Advancing biomass valorization with zeolite catalysts: Focus on oxidative transformations

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ARTICLE INFO

ABSTRACT

The catalytic upgrading of biomass into high-value platform chemicals offers a promising alternative to conventional fossil-based processes, driven by the need for safer, environmentally friendly, and energy-efficient technologies. Zeolites, with their unique structural properties, high surface area, and tunable active sites, are widely used in biomass conversion processes. Metal-modified zeolites, engineered with specific functionalities, exhibit exceptional catalytic activity in key reactions such as glucose isomerization, HMF hydrogenation, fatty acid esterification, and hydrodeoxygenation of phenolics and vegetable oils. This review focuses on the role of zeolites in oxidative biomass transformations, emphasizing their effectiveness in a range of reactions, including functional group oxidation, C=C epoxidation, and C-C bond cleavage. We examine the critical features of zeolites -such as porosity, acidity, and metal incorporation- that influence their catalytic performance, especially in terms of selectivity and diffusion limitations. Special attention is given to the oxidative conversion of bio-derived molecules like glucose, HMF and fatty acids into bio-derived acids and epoxides through sustainable, "green" routes. The review concludes by addressing current challenges and exploring future directions for optimizing zeolite-based catalysts for biomass oxidative transformations and the broader bio-based chemical industry.

1. Introduction

Most global energy systems rely on fossil fuels, which, despite their benefits, pose significant problems such as environmental damage, scarcity, supply risks, and price instability. As non-renewable resources, their long-term availability is uncertain, and thus, more sustainable solutions for the production of fuels and chemicals have to be found [1]. In this context, biomass can be distinguished as the only current sustainable source of organic carbon for the chemical industry [2,3]. Biomass consists mainly of lignocellulosic and related materials (70–75 % of biomass), oils and fatty acids (15–20 % of biomass) and proteins (less than 5 % of biomass) [4]. Among them, lignocellulose and vegetable oils have attracted interest during the last decades due to their broad worldwide availability and their potential for producing renewable fuels and chemicals [5]. The three main components of lignocellulosic biomass are lignin (15–20 %), hemicellulose (25–35 %) and cellulose (40–50 %) [6,7]. Lignin is a 3-D macromolecule consisting mainly of three phenolic building units: sinaphyl alcohol, coniferyl alcohol, and p-coumaryl alcohol. These monomers are linked via C-O and C-C bonds, thus creating highly complex methoxylated phenylpropanoid units [8,9]. After its isolation from the other biomass components, lignin can be used for the production of polymers, such as epoxy resins, or be converted into valuable chemicals such as phenolics, aromatics or carbon materials (e.g., biochar) [10–13]. In the plant structure, lignin surrounds hemicellulose and cellulose, providing rigidity and resistance [14]. Hemicellulose polymer consists of pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose), and sugar acids [15,16]. Likewise, hemicellulose can be used either directly in the production of materials (films, coatings, medical biodegradable materials, etc.) or be converted in a wide range of important chemicals such as xylitol, ethanol, furfural (FUR), 5-hydromethoxyfurfural (HMF) and more [17,18]. Cellulose is a crystalline polymer of glucose units linked by the β-glycosidic bonds, the structural modifications of which can lead to valuable products ranging from biomedical to electronics, as well as coatings, and textiles [19,20]. Important compounds, such as HMF can be derived also from glucose, that are further converted to a plethora of high value chemicals such as formic acid (FA), levulinic acid (LA), 2,5-furandicarboxylic acid (FDCA), 2,5-diformylfuran (DFF), as well as

C7-C15 alkanes after aldol condensation and hydrogenation/hydrodeoxygenation [21].

Vegetable oils (VOs) are historically one of the most important renewable feedstocks of the chemical industry as they are biodegradable, have low ecotoxicity and high availability. From VOs such as sunflower, soybean, castor, and palm oils, a wide range of fuels and materials can be produced [22–26]. VOs consist mainly of triglycerides, which are esters composed of a glycerol part and three fatty acids. Fatty acids can be saturated (e.g., palmitic acid, stearic acid), mono-unsaturated (e.g., oleic acid, palmitoleic acid) or polyunsaturated (e.g., linoleic acid, linolenic acid) [27,28]. Glycerol, obtained from the transesterification process or the hydrolysis of VOs, can be used for the production of biofuels (e.g., hydrogen and syngas, ethanol and methanol), fuel additives and polymer precursors (e.g., olefins, acrolein, propanediols) [29]. Fatty acids can also be valorized through various processes such as hydrogenation, hydrodeoxygenation, transesterification, metathesis, epoxidation, pyrolysis to industrially important materials such as lubricants, biofuels, bio-composites, and chemicals [30–37]. The use of catalysts is crucial for these reactions as well as for lignocellulose conversion. Catalysts can improve reaction rates and product selectivity and are classified into three main categories: enzymes, homogeneous and heterogeneous. Compared to the other two categories, heterogeneous catalysts have attracted the interest for industrial applications due to their chemical and thermal stability as well as easy separation from the reactant/product mixture and recyclability [38–40]. However, biomass catalytic valorization in presence of heterogeneous catalysts is accompanied from some challenges. Firstly, biomass is chemically diverse, often containing oxygen-rich functional groups that require selective transformations [41–43]. Low selectivity is often an issue with undesired side reactions, e.g., over-oxidation or epoxy hydrolysis, leading to low yields of target products [44,45]. Another challenge is that biomass may also contain impurities, like ash or metals, which complicate the catalytic processes. These impurities, together with other byproducts (e.g., water, acids, coke) can deactivate catalysts [46,47]. In addition, often encountered issue is the bulkiness of biomass molecules (e.g., lignin-derived oligomers) which struggle to access active sites in microporous catalysts [48]. Addressing these issues through efficient catalyst development may make biomass a viable resource for commodity and fine chemicals that could compete with current fossil-based strategies.

One of the most important classes of heterogenous catalysts that are widely used in industry is zeolites. Generally, zeolites are crystalline aluminosilicate materials, with porous structure, high surface area, acidic-basic surface properties and high thermal stability that have found application in catalysis, adsorption-separation, and ion exchange [49–51]. Their unique properties make them highly effective in overcoming many challenges associated with biomass conversion. An overview of the role of zeolites in biomass valorization reactions is presented in Fig. 1. Significant progress has been made in recent years to develop novel zeolite catalysts with tailored characteristics, such as hierarchical porosity for enhanced accessibility, precise control over acid site properties (including concentration, type, and strength), the creation of basic sites, and the incorporation of guest metals to produce multifunctional materials. Compared to other supports, such as metal oxides and carbonaceous materials, zeolites have well-defined pore structures that enable size-selective catalysis – a crucial advantage when upgrading biomass-derived molecules with varying sizes. [52]. Moreover, their acid/basic properties can also promote reactions (e.g. dehydration, isomerization) in situ, whereas other supports often require additional acid/base additives [53,54]. This surface chemistry of zeolites is also beneficial for metal deposition, as their stable structure and strong binding of active sites generally lead to less metal leaching and thus lower deactivation rates [55].

Numerous reviews are published, highlighting the role of zeolites in producing biofuels and bio-based chemicals [56–59]. While some reviews cover the entire scope of this field, others focus on specific aspects, such as the use of zeolites to catalyze lignocellulosic biomass pyrolysis [60,61], bio-oil and phenolics upgrading through deoxygenation and catalytic cracking [62–64] as well as the conversion of specific biomass derived compounds to targeted products (e.g., glucose to furans or HMF production) [65,66]. Among the catalytic processes used for biomass upgrading, oxidative transformations for producing acids and epoxides have gained significant interest, as these chemicals can act as building blocks for a renewable chemical and polymer industry. To the best of our knowledge, despite the numerous review articles related to zeolite-catalyzed reactions for biomass upgrading, oxidative transformations are barely discussed.

This review article aims to present a comprehensive overview of the role of zeolites in a representative range of biomass valorization reactions, with particular focus on the oxidative transformations via greener and more sustainable pathways. Specifically, our main focus is to review oxidative reactions (oxidation of functional groups, epoxidation of double bonds, and oxidative C–C bond cleavage) in the context of biomass, more broadly defined. By covering various feedstocks (sugars,
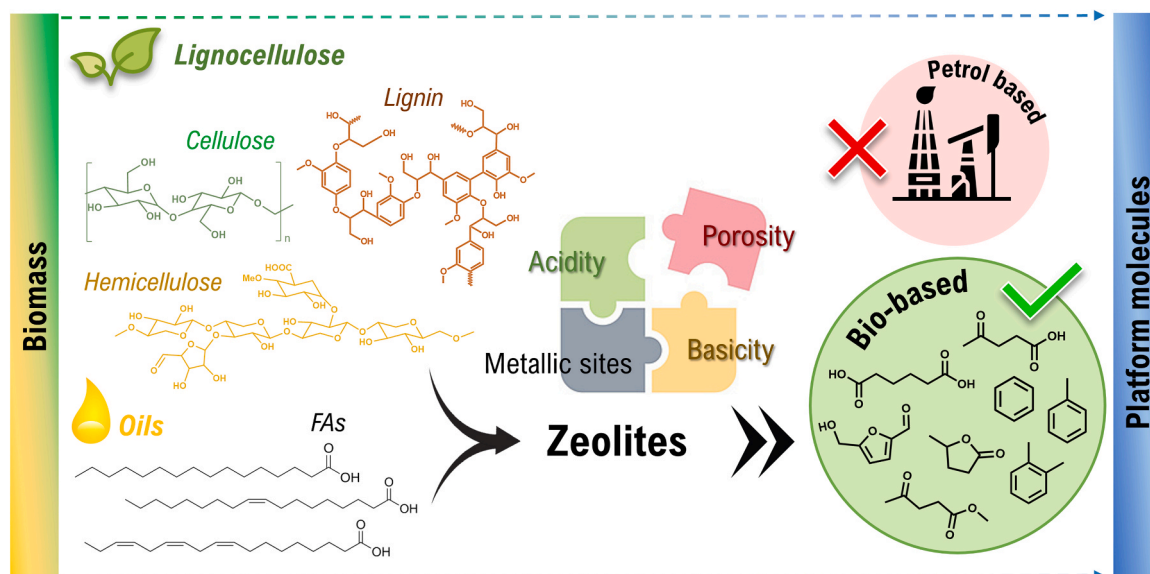

Fig. 1. A schematic representation of the role of zeolite properties in the production of bio-based platform chemicals.

platform chemicals like HMF, lignin-derived aromatics, fatty acids/oils), we want to provide a unified view of how zeolites perform in oxidation reactions across biomass sub-fields. The article begins by examining the zeolite core properties, which often influence the types of reactions which they can effectively catalyze. Following this, a concise overview of biomass transformations involving zeolite catalysts, emphasizing oxidative processes is presented. The focus is centered on the oxidative reactions of specific functional groups and bonds, highlighting the distinctive zeolite properties and active sites required for these reactions. The intrinsic microporosity of the zeolites, while beneficial for many catalytic processes, can also pose limitations, particularly when it comes to the diffusion of large bio-molecules. To address this challenge, a discussion about the use of hierarchically structured zeolites, which feature secondary porosity (mesopores), as a potential strategy for enhancing active sites accessibility is also delivered. Through this overview, we aim to elucidate the relationship between the chemistry of various oxidative transformations and the specific properties required for effective zeolite-based catalysts. The review concludes with a discussion of current challenges and future perspectives.

2. Zeolite's structure, properties, and modifications

Zeolites are crystalline aluminosilicate materials typically consisting of SiO_4 and AlO_4 tetrahedra linked by bridging oxygen atoms, forming secondary building units (SBUs). The SBUs, as shown in Fig. 2, are then organized in more complex structures (e.g., sodalite cages, hexagonal prisms) and finally create 3D frameworks [67–69]. Zeolite frameworks exhibit different sizes, shapes, and connectivity of channels, with pore sizes can range from 0.30 to 0.45 nm for eight-membered ring pores, to 0.8 nm for 12 or 14-membered ring pores [70,71]. Zeolites framework topologies have been classified by the International Zeolite Association (IZA), with a unique three-letter code for each topology [72]. Among the most widely used zeolites in the chemical and petrochemical industries are ZSM-5 (MFI topology), zeolites Y and X (FAU topology), Mordenite (MOR topology), Beta (BEA topology), Chabazite (CHA topology), and Ferrierite (FER topology) [73]. Most of them have been used for the Fluid Catalytic Cracking (FCC) process as well as other reactions such as phenol hydroxylation, ethylbenzene alkylation and olefin epoxidation [74–76]. For the FFC process primarily USY zeolite is used, with this application constituting more than 95 % of the overall zeolite catalyst consumption worldwide. Propylene epoxidation towards propylene oxide formation is also an important process by BASF-Dow joint venture, which employs a zeolite of framework structure type MWW, modified with Ti and Zn, and is established for many years now. For industrial applications, zeolites are selected based on their specific characteristics regarding the structure, the morphology and the composition as well as the needs or limitations of the reaction [75].

