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Review Paper

Transitioning from hydrogen to methane in biorefineries: A sustainable route to clean energy and chemicals

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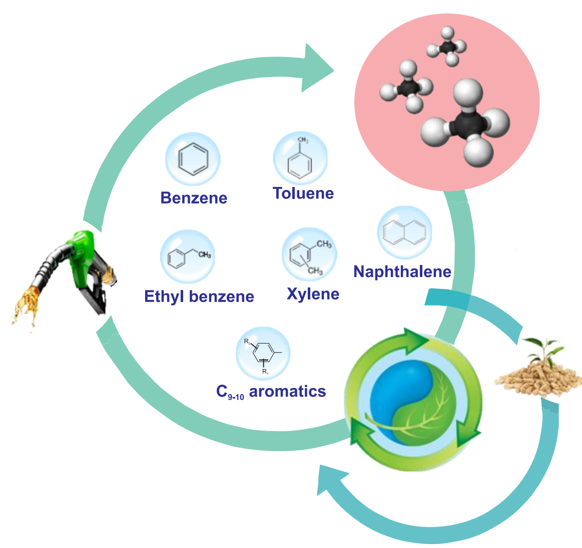
HIGHLIGHTS

- Methanotreating presents a promising alternative to traditional hydrotreating for deoxygenation.
- Methanotreating enhances biomass-derived bio-oil quality, improving fuel and chemical production.
- Methanotreating offers an innovative pathway to reduce environmental impacts and mitigate climate change.

GRAPHICAL ABSTRACT



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ABSTRACT

This review discusses the sustainable transformation of low-quality hydrocarbon fuels, such as biomass-derived bio-oil, into valuable chemicals and clean fuels by introducing the concept of "methanotreating" that uses methane as a hydrogen source for the deoxygenation of bio-oils, thereby addressing environmental concerns associated with conventional hydrogen production. We explore the challenges of methane activation and its potential in biomass upgrading, highlighting the importance of catalyst selection and composition. Methanotreating is a promising and sustainable method for producing high-quality fuels and chemicals, with a deoxygenation performance of over 95%. This present work calls for further research and development in catalyst design and application to advance this innovative approach toward a greener and more efficient energy future.

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Contents

Abbreviations

UNFCC	United Nations Framework Convention on Climate Change
CO_2	Carbon dioxide
ASTM	American Society for Testing and Materials
BTEX	Benzene, toluene, ethylbenzene, and xylene
MDA	Methane dehydroaromatization
CH_4	Methane
H_2	Hydrogen
CO	Carbon monoxide
H/C ratio	Hydrogen to carbon ratio
Pt/Mordenite	Platinum on Mordenite catalyst
Zn	Zinc
Ga	Gallium
Ag	Silver

1. Introduction

In a world addressing the urgent imperative to restrict global temperature increases to just 1.5°C compared to pre-industrial times, the focus has shifted to the sustainable management of both fossil fuels and alternative energy sources (UNFCC, 2015). Despite their abundance, fossil fuels are increasingly recognized as precarious contributors to the ongoing climate crisis (Welsby et al., 2021). Hence, the burden falls on fossil-based oil producers to reevaluate their role in the quest for a more sustainable energy future. Traditional uses of fossil fuels, such as gasoline for automotive transport, are being challenged by an urgent call for responsible utilization. This paradigm shift beckons to explore innovative strategies that not only reduce carbon emissions but also harness the inherent value of these finite resources (Sandaka and Kumar, 2023).

One promising avenue for addressing the aforementioned challenge is the valorization of low-quality hydrocarbon fuels derived from carbon dioxide (CO_2) (Wei et al., 2017; Garba et al., 2021). Innovative approaches can transform such feedstocks into valuable chemical precursors for the thriving chemical industry. Diverging these hydrocarbons from the conventional path of being upgraded into high-octane fuels could open the door to a more economically viable and environmentally friendly route involving their conversion into high-value chemicals. The conversion of low-quality fossil fuel-derived hydrocarbons into valuable chemicals represents a crucial step toward a sustainable energy landscape. This approach reduces the environmental impact while simultaneously extracting maximum value from these resources.

