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REVIEW

Carbon-based and carbon-supported nanomaterials for the catalytic conversion of biomass: a review

Dong Xia[1] · Huayang Yu[2] · Heng Li[3] · Peng Huang[4] · Qun Li[1] · Yuanpeng Wang[1]

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Abstract

Catalytic conversion of biomass and waste into chemicals and fuels is gaining interest to reach a circular economy. Here, we review carbon-based and carbon-supported nanocatalysts for biomass conversion with focus on catalyst types and synthesis, optimization, mechanisms and three-dimension catalytic structures. Catalystic materials include amorphous carbon, graphene, graphene oxide, carbon nanotubes and carbon nanofibers.

Keywords Nanomaterials · Catalysis · Biomass conversion · Biomass-derived compounds · Metallic nanoparticles · Carbon supports · Carbon-supported catalysts

Introduction

The increasing consumption of fossil fuels and the associated air pollution have caused great environmental concerns worldwide. This concern is further exacerbated by the overuse of coals and fossil oils (Goeppert et al. 2014). Fossil fuels have been used as the dominating energy supplements, which contribute to a significant discharge of CO_2 and SO_x gases into the atmosphere and subsequently lead to the greenhouse effect and acid rain (Chandra Srivastava 2012; Zhong et al. 2020). Therefore, it is urgent to search for alternatives for fossil fuels. Biomass, an important industrial substance and the fourth largest energy resource on earth (14% of the primary energy source) (Balat and Ayar 2005), offers great potential to be used as an effective and green energy supplement due to its low cost, renewability, wide availability, and CO_2 cyclability (Wang et al. 2020a). At present, major nations are heading towards the industrialization and commercialization of biomass conversion. The USA pays special focus on the aerobic fermentation of biomass to produce ethanol (Mabee et al. 2011; Wang et al. 2019b), while the European Union concentrates on the production of biomethane and fine chemicals for usage in electricity generation and the manufacturing industry (Hassan et al. 2020; Wang et al. 2021a), with preferential policies enacted to further accelerate their developments (Ben Fradj et al. 2020). China has also formulated government policy to encourage the utilization of biomass, such as biofuels, fine chemicals, combined heat, and power generation (Bi et al. 2015; Tao et al. 2021; Wang et al. 2021a).

Biomass is mainly composed of cellulose, hemicellulose, and lignin (Feng et al. 2021), as presented in Fig. 1. These components can be easily converted into biofuels, fine chemicals, and platform molecules (Das et al. 2021; Navakoteswara Rao et al. 2021), via various catalytic conversion routes (Liang et al. 2021; Zhao et al. 2021). This feature has been frequently exploited to produce other value-added products, such as activated carbons (Adeleye et al. 2021; Ouyang et al. 2020), biochar (Jeyasubramanian et al. 2021; Senthil and Lee 2021) and fertilizers (Castro et al. 2020; Cristina et al. 2020). Additionally, a large number of reviews

Dong Xia and Huayang Yu have contributed equally.

✉ Heng Li
liheng310@foxmail.com

✉ Yuanpeng Wang
wypp@xmu.edu.cn

[1] Key Laboratory for Chemical Biology of Fujian Province, Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, People's Republic of China

[2] School of Design, University of Leeds, Leeds LS2 9JT, UK

[3] Key Laboratory of Estuarine Ecological Security and Environmental Health, Tan Kah Kee College, Xiamen University, Zhangzhou 363105, China

[4] Department of Materials, University of Manchester, Manchester M13 9PL, UK

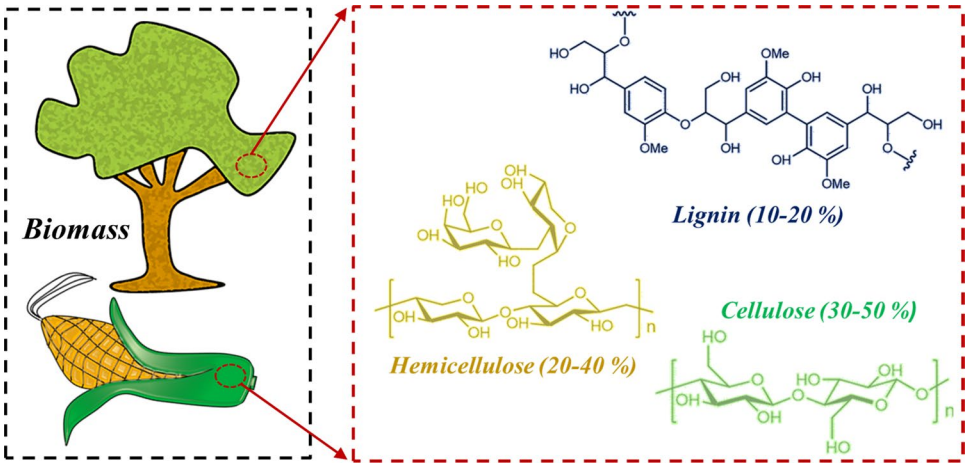

Fig. 1 Typical components of lignocellulosic biomass and their structures. The lignocellulosic biomass is mainly constituted of hemicellulose (20–40%), lignin (10–20%) and cellulose (30–50%)