While some zeolites occur naturally, most of the technical-grade zeolites are synthesized through methods such as hydrothermal synthesis (the most common approach), solvothermal synthesis in non-aqueous solvent medium, ionothermal synthesis in the absence of solvent, or microwave assisted conventional method [77]. In the zeolite framework, the replacement of the Si^{4+} cation in the tetrahedral position by Al^{3+} results in an excess of negative charge, which is usually compensated by inorganic cations or protons (e.g., Na^+, K^+, Mg^{2+}, NH^{4+}, H^+). When protons act as compensating cations, a hydroxyl group is formed between Si and Al atoms, Si-(OH)-Al, which catalytically behave as Brønsted acid site (BAS). For zeolites with a high Si/Al ratio, the thermal stability and hydrophobicity of zeolite structure tend to increase, while low-silicon zeolites are more hydrophilic and have increased ion exchange capacity [78,79]. In addition to Brønsted acid sites, zeolites are also characterized by Lewis acidity. Lewis acid sites (LAS) can be generated through the post-synthesis modifications such as steaming, calcination at high temperature, and acid or base leaching. These treatments lead to the hydrolysis of the framework Si-O-Al bonds, partial removal of aluminum, and the formation of 'extra-framework aluminum' (EFAl) species [80,81]. Alternatively, LAS can be generated by isomorphous substitution, where Al atoms in the zeolite framework are replaced by other tetravalent or pentavalent metal atoms, such as titanium, tin, zirconium, iron, vanadium and more [55,82,83]. These modifications enhance the catalytic properties of zeolites, broadening their applicability in various reactions.

2.1. Metal-modified zeolites

As already mentioned, in the zeolite framework Al atoms can be replaced with other metals via isomorphous substitution without any change in the topological structure, thus leading to the formation of metal-containing zeolite frameworks. The metals are fully coordinated with framework oxygen, forming Si-O-Metal linkages, and/or partially
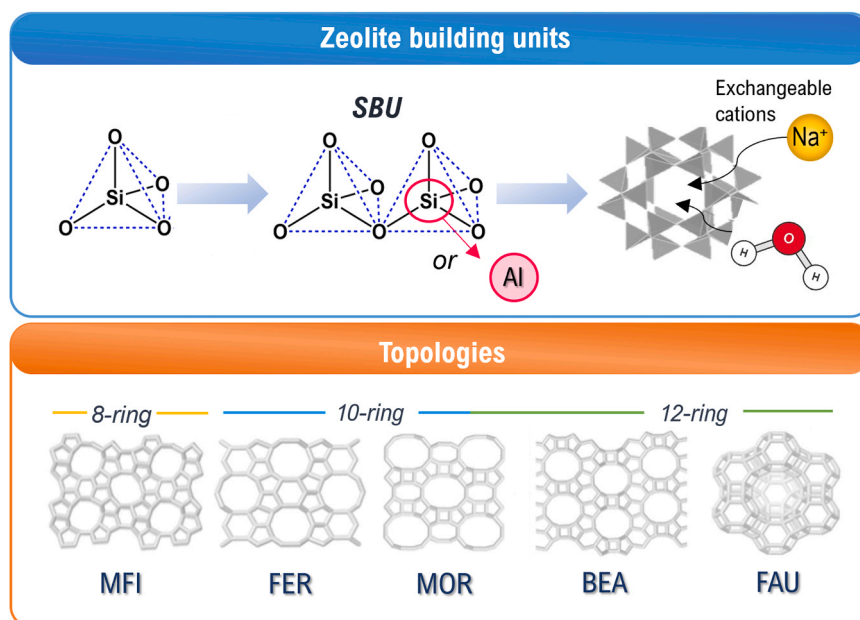

Fig. 2. Schematic representation of zeolite building units and main topologies.

dislodged containing both framework Si-O-Metal linkages and terminal Metal-OH groups. The most common procedure for the preparation of metal-containing zeolites is by adding metal salts or metal organics to the synthesis gel during the hydrothermal procedure. Other methods include the dry-gel conversion (DGC), demetalation−metalation and inter-zeolite transformation [55]. One of the most well-known metal modified frameworks is that of TS-1 catalyst (titanium-silicalite-1), with incorporated titanium into the pure silica MFI framework, which poses unique properties especially for oxidation reactions [84–86].

Except for framework metal species, extra-framework metal species that exist adjacent to the zeolite framework are also important for the catalytic transformations. These metallic sites are located on the zeolite's channels, or pores, due to electrostatic and van der Waals interactions, or chemical interactions between the metal sites and the framework. They can be in the form of metal single sites, metal clusters or nanoparticles [87–90]. Many transition metals, such as Cu, Co, and Fe can be introduced to the zeolite surface via ion-exchange and provide well-defined acidic and redox active sites [91–93]. Noble metals are also often supported on zeolites, providing valuable catalytic activity for a range of reactions, e.g., oxidation of volatile compounds on Pt/ZSM-5 [94]. For noble metals, due to their scarcity and high cost, the creation of highly dispersed metal active sites is very important as it can reduce the required metal amount while maintaining a high catalytic activity. Noble metal cations such as Pt, Pd, Rh, Ru, and have been successfully introduced into the extra-framework positions of zeolites, presenting great catalytic activity in isomerization, oxidation, hydrogenation and deoxygenation reactions [95–99]. Metal clusters, consisting of a few atoms, are confined within zeolite crystals in channels, cages, or intersectional voids, while metal nanoparticles (NPs), with larger sizes, are usually located either on the external surface of the zeolite or close to positions where there are structural defects [100]. Compared to other supports, zeolites are particularly effective at stabilizing metal nanoparticles, preventing leaching and sintering [101]. In Fig. 3, a schematic representation of the location of metal species in framework and extra-framework positions is provided. There are varying methods for the synthesis of zeolite-supported metals, with impregnation (dry or wet), ion-exchange and deposition-precipitation being the most commonly used [52].

2.2. Hierarchically structured zeolites

In the conversion of large substrates, mass transport limitations can negatively impact the reaction rate, as the majority of active metal sites in conventional zeolites are confined within their microporous (< 2 nm) structures [102]. For zeolites with larger crystal sizes in the micrometer range, the contribution of the external surface and the associated active sites is usually minimal. Decreasing the crystal size (e.g., zeolite nanocrystals of ≤200 nm) increases the share of the external surface area, which can improve both the catalytic activity and catalyst lifetime [103]. However, controlling the crystal size remains challenging, and separating small zeolite crystals from the reaction mixture by filtration is difficult due to their colloidal properties. To enhance accessibility to the active sites and reduce steric hindrance, alternative strategies include the synthesis of zeolitic materials that feature mesopores in addition to their typical micropores [104,105]. A schematic representation of the main hierarchical zeolite structures compared to conventional microporous zeolites is displayed in Fig. 4. Hierarchical zeolites have already found application in industrially relevant reactions such as: alcohol dehydration, catalytic cracking, benzene alkylation, methanol to hydrocarbons (MTH) and olefin hydro-isomerization [106–113].

Hierarchical zeolites can be prepared according to various synthesis procedures, with the most common methods being soft templating, hard templating, zeolitization of mesoporous silicates (e.g., MCM-41, SBA-15), desilication and dealumination [114]. In templating-based methods, hierarchy is created during the synthesis process by using templating materials that promote the formation of larger pores. Then the material is calcined at high temperatures in air to remove the template, leaving only the zeolitic framework. In soft templating, surfactants or block co-polymers are typically used to guide the formation of mesopores [115–117]. Hard templating involves the use of various types of carbon materials such as carbon nanotubes and carbon nanofibers to create the desired porous structure [118–122]. Less common templates are metal nanocrystals or nanoparticles [123,124], as well as other macro-templates, such as bacterial threads, natural sponges, and leaves of plants [125–127], offering an alternative route for hierarchical zeolite fabrication.

Mesoporous structures with amorphous walls, such as SBA-15 and MCM-41, can be transformed into crystalline zeolitic structures through a process known as zeolitization. This approach allows for the preparation of zeolite structures with intercrystalline mesopores, which can improve the accessibility of active sites and enhance catalytic performance. Two main procedures are typically used to achieve the crystallization: vapor phase transport (VPT) and steam assisted conversion (SAC). In VPT, both water and a structure-directing agent (SDA) are vaporized and interact with the initial material, promoting zeolite crystallization. In contrast, the SAC method involves only water in the liquid phase, while the SDA is contained in solid gel phase, guiding the formation of the zeolitic structure [128].

Another strategy to enhance the porosity of zeolite materials is through demetalation, a method that introduces additional porosity by selectively removing metal atoms from zeolite's framework. This can be achieved through dealumination or desilication procedures. Dealumination is a post-synthesis method that removes aluminum from the zeolite structure and can be achieved by steaming, acid leaching (e.g.,

Single metal sites in zeolite

Metal@zeolite

Framework metal sites   **Metal-exchanged**   **Metal-clusters**   **Metal-NPs**

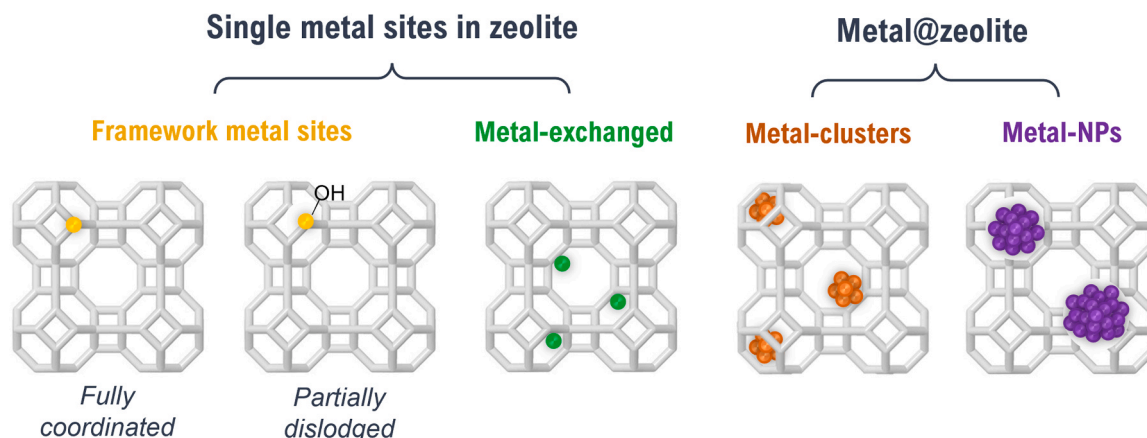*Fully coordinated*   *Partially dislodged*

Fig. 3. Schematic representation of the location of metal species in zeolites.

