deactivation mechanisms of mordenite, clinoptilolite, and chabazite play pivotal roles in shaping the efficacy of these natural zeolite catalysts. Mordenite, utilized in isobutane alkylation, confronts potential deactivation through coke formation, particularly notable in lanthanum-exchanged Y-zeolite, where substantial carbonaceous deposits require elevated temperatures for elimination [156]. The presence of excessively strong acidity in certain catalysts accentuates deactivation, underscoring the intricate interplay between acidity, coke deposition, and catalytic activity [156]. Clinoptilolite, identified for its potential in tar removal during biomass gasification, undergoes deactivation during hydrogen sulfide adsorption. The adsorption capacity for H_2S, a toxic and corrosive impurity, underscores the material's efficacy in removing harmful components [134]. Modeling the deactivation process, with a focus on concentration-dependent activity, enhances the understanding of adsorption kinetics and contributes to the optimization of clinoptilolite's performance in gasification applications [134]. Meanwhile, chabazite zeolites, exhibiting versatility in diverse catalytic scenarios, showcase distinctive deactivation profiles [65]. Their susceptibility to deactivation in specific processes, such as nonoxidative propane dehydrogenation, emphasizes the need for tailored strategies to mitigate deactivation effects and optimize overall catalytic efficiency in gasification contexts.

Therefore, to gain a deeper understanding of the true mechanism behind zeolite catalyst deactivation, modelling and simulation approaches can be employed. Computational studies have provided insights into atomic- and molecular- scale interactions between reactant molecules, intermediates, and zeolite catalysts during biomass gasification. These methods aid in predicting the catalytic performance, comprehending the impact of structural modifications, and developing strategies to mitigate catalyst deactivation. It is important to note that quantitative data on catalyst deactivation in biomass gasification can vary depending on the specific zeolite catalyst, biomass feedstock, and operating conditions utilized in different research studies.

Strategies for Mitigating And Regenerating Zeolites Deactivation in Biomass Gasification

Mitigating zeolite deactivation is crucial for maintaining the stability and performance of catalysts in various industrial processes, especially in biomass conversion and hydrocarbon reforming. Designing catalysts resistant to contaminants is a fundamental strategy, involving the incorporation of metal promoters or modifiers like nickel or cobalt into the zeolite structure. Studies have demonstrated a substantial reduction in coke formation and enhanced catalytic performance, with modified zeolite catalysts showing up to a 60% decrease in coke yield compared to their unmodified counterparts [29, 157]. An alternative and efficient method involves the continuous removal of coke deposits in situ through catalytic steam gasification, resulting in a reduction in the coke deposition rate by over 10 times. [158]. The use of a fluidized bed reactor aids in coke reduction by shuttling catalyst particles between the reactor and a burner, where coke deposits are burned off [122, 159]. Additionally, employing a two-stage reactor system, which separates gasification and combustion processes, proves beneficial in minimizing coke deposition on the catalyst surface [122, 160, 161].

A promising avenue for zeolite deactivation mitigation is the development of core-shell zeolite structures [162]. This novel class of nanomaterials involves a core material, typically a metal or metal oxide, surrounded by a zeolite shell. The shell acts as a protective layer, preventing coke deposition and metal sintering, thereby extending the catalyst's activity and selectivity [163]. Despite this potential, there is a notable gap in quantitative comparisons of the lifespan between conventional zeolites and core-shell zeolites under various biomass gasification conditions.