regarding the conversion of biomass and biomass-derived chemicals into high-quality products have been outlined, which involve the deployment of both non-catalytic and catalytic methods (Calcio Gaudino et al. 2019; Gallezot, 2012; Hou et al. 2021; Lee et al. 2010; Zhang et al. 2017b). For example, Sivagurunathan et al. (2021) reviewed and outlooked the transformation of waste lignin into biofuel and value-added chemicals. Yu et al. (2021) commented on the recent advances in biomass gasification over alkali and alkaline metals. Layered double hydroxides as catalysts also have been summarised for the catalytic conversion of biomass (Song et al. 2020). Sudarsanam et al. (2019) reviewed different types of heterogenous catalysts in converting biomass into fuels and chemicals. Moreover, zeolite as support for metallic nanoparticulate catalysts in catalytic hydrodeoxygenation of biomass-derived compounds was also systemically reviewed (Luo et al. 2019). The progress regarding employing different catalytic approaches using specific catalysts in transforming lignocellulosic biomass into fuels and fine chemicals was also comprehensively commented on (Zhou et al. 2011). Temperature-induced biomass conversion to biofuels and the associated environmental impacts were reviewed by Osman et al. (2021). Functional hydrogels derived from cellulosic biomass showed remarkable performances in decontaminating wastewaters (Thakur et al. 2022a). Interestingly, monomers and polymers can also be produced from biomass via the microbial fermentation approach (Thakur et al. 2022b). Nevertheless, a detailed review that covers recently reported nanomaterials in catalyzing biomass-derived molecules and pure biomass into high-value chemicals is highly desirable and urgent, particularly those that were frequently reported and show rising trends in the field of biomass valorization. The catalytic conversion of pure biomass and biomass-derived molecules by different types of nanomaterials will be reviewed at the beginning of this review for clarity and straightforward understanding.

Carbon materials possess remarkable hydrothermal stability and are easy to modify, thus presenting superior capability of anchoring various types of metal particles and restoring catalytic activity under mild regeneration conditions (Huo et al. 2021). The excellent physiochemical properties of carbon materials, such as high surface areas, abundant functional groups (e.g. hydroxyl, carboxyl, epoxide, amino), tunable porous microstructures, high thermal stabilities, pronounced stabilities under strong acidic and alkaline conditions, ease of modification and impregnation with functionality-varied catalysts, are highly beneficial for catalytic biomass conversion (Furimsky 2017; Ledesma and Beltramone 2021; Xia et al. 2021a, b). Moreover, carbon materials are also essential components for forming highly efficient single-atom catalysts with enhanced conductivity (Lu et al. 2021). These excellent features underpin their great feasibilities and wide applicability in the fields of biomass utilization and resourcelization. Therefore, carbon-based materials, such as amorphous carbon (Cao et al. 2017), carbon nanotube (Chen et al. 2015), graphene, graphene oxide, reduced graphene oxide (Das et al. 2017; Jin et al. 2013; Zhu et al. 2015), graphite (Sharma et al. 2020; Tian et al. 2020) and graphite oxide (Li et al. 2020c; Zhang and Li 2020) in catalytic conversion of biomass have drawn enormous attention. Nevertheless, the up-to-date reviews of these nanocarbon materials for biomass conversion are rare. Notably, nanocarbon materials are also an outstanding supporting framework for functional catalytic nanoparticles (Devadoss et al. 2014; Meng et al. 2020a; Shi et al. 2021; Wang et al. 2017). This type of hybrid catalyst, namely nanocarbon supported nanoparticles, have found important applications in biomass upgrading and conversion (Xu et al. 2020). Previous reviews regarding the utilization of graphene, graphene derivatives and graphene-like substances as nanomaterials for catalytic biomass conversion have also been published (Das et al. 2017; Zhu et al. 2015).

To the best of our knowledge, no systematic review about carbon-based nanomaterials and carbon-supported hybrid nanomaterials for catalytic biomass conversion focussing on recent advancements have been reported. To fill the gap, we have summarized the frequently exploited amorphous carbon, carbon nanotube and graphene-related catalysts that are exploited in biomass valorization, including catalyst preparation, design, screening, and optimization. Specifically, this review outlines the up-to-date studies for the catalytic conversion of biomass using carbon-based nanocatalysts and carbon-supported hybrid nanocatalysts, which encompass amorphous and crystalline carbon-based catalysts, and their supported monometallic/multimetallic nanoparticles. Carbon nanostructure precursors can be assembled into carbon-based 3D macroscopic structures or monoliths, which inherit the superlative physical–chemical–mechanical properties from their parent carbon nanostructures. Consequently, this review also includes a subsection dedicated to carbon-based 3D macroscopic structures or monoliths and outlines their outlooks in the field of transforming biomass into high-value chemicals and commercial commodities. Currently, catalysts derived from carbon-based 3D macroscopic structures have not been widely investigated for biomass conversion, but relevant research is gaining popularity. Nanomaterials-based catalysts belong to a large category and are mainly exploited in the catalysis of biomass-related compounds, and piles of new scenarios have been continually emerging each year. Therefore, systematic summarization of the reported literature is important to make them more impactful. In addition, a clear understanding of this area is essential to considerably advance its developments. The general information and structure of this review are illustrated in Fig. 2.

Catalytic conversion of biomass

Converting naturally abundant and renewable biomass into high-quality transport fuels, alternative chemicals or other material intermediates is a sustainable way to provide resources for modern society, especially to ease the severe environmental pollution caused by fossil fuels. Undoubtedly, catalysis is one of the most effective approaches to obtain the desired chemical feedstocks from biomass, thus exhibiting great potential.

Catalytic conversion of pure biomass

Nanomaterial catalysts play important roles in transforming both biomass and biomass-derived molecules into value-added and high-quality products, consequently, they have been widely studied. This section covers the recent work concerning the catalytic conversion of pure biomass (algae-based biomass, non-algae-based biomass) using several functionality-different catalysts.