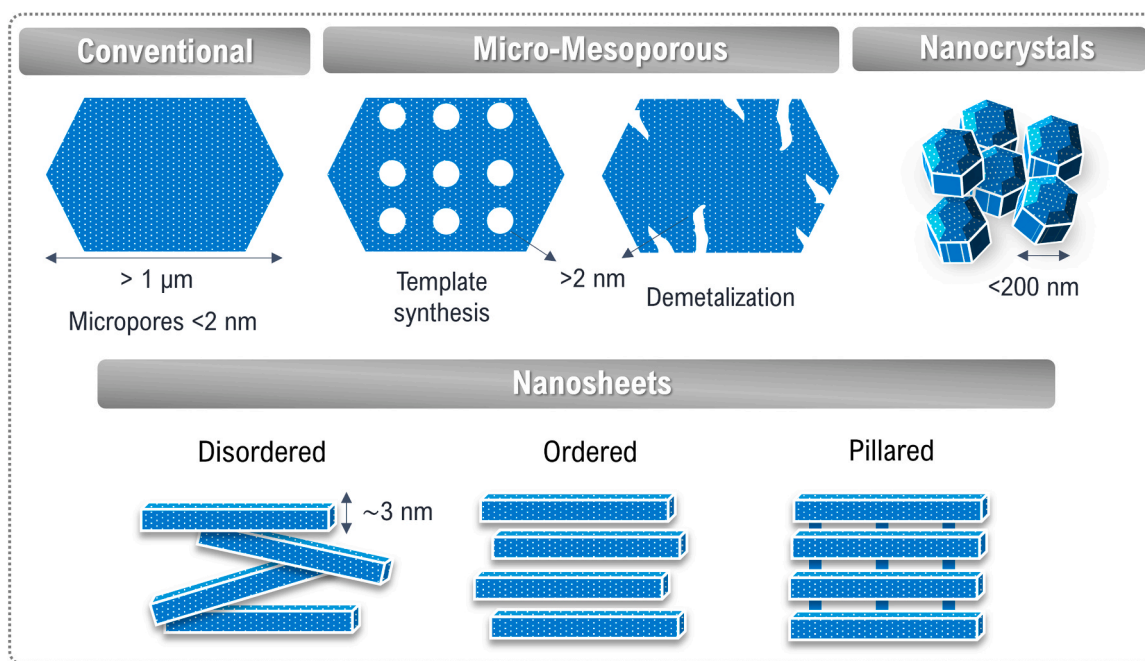**Fig. 4.** Schematic representation of hierarchical zeolite structures.

HNO$_3$, H$_2$SO$_4$, HCl or organic acids) or other chemical treatments [129, 130]. While dealumination increases porosity, it can also affect the acidic properties of zeolite, often leading to a decrease in surface acidity due to the Al framework extraction [131]. Desilication is defined as the extraction of silicon by using an alkaline medium [132–134]. This technique has been known to yield lower Si/Al ratios with only small changes in framework acidity. Extraction of silicon atoms leads to a significant amount of extra porosity, which starts in the boundaries or defect sites of the zeolite crystals and preserve the structural integrity. The formed mesopores are interconnected, enhancing their accessibility from the external surface of zeolite and improving mass transport properties [130].

Two -dimensional zeolites, composed of thin nanosheet layers up to 3 nm in thickness, have also attracted the interest as catalytic materials that can mitigate diffusion limitations. They can self-assemble into various hierarchical structures, including disordered unilamellar assemblies, ordered multilamellar stack or pillared frameworks [135,136]. These two-dimensional zeolites offer significant advantages in terms of accessibility to active sites and catalytic performance due to their unique structural characteristics. There are varying methods for the synthesis of zeolite nanosheets, with the most common being crystallization from unique organic structural directing agents [135], additive-assisted synthesis with the use of organic and inorganic compounds (e.g., urea and fluorinated surfactants) [137], seed-directed synthesis [138] and exfoliation of layered zeolites precursors by post-synthesis treatment [139].

3. Zeolites in biomass valorization reactions

Over the last years, the use of zeolitic materials in biomass valorization reactions has gained increased attention, especially due to zeolite's special features such as shape-selectivity, acidity and thermal stability [140,141]. According to the existing literature summarized in Table 1, modified zeolites have been employed in various important reactions, including glucose isomerization-dehydration, LA hydrogenation, sugars esterification, aldol condensation, and hydrodeoxygenation (HDO).

One of the most important transformations in biomass valorization is the conversion of glucose to HMF and LA, which are important platform molecules for biopolymer synthesis. The process typically involves a multi-step reaction, starting with glucose isomerization to fructose, followed by fructose dehydration. While glucose isomerization to fructose was conventionally catalyzed by enzymes, the use of heterogeneous catalysts offers advantages such as milder reaction conditions and catalyst reusability [142–144]. Tin-containing zeolites, particularly Sn-Beta, have shown great activity for glucose isomerization to fructose due to their Lewis acidity [145,146]. Framework Sn sites, incorporated as tetrahedral (or T-) atoms in the zeolite framework, are considered catalytically the more active [147], and can be easily created via the solid-state incorporation of Sn into Beta zeolites [148,149]. When Brønsted acidity is present due to Al atoms in the zeolite framework, the further dehydration of fructose to HMF can be achieved. Brønsted acidic sites are known for their dehydration activity over also other alcohols

Table 1
Representative examples of the use of zeolites in biomass valorization reactions.

Reactant	Reaction type	Catalyst	Reaction conditions	Main product	Ref.
Glucose	Isomerization-dehydration	Sn-Al-Beta	120 °C, ionic liquid	HMF	[152]
LA	Hydrogenation	Ru/HZSM−5	100 °C, H$_2$	GVL	[163]
FUR	Hydrogenation	Zr/SAPO−34, ZrP/HZSM−5	150–180 °C, N$_2$, alcohols	GVL	[165,166]
Glucose	Esterification	ZrY6	180 °C, methanol	Methyl levulinate	[170]
Palmitic acid	Esterification	H-Y, ZSM−5	70 °C, methanol	Methyl palmitate	[173]
FUR	Aldol condensation	H-BEA	100 °C, acetone	Aldol condensation product	[178]
Phenolics	HDO	Ni/ZSM−5, Ni/BEA	220 °C, H$_2$	Cycloalkanes	[185]
Methyl stearate, algae oil	HDO	Ni/nano-ZSM−5	280 °C, H$_2$	Alkanes	[189]

and ketones [150,151]. According to Zhang et al. [152], Sn-Al-Beta catalyst with both Sn and Al framework species showed high HMF yield (54 %) which was stable after 5 cycles and catalyst regeneration. Sn-Beta zeolites have been found also effective to catalyze the cyclo-addition of isoprene and methyl acrylate for the production of bio-derived monomers [149]. Zeolites with surface metal species, such as those containing Cr, Fe, or Hf, have been found active for glucose and cellulose conversion to HMF [153–156]. From the same reaction path LA can be produced after the hydrolytic ring opening of HMF [157], or directly from the hydrolysis reaction of furfuryl alcohol or xylose. Zeolites with low Si/Al ratio, such as HZSM-5, have shown high activity for LA production, comparable or even better than that of the homogeneous sulfuric acid, with much better recyclability potential [158,159].

Metal modified zeolites have also been used in biomass hydrogenation reactions [160,161]. One important example is LA conversion to GVL (γ-valerolactone), a value-added platform chemical for the production of biofuels, fuel additives, and polymers [162]. Ruthenium and nickel supported zeolites have shown good activity during LA hydrogenation to GVL at temperatures ranging from 100 to 220 °C under H_2 atmosphere [163,164]. Zeolite acidity can facilitate the dehydration step of 4-hydroxypentanoic acid, which is formed after LA hydrogenation and is the main intermediate in GVL synthesis. The beneficial role of acid sites of zeolites was evident in LA hydrogenation at 100 °C, where Ru/HZSM-5 presented much higher GVL yield compared to RuO_2 deposited on carbon-based supports [163]. Zirconium supported zeolites have been used for FUR transformation to GVL, employing alcohols as hydrogen donors under N_2 atmosphere, with excellent results at temperatures between 150 and 180 °C [165,166]. As it was revealed, ZrP-modified H-ZSM-5 catalyst showed almost complete FUR conversion and over 90 % GVL yield in the first run. However, the catalyst activity was decreased after four runs due to the formation of carbon deposits, which easily blocked the zeolite micropores and obstructed access to active sites [166].

Esterification reactions are important for the production of chemicals and biofuels from biomass-derived molecules [167,168]. For example, methyl levulinate, a fuel additive that is used in the food, polymer and pharmaceutical industries, can be produced from the reaction of sugars with methanol [169]. According to Li et al. [170], the hybrid zirconia-modified zeolite HY (ZrY6), which possesses both acid and basic sites, could effectively convert a range of sugars including glucose, mannose, galactose and sucrose to methyl levulinate at 180 °C. Compared to ZrO_2, which promotes isomerization of glucose to fructose through its basic sites, the acidity provided by HY support could facilitate the subsequent dehydration, esterification and rehydration reactions. Under similar reaction conditions, the moderate acidity of silicoaluminophosphate (SAPO) based zeolite zirconia composites enhanced ethyl levulinate synthesis from furfuryl alcohol, resulting in much higher conversion and product yield compared to t-ZrO_2 [171]. SAPO-type zeolites, while important in other biomass conversions (e.g. hydrodeoxygenation), have seen little application in oxidative biomass valorization. From the esterification reaction of fatty acids green biodiesel is produced [172]. Zeolites H-Y and ZSM-5 have been successfully utilized for linoleic acid and palmitic acid esterification with methanol, at 60–180 °C, presenting almost complete conversion and high product yield (~70–80 %) even after 5 catalytic cycles. Here, pore size and the hydrophobicity/hydrophilicity balance were critical for the efficient product formation [173,174]. It was shown that the use of HZSM-5–50 resulted in very low conversion (lower than 10 %), which was slightly improved in the case of H-ZSM-5–30 and H-Y-5.2 (20–27 % conversion). The H-Y-60 catalyst, with higher average pore size, large cavities and more hydrophobic surface, showed full conversion (100 %) [173].

Aldol condensation of aldehydes and ketones is another important reaction for producing biofuels. While homogeneous sodium hydroxide aqueous solutions are very effective for aldol condensation [175], zeolites with both acidic and basic properties have been successfully used as alternatives [176,177]. Kubička and co-workers [178], tested different structural types, including H-ZSM-5, H-BEA, H-MOR and H-USY, for the condensation of FUR with acetone. Among these, H-BEA owning a wide pore, three-dimensional crystalline framework, exhibited the best catalytic performance producing high amounts of condensation products after 2 h reaction at 100 °C. Unlike materials with basic character that result in the formation of only the first condensation C8 product, FAc, Brønsted acid sites of H-BEA contributed to the formation of also the second condensation C8 product, $(Fac)_2$, due to the dimerization of the olefinic FAc on the acid sites.

Finally, zeolites have presented great performance in HDO reactions, which are crucial for upgrading pyrolysis oils and fatty acids. Pyrolysis oils, derived from lignocellulose pyrolysis at elevated temperatures in the absence of oxygen, contain a mixture of phenolic compounds, alkoxy-aromatics and monolignols, with high water content that limit their use in the production of fuels [179]. The utilization of zeolites in the step of pyrolysis can enhance the formation of aromatic hydrocarbons [180]. Appropriate zeolite topology and acidity can promote the formation of bio-oils enriched in monoaromatic compounds, without further condensation into PAHs (polyaromatic hydrocarbons) [181]. However, due to the low organic fraction of bio-oils and rapid catalyst deactivation, ex-situ upgrading of the pyrolysis oils is often preferred. Metals such as nickel, iron, palladium supported on acidic materials have shown great catalytic activity in HDO reaction of biomass derived oils [182–185]. Especially nickel modified zeolites showed impressive results in phenolics HDO, resulting in high deoxygenation degree and cyclohexane/methyl-cyclohexane selectivity [185,186]. The Ni-ITQ-2 composite achieved 99 % yield of methylcyclohexane from m-cresol (a lignin-derived phenolic). Additionally, zeolite acid-base sites can catalyze the isomerization of long-chain alkanes produced during fatty acid HDO, leading to the formation of iso-alkanes, which are valuable components in second-generation biodiesel production [187–189].

4. The use of zeolites in oxidative biomass transformations

During the recent years, oxidative reactions of biomass have attracted the interest as important pathways for producing valuable intermediates used in the food, chemical and polymer industries. As presented in Fig. 5, oxidative transformations of biomass derived molecules can be broadly divided into three main categories: i) oxidation of functional groups, ii) epoxidation of carbon-carbon double (C=C) bonds, and iii) oxidative cleavage of carbon-carbon bonds.

Regarding the oxidation of functional groups, much of the focus has been on glucose and HMF. Both these molecules contain -OH and -CHO groups that can be oxidized towards carboxyl (-COOH) groups. From glucose oxidation, important organic acids such as gluconic acid (GOA), glucuronic acid (GUA) and glucaric acid (GAA) can be produced. Especially GOA has found extensive application as food additive, in pharmaceuticals and polymers, and as cement additive in construction industries. Following the conventional practice, GOA and GAA can be produced by biochemical oxidation using fungi, bacteria, enzymes or chemically by using nitric acid. However, these strategies suffer from low productivity, lack of catalyst recyclability and environmental pollution [190]. In the polymer industry, HMF oxidation to FDCA has opened new opportunities for the production of bio-based polymers, as FDCA is an important substitute for a variety of petrochemicals, such as terephthalic and adipic acid [191,192]. In addition to FDCA, HMF can be partially oxidized to DFF, an important intermediate for the synthesis of ligands, pesticide, antifungal agents, fluorescent materials and polymeric materials [193,194].