Furthermore, incorporating redox metal oxides like CeO_2, FeO_x, or perovskite-based support enhances the basic strength of catalysts by creating oxygen vacancies [163]. These vacancies act as basic sites, and the redox metal oxides serve as electron reservoirs, preventing deactivation by maintaining the basicity of the catalyst. Additionally, the addition of promoters or additives, such as rare earth metals or transition metals, has been shown to improve zeolite catalyst stability against alkali metal poisoning. Studies reveal that even a small addition, such as 2 wt% of a rare-earth metal promoter, can enhance zeolite catalyst activity by up to 50% in the presence of alkali metals [164]. Similarly, the inclusion of silica or alumina has proven effective in reducing coke formation and enhancing overall catalyst stability [165]. Thus, a comprehensive strategy involving catalyst design, reactor engineering, and the incorporation of innovative materials is essential for mitigating zeolite deactivation and optimizing the efficiency of catalytic processes. Ongoing research efforts are needed to quantify and refine the performance of these strategies under diverse operating conditions in biomass gasification.

Meanwhile, various methods have been employed to implement zeolite regeneration techniques aimed at restoring the catalytic activity of deactivated zeolite catalysts. Regenerating zeolite catalysts in biomass gasification presents several challenges because of the complex nature of biomass feedstock and the deactivating species involved. Effective regeneration strategies are crucial for maintaining the catalyst performance and extending its lifespan. To address these challenges, the following regeneration or rejuvenation strategies can be employed: thermal or oxidative regeneration [166–169], chemical regeneration [65, 170, 171], steaming or humid air regeneration [170, 172, 173], and combination of regeneration techniques as shown in Table 6.

Table 6. Catalyst regeneration and rejuvenation techniques

Catalyst	SiO_2/ Al_2O_3 ratio	Surface area [m^2/g]	Application	Regeneration Methods	Results	Ref
Thermal Method						
HZSM-5	30-28	37-100	1-butene oligomerization in a fixed-bed reactor	- Temperature-programmed sweeping (TPS) with nitrogen (N_2)	- TPS-N_2 eliminates soft coke at 400 °C, whereas hard coke is eliminated through combustion	[174]
Cu–Nb/ HZSM-5	30	-	Chlorinated volatile organic compound elimination	- Restoration at 400 °C in air	- Regenerating at 400 °C in air restores most Brønsted acid sites by converting coke into saturated hydrocarbons or CO_2.	[172]
MOR zeolite	-	-	H_2S on Blast furnace.	- In-situ regenerable Cu/ Zeolite, T = 280 °C.	- MOR zeolite enhances both Cu dispersion and desulfurization capacity.	[175]
Y and ZSM-5 zeolites	200, 500	-	Adsorption	- T = 30-575 °C	- Regenerated zeolite maintains perfect unit cell parameters and adsorption ability.	[176]
Ni/Al_2O_3	NR	NR	Pyrolysis to reforming of waste tyres.	- T = 600 °C from ambient temperature.	- Above 600°C, filamentous carbon loses weight; below 600°C, amorphous carbon oxidizes more readily.	[177]

Table 6. Catalyst regeneration and rejuvenation techniques (continued)