Algae-based biomass presents outstanding reproduction capability, high yield productivity (Carpita et al. 2012), as well as contains large amounts of carbohydrates, therefore exceedingly benefits the production of important chemical agents (Pendyala et al. 2020). Karpagam et al. (2020) fabricated heterogeneous bio-nano particles CaO and $CaCO_3$, originating from small-sized and powdered seashells, respectively, for direct catalytic transesterification of wet microalgal biomass of *Coelastrella* sp. M-60 into biodiesel, e.g. fatty acid methyl esters. The results showed that both the bio-nano particles CaO and $CaCO_3$ possessed significantly improved fatty acid methyl esters productivity than the commercial acid catalyst (increment of 102 and

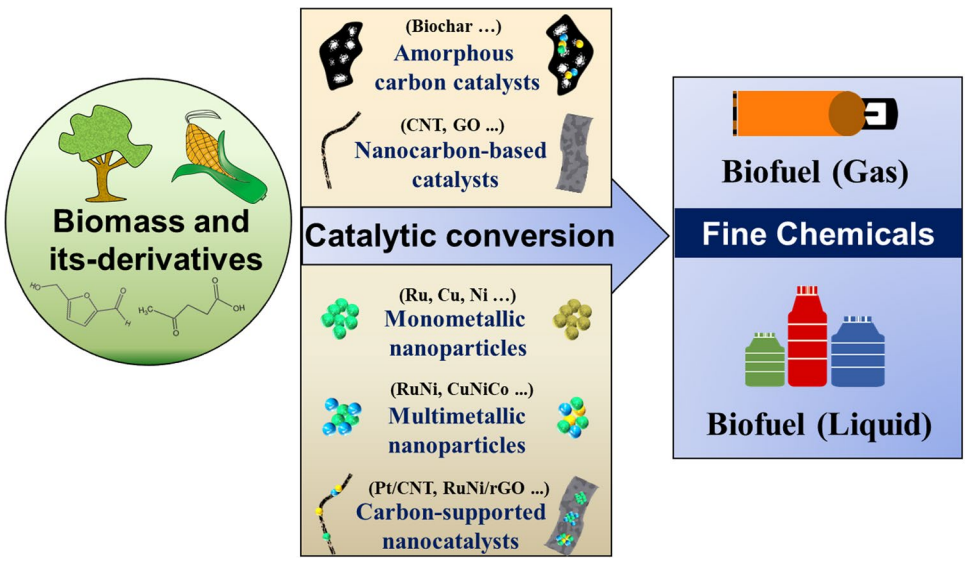

Fig. 2 Various nanomaterials-based catalysts for catalytically transforming biomass and its derivatives into biofuels and fine chemicals of this review, including monometallic nanoparticles, multimetallic nanoparticles, other nanoparticulate catalyst (*MOF* metal–organic framework), amorphous carbon catalysts, nanocarbon-based catalyst (*CNT* carbon nanotube; *GO* graphene oxide), carbon-supported nanocatalysts (*rGO* reduced graphene oxide)

139%, respectively). N_2P-loaded zeolite synthesised by a wet impregnation approach has also been proven to be effective for catalytic pyrolysis of water hyacinth and algae bloom into the respective bio-oil and biochar (Li et al. 2020a). These studies demonstrated that nanoparticles play important roles in the catalytic conversion of earth-abundant algae-based biomass into biofuels or alternative chemicals.

Recently, a large number of excellent works using a variety of solid nanomaterials for non-algae-based biomass conversion have been exploited. For example, Emara et al. (2020) synthesized CuO and hybridized CuNi-, CuCo-, CuNiCo-based mixed oxide nanoparticles for the catalytic pyrolysis of sugarcane-bagasse. The results demonstrated that the Cu-containing mixed oxide catalysts, especially the triple mixed oxides, displayed significantly improved catalytic activities for cellulose, hemicellulose and lignin degradation. The utilization of function-different nanocatalysts towards the conversion of bamboo shoot shell leads to the formation of different chemicals and derivatives, such as furoic acid (Yang et al. 2020b) and furfurals (Feng et al. 2020a). Modification and hybridization of known catalysts are effective and efficient approaches to further improve their catalytic performances in biomass conversion. For instance, in the process of hydrogen production from fir sawdust in a fixed-bed reactor, the hydrogen volume fraction was 30.39% higher when using the Co and La co-doped Ni/Al_2O_3 catalyst, compared with that of the un-coped catalyst (Wang et al. 2020c). The light olefins productions from pine sawdust using the dual catalyst of CaO and Al-MCM-41 were increased by 56.0 and 44.7% (Wang et al. 2020b). Therefore, nanomaterials as promising non-aqueous catalysts for biomass upgrading are the main foci to obtain high yields of important biomass-derived chemicals and value-added alternative fuels.

Direct catalytic conversion of pure biomass is challenging, however, these reported studies offered feasible approaches to achieve the goals of direct biomass conversion into valuable products, from simple natural minerals, single metal oxides/multi-metal oxides to doped metal catalysts. Designing catalysts with suitable mineral components, metallic species and substrates are crucial in improving the catalytic performance of biomass transformation. Besides, modification and hybridization of known catalysts are effective and important approaches to further improve their catalytic performances in biomass utilization.

Catalytic conversion of biomass-derived molecules

Biomass-derived molecules, such as levulinic acid, furfuryl alcohol, 5-hydroxymethylfurfural, 2,5-diformylfuran, glucose, fructose, xylose, inulin and sucrose, can be catalyzed into useful chemicals by nanomaterials catalysts. These processes are usually achieved by catalyzing a variety of reaction processes, hence the associated reactions in biomass upgrading and valorization were reviewed in this section. These include catalysis-based hydrogenation, hydrodeoxygenation, dehydration, deoxydehydration and amination, as shown in Fig. 3.

For catalytic hydrogenation of levulinic acid to γ-valerolactone with marked selectivity, Krushna et al. (Barla et al. 2021) prepared a highly efficient Y-zeolite supported Co catalyst, CoZ, via a wet impregnation approach. The CoZ catalysts were able to convert 60% of levulinic acid to γ-valerolactone with 70% selectivity. The high selectivity of γ-valerolactone was attributed to the surface Lewis acidic sites of the catalyst and the mild reaction temperatures. The selectivity of γ-valerolactone can be further enhanced by using metal–organic framework-based nanomaterial catalysts (Vasanthakumar et al. 2020). Catalytic transfer hydrogenation of 5-hydroxymethylfurfural and aldehydes to the corresponding alcohols was exploited by Feng et al. (2020b). In the study, earth-abundant MnO nanoparticles were incorporated into N-doped carbon, MnO@C-N, as the efficient catalyst, which showed excellent catalytic capacity and recyclability. Isopropanol was used as the H-donor/solvent to directly donate hydrogen to dramatically enhance the catalytic conversion and selectivity performances: 5-hydroxymethylfurfural to 2,5-dihydroxymethylfuran with 93% yield and 91% selectivity; aldehydes to the corresponding alcohols with at least 95% selectivity and 97% conversions. The above examples guide the design of different multifunctional