Regarding the **epoxidation of fatty acids**, which are the major component of VOs, they contain C=C bonds that can be epoxidized towards derivatives used in the production of polymers, cosmetics, pharmaceuticals and lubricants. Bio-based polyols and polyurethanes can be produced from the epoxidation of fatty acids or directly from VOs [195,196]. The reaction was conventionally conducted with the use of percarboxylic acids, such as peracetic or performic acid, which can be
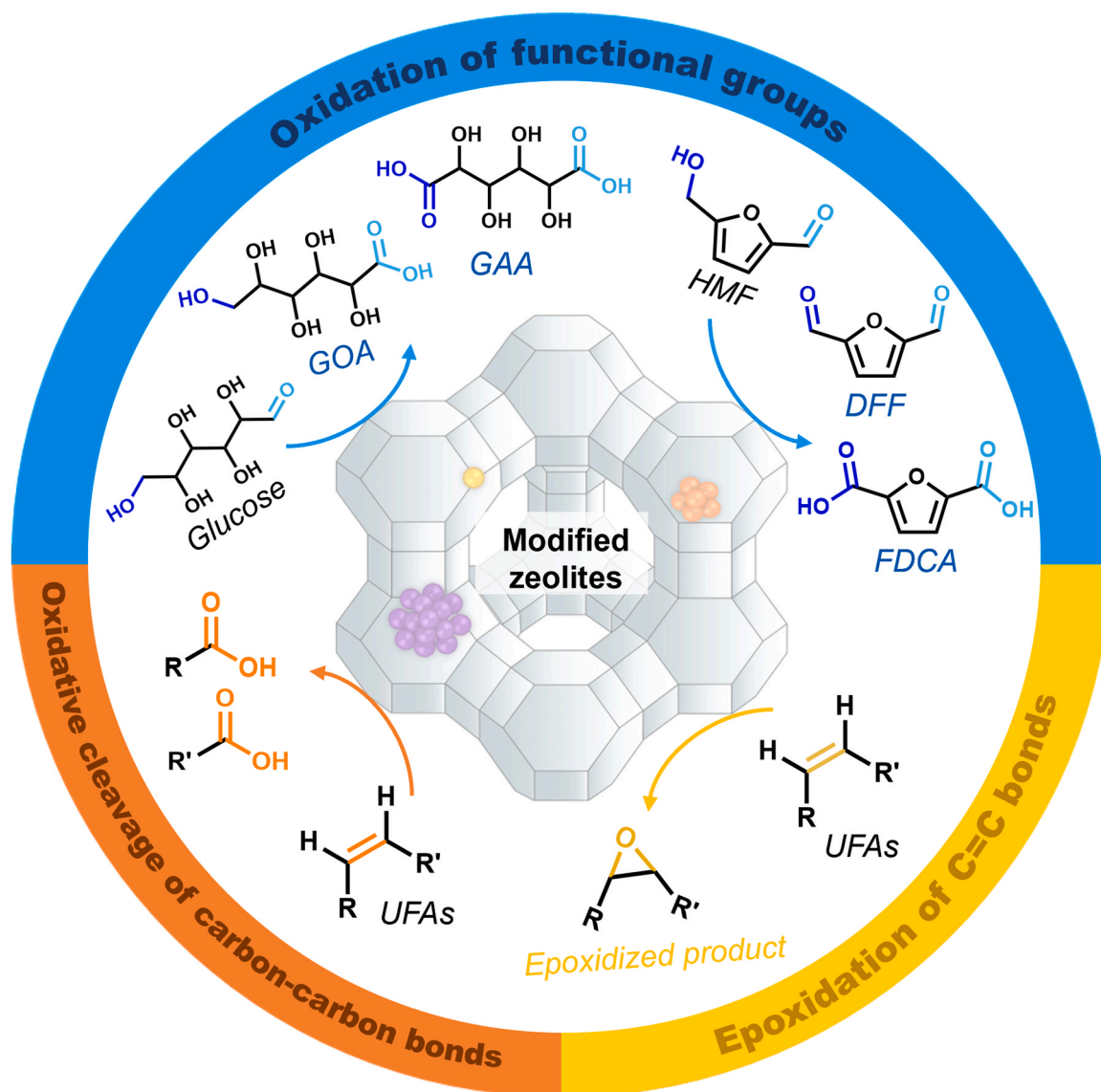
Fig. 5. Schematic illustration of the possible oxidative reactions of biomass derived molecules that modified zeolites can catalyze.

formed in situ from hydrogen peroxide and the corresponding acid in the presence of a strong mineral acid. However, this process has many disadvantages, including low epoxide selectivity due to competing ring-opening reactions, the formation of strongly corrosive by-products, and the production of unstable and explosive peracids [197].

In addition to epoxidation, fatty acids can be subjected to **oxidative cleavage** of C═C bonds, which leads to the production of a wide range of useful bio-based mono-and di-carboxylic acids. Similar to FDCA, these acids are considered as renewable, carbon-neutral monomers for polymers production [198,199]. The direct oxidative cleavage of olefins by ozone-based methods pose significant concerns due to the risk of explosive reactions, which have been previously reported [200].

Given the challenges and opportunities in these transformations, the production of biomass-derived acids and epoxidized monomers represents a pivotal area of ongoing research. The use of environmentally friendly solvents (e.g., water), "green" oxidants (e.g., O_2 or aqueous solutions of peroxides) along with catalysts with stable activity and easy recyclability, is crucial for developing more sustainable technologies to the chemical industry. Zeolites, with their unique structural and chemical properties, have already found extensive use in a variety of industrial catalytic processes, and they offer significant advantages for the oxidative biomass transformations. Advances in zeolite synthesis and

post-synthesis modifications enable the design of materials with tailored pore sizes, morphologies, and compositions, with tunable acidity that can be used for oxidative reactions opening the path for the establishment of new eco-friendly processes for acids and epoxides production.

4.1. Oxidative reactions of functional groups

Glucose aerobic oxidation is usually conducted at a temperature range of 40–110 °C, in presence of noble metal catalysts and in the presence of a base [190]. Gold catalysts, in particular, have shown remarkable activity and high selectivity for gluconic acid formation in both basic and base-free reactions [201–203]. The use of reduced amount of base is beneficial, as under alkaline conditions, glucose can undergo isomerization to fructose, and undesired gluconate salts and basic by-products can be formed. Zeolites, due to their compatibility with water, porous system that enhances the transport of molecules to and from the active sites, as well as surface -OH groups that can interact with the functional groups of glucose, are attractive supports for this kind of liquid-phase oxidation reactions [204,205].

The catalyst preparation method was found to have an impact on glucose oxidation under base-free aerobic conditions as demonstrated by Wolska et al. [205], who explored the impact of different synthesis

methods for gold-supported zeolites. They found that deposition method can affect gold loading, particle size and the support acidity. The highest glucose conversion (91 %) and GOA selectivity (99 %) were achieved with a 2 % Au-HBeta(AP) catalyst prepared by anchoring gold species onto (3-aminopropyl)trimethoxysilane (APTMS).This method produced small and very homogeneously distributed gold nanoparticles (~ 6 nm). In contrast, the ion-exchange method, resulting in larger nanoparticles (15–30 nm) in the Au-HBeta(IE) catalyst, allowed the simultaneous adsorption of glucose and oxygen to gold particles, thus increasing the reaction rate (Fig. 6a). According to the proposed reaction mechanism (Fig. 6b), in the base-free oxidation, BAS can facilitate the initial glucose adsorption through the carbonyl oxygen and the protonation of the aldehyde group, emphasizing the role of BAS in the zeolite supports. This leads to the formation of a geminal diol, for which one of its -OH groups can be oxidized with the adsorbed oxygen activated on Au NPs, thus forming GOA. Catalyst stability tests showed that 2 % Au-HBeta (AP) preserved high conversion (over 75 %) and 100 % gluconic acid selectivity even after 6 catalytic cycles. The doping of Au-Beta zeolites with a second metal (Nb or Ce) presented interesting results as niobium dopant, despite acting as a structural promoter for better gold dispersion, decreased the activity of the catalyst. This result could be attributed to the very strong gold-niobium interaction that resulted in a decrease of both conversion and GOA selectivity. On the other hand, cerium nanoparticles in neighboring positions regarding gold nanoparticles probably increased the number of total active sites, and thus had a positive influence on the conversion and GOA selectivity.

Another approach for glucose oxidation towards the corresponding acids is **photocatalysis** [206,207]. Photocatalytic conversion is considered as a promising technology for producing chemicals from biomass as the reaction is driven by solar energy, at low temperatures, atmospheric pressures, using non-toxic and low-cost catalysts [208, 209]. Heterogeneous photocatalysts are mainly semiconductor materials, such as metal oxides, which are active in presence of UV or visible light [210]. Metallothioporphyrzines (MPz) have also been used in selective organic transformations due to their distinct optical and electronic properties [211,212]. The deposition of $FePz(SBu)_8$ complex on H-ZSM-5 resulted in a highly active photocatalyst for glucose oxidation under visible light ($\lambda \geq 420$ nm) in water. The large specific surface area and high chemical stability provided by the zeolitic support was proved beneficial as $FePz(SBu)_8$/H-ZSM-5 achieved glucose conversion of 35.8 %, compared to the unsupported $FePz(SBu)_8$ that had only 4.9 % conversion [212]. Other photocatalysts, such as TiO_2, have also been explored for glucose oxidation [213,214]. According to Colmenares et al. [215], the use of a TiO_2 supported zeolite Y catalyst, prepared by a modified sol-gel method assisted by ultrasonic irradiation, showed high GAA-GOA selectivity (68.1 %) during glucose photooxidation in a water-acetonitrile system at 30 °C. The negatively charged framework of zeolite Y and its high surface area helped to facilitate the selective photocatalytic oxidation of glucose, compared to the bulk TiO_2. Under similar reaction conditions, the use of chromium-dopped TiO_2/-zeolite Y catalyst, prepared via the improved wet impregnation-ultrasonic irradiation method, resulted in only 7 % glucose conversion, however, carboxylic acid selectivity increased to 87 % [216].

The complete oxidation of HMF to FDCA is usually conducted in presence of noble metal catalysts supported on oxides or carbon materials in basic conditions [217–219]. Similar as in glucose oxidation, a decrease of the additional base is required. According to the findings of Liao et al. [54], complete aerobic oxidation of HMF and 98 % FDCA yield were achieved, at 140 °C, with the use of 1 %Au/Sn-Beta, prepared using the sol-immobilization method. LAS generated by the incorporation of Sn^{4+} ions into the framework of Beta, facilitated the initial HMF adsorption via the -CHO group and the breakage of O-H bond of hydroxyl group, resulting in increased FDCA formation. The presence of
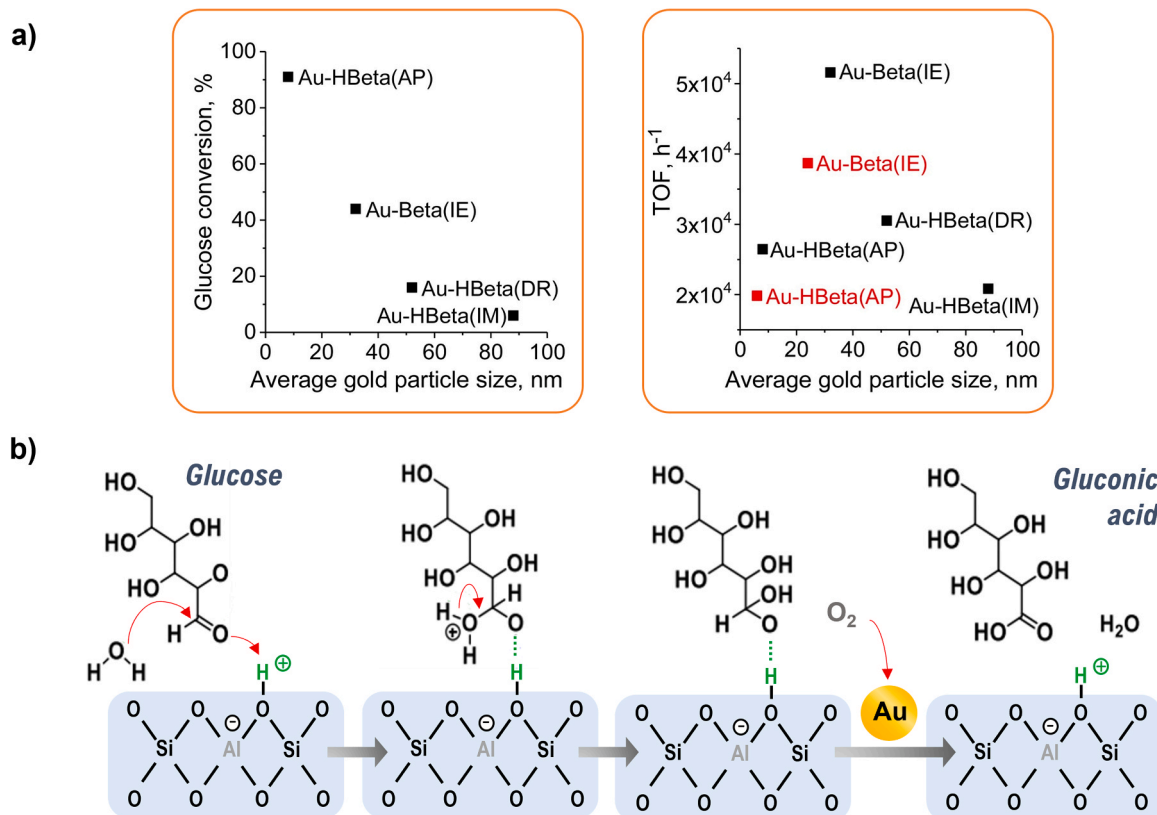