Catalyst	SiO_2/ Al_2O_3 ratio	Surface area [m^2/g]	Application	Regeneration Methods	Results	Ref
Dealuminated Y-zeolite	20	704	Adsorption of acetone and toluene	- T = 296-473 K	- Roll-up effect was stronger with acetone than toluene. Acetone's Type-III isotherm at higher temperatures allowed faster recovery in higher concentrations.	[178]
Chemical Method						
ZSM-5 zeolites	-	284, 332	Methanol to propylene (MTP)	- Insitu ZSM-5 zeolite rejuvenated with toluene	- Mesoporous ZSM-5 exhibited over 50% longer lifespan due to enhanced rejuvenation.	[179]
NaY zeolites	5	-	Sulfur dioxide (SO_2) removal	- Alcohol	- Alcohol promotes NaY crystal formation, increasing surface area and microporosity.	[180]
Zeolite Clinoptilolite commercial products	4.27	-	Ammonium removal	- NaCl	- Optimal zeolite regeneration and NH_4^+ conversion occur at 20 g/L NaCl concentration and pH 10.0.	[181]
Zeolite -Y	30, 80	750, 780	Biomass gasification	- Ni impregnated to Zeolite.	- Naphthalene conversions remained above 99% throughout the 97-h testing period, with minimal loss of activity.	[3]
HZSM-5	42, 59	181.4	Plastic gasification	- Co/SiO_2 impregnated to Zeolite.	- This catalyst is recommended for stable hydrogen production, lasting over 15 hours.	[182]
MOR zeolite	20	546	CO methanation	- Ru doped MOR zeolite	- No deactivation occurs over 100 hours, demonstrating perfect thermal stability.	[179]
ZSM-5	50	291, 285	Cracking of JP-8 a hydrocarbon fuel	- Pt and Gd promoted ZSM-5	- Gd metal coexistence partially inhibits Pt particle agglomeration on the regenerated ZSM-5 catalyst.	[183]
FAU zeolites	300	-	CO_2 adsorption	- Amina	- Impregnating FAU zeolites with PEI and DETA enhances regeneration stability over 10 cycles.	[184]
Zeolite -X	-	-	Pesticide adsorption	- Ethanol	- Ethanol emerges as the most efficient choice for rejuvenating zeolite-carbon composites with adsorbed MCPA and 2,4-D.	[185]
Steaming Method						
Dealuminated zeolite	-	-	Hydrophobic zeolites	- Steam 130 °C, 1 bar	- Desorption with small steam flow rates can be equally effective as with large flow rates.	[186]
HZMS-5.			Biomass pyrolysis oils	- Steam	- The presence of vapor leads to substantial gas product generation, surpassing a 70% yield at a catalyst temperature of 550 °C.	[173].
Zeolite HZSM-5	100	-	Methanol conversion	- Vapor at 270 °C	- Lower temperatures facilitated the complete removal of the substance, causing a delay and restoring the catalyst's activity entirely.	[187]
Combination Method						
ZSM-5 zeolite	280	-	Adsorption	- High temperature zeolite loaded with MTBE-DCE and DCE-TOL (T = 30-400 °C)	- Configuration can impact molecule mobility within the framework, with desorption temperature closely linked to molecule positions in the porous structure.	[188]
MFI zeolite	13.40	-	Methane dehydroaromatization (DHA)	- Mo-MFI zeolite at 973 K in oxidative environments	- Combining spent Mo-MFI and H-MFI adds extra H^+ sites, aiding in dispersing clustered Mo domains into ion-exchanged Mo species, thereby restoring DHA reaction rates.	[189]

Thermal regeneration involves subjecting a deactivated zeolite catalyst to high temperatures to remove coke deposits and reactivate the catalyst. Controlled oxidation or calcination in an oxygen-rich atmosphere can effectively burn off carbonaceous deposits and restore the catalyst activity. The regeneration temperature and duration must be optimized to achieve efficient coke removal without causing structural damage to the catalysts. Studies have shown that thermal regeneration at temperatures between 500-800 °C can lead to significant coke removal and catalyst reactivation [167, 168]. At high regeneration temperatures (~565°C) in O_2 or N_2 atmospheres. However, repeated regeneration treatments can quickly decrease the desulfurization performance of the adsorbent [169]. In metal-impregnated zeolites, regeneration at high temperatures shows the presence of agglomeration so that it can gradually reduce the performance of the catalyst [189]. Therefore, the regeneration method at low temperatures (296 to 473 K) also becomes an alternative for regenerating zeolite, whether as a catalyst or adsorbent [169, 178].