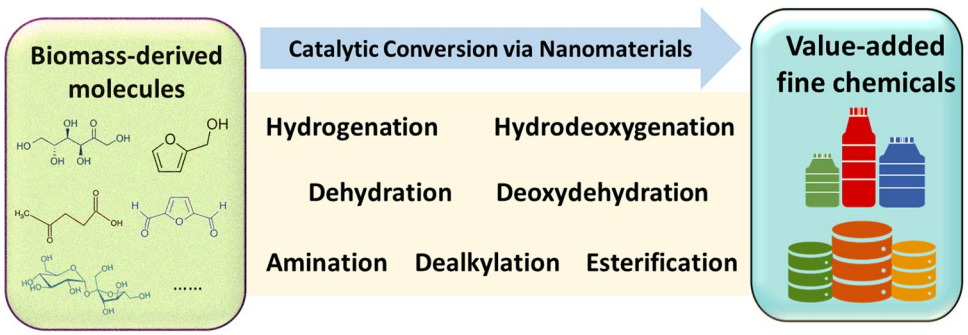

Fig. 3 Catalytic conversion of biomass-derived molecules into value-added fine chemicals via nanomaterials. Enhanced catalytic performances regrading different catalytic reactions are summarized in this review, including hydrogenation, hydrodeoxygenation, dehydration, deoxydehydration, amination, dealkylation and esterification

nanomaterial catalysts with high efficiency and selectivity towards catalytic biomass conversion.

A recent study concerning the selective hydrodeoxygenation of biomass-derived glycerol to 1,3-propanediol was reported by Miao and co-authors (Miao et al. 2020), who initially proposed using density functional theory calculation to conclude that the hybridized Pt/WO_x were the suitable and favourable catalysts to produce 1,3-propanediol (thermodynamic instability) over the competitive 1,2-propanediol and *n*-propanol. As expected, the experimental results revealed that the high surface area of Zeolite β supported Pt/WO_x (Pt/W/β) catalysts followed well with the density functional theory calculation, based on the results of the outstanding glycerol conversion of 84.2% and 1,3-propanediol selectivity of 46.1%, owing to the interfacial structure of Pt/WO_x benefiting H_2 chemisorption and the introduction of WO_x increasing Brønsted acid sites. In addition, the as-synthesized Pt/W/β catalysts displayed superior recyclability and renewability. This study clearly emphasized the importance of theoretical calculation in the instruction of experimental design.

The catalytic dehydration of carbohydrates, e.g. glucose and fructose, using different nanomaterials are frequently exploited in recent studies. Zhang et al. (2021) fabricated a H_3PO_4 modified silica-tin oxide composite (SiSnPO), for catalytic hydrolyzing glucose to 5-hydroxymethylfurfural. The high yield of 70.3% was attributed to the well-distributed Lewis acid sites and Brønsted acid sites. In another study, Bounoukta et al. (2021) discussed the acidity of the catalyst in hydrolyzing glucose to 5-hydroxymethylfurfural by designing a *p*-toluenesulfonic-sulfonated and Ca-impregnated bifunctional activated carbon catalyst, which exhibited a 5-hydroxymethylfurfural yield of 57%. Despite the low yield, this study manifested the impact of the functionalities of Lewis acid sites and Brønsted acid sites in the catalytic process of glucose. For nanomaterial catalysts, both the Lewis acid sites and Brønsted acid sites play dominant roles in the conversion ratio and yield.

As for deoxydehydration, Li et al. (2020b) systematically analyzed the catalytic deoxydehydration performance of biomass-derived diols using the $[Cp^*MoO_2]_2O$ catalysts (Cp* represents 1,2,3,4,5-pentamethylcyclopentadienyl). A 55% yield of 1-octene at a full conversion of 1,2-octanediol using anisole as the solvent was obtained. This case manifested that both reductant and solvent were key to enhancing catalytic performances.

The hydrotalcite-derived nickel catalysts synthesised by Zhou et al. (2021) showed high efficiency for obtaining high-value products of furfurylamine with an 84.1% yield from the complete conversion of furfuryl alcohol when using ammonia as the hydrogen donor. This study also showed that the Ni_2Al-600 catalyst with a Ni content of 50.5 wt% and surface area of 179 m^2/g exhibited high catalytic conversion and yield of 5-(aminomethyl)-2-furanmethanol to 2,5-bis(aminomethyl) furan at 160 °C for 18 h. The above example indicated that tuning the physicochemical properties of nanomaterials is essential in obtaining their optimal catalyst performances.

A recent study on the selective conversion of biomass-derived substances into fine and bulk chemicals has been investigated by Liao et al. (2020b), who transformed the commercial microporous ZSM-5 zeolite catalysts to serials of the Lewis acidic sites enriched hierarchical ZSM-5 catalysts, for the catalytic dealkylation of lignin-derived 4-n-propylphenol into small aromatics, i.e. phenol and propylene. The altered ZSM-5 catalysts with enlarged surface area and mesopore volume displayed higher catalytic dealkylation activity because of the hierarchization resulting in more Lewis acidic sites which favoured a high reaction temperature of 470 °C. As evidenced above, modification of existing nanomaterials is a good strategy to further enhance their catalytic capabilities.

The TBA_6-P_2W_{17}-SO_3H (TBA represents tetrabutylammonium), with a large percentage of Brønsted acid sites, as a typical solid acid catalyst, was synthesized by Lian and co-workers (Lian et al. 2020). The results demonstrated pronounced catalytic esterification functionalities towards the production of 5-hydroxymethylfurfural from several biomass-relevant carbohydrates, e.g. fructose, glucose, sucrose, inulin, and cellulose. Notably, the fructose reached the highest conversion of 99% to 5-hydroxymethylfurfural in the presence of 1,4-dioxane at 100 °C for 2 h. By contrast, cellulose exhibited the lowest conversion of only 1.6% amongst these tested carbohydrates. This study also suggested that the lack of Lewis acidic sites in the TBA_6-P_2W_{17}-SO_3H catalysts resulted in unfavourable catalytic conversion of cellulose.