As the exploration of responsible utilization of fossil-based hydrocarbons progresses, there is a parallel need to seek alternative energy sources, particularly for applications like automotive road transport. One prevailing approach to achieving this transition involves the utilization of biomass, which is recognized as a sustainable and renewable resource. Biomass, typically subjected to pyrolysis, results in the production of bio-oil characterized by its low quality and rich oxygenate content (Wang et al., 2022). To transform this bio-oil into a suitable fuel, it must undergo hydrotreatment, a critical step often conducted under high-pressure hydrogen (Zhang et al., 2021). Hydrogen plays a pivotal role in facilitating the deoxygenation and saturation reactions necessary for refining bio-oil (Rogers and Zheng, 2016). A key advantage of biomass-derived bio-oil is its carbon-neutral potential, attributed to the utilization of plants in the initial biomass production process, effectively offsetting the carbon emissions associated with its combustion (Srivastava et al., 2021). However, what often remains obscured in the background is the environmentally unfriendly and carbon-intensive hydrogen production process.

Hydrogen, an essential element in the hydrotreatment process, is primarily generated through methods like steam methane reforming, which is responsible for a significant portion of global hydrogen production and the emission of substantial amounts of CO_2 into the atmosphere (Oni et al., 2022). In this context, a critical question arises: Is there a more sustainable and environmentally friendly means of producing hydrogen, particularly for bio-oil hydrotreatment, that aligns with the imperative of carbon neutrality? In light of this question, the present work introduces a forward-thinking approach to address the sustainability problem of hydrotreatment in the biomass-derived bio-oil refining process. The term "methanotreating" centers on directly utilizing methane as an alternative hydrogen source for deoxygenating bio-oils. Harnessing methane's potential, the aim is to transform the hydrotreatment process, thereby reducing its environmental impact and supporting the transition towards a greener, more sustainable energy future. The network visualization map representing the most frequently used keywords in methane-assisted biomass upgrading is illustrated in **Figure 1**.

This critical review aims to delve into the ability of methanotreating to transform biomass-derived bio-oil into clean, carbon-neutral fuels, thereby addressing the environmental concerns associated with using hydrogen produced by conventional production methods. The comparison of the present review with previously published reviews is provided in **Table 1**.

2. Hydrotreating

Biomass is renewable, which addresses the issue of resource depletion, and has a lower carbon footprint, contributing to the reduction of greenhouse gas emissions and other pollutants (Sanchez et al., 2015). Moreover, biomass can be locally sourced, reducing reliance on export energy supplies and transportation requirements. One key aspect contributing to the viability of biomass as an energy source is its energy efficiency, offering greater returns on energy units compared to fossil fuels (Qu et al., 2021).

Converting biomass through pyrolysis into a suitable fuel alternative involves a series of intricate steps, with hydrotreating playing a pivotal role in addressing some of the unique challenges associated with bio-oil production (Doukeh et al., 2021). Bio-oil, a key product derived from biomass, contains significant oxygen levels and various oxygen functional groups, including carboxylic acids, ketones, aldehydes, furans, alcohols, esters, and ethers. The presence of oxygen in bio-oil leads to a lower energy density, high acidity, and thermochemical instability, rendering it unsuitable as a fuel. Therefore, effective hydrotreating is essential to reduce the oxygen content, making bio-oil suitable for use (Yang et al., 2023).

Hydrotreating of bio-oil involves the removal of oxygen functional groups through various mechanisms (Gandarias and Arias, 2013). This process is complex due to the diverse nature of these functional groups and their different responses to deoxygenation. Hydrogen is a critical component in hydrotreating, as it plays a central role in decarbonylation, decarboxylation, and the saturation of unsaturated bonds in the oil, which can form coke and deactivate catalysts (Rogers and Zheng, 2016). Additionally, syngas, a mixture of hydrogen and carbon monoxide (CO),