Fig. 6. a) Glucose conversion and TOF over average Au NPs size for 2 %Au-HBeta, and b) Proposed reaction mechanism for the conversion of glucose to GOA in presence of Au supported zeolite [205].

both Au and Sn led to higher FDCA yield (46.7 %) compared to Au/Beta and Sn-Beta separately, suggesting a synergistic effect between Au particles and zeolite framework Sn^{4+} ions. Indeed, the versatility of introducing various metals (e.g., Sn, Mg, Cu) within the zeolite framework allows for tuning its acidic/basic sites, thereby improving the efficiency of additional metal active sites (e.g., Au). A comparison with other similar works that use Au supported on carbon materials and oxides, showed that Au/Sn-Beta provided higher FDCA productivity (millimoles of FDCA produced hourly per gram of noble metals), despite the lower amount of additional base that was used. Stability tests were performed with the 2 %Au/Sn-Beta, for which HMF conversion was maintained at 95–100 % even after 4 catalytic cycles, indicating a relatively stable activity for these catalysts. High HMF conversion and product selectivity were also achieved in the case of magnesium modified zeolites. According to Zhu et al. [220], the basic sites of 2 % Au/Mg-zeolites (Beta, MOR, FAU), promoted HMF oxidation under base-free conditions, achieving 98.1 % FDCA selectivity at 130 °C. The Mg^{2+} ions substituted into the zeolitic framework can provide the basic sites that facilitate HMF oxidation through the high HMF adsorption, even under base-free conditions [53]. Other noble metals, such as platinum and ruthenium supported on zeolites, have shown remarkable activity in HMF oxidation to FDCA [221–223]. Despite the low metal content (0.2 %), platinum nanoparticles encapsulated in the framework of Beta zeolite (0.2 %Pt@Beta) presented near-complete HMF oxidation at 90 °C in presence of O_2, resulting in 99 % FDCA yield. When comparing Pt@Beta with Pt/C, despite the > 99 % HMF conversion in both cases, the carbon supported catalyst showed a FDCA yield decrease to 32 %. This dramatic difference highlights how zeolite's confined environment suppresses over-oxidation or side reactions on Pt, whereas carbon allows unselective pathways. Additionally, the encapsulation of metal nanoparticles within zeolite Beta framework enhanced the stability of the active sites, as rare deactivation was observed after a five-run test [221].

An alternative way for FDCA production is the **electrochemical HMF oxidation** [224,225], which usually operates at room temperature and in absence of additional oxidants, as the reaction is driven by the electric potential [226,227]. Tantisriyanurak et al. [228], reported a hybrid NiAl-MOR-CNTs catalyst for HMF oxidation, leading to complete substrate conversion and 92 % FDCA selectivity. The prepared electrode, composed of the synthesized catalyst and a Nafion binder, preserved the high catalytic activity even after several experimental cycles. MOR zeolite was used as support for the homogeneous dispersion of NiAl-LDH, forming a composite that was then calcined to produce highly dispersed metal oxides.

For the **partial HMF oxidation to DFF**, vanadium supported zeolites have been found to selectively oxidize only the hydroxyl group of HMF, leaving the aldehyde group intact to form DFF [229,230]. A high silica MOR zeolite with isolated vanadium species was used for the aerobic oxidation of fructose, at 120–130 °C, giving 100 % fructose conversion and 96.0 % DFF yield in the presence of HCl [230]. The isolated tetrahedral $[V_2O_8]^{6-}$ species, deposited on zeolites surface, presented high activity in the oxidation of HMF to DFF and resistance to the over-oxidation of fructose. The high-silica MOR framework provided satisfactory acidity for the formation of the intermediate HMF and preserved the zeolite structure under acidic conditions. Reusability tests showed that V_2O_5@MOR catalysts with Si/Al ratio 60 maintained a DFF yield over 90 % even after 5 catalytic tests, with preserving both the crystallinity as well as porous and morphological features. In contrast, for catalysts with low Si/Al, Al and V leaching was observed, decreasing thus DFF yield to 78.8 % after the 5 cycles. In the direct HMF aerobic oxidation to DFF at 120 °C, the use of V_2O_5/Cu−MOR zeolite exhibited high DFF yield (91.5 %) with 99 % conversion [231]. HMF was adsorbed on the catalyst surface and was then oxidized to DFF mainly by lattice oxygen (V^{5+}-O^{2-}). Due to the presence of O_2, the lattice oxygen vacancies of V^{4+} transition active site could be re-oxidized to regenerate V^{5+}-O^{2-} species. According to the authors, the strong interaction between the framework Cu species with the vanadium atoms on the zeolite's surface promoted both the activity and the stability of the supported V active sites, resulting in a good catalyst reusability. Contrary to the V_2O_5@MOR for which HMF conversion was decreased from 99 % to 75.4 % and DFF yield from 63.4 % to 25.8 % after 5 cycles, V_2O_5@Cu-MOR maintained a conversion of 99 % and a DFF yield higher than 80 %. This improvement is due to the robust and well-defined pore system of zeolite supports that stabilize metals incorporated into their framework, assuring a high dispersion of active species, i.e. V^{5+}-O^{2-}. In Fig. 7 a schematic representation of the two pathways for HMF oxidation towards DFF and FDCA over zeolite-based catalysts is presented.

The selective oxidation of the aldehyde group of HMF can lead to the formation of hydroxymethyl-2-furancarboxylic acid (HMFCA), an important compound for the synthesis of furanic polyesters [232,233]. Niobium modified zeolites with surface metal oxides (MO_x@Nb-zeolite, where MO_x = CoO_x, MnO_x or FeO_x, and zeolite = USY and Beta) demonstrated great catalytic behavior in the oxidation of HMF to HMFCA, at 170 °C in presence of t-BuOOH. The catalysts, prepared via the dealumination of zeolites H-USY and H-BEA followed by impregnation with niobium ethoxide, resulted in acid-base properties and led to complete HMF conversion with 97.0 % HMFCA selectivity [233].

In summary, the selective oxidation of glucose and HMF using zeolite-supported noble metals has proven to be a highly efficient and sustainable method for producing valuable bio-based chemicals such as GOA, FDCA, and DFF. The development of base-free conditions, as well as alternative methods such as photocatalysis and electrochemical oxidation, has opened new avenues for greener and more efficient biomass valorization routes. The use of zeolites as catalyst supports in these reactions offers significant advantages, including tunable acidity, high surface area, and the potential for easy catalyst recycling. In Table 2, a summary of the zeolite catalyzed oxidation reactions of glucose and HMF towards the corresponding acids is presented.

4.2. Epoxidation of double bonds

The conventional industrial process for the epoxidation of double bonds involves the use of highly acidic media that have many drawbacks, such as low selectivity towards the targeted epoxides, hazards associated with highly concentrated peroxides and corrosiveness issues. The use of heterogeneous catalysts based on W and Ti have shown great potential as alternatives, offering high product yields and/or selectivity under mild conditions [234–236]. In the early 1980s, EniChem's discovery of TS-1 zeolite enabled the development of a new approach for the selective epoxidation of propylene. This method was using H_2O_2 as oxidizing agent with water being as the main byproduct, making it a more environmentally friendly alternative [237,238]. Among solid epoxidation catalysts, those based on titanium and silica are the most extensively studied as they provide a favorable balance between effective catalytic performance under mild conditions, low cost and reusability potentials due to the relatively stable Ti-O-Si bonds against leaching [234].

TS-1 catalysts have demonstrated remarkable efficacy in epoxidation reactions. Wilde et al. [239], reported that the industrial TS-1 catalyst achieved methyl oleate (MO) epoxidation to epoxidized methyl oleate (EMO) with a selectivity of 87 % at 93 % conversion after 24 hours at 50 °C. Compared to other titanium-containing catalysts, such as TiO_x-SiO_2 and Ti-MCM-41, the tetrahedrally coordinated Ti species in TS-1 zeolite promoted H_2O_2 activation, thus forming Ti-OOH active sites, which could epoxidize effectively the carbon-carbon double bonds. After three catalytic runs conversion was steadily decreased while the epoxide selectivity slightly increased. However, the initial activity and selectivity of the catalyst were completely recovered by calcining TS-1 at 400 °C for 24 hours. In the same work, TS-1 was also used for the epoxidation of biodiesel (mixture of methyl oleate, methyl linolate and methyl linolenate) derived from rapeseed oil, achieving 90 % conversion with 76 % selectivity. Here it was found that TS-1 with crystallite sizes in the
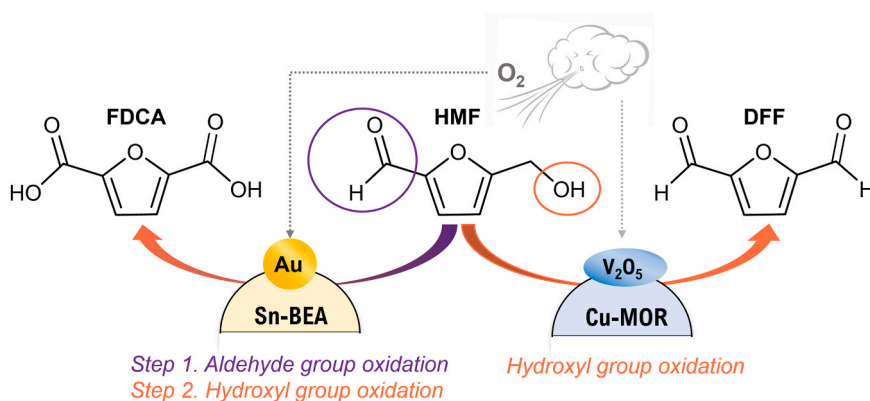
Fig. 7. HMF aerobic oxidation to DFF (partial oxidation) and FDCA (fully oxidation) in presence of metal modified zeolites.