Due to the wide variety of biomass-derived compounds, different catalytic reaction types will be involved in synthesizing targeted chemicals. Consequently, designing catalysts with Lewis acidic sites or Lewis basic sites should be considered carefully for a specified catalytic reaction. It is also important to take into account the durability of the catalysts while performing in harsh reaction conditions, e.g. high temperature, high pressure, impurity, and leaching. Achieving high conversion of biomass-derived molecules and high yield of value-added products are of great importance, which can be realized by introducing new reagents and fabrication methods, tuning physicochemical parameters, hybridizing, and incorporating catalytic nanoparticles.

Carbon-based nanomaterial catalysts for biomass-related conversion

Different types of carbon materials as efficient catalysts for converting biomass into value-added and energy-related products have been widely investigated, including

amorphous carbon (Elsayed et al. 2021; Li et al. 2021), carbon nanotube (Liao et al. 2020a; Zhang et al. 2015), carbon nanofiber (Jongerius et al. 2013), graphene (Zhu et al. 2015), graphene oxide (Hou et al. 2016), reduced graphene oxide (Cheng et al. 2016b; Parrilla-Lahoz et al. 2021), graphite (Faba et al. 2016; Feng et al. 2020a) and graphite oxide (Nie et al. 2014). Among them, the specific structures of graphene family materials (Clancy et al. 2018) and their fabrication methods, as well as applications, have all been well exploited (Chen et al. 2013; Geim and Novoselov 2007; Papageorgiou et al. 2017; Wang and Shi 2015).

The carbon-based nanomaterials show a broad spectrum of advantages as catalysts, such as tunable physicochemical properties, tailorable porous structures (micro-, meso-, macropore or hierarchical), high surface areas, exceptional thermal stabilities, and pronounced chemical inertness (Cheng et al. 2017; Kundu et al. 2020; Ng et al. 2012; Panwar et al. 2019). Besides, they are also widely used as supporting frameworks or skeletons for nanoparticulate catalysts to achieve syngenetic effects on improving the catalytic functionalities. Their unique structures facilitate effective separation, distribution and anchoring of the nanoparticles, as well as inhibiting nanoparticles aggregations, and sintering (Bhattacharya and Samanta 2016; Borenstein et al. 2017; Gerber and Serp 2020). The carbon-based nanomaterials contain a variety of oxygen-contained functional groups, which allow them to be grafted, impregnated or introduced with other functional groups to impart varied catalytic abilities for different biomass conversion (Sudarsanam et al. 2018; Wang et al. 2018). As studies related to graphene-based nanomaterials for biomass conversion, before 2017, have already been published (Das et al. 2017; Zhu et al. 2015), this chapter will pay attention to the recent works involving carbon nanomaterials published in the last five years, as listed in Table 1.

Amorphous carbon-based catalysts for biomass-related conversion

Amorphous carbon, e.g. activated carbon and biochar, is a common catalyst for applications in the conversion of biomass in the scientific community, which also has been considerably implemented and exploited. In this section, an unsupported amorphous carbon catalyst for biomass-related conversion will be discussed. Ren et al. (2018) reported a set of nitrogen-doped carbon catalysts for catalyzing biomass-derived 5-hydroxymethylfurfural to 2,5-diformylfuran. Amongst the as-prepared catalysts, the NC-950, treated at 950 °C, enabled a complete conversion of 5-hydroxymethylfurfural in the presence of acetonitrile and nitric acid and exhibited the highest 2,5-diformylfuran selectivity (95.1%), as well as maintained excellent cyclability. Additionally, Nguyen et al. (2020) fabricated a multifunctional nitrogen-doped carbon catalyst, NC-900, which displayed a 100% conversion of biomass-derived furfural and yielded 61% maleic acid. The two cases indicate that the amorphous carbon catalysts can be derived from different precursors. Other amorphous carbon-based catalysts, such as acidic ion modified nitrogen-doped carbon catalyst (Zhang et al. 2020) and bifunctional carbon nanoplatelets with plenty of oxygenic groups (Zhao et al. 2020a), have also been used for catalytic conversion of biomass-derived molecules and showed good conversion rates, as listed in Table 1.

For amorphous carbon catalysts directly derived from biomass, Abdu et al. (2020) utilized the eucalyptus plant as the original biomass to prepare carboxylated carbon catalysts. The carboxylated carbon catalyst was exploited for the catalytic hydrolysis of eucalyptus biomass, and its remarkable catalytic capacities were demonstrated by the high product yields of xylose and glucose (95.1 and 81%, respectively). Similarly, Ma et al. (2020) prepared nitrogen-doped activated carbon catalysts using the walnut shell. The sample was soaked in ammonia solution followed by carbonization, which results in a high surface area of 1259 m^2/g. This work also exploited the catalytic performance of nitrogen-doped activated carbon for the pyrolysis of walnut shells. The results indicated that it displayed a high yield of 44.19 mg/g and a selectivity of 34.7% in the generation of alkylphenols, such as 4-ethylphenol, cresol, phenol. In addition, the pyrolysis products in this study also contained several other aromatics, such as alkoxyphenols, catechols, and furans. The two studies demonstrate the multifunctional utilization and feasibility of biomass resourcelization, from wastes to high-value products and chemicals, as well as efficient catalysts.

Biomass not only shows great feasibilities in conversion into high-quality chemicals but can also be used as a raw material for directly making catalysts, which serves as an excellent alternative to replace precious or expensive catalysts. Even though amorphous carbon-based catalysts have been extensively exploited, most reported amorphous carbon only displayed limited catalytic abilities towards the production of fine chemicals during the biomass conversion, namely only disclosing single functionality. Developing multifunctional amorphous carbon catalysts is urgent, which can be realized by introducing various functional groups, generating hierarchical porous microstructures or enlarging specific surface areas by adding activation/porogen agents, and forming single- or multi-atom catalysts.