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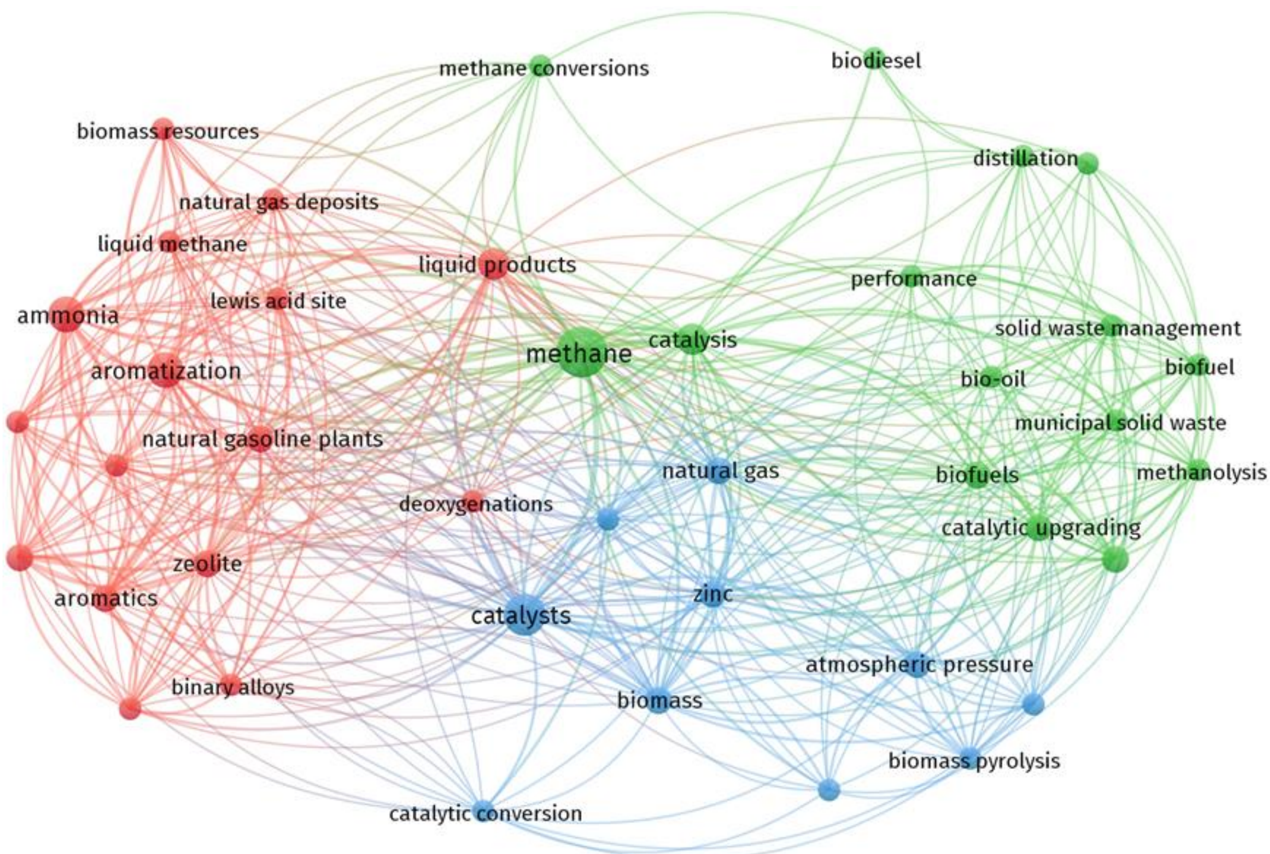

Fig. 1. Network visualizaton map of keywords used in methanotreating of biomass.

Table 1.
Comparison of coverage of this review with previously published articles on methanotreating.

Reference	Comparative analysis	Practical implications	Challenges	Roadmap, pathways
Wang et al. (2019b)	√	√	√	-
Song et al. (2022)	√	-	√	-
This review	√	√	√	√

can be used directly in hydrotreating, bypassing the need for a separate water-gas-shift reaction and facilitating integrated processes (Sircar and Golden, 2000). Moreover, the challenges in hydrotreating biomass-based bio-oil arise from the diversity of oxygen-containing species and their distinct reactivity patterns. These challenges include the removal of hydroxyl groups bound to aromatic rings and the preservation of desirable functional groups, such as furan rings (Pang and Medlin, 2011). Monometallic catalysts, such as nickel and noble metals, are often unsuitable for retaining these functionalities (Sitthisa and Resasco, 2011). Bimetallic catalysts, on the other hand, can show promise in achieving selectivity toward desired products (Sun et al., 2013). The use of hydrogen and syngas for hydrotreating bio-oils holds great promise, but removing specific oxygen functional groups, such as hydroxyl groups and phenol derivatives, needs further research.

3. Methane activation

Methane, the primary component of natural gas, has become a focal point for the petrochemical industry due to various factors, such as dwindling easily accessible oil reserves and the abundant reserves of natural gas, especially shale gas and hydrates (Kerr, 2010; Martín, 2016). As a result, there is a growing interest in converting methane into valuable fuels and chemical precursors.