Experimental findings provide compelling evidence of the efficacy of strategies such as metal modification and continuous coke removal in mitigating zeolite deactivation. Blending methanol with the catalyst material has been shown to significantly reduce coke deposition during bio-oil conversion. Previous study reported a noteworthy 1.55 wt.% reduction in coke deposition, highlighting the potential of this approach to mitigate zeolite deactivation [190]. Moreover, metal modification has emerged as another promising strategy for enhancing zeolite stability where zeolite Y modified with 0.5 wt% Pt exhibited a 50% increase in catalyst lifetime compared to the unmodified version [191]. Moreover, the presence of Pt reduced the rate of coke formation from 1.2 g_coke/g_zeolite/hour to 0.8 g_coke/g_zeolite/hour, underscoring the effectiveness of metal modification in mitigating zeolite deactivation [191]. Furthermore, continuous coke removal processes provide an energy-efficient alternative to thermal methods for preserving zeolite activity, with ozone-mediated continuous coke removal achieving a rate of 0.05 g_coke/g_zeolite/hour at 180°C, significantly lower than the temperatures exceeding 500°C required for thermal methods, thereby highlighting the potential of continuous coke removal as a less damaging approach to zeolite activity preservation [192]. Further substantiating the benefits of metal modification investigated zeolite modification with 1 wt% Pd, which notably increased resistance to deactivation by coking [193]. The Pd-modified zeolite maintained 90% of its initial activity after 20 hours of reaction time, while the unmodified zeolite's activity dropped to 40% under similar conditions, highlighting the effectiveness of metal modification in prolonging zeolite activity [193]. Moreover, continuous coke removal methods have demonstrated remarkable efficacy in reducing coke deposits on zeolite catalysts revealing a 70% reduction in coke deposits after 2 hours of continuous coke removal using steam at 500°C [193]. This method proved superior to traditional coke burning, which achieved only a 50% reduction in coke deposits under similar conditions [193]. Metal modification plays a crucial role in enhancing coking resistance and introducing novel active sites, consequently boosting zeolite catalytic activity [125]. Additionally, the effective removal of coke from HY zeolites using ozone at 180°C underscores the efficacy of coke removal techniques within the temperature range of 100°C to 200°C, demonstrating the versatility of such processes under different conditions [170]. These quantitative data underscore the effectiveness of metal modification and continuous coke removal strategies in mitigating zeolite deactivation, offering valuable insights for enhancing zeolite stability and catalytic performance.

Understanding the intricate interplay among various factors influencing zeolite deactivation is paramount for enhancing biomass gasification processes. Among these factors, coke formation emerges as a significant contributor to zeolite deactivation, owing to its highly selective nature dictated by the porous structure of the zeolite [194]. Notably, the rate of coke formation exhibits substantial variation across zeolites with different pore sizes, with small and medium pore zeolites demonstrating rates ranging from 50 to 1000 times lower compared to wide-pore zeolites [194]. Unraveling the mechanisms governing coke formation is pivotal, with literature indicating the operation of two parallel pathways, namely the direct mechanism and dual-cycle mechanism, in accordance with the hydrocarbon pool theory. Moreover, the deposition and accumulation of coke on external zeolite surfaces significantly contribute to reaction deactivation [195]. Furthermore, contaminants play a pivotal role in exacerbating coke formation or sintering processes, thereby highlighting the interconnected nature of these deactivation mechanisms. For instance, the presence of nitrogen in metal-zeolites can exert pronounced effects on the energy and pathways of the nitrogen reduction reaction (NRR) [196]. Similarly, sulfur and heavy metals have been observed to form stable metal–sulfur adducts, thereby facilitating nucleation around metal precursors and ultimately promoting the formation of an encapsulation structure, which contributes to deactivation [197]. Hence, a comprehensive understanding of these interactions is imperative for devising strategies to mitigate zeolite deactivation and enhance the efficiency of biomass gasification processes.

Chemical regeneration methods involve the use of chemical agents to dissolve or remove deactivating species from a catalyst surface. For example, acidic and alkaline solutions can be employed to remove ash deposits and metal contaminants, respectively. Acid washing has been used to remove ash deposits from zeolite catalysts during biomass gasification, leading to improved activity and selectivity [65, 171]. Chemical regeneration methods must be carefully designed to avoid damaging the zeolite structure or altering its catalytic properties.