Table 2
Oxidative reactions of functional groups of biomass derived molecules in presence of modified zeolites.

| Reactant	Catalyst	Reaction conditions	Conv., %	Main product	Sel., %	Ref.
Glucose	2 %Au/Beta	Aerobic ox. (110 °C, water, 0.5 MPa O_2)	91	gluconic acid	99	[205]
Glucose	FePz(SBu)$_8$/H-ZSM−5	Photocatalytic ox. (r.t., Xe lamp)	36	Glucaric/ gluconic acid	45	[212]
Glucose	TiO$_2$/zeolite Y	Photocatalytic ox. (30 °C, 1 bar, 125 W mercury lamp)	15	glucaric/ gluconic acid	68	[215]
Glucose	Cr-TiO$_2$/zeolite Y	Photocatalytic ox. (30 °C, 1 atm., 125 W UV-lamp)	7	glucaric/ gluconic acid	87	[216]
HMF	1 %Au/Sn-Beta	Aerobic ox. (140 °C, water, Na$_2$CO$_3$, 1 MPa O_2)	100	FDCA	46	[54]
HMF	2 %Au/Mg-Beta	Aerobic ox. (130 °C, water, Na$_2$CO$_3$, 2 MPa O_2)	95	FDCA	98	[220]
HMF	0.2 %Pt@Beta	Aerobic ox. (90 °C, water, O_2 balloon)	> 99	FDCA	99	[221]
HMF	NiAl-MOR-CNTs	Electrochemical ox. (r.t, KOH, 1.67 V)	100	FDCA	92	[228]
HMF	V$_2$O$_5$/Cu-MOR	Aerobic ox. (120 °C, DMSO, O_2 balloon)	> 99	DFF	91	[231]
Fructose	[V$_2$O$_8$]$^{6-}$/MOR	Aerobic ox. (120–130 °C, DMSO, HCl, O_2 balloon)	100	DFF	96	[230]
HMF	MO$_x$@Nb-Y30	Wet ox. 170 °C, ACN, t-BuOOH,	95	HMFCA	97	[233]
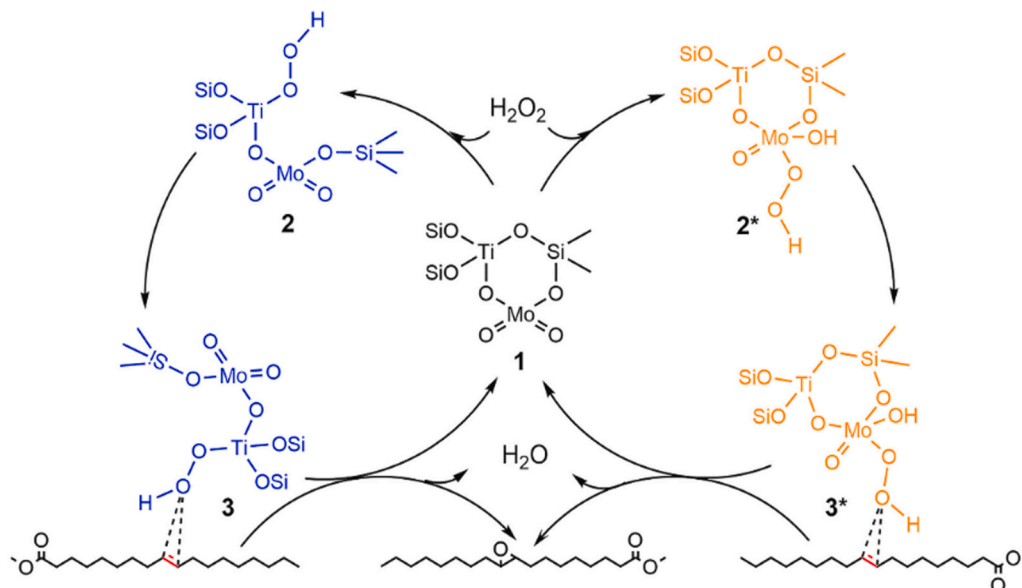
Fig. 8. Proposed mechanism for the role Mo/TS-1 catalyst in methyl oleate epoxidation [241].

sub-micrometer scale and with stacked morphology exhibited a significantly higher turnover number than the industrial TS-1.

The **influence of Si/Ti ratio** of TS-1 on the epoxidation effectiveness is significant. TS-1 catalysts with Si/Ti ratios ranging from 40 to 80 were hydrothermally synthesized and tested for the epoxidation reaction of soybean oil (SO) at 60 °C [240]. Among the catalysts, TS-1–40 (Si/Ti ratio of 40) demonstrated the best performance, with 40.9 % conversion and 88.2 % selectivity towards epoxidized soybean oil (ESO). The higher amount of framework titanium species in TS-1–40 improved reactant conversion and epoxy-product formation. Although the TiO_2 catalysts also presented high catalytic activity, they showed severe decomposition of H_2O_2, limiting their use in industrial applications. Additionally, TS-1–40 showed excellent reusability after high-temperature calcination, making it a viable candidate for scaling up clean, acid-free epoxidation processes for ESO production.

Metal-modified TS-1 catalyst by introducing other metals has also been investigated for the epoxidation of fatty acids [241–243]. For instance, 2 %Mo/TS-1 with highly dispersed surface Mo^{6+} species, increased MO conversion from 27.3 % (unmodified TS-1) to 51.6 % at 80 °C within 12 hours [241]. The enhanced activity is linked to the dual role of Mo^{6+} species in H_2O_2 activation and weakening of Ti-O bond in the TS-1 framework. As shown in the proposed reaction mechanism of Fig. 8, in the TS-1 catalyzed epoxidation of methyl oleate, the isolated Ti^{4+} sites in TS-1 activate H_2O_2 to form peroxo (Ti–OOH) species. These Ti–OOH sites are highly selective oxidants for C═C bonds (forming epoxides) but are less prone to over-oxidation (due to the controlled pore environment). This metal-site/reactant interaction – essentially in-situ generation of a selective oxidizing agent within the zeolite pore – is key to TS-1's success in epoxidations. Higher Mo loadings increased total acidity and led to unwanted epoxy ring-opening side reactions (glycol formation) – an issue mitigated by using an optimal 2 wt% Mo loading. In addition, the higher metal content and/or larger metal particle sizes can obstruct the active Ti sites in TS-1, resulting in poorer catalyst performance. Recyclability tests showed that 2 %Mo/TS-1 maintained a high EMO selectivity even after 3 cycles, however, MO conversion was decreased rapidly. This could be attributed to both the loss of a small Mo species on the catalyst surface as well as the blockage of some active sites from adsorbed MO and EMO macromolecules. Similarly, in the epoxidation reaction of soybean oil at 80 °C, Cd loaded TS-1 catalysts presented good activity in terms of conversion and product selectivity [243]. For Cd/TS-1 catalysts, by increasing Cd loading from 0.5 % to 2 %, both SO and H_2O_2 conversion increased. With 2 %Cd/TS-1 SO conversion reached 33.9 %, with epoxidized SO product selectivity 100 %. Higher Cd loadings adversely affected performance, mirroring trends seen with Mo-modified TS-1. In this work, varying catalyst regeneration procedures were also evaluated indicating that compared to washing and oxidation, with the calcination of the used catalyst the initial SO conversion levels could be reestablished. As it can be distinguished in Table 3, the use of metal-supported TS-1 zeolites can lead to high product selectivities in shorter reaction times, underscoring their industrial potential in green epoxidation processes.

Apart from the epoxidation of carbon double bonds of biomass derived molecules, zeolites can also be used for the **hydrolysis of epoxides to vicinal diols** [244]. Vicinal diols produced from the direct ring-opening of epoxides are widely used as intermediates in the production of polymers, cosmetics, medicines, and more [245]. While the direct dihydroxylation of double bonds to vicinal diols is possible, it typically involves the use of harmful reagents such as OsO_4. As a result, an indirect two-step process – comprising double bond epoxidation followed by epoxy hydrolysis – has gained attention as a more sustainable and environmentally friendly alternative [246]. This approach employs heterogeneous catalysts and diluted oxidants, such as aqueous solutions of hydrogen peroxide in low concentrations, making it both safer and more efficient. The inherent acidic functionalities of epoxidation catalysts, combined with the water content in the oxidant allow the two-step reaction to be carried in out in a one-pot process [247]. Ring-opening reactions are commonly catalyzed using strong acids or Lewis acids in the presence of alcohols, which act as nucleophiles [248, 249]. Modified zeolites featuring Lewis acidity offer a promising catalytic system, as these materials combine high activity for epoxy hydrolysis with benefits such as recyclability, stability and process safety. Zeolites incorporating metals such as tin, titanium, hafnium, and zirconium have shown remarkable catalytic activity in epoxide hydrolysis to vicinal diols [245]. Their activity stems from the tailored acidity of the incorporated metal sites, which effectively activate the epoxide ring while maintaining the advantages of a heterogeneous catalytic system.

4.3. Oxidative cleavage of carbon-carbon bonds

The conventional oxidative cleavage of C═C double bonds was typically conducted in presence of ozone, which, while effective, possess environmental and safety concerns. To mitigate these issues, alternative oxidants such as H_2O_2 and O_2 are more desirable, offering a safer and more sustainable approach to cleaving fatty acid C═C bonds [250]. Among these methods, the most relevant follows a three-step mechanism: i) double bond epoxidation, ii) epoxide hydrolysis to yield vicinal diols, and iii) oxidative vicinal diol cleavage [251–253]. While modified zeolites have been successfully employed for the first two steps, their application in vicinal diol cleavage remains limited. Homogeneous catalysts based on Fe, W, Co and Ru have been the primary focus of research for this step [254–259]. Recent studies, however, highlight the potential of metal supported catalysts for achieving efficient C-C bond cleavage.

Ethylene glycol (EG), the simplest biomass-derived vicinal diol, serves as a key feedstock for producing formic acid (FA), an important substance for the chemical, agricultural, textile, leather and pharmaceutical industries [260]. In the oxidative cleavage of EG with H_2O_2 at 50 °C, the use of 0.5 %Fe/ZSM-5 zeolite catalyst resulted in 100 % EG conversion and 47.7 % FA selectivity [261]. Spectroscopic and kinetic studies showed monomeric Fe^{3+} sites are the most active for C–C cleavage, whereas Fe-oxide clusters are far less active. The zeolite stabilizes these isolated Fe sites and the confinement may also orient diol molecules for selective C–C scission to acids. This structure–function relationship (isolated vs clustered metal sites) dramatically affects efficiency and selectivity. Lower catalytic activities were observed in the case of 0.5 %Fe/BEA and 0.5 %Fe/MOR, likely due to their bigger 12-membered ring pores, compared to 10-membered ring pores in ZSM-5, facilitating the formation of undesired FeO_x aggregates which suppressed EG conversion. Even lower EG conversion (lower than 5 %) was obtained with the use of 0.5Fe/SiO_2 and 0.5Fe/Al_2O_3 catalysts, fact that further underly the need of structured microporous environment in zeolites. Under mild reaction conditions, 0.5 %Fe/ZSM-5 could also

Table 3
The use of zeolites in epoxidation reaction of biomass derived molecules.

Reactant	Catalyst	Reaction conditions	Conv., %	Main product	Sel., %	Ref.
Methyl oleate	TS−1	50 °C, CH_3CN, H_2O_2, 24 h	93	Methyl 9,10-epoxy stearate	87	[239]
Biodiesel	TS−1	50 °C, CH_3CN, H_2O_2, 24 h	90	Epoxidized products	76	[239]
Soybean oil	TS−1−40	60 °C, t-butanol, H_2O_2, 24 h	40	Epoxidized SO	88	[240]
Methyl oleate	2 %Mo/TS−1	80 °C, CH_3CN, H_2O_2, 12 h	51	Methyl 9,10-epoxy stearate	~60	[241]
Soybean oil	2 %Cd/TS−1	80 °C, t-butanol, H_2O_2, 12 h	33.9	Epoxidized SO	100.0	[243]

convert larger molecules, such as glycerol (86 % conversion, 48 % FA selectivity), glucose (49 % conversion, 18 % FA selectivity) and sorbitol (36 % conversion, 25 % FA selectivity). In these cases, the decreased catalytic activity of Fe/ZSM-5 could be attributed to the lower accessibility of the larger molecules to the active Fe-sites inside the zeolite micropores. The combination of Fe/ZSM-5 with TS-1 has shown promise for the direct ethylene oxidation to FA [262]. As shown in Fig. 9, in presence of H_2O_2, TS-1 catalyze the epoxidation of C=C bonds, while Fe/ZSM-5 provide the desired acidity for the epoxide hydrolysis and Fe active sites for the vicinal diol cleavage.