However, the current industrial practice involves indirect methods that are costly, energy-intensive, and reliant on multi-step processes. The main approach is the conversion of methane into syngas, followed by additional steps requiring oxygen input to remove CO species, ultimately leading to desired hydrocarbon production. The complexity of indirect processes, including Fischer Tropsch synthesis and methanol to gasoline, both derived from syngas through steam reforming, is well-established but burdened by high energy requirements, resulting in unselective products and catalyst deactivation due to coke formation (Wilhelm et al., 2001; Dry, 2002). However, the emergence of direct oxidative routes, like the oxidative coupling of methane and the nonoxidative system, offers a promising alternative (Ortiz-Bravo et al., 2021). While not yet commercially viable, these systems have attracted substantial research attention as they promise to reduce costs and improve energy efficiency by directly utilizing methane. Conversely, methane activation presents a significant challenge due to its high bond energy (435 kJ/mol) (**Fig. 2**).

Methane dehydroaromatization (MDA) reaction, which yields benzene, requires a substantial input of energy ($\Delta G^0_{450°C}$ = 267 kJ/mol), necessitating high temperatures and catalysts (Xu et al., 2003). This process results in unselective products and catalyst deactivation through coke formation, necessitating frequent regeneration (Kosinov et al., 2019). Two mechanisms have been considered for the MDA reaction system, such as the bifunctional mechanism and the hydrocarbon pool mechanism. The bifunctional mechanism involves C-H bond activation and C-C coupling at active sites like molybdenum carbides (Razdan et al., 2020). Conversely, the hydrocarbon pool mechanism proposes that Brønsted acid sites assist

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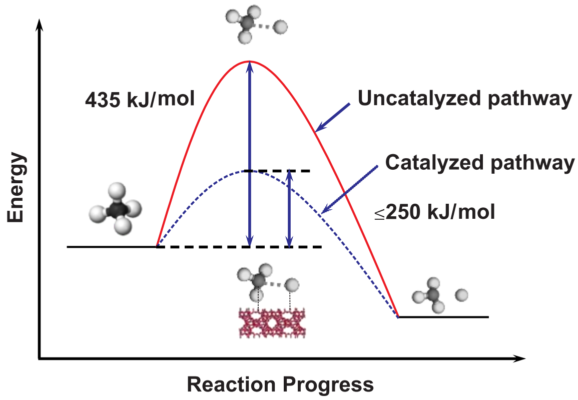

Fig. 2. Representation of methane activation under uncatalyzed and catalyzed pathways.

molybdenum species in zeolite structures, affecting their shape-selectivity toward benzene by confining and transforming hydrocarbon intermediates. The representation of the bifunctional and hydrocarbon pool mechanisms is provided in **Figure 3**. One approach to overcoming the high activation energy of methane is cross-coupling with higher carbon number hydrocarbons, allowing methane activation at lower temperatures (Choudhary et al., 1997). Co-feeding methane with feedstocks, such as naphtha, has shown promise (Jarvis et al., 2018).

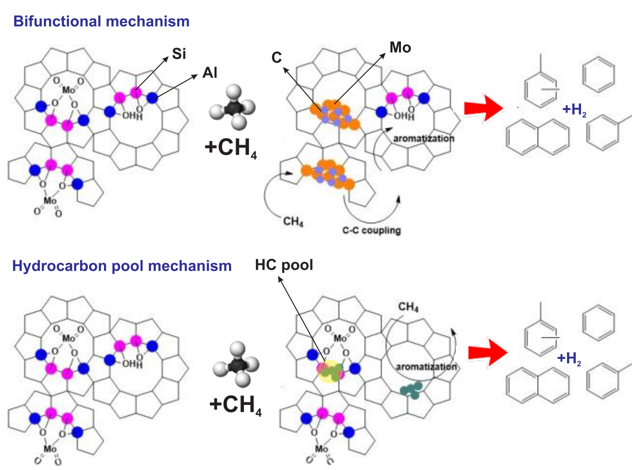

Fig. 3. Mechanisms for the methane dehydroaromatization (MDA) reaction.

3.1. Cross-coupling of methane with light naphtha

Light naphtha, predominantly consisting of C_5 and C_6 paraffin, serves as a simpler fossil fuel feedstock. Isomerization of these paraffins is critical for increasing the octane number of gasoline fuel (Fan et al., 2004). Branched paraffins, like i-pentane and i-hexane, are particularly valuable due to their higher research octane numbers and environmental friendliness than normal paraffins (Ghosh et al., 2006). Bifunctional catalysts, including Pt/Mordenite, have been found effective for isomerization by facilitating dehydrogenation, protonation, rearrangement, β-scission, and hydrogenation reactions (Arribas and Martínez, 2001).