Carbon nanotube-based catalysts for biomass-related conversion

Comparatively, the up-to-date reports regarding adopting carbon nanotubes as catalysts for biomass-related conversions are rare, although they have been frequently utilized

Table 1 Carbon-based nanomaterial catalysts for biomass-related conversion in previously reported literature

Nano-catalysts	Biomass	Products	Conditions	Conversion	Selectivity	Ref
Nitrogen-doped carbon catalysts	Biomass-derived 5-hydroxymethyl-furfural	2,5-diformylfuran	100 °C, 14 h, 10 bar oxygen pressure	100%	95.1%	Ren et al. (2018)
Nitrogen-doped carbon catalysts	Furfural	Maleic acid	80 °C, hydrogen peroxide as an oxidant	100%	61%	Van Nguyen et al. (2020)
Acidic ion modified nitrogen-doped carbon catalyst	Levulinic acid	Ethyl levulinic acid	70 °C	94.17%	-	Zhang et al. (2020)
Bifunctional carbon nanoplatelet	Fructose	2,5-diformylfuran	110 °C, 2 h, dimethyl sulfoxide	100%	70.3%	Zhao et al. (2020a)
Carboxylate heterogeneous catalysts from eucalyptus	Eucalyptus biomass	Xylose/glucose	180 °C, 17 min, HCl	–	95.1%/81%	Abdu et al. (2020)
Nitrogen-doped activated carbon by using walnut shell	Walnut shells	Alkylphenols	400 °C	12.8%	34.6%	Ma et al. (2020)
Carbon-nanotube-N-heterocyclic carbene ruthenium complex	Hydrogenating ethyl levulinate	γ-valerolactone	N_2 atmosphere, 60 °C, 6 h, 3.0 MPa	100%	100%	Shen et al. (2019)
Graphene oxide	Cellulose	Glucose	Microwave irradiation, 473 K, 30 s, 800 W	–	73%	Mission et al. (2017)
Graphene oxide	Biomass-derived furfural alcohol	Ethyl levulinate	130 °C, 2 h	100%	38.3%- 62.9%	Wu et al. (2019)
Reduced graphene oxide	Rearranging Cyclopentanol, methylcyclopentane molecules	High-quality jet oil	Room temperature, 30 min	71.8%	97.3%	Dai et al. (2020)
Nitrogen-doped graphene oxide	Glucose	Succinic acid	160 °C, 18 atm O_2 pressure, 20 h	100%	67.9%	Rizescu et al. (2017)
Sulfonated graphene oxide	Cellulose	Glucose	130 °C, 10 h	78.3%	89%	Huang et al. (2018)
Sulfonated graphene oxide	Cellulose	Glucose	150 °C, 3 h	47.6%	95.5%	Tondro et al. (2020)
Sulfonated graphene oxide	Cellulose	Glucose	160 °C, 3 h	36.1%	72.8%	Tondro et al. (2021)
Carbon nanotube	Cellulose	Glucose	423 K,15 h	35.3%	76.5%	Qin et al. (2020)
Reduced graphene oxide	Cellulose	Glucose	423 K,15 h	37.9%	77.8%	(Qin et al. (2020)
Activated carbon	Cellulose	Glucose	423 K,15 h	36.6%	75.1%	Qin et al. (2020)
Sulfonated graphene	Corn stalk	Furfural	150 min, 190 °C	–	48%	Ma et al. (2019)
Sulfonated graphene	Xylose	Furfural	150 min, 150 °C	–	96%	Ma et al. (2019)
Sulfonated graphene quantum dot	Fructose	5-hydroxymethylfurfural	170 °C, 2 h	91.8	56.3%	Li et al. (2018b)
Edge-selectively carboxylated graphene	Cellulose	Glucose	180 °C, 20 min, HCl	-	87%	Idris Abdu et al. (2020)
Edge-selectively carboxylated graphene	eucalyptus lignocellulose	Xylose and glucose	180 °C, 20 min, HCl	-	89 and 65%	Idris Abdu et al. (2020)

as supporting materials for functional nanoparticles. A recent study conducted by Zhao et al. (2020a) used carbon nanotube as a catalyst for transforming 5-hydroxymethylfurfural into 2,5-diformylfuran, but only 25.78% conversion of 5-hydroxymethylfurfural and 11.43% yield of 2,5-diformylfuran were achieved. However, the conversion ratio and yield can be significantly improved by adding $NaNO_2$ into the system. Using carbon nanotube as a substrate for grafting of

a high-performance metal complex for the conversion of biomass-derived compounds was tested by Shen and co-workers (2019). In the work, the N-heterocyclic carbene ruthenium complex was grafted onto carbon nanotube to produce effective CNT-Ru-1 catalysts, with both catalytic yield and conversion exceeding 99%. In another study, the functionalized carbon nanotube was used to catalyze 5-hydroxymethylfurfural, but with no value-added products were generated (Sharma et al. 2019). As evidenced above, carbon nanotube as a catalyst by itself for biomass transformation into useful chemicals shows limitations but exhibits great prospects as a supporting framework for highly effective nanomaterials-based catalysts.

Commonly used carbon nanotube has plenty of carboxylic acid functional groups but lacks nitrogen-containing functional groups compared to the amorphous carbon catalysts, hence, restricting its applicability in catalytic biomass conversion. As such, initiating or grafting functional catalytic active sites with highly active carboxylic acid functional groups are important routes to broaden its catalytic applications for the effective valorization of biomass.

Graphene-based catalysts for biomass-related conversion

The 2D materials, graphene and its derivatives are the most representative since it won the Nobel Prize in 2010, therefore graphene-based nanomaterials have already been extensively studied in catalytic conversion and upgrading of biomass-related applications. Therefore, the recent advance of graphene-based catalysts will be reviewed in this section. Graphene-derived catalysts, such as graphene oxide (GO), reduced graphene oxide (rGO), nitrogen-doped graphene oxide (NGO) and sulfonated graphene oxide (SGO), are not uncommonly used for biomass conversion, as indicated in Fig. 4.