Mesoporous materials can be a promising strategy for the conversion of large molecules during oxidative cleavage, where diffusion limitations in microporous zeolites are a major challenge. In 1992 a new family of mesoporous silicate and aluminosilicate materials referred as M41S was designated by researchers at Mobil [263]. One of the most extensively investigated members of this family of materials is MCM-41, featuring one-dimensional hexagonal arrangement of uniform mesopores of 0.2–10 nm. This material resembles a zeolite with respect to its regular system of pores with uniform width, however, one significant difference is the non-crystallinity of the silica or silica–alumina pore walls in MCM-41 [264]. In the oxidative cleavage of methyl-epoxy-stearate at 60 °C in presence of H_2O_2, the addition of Al-MCM-41 to $WO_3 \cdot H_2O$ significantly improved catalyst reusability [265]. While $WO_3 \cdot H_2O$ alone resulted in 90 % conversion with 80 % selectivity for nonanal and methyl 9-oxononanoate, combining it with Al-MCM-41 increased conversion to 99 % with aldehydes selectivity of 65 %, maintaining performance over four cycles. The impregnation of tungsten species to the surface of MCM-41 further enhanced catalytic activity, achieving 99 % conversion and 78 % methyl 9-oxononanoate selectivity [266]. Compared to other previous works, here the catalyst presented excellent catalytic activity for 4 cycles, with no soluble tungsten species being detected in the liquid medium. The use of Cr/MCM-41 in the oxidative cleavage of oleic acid at 80 °C with supercritical carbon dioxide resulted in 99 % conversion, producing pelargonic acid and azelaic acid with concentrations of 31.7 % and 32.0 %, respectively [267]. Although Co/MCM-41 and Mn/MCM-41 maintained similar conversions, their selectivity for targeted acids was lower, and these catalysts showed greater susceptibility towards leaching.

The **single carbon bond (C-C bond) cleavage** is also a challenge in the valorization of lignin derived molecules. Compared to the relatively high reactivity of C-O bonds, the selective cleavage of C-C bonds is more difficult because of their non-polar nature, high robustness and bond dissociation energies [268]. However, oxidative techniques using metal-loaded zeolites have shown promise. These methods not only break C-C bonds but also yield highly functionalized oxygenates like aldehydes, ketones and organic acids [269]. Bio-derived vanillin, a very important intermediate for the synthesis of polymers [270], can be produced from the selective oxidation of isoeugenol [271–274]. Sahu

et al. [275], reported a 19 % isoeugenol conversion and 70 % vanillin selectivity using only H_2O_2 at 60 °C. Introducing cerium into MCM-22 (Ce-MCM-22) improved isoeugenol conversion to 61 %, by keeping stable vanillin selectivity (73 %). The use of bulk CeO_2 showed only 24 % conversion with various product distribution. The two independent 2-dimensional channel systems accessible by ten-membered ring pores of MCM-22 (MWW framework type) facilitated the dispersion of Ce active species and efficient diffusion of molecules inside the pores. No metal leaching was observed from the catalyst recyclability tests, with Ce-MCM-22 maintaining high conversion and vanillin selectivity for at least five cycles.

Cerium-modified zeolites have also been effective for the oxidative C-C cleavage in lignin-derived 2-phenoxy-1-phenylethan-1-one towards benzoic acid. Benzoic acid is used in a wide range of applications including plasticizers, preservatives, dyes/perfumes and as a feed for chemicals production [276]. Under aerobic conditions, at 100 °C, this lignin monomer presented 84.6 % conversion, with 71.4 % benzoic acid and 53.4 % phenol yield, in presence of 15 %Ce-5 %Cu/ZSM-5 catalyst [269]. This bimetallic catalyst leveraged the synergistic redox interaction between Cu^{2+}/Cu^{+} and Ce^{4+}/Ce^{3+} redox pairs, outperforming bulk CeO_2 catalysts with only 15 % conversion. The zeolite's two-dimensional 10-ring channels dispersed Ce active sites and facilitated molecular diffusion, leading to higher yield and selectivity. The bimetallic catalyst was also tested in the aerobic oxidation of organosolv lignin at 150 °C, resulting in 65.9 % conversion and 39.7 % product selectivity. For the oxidative cleavage of palm kernel shell biomass at 180 °C with H_2O_2, metal loaded zeolites like 10 %Co/H-Y and 10 % Cu/H-Y increased conversion from 75 % to 80–86 % [277]. Yields of oxidized products, including phenols, aldehydes, and carboxylic acids increased from 7.54 % to 23–32 %, demonstrating the effectiveness of the addition of Co and Cu metal modifications of zeolites in promoting oxidative transformations. A comprehensive summary of the oxidative cleavage of C-C bonds in biomass-derived feedstocks using zeolitic materials is presented in Table 4, highlighting their potential in green and sustainable chemical processes.

5. Biomass oxidative reactions over hierarchical zeolites

The use of hierarchical zeolites has been extensively researched to address mass transport limitations that arise for larger biomass-derived molecule transformations. More specifically, the kinetic dimeter for many of the biomass-derived molecules is in the range of 0.5–0.9 nm for the lignocellulosic components, such as glucose and HMF, and over 10 nm for branched chain fatty acids [278,279]. As showed in the previous paragraphs, the conventional microporous zeolite structures have successfully been used for many biomass oxidative reactions. However, a better distribution of the active sites within the whole zeolite surface and easy accessibility to these active sites from the larger molecules would establish even more the suitability of these materials for biomass valorization. Hierarchical zeolites, with micropores (0.5–2 nm) and mesopores (larger than 2 nm) offer high potentials as they preserve the benefits of conventional zeolites such as crystallinity, acidity/basicity, high surface area and heating resistance, and simultaneously offer large pores for converting most of the biomass components. Table 5 summarizes previously published works on hierarchical zeolites in oxidative biomass transformations. For lignocellulosic biomass, hierarchical zeolites have been used for the **selective HMF oxidation** [233,280,281]. Salakhum et al. [280], prepared hierarchical zeolitic materials as supports for Pt deposition, which were used in the base-free aerobic HMF oxidation at 110 °C. According to the authors, hierarchical Pt/Na-Hie-ZSM-5 and Pt/Ca-Hie-ZSM-5 catalysts presented 100 % HMF conversion, yielding FDCA as the main product with selectivities of 35.8 % and 67.8 %, respectively. In contrast, the conventional microporous Pt/Na-ZSM-5 catalyst achieved only 67.1 % conversion, favoring DFF formation with 38.8 % selectivity and 6.4 % FDCA yield. The enhanced activity of hierarchical materials, especially Pt/Ca-Hie-ZSM-5,
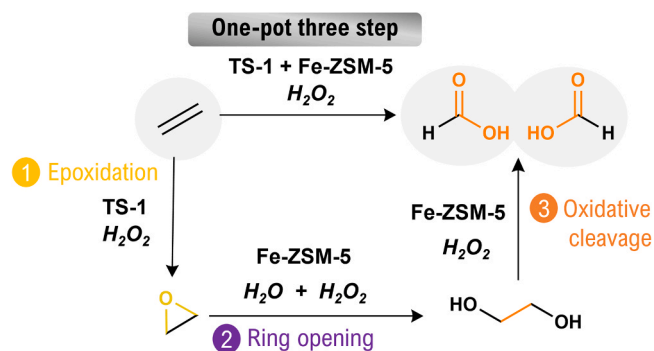

Fig. 9. Reaction scheme for the oxidative cleavage of ethylene into FA in presence of Fe-ZSM-5 and TS-1 catalysts [262].

Table 4

The use of zeolites in the oxidative cleavage of carbon bonds of biomass derived molecules.

Reactant	Catalyst	Reaction conditions	Conv., %	Main product	Sel., %	Ref.
Ethylene glycol	Fe/ZSM−5	50 °C, water, H_2O_2, 2 h	100	Formic acid	47	[261]
Methyl Epoxystearate	$WO_3 \cdot H_2O$ Al-MCM−41	60 °C, H_2O_2, 40 min	99	Nonanal, methyl−9-oxonanoate	65 (total)	[265]
Methyl 9,10-Epoxystearate	WO_3/MCM−41	80 °C, butanol, H_2O_2, 20 min	99	Nonanal, methyl 9-oxononanoate	78	[266]
Oleic acid	Cr/MCM−41	80 °C, $scCO_2$, O_2, 8 h	99	pelargonic acid, azelaic acid	31, 32	[267]
Isoeugenol	Ce-MCM−22	60 °C, H_2O_2, 90 min	61	vanillin	73	[275]
2-phenoxy−1-phenylethan−1-one	15Ce−5Cu/ZSM−5	100 °C, ethanol, O_2, 4 h	84	Benzoic acid	-	[269]
Organosolv lignin		150 °C, ethanol, O_2, 24 h	65	DEM	39 (total)	
Palm kernel shell	10 %Cu/H-Y 10 %Co/H-Y	180 °C, isopropanol, H_2O, H_2O_2, 2 h	80 86	Phenols, aldehydes, acids	- -	[277]

Table 5

Hierarchical zeolites for biomass oxidative transformations.

Catalyst	Preparation method, SDAs/ Support	Reaction	Conv., %	Product sel., %	Ref.
1 %Pt/Ca-Hie-ZSM−5	Soft templ., TBPOH	HMF ox.	100	FDCA, 67	[280]
0.8 %Au/Ca-hie-ZSM−5	Soft templ., TBPOH	HMF ox.	100	FDCA, 75	[281]
TS-SP	Soft templ., DATMS	MO epox.	100	Epox.MO, 91	[282]
Layered TS−1	Soft templ., C16−6−6	MO epox.	92	Methyl 9,10-di-hydroxystearate, 89–92 %	[284]
Pillared TS−1	Soft templ., C16−6−6		44		
Meso-TS−1	Hard templ., Carbon black		76		
Ti-M41p-6h	SAC, MCM−41	MO epox. ML epox.	66 66	Epox.MO, 94 Mono-Epox.ML, 50 Di-Epox.ML, 46	[285]
micro-/meso TS_ns	Des-Recrystal., TS−1_n	FAME epox.	65	Epox. FAME, 82	[44]

could be attributed to enhanced molecular diffusion within the nanosheets, smaller Pt nanoparticle size (2.5–4.5 nm), and higher support basicity. The hierarchical catalyst maintained high HMF conversion and FDCA yield even after five catalytic cycles by preserving Pt content% and showing resistance over metal sintering, contrary to Pt/Na-ZSM-5 catalyst for which a larger aggregation of Pt was found as well as severe leaching.

As in the case of microporous zeolites, the choice of metal deposition method also significantly affected the catalytic activity of hierarchical zeolites. Somsri and co-workers [281], investigated deposition-precipitation (DP) and wet impregnation methods for Au deposition on hierarchical Ca-ZSM-5. The catalyst prepared via DP, Au/Ca-hie-ZSM-5 (DP), displayed smaller Au particles (~ 1.3 nm) and exhibited complete HMF conversion with 75.1 % FDCA selectivity, whereas the wet impregnation method yielded a catalyst (Au/Ca-hie-ZSM-5-imp) with larger particles (3.6 nm) with only 43.6 % FDCA selectivity. These results highlight the importance of preparation techniques in achieving optimal catalytic performance.

Hierarchical zeolites have also shown remarkable activity in the epoxidation of fatty acids. For the epoxidation of methyl oleate (MO), a hierarchical titanosilicate zeolite (TS-SP) with sponge-like morphology and mesopore diameter of 3–5.5 nm, demonstrated 100 % conversion and 91 % selectivity for epoxidized products at 90 °C [282]. In comparison, the use of microporous TS-1 increased MO conversion from 23 % (in absence of a catalyst) to only 39 %, with 62 % product selectivity. In a similar work, a catalyst system combining WO_3 in physical mixture with a spongy titanosilicate (STS) not only facilitated the epoxidation of MO but also enabled the hydrolysis and oxidative cleavage of the formed vicinal diol [283]. The WO_3-STS catalyst showed enhanced catalytic performance, having 94.4 % MO conversion and more than 63 % selectivity towards oxidative cleavage products, with significantly reduced WO_3 leaching compared to conventional TS-1 catalyst.

TS-1-based catalysts with different textural features, namely layered TS-1, pillared TS-1, and Ti-pillared TS-1 as well as mesoporous TS-1, were investigated in the liquid-phase epoxidation of MO with hydrogen peroxide at 50 °C [284]. After synthesizing layered TS-1, the obtained nanosheets were used for the preparation of pillared TS-1, in which zeolite nanosheets were connected forming a bulkier, more stable material. The catalytic activity of these materials was compared with that of microporous TS-1 and mesoporous TS-1, prepared by using carbon black pearls as a secondary templating agent. After 5 h, layered TS-1 achieved 92 % MO conversion, while mesoporous TS-1 reached 76 %, compared to 44 % for pillared TS-1 and much lower values for conventional TS-1. Despite the expansion of the interlayer distance of the pillared TS-1, the accessibility of the active sites is likely limited due to the high steric demand of MO molecules. For longer reaction time (more than 24 h), MO conversion reached 76 % for the pillared sample. For MO epoxidation with H_2O_2, the tetrahedrally coordinated Ti atoms in TS-1 samples in combination with the hierarchical structure were found to be much more effective, compared to Ti-MCM-36 catalyst with mesopores and mainly octahedrally coordinated Ti-sites.