Apart from isomerization, the upgrading of light naphtha can also yield valuable products like benzene, toluene, ethylbenzene, and xylenes (BTEX), which enhance octane numbers in fuels and find applications in the chemical industry, such as the synthesis of pharmaceuticals, cosmetics, inks, and rubber products. The aromatization of light naphtha results in the production of BTEX and hydrogen as a by-product (Ellouh et al., 2020).

3.2. Cross-coupling of methane with heavy naphtha

Heavy naphtha fractions, containing a mix of paraffins, naphthenes, aromatics, and olefins, are usually less desirable due to their environmental impact and economic viability concerns (Saxena et al., 2013). Hydrocracking is required to reduce the larger carbon number components in these fractions, and this process also demands hydrogen. HZSM-5 is a preferred catalyst for cracking heavy naphtha hydrocarbons, primarily through two mechanistic pathways: protolytic cracking and hydride transfer (Kotrel et al., 2000).

4. Methanotreating for the production of fuels and chemicals

Methanotreating involves the utilization of methane as a co-feed alongside various organic compounds to upgrade and convert them into valuable fuels and chemicals (Wang et al., 2019b; Peng et al., 2020). While methane is known for its high carbon-to-hydrogen ratio, making it a potential alternative to hydrogen and syngas, its stable molecular structure presents challenges for participation in chemical reactions at lower temperatures. However, the abundance of methane in natural and shale gas and its low cost make it an attractive option for deoxygenation processes in biofuel production.

Methanotreating is particularly relevant for converting oxygen-containing compounds in bio-oil and other biomass feedstocks. These oxygen moieties, such as carbonyl groups (in ketones and aldehydes) and carboxylic compounds, can impart undesirable properties like poor stability and high viscosity to biofuels (Shun et al., 2013). Methane, when employed as a co-feed, offers a unique opportunity to remove these oxygen functionalities, thus improving the quality and properties of biofuels and chemical products. Several studies have explored the methanotreating process with biomass-derived model compounds to better understand the reaction mechanisms (**Fig. 4**). The results indicate that the presence of methane improved the selectivity towards BTEX, resulting in a more desirable product composition.

Studies demonstrate the potential of modified zeolite catalysts for transforming these compounds into valuable products for applications in the chemical and fuel industries. It was observed that the addition of metal species in the catalyst enhanced methane conversion and activation (**Fig. 5**). The choice of catalyst composition plays a crucial role in product distribution. Transition metals like Zn and Ga, in combination with zeolite, facilitate methane activation, deoxygenation, and aromatization reactions (Luzgin et al., 2010; Gabrienko et al., 2017). Chromium species in zeolite enhance deoxygenation reactions and CO_2 production (Aishah et al., 2003; Mimura et al., 2006; Peng et al., 2019). Silver (Ag) in zeolite-based catalysts has a dual role, activating methane and improving the H/C atomic ratio and oil yield, but it can lead to overcracking. Surface modification with lanthanides, phosphorus, or silicon can control cracking activity, enhancing bio-oil quality and yield (Ding et al., 2002; Yaripour et al., 2005; Jin et al., 2007; Li et al., 2010).

In summary, the liquid product yield can be increased by methanotreating, with a significant boost in BTEX selectivity, demonstrating the importance of methane in the methanotreating process and suggesting its potential as a co-reactant for biofuel and chemical production. Methane, when used in conjunction with appropriate catalysts, enhances the activation of organic compounds, facilitating the production of valuable fuels and chemicals. It acts as a hydrogen or methyl donor, aiding in the conversion of various functional groups present in the feedstock molecules. This unique approach not only offers economic advantages but also addresses environmental concerns by reducing the oxygen content in biofuels. Overall, methanotreating holds promise as a sustainable and efficient method for producing high-quality fuels and chemicals from biomass feedstocks, utilizing the abundance of methane resources available worldwide.