Graphene oxide catalysts for biomass conversion

Graphene oxide as a solid catalyst for depolymerizing cellulose with the assistance of microwave irradiation was exploited by Mission et al. (2017). Graphene oxide exhibited a ~46% yield of glucose at 200 °C for 60 min with a microwave power of 200 W, and the yield can be further improved to 73% using a cellulose-to-water ratio of 1:50. The excellent catalytic activity of graphene oxide was attributed to its high absorption capacity of microwave, and its high concentrations of hydroxyl as well as carboxyl groups. To convert biomass-derived furfural alcohol into ethyl levulinate, Wu et al. (2019) controlled the fractions of catalytically active oxygen-containing groups and organosulfur groups on graphene oxide nanosheets by adjusting the synthetic parameters. All the as-synthesized graphene oxide catalysts were able to fully convert furfural alcohol with the yield of ethyl

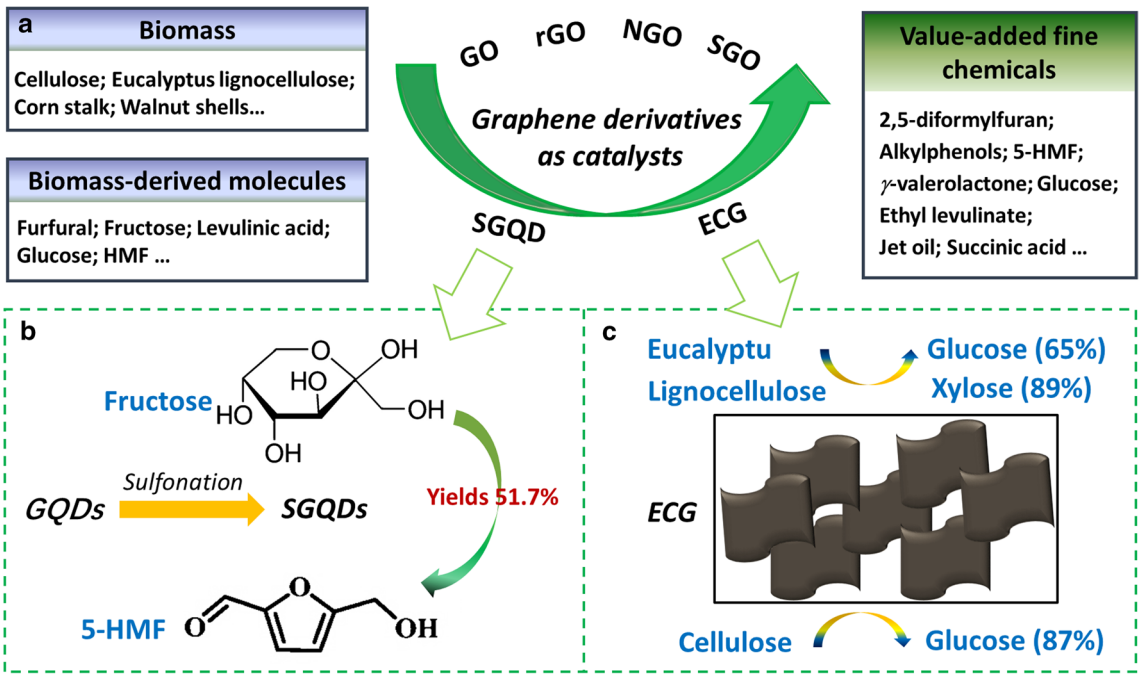

Fig. 4 (**a**) Catalytic conversion of biomass-derived molecules into fine chemicals via graphene-derived nanomaterials: GO, graphene oxide; rGO, reduced graphene oxide; NGO, nitrogen-doped graphene oxide; SGO, sulfonated graphene oxide. (**b**) Synthesis of sulfonated graphene quantum dots (SGQDs) from graphene quantum dots (GQDs) and dehydration of fructose to 5-hydroxymethylfurfural (5-HMF). (**c**) Description of edge-selectively carboxylated graphene (ECG) for hydrolysis of cellulose and eucalyptus lignocellulose

levulinate ranging from 38.3 to 62.9%, owing to the strong acidities. These oxygenic functional groups within the graphene oxide nanosheets enable them to perform different types of catalytic functionalities in various systems.

Reduced graphene oxide catalysts for biomass conversion

Not just focussing on graphene oxide catalysts, Mission et al. (2018) also considered using reduced graphene oxide as a catalyst for depolymerizing cellulose. In the study, a high yield of glucose was achieved in a much shorter time in the presence of subcritical water at 473–513 K for 5 min using a 200 W microwave power. This was because reduced graphene oxide was microwave sensitive and full of nano defects. Based on the above studies, the microwave irradiation method can be extended to another carbon-based catalytic system to improve efficiency. In a different application, reduced graphene oxide as functional additives in the sulfuric acid-catalyzed reaction was systematically studied by Dai et al. (2020). The authors produced high-quality jet oil from rearranging cyclopentanol and methylcyclopentane molecules. In this case, the addition of reduced graphene oxide increased the contact area of reactants with sulfuric acid, therefore leading to enhanced conversion, yield and selectivity, especially for methylcyclopentane. The above examples demonstrated that reduced graphene oxide can be exploited as efficient catalysts for biomass conversion by using appropriate strategies.

Nitrogen-doped graphene oxide catalysts for biomass conversion

As a metal-free catalyst, nitrogen-doped graphene oxide is attracting enormous attention. A typical case study concerning nitrogen-doped graphene oxide catalysts for efficiently oxidizing glucose into succinic acid was reported by Rizescu et al. (2017). In their study, various nitrogen contents of 3.8, 5.3 and 8.5% were imported into GO precursors in ammonia followed by reduction to form the NH_2-functionalized, reduced graphene oxide catalysts, namely NH_2-rGO, in which the NH_2-rGO with a nitrogen content of 5.3% displayed a complete conversion of glucose and a 67.9% high selectivity value towards succinic acid. The reduced graphene oxide as a control in this study showed nearly no catalytic activity, confirming the activity was originated from the introduced nitrogen atoms.