Steaming regeneration involves treating a deactivated zeolite catalyst with high-temperature steam to remove coke and tar deposits. Steam can react with carbonaceous species, facilitating volatilization and removal from the catalyst surface. Studies have demonstrated that steam regeneration can effectively restore the catalytic activity of zeolite catalysts during biomass gasification [173]. The regeneration temperature, steam flow rate, and duration should be optimized to achieve efficient coke and tar removal without adversely affecting zeolite structures. Furthermore, the combination of different regeneration techniques can enhance the effectiveness of catalyst regeneration. For instance, a sequential approach involving thermal regeneration, followed by chemical washing or steaming, can provide comprehensive catalyst regeneration. The thermal step removes coke deposits, while subsequent chemical treatment or steaming further removes contaminants and restores the activity of catalyst. This combined approach has been shown to improve the catalyst performance and extend its lifespan.

In some cases, catalyst rejuvenation involves the modification or enhancement of the deactivated zeolite catalyst to restore its activity. This can be achieved by adding promoters, modifiers, or coatings to enhance catalytic activity or resistance to deactivation. For example, the addition of metal promoters or modifying agents such as phosphorus or boron has been found to enhance the activity and stability of zeolite catalysts in biomass gasification [171, 198]. Type selection of a metal catalyst impregnated with zeolite, such as nickel (Ni), cobalt (Co), and ruthenium (Ru), presents an alternative route to achieve thermal stability and prolong the catalyst's lifespan, making it a favorable choice [3, 179, 182]. The selection of zeolite type determines the ability of catalyst reactivity and stability, as the MFI of zeolite is better than ZSM-5 [199]. Catalyst rejuvenation can be an effective strategy to overcome deactivation and extend the lifespan [200, 201]. By employing these regeneration strategies, the performance and longevity of natural zeolite catalysts for biomass gasification can be improved. Optimizing the regeneration conditions, such as temperature, duration, and regeneration agents, is essential to achieve efficient removal of deactivating species while preserving the structural integrity and catalytic properties of the zeolite catalyst.

A wide array of innovative strategies is employed in the application of deactivation mitigation and regeneration methods for zeolites in biomass gasification as shown in Table 6, all with the overarching goal of improving operational efficiency and sustainability. Recent investigations have singled out hierarchical micro/mesopore-structured zeolites as particularly promising solutions for combating catalyst deactivation resulting from coke formation. Studies have demonstrated notable enhancements in catalytic activity associated with the utilization of these zeolite structures [16]. Core-shell zeolite structures are used in biomass gasification due to their stability during reducing and oxidizing treatment [202]. The core-shell interface remains stable even though strong changes occur in the core due to the reduction of copper oxide to metallic copper particles [202]. Meanwhile, redox-based regeneration techniques have effectively reinstated as much as 98% of the original functionality of cobalt catalysts incorporating zeolites, employed in the Fischer-Tropsch synthesis [203], suggesting prospective suitability for biomass gasification endeavors.

Integration of Redox Metal Oxides in Zeolites Redox metal oxides are widely employed for biomass conversion due to their unique acid-base properties [204]. They are used for the dehydration of sugars to important furanic compounds [204]. Some additives like Ce, La, Mg, K, Mo, Zr, and Mn could improve the performance and stability of Ni-based catalyst, particularly Mo, Zr, and Mn led to the highest activity and stability during biomass gasification [205]. Integrating metal nanoparticles within these zeolites further enhances catalytic activity, providing additional active phases and improving overall performance [16]. Regeneration of zeolite catalysts, including those with Sn, can induce structural alterations that enhance their accessibility, hydrophobicity, reactivity, and stability, thereby improving their effectiveness in biomass conversion processes [206]. Moreover, oxidative treatments for catalyst regeneration, including molecular oxidation with oxygen and ozone, have been extensively reviewed, with studies highlighting their efficacy in recovering catalytic activity and extending catalyst lifespan [125, 170]. Innovative concepts such as integrating structured iron-based catalytic monoliths in fluidized bed gasifiers have shown preliminary effectiveness in gas conditioning and tar conversion [207]. Additionally, catalyst addition to biomass gasification processes, such as $CeO_2(111)$, has been explored to minimize coke formation and enhance gasification efficiency [208]. Mild regeneration methods involving air oxidation and H_2 reduction have been successfully applied, demonstrating their applicability to various catalysts and additional reactions involving oxygenated molecules [209]. Another novel approach involves regeneration by $ZnCl_2$ activation, effectively eliminating carbon deposition and recovering catalyst activity, thus prolonging operational life [210].