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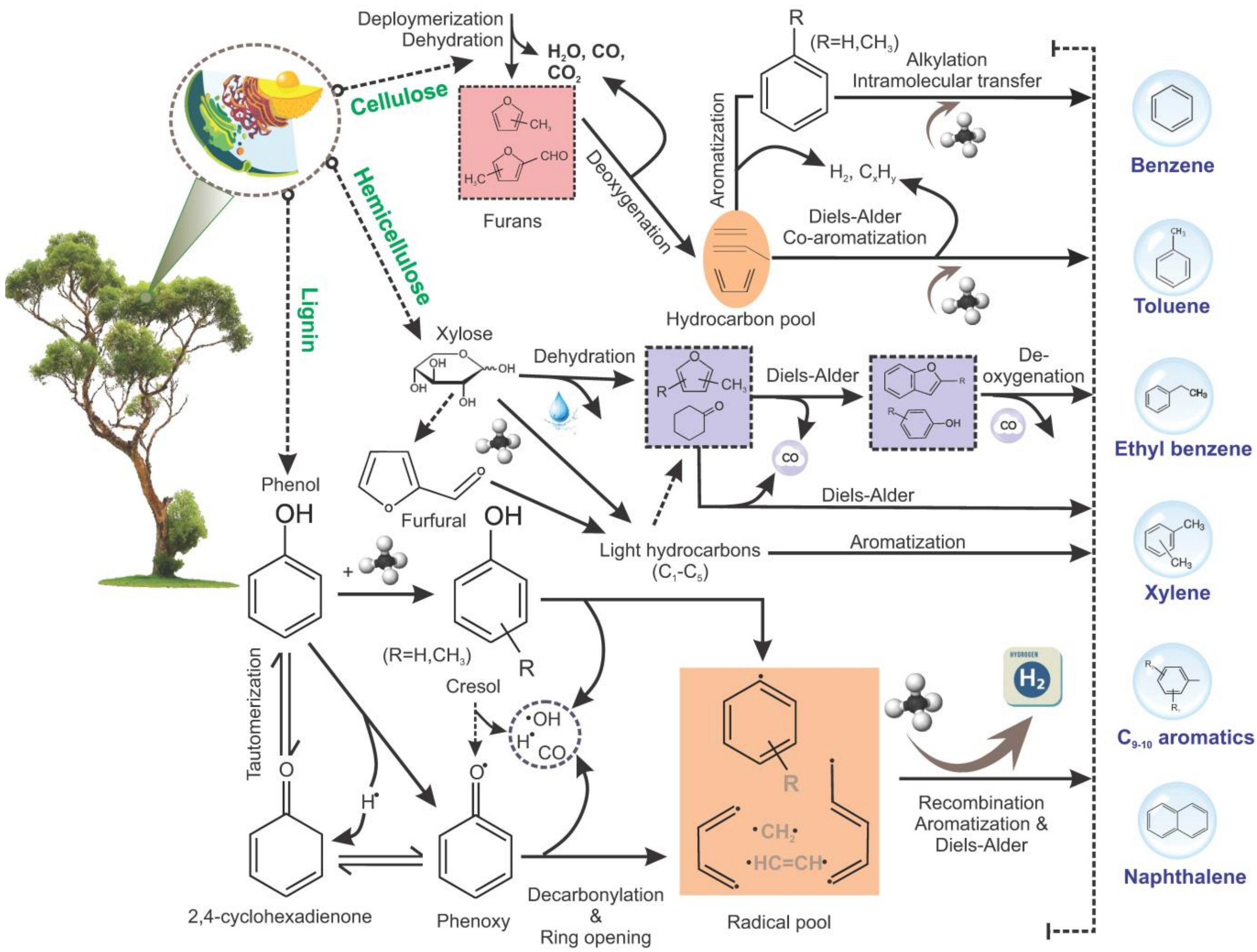

Fig. 4. The possible reaction pathways involved in converting cellulose, hemicellulose, and lignin from biomass to aromatics under a methane environment. Redrawn based on Peng et al. (2019) and Wang et al. (2018a and b, 2019a).