Steam-assisted conversion (SAC) has been used to transform amorphous Ti-MCM-41 into hierarchical zeolites with varying degrees of crystallinity, significantly enhancing catalytic performance. SAC-treated Ti-MCM-41 samples (Ti-M41p), were effectively used for the epoxidation reaction of methyl oleate (MO) and methyl linolate (ML). The different treatment times generated catalysts with pores of 3 nm, which were maintained for Ti-MCM-41p-6h but totally disappeared in Ti-M41p-24h. The SAC treated samples demonstrated superior catalytic activity, with Ti-M41p-6h and Ti-M41p-12h presenting the highest conversion (66–69 %) and product selectivity (94 %). Ti-M41p sample that was treated for 24 h under steam had similar activity as the microporous TS-1, having high product selectivity (80–88 %) but very low conversion (less than 8 %). The improved catalytic performance of SAC transformed Ti-MCM-41 samples was attributed to the mesoporous surface area and crystallinity of the material. In ML epoxidation, Ti-M41p-6h facilitated the epoxidation of both C═C bonds, achieving 66 % conversion and balanced product selectivity for mono- and di-epoxides, unlike microporous TS-1, which achieved only 6 % conversion [285].

In the epoxidation of fatty acids methyl esters (FAME), nanosized TS-1 (TS-1_ns), synthesized via microwave-assisted hydrothermal method and subsequently recrystallized, exhibited outstanding catalytic performance. Recrystallized TS-1_ns with mesopores of 3 – 10 nm achieved 65 % FAME conversion and 82 % epoxide selectivity at 50 °C,

outperforming both microporous TS-1 and desilicated TS-1 samples. Despite the larger pores of desilicated materials (10 – 40 nm) that enhance molecule diffusion, their increased surface hydrophilicity was probably unfavorable during FAME epoxidation in acetonitrile, as the alkaline-treated samples showed much lower catalytic activity even than the microporous material. Contrary, in the case of TS-1_ns, the stacked morphology through condensation of hydroxyl groups on the crystal surface was associated with an increase of the surface hydrophobicity, which enhance the adsorption of FAME molecules and thus promote their epoxidation [44]. Overall, these findings underscore the significant advantages of hierarchical zeolites in biomass oxidative transformations, with improved molecule diffusion, active site accessibility, and reduced steric hindrance contributing to their superior catalytic activity.

6. Challenges and perspectives

The literature summarized in this review highlights significant advances in the field of biomass upgrading, focusing on oxidative transformations, with the use of modified zeolites over the recent years. Biomass conversion reactions demand catalysts with high thermal and chemical stability, as well as reusability. Zeolites have already been established as an important class of heterogeneous catalysts that can meet these requirements. The varying number and nature of functional groups of biomass derived molecules require the use of materials with specific functionalities (active metal sites, acidity, basicity, mesoporosity). The flexibility that zeolite synthesis procedures give for preparing materials with tailored features is considered as a big advantage of zeolites compared to other heterogeneous catalysts. Especially for biomass oxidative transformations, the use of zeolites increased the sustainability factor by facilitating the use of "green" oxidants, such as O_2 and H_2O_2, employing safer chemicals, and operating under mild reaction conditions compared to conventional processes. Metal–biomass interactions are modulated by the zeolite's environment: the zeolite can enforce proximity of reactants to active sites, stabilize certain intermediates, or prevent bimolecular side reactions, thereby improving selectivity. Zeolite-supported catalysts often exhibit superior activity or selectivity relative to common supports (alumina, carbon, bulk oxides), due to zeolites' structural stability, shape-selective pores, and ability to stabilize active sites (preventing metal sintering or leaching). However, microporous zeolites often face diffusion limitations, side reactions, and coke deposition in reactions involving biomass-derived molecules. Addressing these challenges and perspectives will be critical to fully exploring the potential of these materials in the sustainable development of biomass oxidative upgrading.

In the oxidation of functional groups of biomass-derived molecules such as HMF and glucose, achieving high product selectivity is of high priority. While Au supported on zeolites have shown promise, a deeper understanding of the role of metal nanoparticle size, metal loading and the interactions between Au and other metals in bimetallic catalysts should be further investigated. In addition, the use of non-noble metals, which are more abundant and cost-effective, is equally important for the scale-up of these reactions to industrial applications. Moreover, zeolites have the potential to minimize or eliminate the need for additional base that is often required with other catalyst supports. Despite this, the exact role of BAS, LAS and basic sites in metal-modified zeolites remains unclear. Both glucose and HMF contain -CHO and -OH groups that can be adsorbed to acid and basic sites of zeolites, initiating the oxidation reaction. Further studies using simpler model compounds with similar functional groups (e.g., -CHO or -OH) can be used to elucidate the relationship between functional group reactivity and zeolite surface chemistry (acid/basic sites). For these studies small alcohols or aldehydes are preferred in order to avoid the influence of diffusion limitations and reveal the intrinsic catalytic activity. In such investigations, operando techniques could provide valuable insights into the interactions of reactants, intermediates and products with the catalyst

during reaction. For photocatalytic reactions, research is still in its infancy, with zeolites applied mainly for glucose oxidation thus far. Despite the lower energy demands of photocatalysis compared to the thermochemical reactions and the high selectivity towards GOA/GAA, conversion values remain low. Zeolites with higher external surface areas and hierarchical structures, containing both micro- and mesopores, could significantly enhance accessibility to active sites and improve catalytic performance.

Diffusion limitations also pose challenges in reactions such as C=C bond epoxidation and C-C bond oxidative cleavage. For instance, the epoxidation of unsaturated fatty acids (UFAs) derived from vegetable oils and subsequent cleavage of the corresponding vicinal diols to produce mono- or dicarboxylic acids suffer from restricted activity with microporous zeolites, which rely predominantly on their external surface areas. Hierarchical zeolites, such as mesoporous TS-1, have been successfully used for overcoming these limitations in UFAs epoxidation. Further modification of these catalysts with surface active metals such as Fe, W, or Cr could promote not only the step of epoxidation but also the oxidative cleavage of C-C bonds. However, most of the currently used supports (e.g., MCM-41), despite the high conversion and product selectivity suffer from metal leaching issues and catalyst instability. The crystalline structure of zeolites could mitigate stability issues by forming strong interactions with the metal species, whether as single sites, clusters, or nanoparticles, thereby enhancing overall catalyst durability. Optimizing the oxidative cleavage of mono-unsaturated fatty acids can also open new potentials for the valorization of polyunsaturated fatty acids and lignin derived molecules that contain C=C bonds (e.g., isoeugenol).

While the broad use of zeolites in many of industrial processes demonstrates their potential for large-scale applications, scaling oxidative biomass conversions faces challenges – e.g. handling of solid biomass-slurry feeds, water tolerance of catalysts, and catalyst lifetime in presence of bio-impurities (N/S compounds, etc.).

Addressing these challenges through targeted research will allow for the development of robust, efficient, and sustainable zeolite-based catalysts. Such advancements will not only contribute to overcoming current limitations in oxidative transformations but will also unlock new opportunities for the broader application of zeolites in biomass upgrading, fostering progress toward sustainable chemical processes.

7. Conclusions

The transition from fossil resources to biomass as a feedstock is of high importance for advancing a sustainable and environmentally friendly chemical industry. Biomass provides a renewable alternative, decreasing the carbon footprint and reliance on non-renewable resources. Zeolites play a pivotal role in the catalytic upgrading of biomass, thanks to their high surface area, tunable pore structures, and strong acid-base sites. The modification of zeolites with metals further enhances their catalytic properties, facilitating critical reactions such as glucose isomerization and dehydration, LA and FUR hydrogenation, sugars and fatty acids esterification, phenolics and vegetable oils hydrodeoxygenation. All of these reactions are important for the production of chemicals, materials and fuels.

In oxidative biomass transformations, the use of zeolites has enabled the establishment of more safe and sustainable processes by leveraging "green" oxidizing agents such as O_2 and H_2O_2, employing neutral solvents, and operating under mild, energy-efficient conditions. In glucose and HMF oxidation, Au supported on zeolites have showed great activity, particularly in decreasing the demands for additional base. For the partial HMF oxidation to DFF and HMFCA, zeolites modified with vanadium, cobalt and iron have exhibited high product selectivities, emphasizing the versatility of metal-modified zeolites. The role of BAS, LAS, and basic sites in facilitating the initial aldehyde and hydroxyl groups adsorption has been a key factor in promoting the overall reaction efficiency.

For the epoxidation of C=C bonds in unsaturated fatty acids, titanium-containing zeolites, such as TS-1, have showed great activity, particularly in reactions involving methyl oleate and vegetable oils. Further modification of TS-1 with metals such as Mo and Cd have decreased reaction times and increased product selectivity. Beyond epoxidation, unsaturated fatty acids can also be subjected to carbon-carbon bond cleavage towards the formation of bio-carboxylic acids. However, this reaction remains challenging, mainly due to the diffusion limitations of larger molecules in conventional zeolite structures.

Hierarchical zeolites containing both micro- and mesopores, have shown promise in overcoming these challenges. They have delivered improved catalytic performance in reactions such as HMF oxidation and fatty acids epoxidation, and they hold significant potential for oxidative cleavage reactions. This progress highlights the significant potential of tailored zeolite-based catalysts in mitigating mass transport limitations and enhancing catalytic efficiency.

Collectively, the findings reviewed in this article highlight the transformative potential of zeolite-based catalysts in biomass valorization. These materials provide a platform for developing sustainable, efficient, and scalable processes that align with the goals of a bio-based chemical industry. Future research should focus in optimizing catalyst design rationally, improving reaction selectivities, and addressing challenges such as diffusion limitations and catalyst stability. By doing so, zeolites will continue to be at the forefront of innovations driving the transition towards a sustainable, circular economy.

Abbreviations

BAS	Brønsted acid site
B/L ratio	The ratio of Brønsted to Lewis acid sites
C-C	Carbon-carbon single bond
C=C	Carbon-carbon double bond
CTAOH	Cetyltrimethyl ammonium hydroxide
DATMS	N,N-Diethyl−3-(trimethoxysilyl) propan−1-amine
DFF	2,5-diformylfuran
DGC	Dry-gel conversion
EFAl	Extra-framework aluminum
EG	Ethylene glycol
EMO	Epoxidized methyl oleate
ESO	Epoxidized soybean oil
FA	Formic acid
FCC	Fluid Catalytic Cracking
FDCA	2,5-furandicarboxylic acid
FUR	Furfural
GAA	Glucaric acid
GOA	Gluconic acid
GUA	Glucuronic acid
GVL	γ- valerolactone
HDO	Hydrodeoxygenation
HMF	5-hydromethoxyfurfural
HMFCA	Hydroxymethyl−2-furancarboxylic acid
IZA	International Zeolite Association
LA	Levulinic acid
LAS	Lewis acid sites
ML	Methyl linolate
MO	Methyl oleate
MPz	Metallothioporphyrzines
MTH	Methanol to hydrocarbons
NPs	Nanoparticles
PAHs	Polyaromatic hydrocarbons
SAC	Steam assisted conversion
SAPO	Silicoaluminophosphate
SBU	Secondary building unit
SDA	Structure directing agent
SO	soybean oil
STS	spongy titanosilicate
TBHP	tert-butyl hydroperoxide
TBPOH	tetrabutylphosphonium hydroxide
TPAOH	tetrapropylammonium hydroxide
TS−1	Titanosilicate−1
VOs	Vegetable oils

CRediT authorship contribution statement

Zormpa Foteini: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation. **Saraçi Erisa:** Writing – review & editing, Visualization, Supervision, Conceptualization. **Treu Philipp:** Writing – review & editing.

Author agreement statement

We the undersigned declare that this manuscript is original, has not been published before and is not currently being considered for publication elsewhere. We confirm that the manuscript has been read and approved by all named authors. The Corresponding Author is the sole contact for the Editorial process. He/she is responsible for communicating with the other authors about progress, submissions of revisions and final approval of proofs.

Declaration of Competing Interest

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

Data availability

No data was used for the research described in the article.

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