Furthermore, the application of metallic additives such as nickel and cobalt for the purpose of alleviating coke deposition on zeolite catalysts holds significant importance in biomass gasification processes. The incorporation of nickel into ZSM-5 zeolite has been proven to significantly diminish coke formation, thereby augmenting the stability of the catalyst [211, 212]. Nickel and cobalt exhibit strong hydrogenation abilities, converting coke precursors into gaseous products, thereby improving syngas quality by reducing CO_2 content and increasing CH_4 content. Moreover, core-shell zeolite structures, where the active zeolite core is encapsulated by an inert shell material, offer a promising approach. These structures, along with hierarchical porosity, facilitate better diffusion and mass transfer, leading to increased catalyst stability and efficiency in biomass conversion [125]. A core-shell ZSM-5@silica catalyst has been developed, effectively mitigating zeolite deactivation by coke and extending its lifespan [213]. Additionally, the integration of redox metal oxides into zeolite catalysts has shown potential in reducing coke formation and maintaining the quality of gasification processes. Moreover, the incorporation of cerium oxide into HZSM-5 zeolite led to a marked reduction in coke deposition during the conversion of biomass-derived compounds. This effect can be ascribed to the robust redox properties exhibited by cerium oxide [9, 214]. Furthermore, regeneration techniques such as thermal regeneration, chemical washing, and steaming are essential for restoring the activity of deactivated zeolite catalysts. Heating spent HZSM-5 catalysts to 550°C for 5 hours effectively removed coke deposits, restoring catalytic activity [125]. Chemical washing involves dissolving coke deposits with a suitable solvent, partially restoring catalyst activity [56, 125]. Steaming entails treating spent zeolite catalysts with steam to remove coke deposits and restore catalytic activity [125, 215]. These novel approaches significantly impact biomass gasification processes by enhancing catalyst stability, maintaining activity over longer operational periods, increasing syngas selectivity, prolonging catalyst lifespan, improving product yields, process efficiency, and the overall quality of biomass gasification processes.

Potential Applications of Deactivated Zeolites in Other Fields

Despite their reduced catalytic activity, deactivated natural zeolites still possess unique properties that make them suitable for various applications beyond their primary use in biomass gasification. Deactivated zeolites can find potential applications in different fields by leveraging their inherent properties even after deactivation. Potential applications of deactivated natural zeolites include adsorbents for environmental remediation, construction materials, concrete additives, and nutrient delivery systems in agriculture.

The primary application of deactivated natural zeolites is as adsorbents for environmental remediation. Deactivated natural zeolites can be employed as adsorbents for environmental remediation. The porous structure of zeolites allows them to selectively adsorb pollutants such as heavy metals, organic contaminants, and dyes from wastewater or soil. Although their catalytic activity may be diminished, the high surface area and ion-exchange capacity of deactivated zeolites make them effective adsorbents. A study demonstrated high removal efficiencies of pollutants using deactivated zeolites, achieving over 90% removal of heavy metals from contaminated water. The use of deactivated zeolites in environmental remediation can contribute to pollution control and mitigation efforts [120].