5. Practical implications of this review

As we strive to combat climate change, it is clear that moving away from fossil fuels is imperative. But the journey does not stop at abandonment; it also involves finding innovative ways to maximize the remaining fossil fuel resources and seeking alternative fuels for combustion engines. One promising route discussed herein is the methanotreating of bio-oil into a sustainable fuel source by developing catalysts that can directly activate methane during the process, a move that avoids environmentally harmful hydrogen production and capitalizes on an abundant natural resource. Thus, there is a need to develop a range of catalysts tailored to specific goals. These catalysts should be tested on various model compounds to understand their mechanisms, and then they need to be applied to real-world feedstocks to assess their feasibility. Furthermore, researchers need to reshape the landscape of catalysis and develop efficient catalytic methane-assisted biomass upgrading (**Fig. 6**). One such avenue involves exploring diverse catalyst support structures, each with varying pore morphologies. This innovative approach enables the fine-tuning of product selectivity, holding the potential to benefit a wide range of industrial processes. Furthermore, a deeper understanding of the anti-sintering mechanisms in catalysts promises to shed light on catalyst stability beyond the role of sulfur in noble metal affinity. Additionally, the intriguing concept of memory effects in catalyst synthesis opens up exciting possibilities where further investigations can uncover synthesis-assisting species that enhance catalytic performance.

Expanding the scope of research beyond alcohols, scientists can investigate other oxygenate compounds present in bio-oils, broadening the potential applications of these catalytic processes. To make these innovations more practical and impactful, a comprehensive techno-economic analysis is necessary, quantifying the economic and environmental benefits of these technologies. Moreover, investigating more effective systems for methane activation, such as non-thermal plasma, holds the promise of streamlining processes and potentially eliminating the need for a dedicated methane activation function on the catalyst. Together, these research avenues offer a compelling vision for the future of catalysis, with the potential to revolutionize various industries and enhance the sustainability of chemical processes. These endeavors promise to revolutionize the biofuels industry, offering improved sustainability and economic viability.

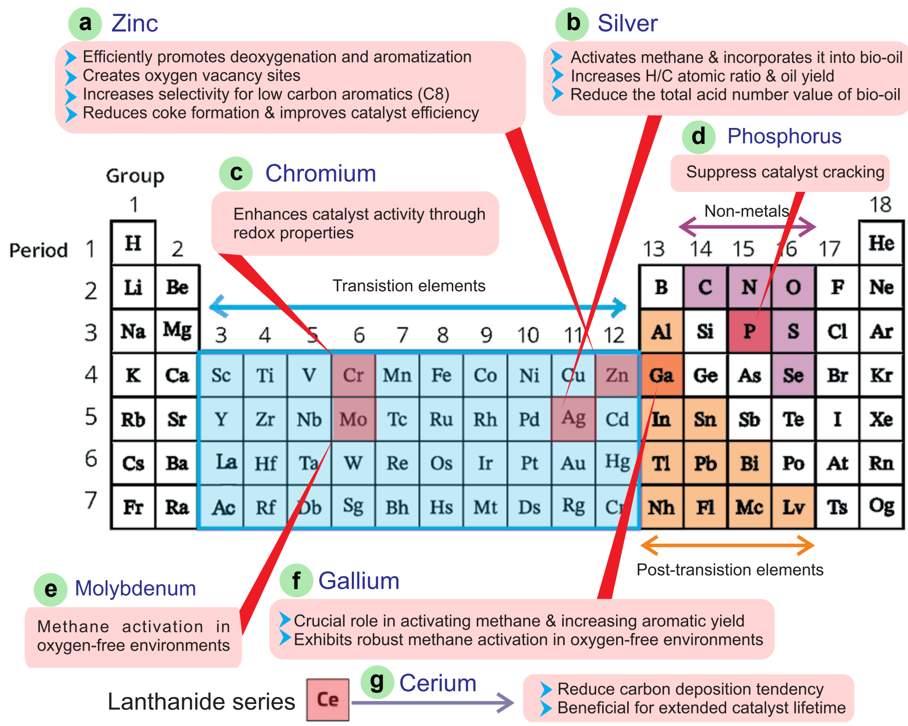

Fig. 5. The Role of metal loading in zeolite catalysts to enhance deoxygenation, aromatization, and methane activation in biomass upgrading: **(a)** Zinc (He and Song, 2017), **(b)** Silver (He and Song, 2014), **(c)** Chromium (Peng et al., 2019), **(d)** Phosphorus (Yaripour et al., 2005; Li et al., 2010), **(e)** Molybdenum (Gunawardena and Fernando, 2017), **(f)** Gallium, and **(g)** Cerium (Jin et al., 2007).