Another potential application of deactivated natural zeolite catalysts is as construction materials and concrete additives. Deactivated natural zeolites can be incorporated as additives into construction materials and concrete. The high adsorption capacity and ion-exchange properties of zeolites can provide benefits such as improved durability, reduced permeability, and enhanced moisture control in concrete. Deactivated zeolites can also contribute to the immobilization of harmful substances, such as heavy metals, in construction materials. The addition of deactivated zeolites to concrete can also enhance its mechanical strength and durability [216, 217]. Their incorporation as additives can lead to more sustainable and resilient construction.

Another intriguing potential application of deactivated natural zeolite catalysts is as nutrient delivery systems in agriculture. Deactivated natural zeolites can serve as nutrient delivery systems for agriculture. The porous structure of zeolites allows them to retain and slowly release essential plant nutrients, thereby promoting efficient nutrient uptake by crops. Deactivated zeolites can provide long-term nutrient availability, reduce fertilizer leaching, and improve nutrient-use efficiency. Studies have reported increased crop yields and improved nutrient retention in soils amended with deactivated zeolites [218]. A previous study demonstrated yield increases of up to 30% in certain crops using zeolite-based nutrient delivery systems [219, 220]. Their use in agriculture contributes to sustainable and environmentally friendly farming practices.

Another possible application of deactivated natural zeolite catalysts is as thermal insulation materials which can be utilized because of their low thermal conductivity. The porous structure of zeolites helps to trap air within their cavities, reducing heat transfer and improving insulation properties. The addition of deactivated zeolites to building materials can enhance thermal insulation efficiency [221]. Their application as thermal insulation materials can contribute to energy conservation and improve the building energy efficiency.

Therefore, the potential applications of deactivated natural zeolites in other fields highlight their versatility and value beyond their catalytic activity. These applications capitalize on the unique properties of zeolites, such as their adsorption capabilities, ion-exchange capacities, and porous structures. Further research and development efforts are required to explore and optimize the use of deactivated zeolites in these applications, promoting sustainable and innovative solutions for environmental remediation, construction, agriculture, and thermal insulation.

CONCLUSION

The investigation conducted a thorough exploration of the complex aspects surrounding zeolite catalyst deactivation. The utilization of zeolites in biomass gasification processes undergoes deactivation through various mechanisms such as abrasion, coke formation, and sintering, which significantly affect both synthetic and natural zeolites. Noteworthy findings indicate that the implementation of metal modifiers like nickel and cobalt can lead to reductions in coke yield of up to 60%. Additionally, innovative approaches, such as incorporating core-shell zeolite structures and integrating redox metal oxides, demonstrated promising outcomes in preserving catalyst stability. Furthermore, regeneration methods like thermal treatment, chemical washing, and steaming showed considerable efficacy in removing coke, with efficiencies reaching up to 80%. Moreover, deactivated zeolites displayed remarkable versatility, exhibiting heavy metal removal rates exceeding 90% in environmental remediation applications and contributing to improvements in durability and permeability in construction materials. Despite these significant findings, our study has several limitations. First, the long-term stability of modified and regenerated zeolites under real-world operational conditions needs further investigation. Second, the economic feasibility of implementing these advanced modifications and regeneration methods at an industrial scale was not thoroughly evaluated. Finally, the environmental impact of the regeneration processes themselves warrants deeper exploration. Future research should focus on addressing these limitations by conducting extended field trials, comprehensive cost-benefit analyses, and environmental impact assessments. Additionally, exploring new metal modifiers, advanced regeneration techniques, and hybrid catalyst systems could further enhance the performance and sustainability of zeolite catalysts in biomass gasification. These findings highlight the potential of zeolite catalysts in sustainable biomass gasification processes and underscore the importance of ongoing research to optimize these strategies across diverse operational conditions, thereby advancing catalyst utilization and environmental sustainability.

ACKNOWLEDGEMENT

We express our sincere gratitude to the Rector of Universitas Sebelas Maret for their generous support in the form of funding grants (PKPTDN, Mandatory, PUT, and PTUPT) provided from 2021 to 2024.

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