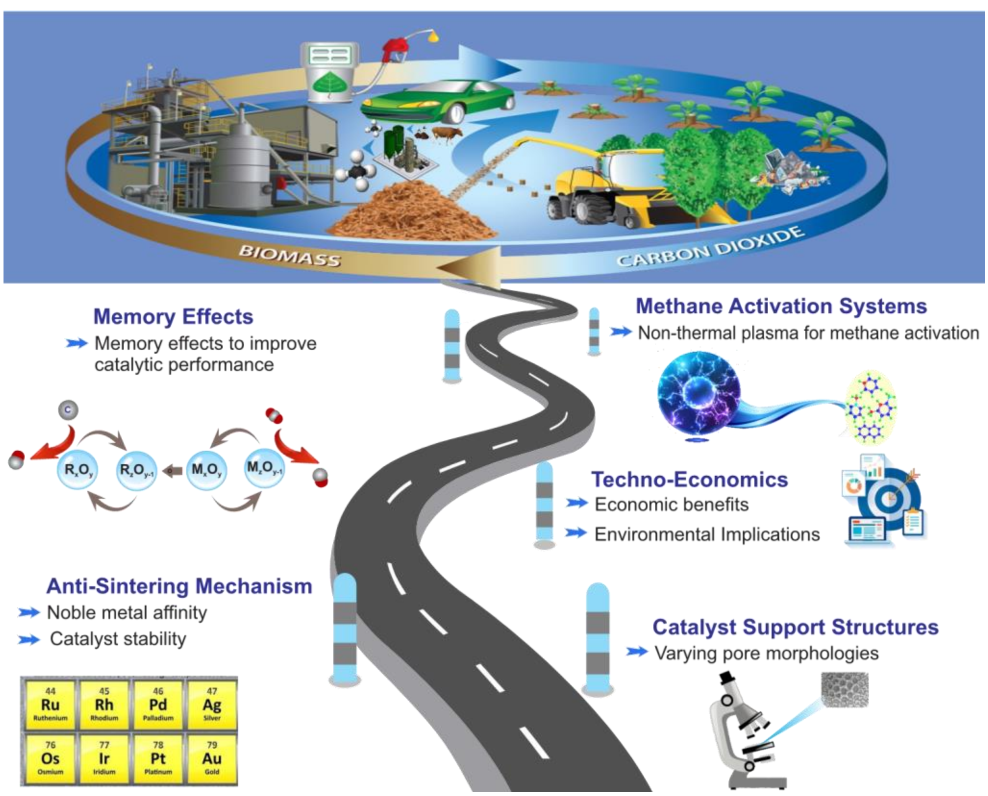

Fig. 6. Roadmap to advancing catalytic methane-assisted upgrading.

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6. Challenges and promises

The methanotreating process leverages methane as a co-feed for upgrading biomass-derived bio-oil, presenting challenges and exciting promises. Overcoming challenges such as efficiently activating methane, designing effective catalysts, ensuring economic viability, and successfully scaling up from laboratory experiments to industrial applications is crucial. However, the promises it holds are equally compelling. Methanotreating offers a sustainable and eco-friendly approach, resulting in higher product yields, reduced carbon footprints, and the potential to convert various oxygenate compounds in bio-oils into valuable fuels and chemicals. Furthermore, it aligns with the global push for cleaner and renewable energy sources, and with further research and development, this field has the potential to revolutionize the energy industry and play a central role in addressing the pressing challenges of climate change.

7. Conclusions and prospects

Methanotreating, as discussed in this review, represents a forward-thinking approach to the environmental and economic challenges associated with biomass-derived bio-oil conversion. By harnessing the unique capabilities of methane as a co-feed for biomass upgrading, we can achieve not only higher liquid product yields but also a significant increase in the selectivity of valuable compounds. This innovative approach offers the potential to revolutionize the biofuels industry, providing a pathway to more sustainable and economically viable fuel and chemical production. To realize the full potential of methanotreating, further research and development are essential, focusing on catalyst design, memory effects in synthesis, techno-economic assessments, and more efficient methane-assisted biomass upgrading. Exploring how methanotreating can be integrated with renewable energy sources, such as solar or wind power, can make the process even more sustainable. Research should also focus on scaling the methanotreating process from a laboratory to an industrial scale. In this way, we can move closer to a future where sustainable and clean energy sources play a central role in addressing the global climate challenge while efficiently utilizing abundant methane resources.

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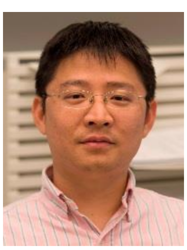

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