Sulfonated graphene oxide catalysts for biomass conversion

The above example involved the usage of organosulfate group modified GO, the sulfonated graphene oxide is an important catalyst that has been frequently exploited in transforming biomass-related materials. For example, Huang et al. (2018) prepared the sulfonated graphene oxide catalyst and addressed its restacking problem for catalytic hydrolysis of cellulose to form glucose. In this study, the sulfonated graphene oxide catalyst showed excellent capacities in converting 78.3% of cellulose and yielding 69.7% glucose at 130 °C for 10 h. Similarly, Tondro et al. (2020) adopted sulfonated graphene oxide catalyst to hydrolyze cellulose in water, in which the sulfonated graphene oxide catalyst exhibited an ultrahigh catalytic capability towards the yield and selectivity of glucose. Other sulfonated graphene oxide catalysts, such as the ones using GO as starting materials that were prepared from the graphitization of nettle leaves (Tondro et al. 2021), the sulfonated graphene oxide catalysts by an advanced gas–liquid interfacial plasma technique (Qin et al. 2020), the sulfonated graphene oxide catalysts fabricated by the typical acid-treatment of graphene oxide in acidic solution (Ma et al. 2019), have also been adapted for catalytic conversion of biomass-derived molecules, as listed in Table 1. Graphene quantum dot, GQD, a graphene derivative, that was sulfonated to possess -SO_3H groups to improve its catalytic activity in converting various biomass-based carbohydrates (e.g. cellulose, glucose, xylose, fructose, inulin, sucrose and cellobiose), has seen conversions of carbohydrates ranging from 45.1 to 91.8% and the yields of 5-hydroxymethylfurfural up to 51.7%, as presented in Fig. 4b (Li et al. 2018b). Early studies of sulfonated graphene oxide catalysts have also been used in converting microalgae to biodiesel (Cheng et al. 2016a), hexose sugars to levulinic acid (Upare et al. 2013), 5-(Hydroxymethyl)-2-furfural to biofuels (Upare et al. 2013). These literature reports indicate that the sulfonated graphene oxide catalysts are promising and beneficial materials for biomass conversion.

Other graphene-related catalysts for biomass conversion

Graphene oxide and reduced graphene oxide can catalyze furfural alcohol into butyl levulinate. Both catalysts exhibited complete conversion and 100% selectivity for butyl levulinate at 110 °C, owing to their tunable oxygenic functional groups on the surface (Gitis et al. 2018). As the functional groups play a pivotal role in affecting the catalytic activity of graphene-based solid catalysts, carboxyl group has been introduced into the graphite oxide catalysts. Specifically, Abdu et al. (2020) used a ball mill to obtain graphite oxide with 26.45% contents of carboxyl groups. The as-obtained catalysts exhibited 87% yield of glucose from cellulose hydrolysis, as well as 89% yield of xylose and 65% yield of glucose from eucalyptus hydrolysis under mild conditions (Fig. 4c). These results show that graphene derivatives embrace high potentials in catalytic conversion and upgrading of biomass-related applications. As can be seen in Fig. 4,

multifunctional graphene derivatives can transform different types of biomass and biomass-derived molecules.

The ability of graphene-related materials in catalyzing biomass-related substances derives from their different functional groups. However, most reported studies were focused on their catalytic capability and selectivity, the structure-property relationship in biomass conversion was scarcely discussed. Future studies that focus on tuning the contents of the catalytically active functional groups in graphene-related catalysts will help to establish the structure-property correlations, which is of crucial significance in revealing the catalytic mechanisms and guiding the accurate design of proper catalysts in complex catalysis systems. Avoiding the restacking of graphene sheets during the catalyst fabrication is also important, therefore, tactics to prevent aggregation should be considered. Additionally, doping is still one of the most effective approaches to alter the microstructures and electronic structures of graphene materials. In-depth understandings of the impact of locally doped atoms on the catalytic behaviours are urgent to be exploited.

Carbon-supported nanomaterial catalysts for biomass-related conversion

Carbon-supported nanomaterial catalysts inevitably present extensive research interests, which are based on the preeminent physicochemical properties of carbon materials as abovementioned. This section will review amorphous carbon, carbon nanofiber, carbon nanotube and graphene as supports for nanomaterial catalysts in biomass-related transformation applications (Table 2, Figs. 5, 6 and 7).

Supported amorphous carbon catalysts

Amorphous carbon features high surface area, hieratical porosity, various oxygenic functional groups, and negative charge (Creamer and Gao 2016; Huve et al. 2018; Sevilla and Mokaya 2014). It is also an ideal supporting material for functional nanoparticle catalysts to enhance their catalytic performances. To broaden the applicability of amorphous carbon, diverse nanoparticle catalysts were incorporated onto amorphous carbon for upgrading the catalytic conversion and productivity of biomass-related projects. A typical example was the decoration of metallic Ni nanoparticles onto nitrogen-doped activated carbon, NAC, to form the Ni/NAC catalysts, for the considerably enhanced hydrogenation of furfural to tetrahydrofurfuryl alcohol (Gong et al. 2017). Results verified that nitrogen doping significantly affected the catalytic performance of Ni/NAC, showing 100% conversion of furfural and a nearly 100% selectivity for tetrahydrofurfuryl alcohol, which was supported by comparing the catalytic results with the non-doped Ni/AC catalyst. Yang et al. (2020a) prepared nitrogen-doped carbon, NC-800, as supporting material for Pt nanoparticles to obtain the hybrid catalyst Pt/NC-800, which was used for aerobic oxidation of biomass-derived 5-hydroxymethylfurfural. The Pt/NC-800 catalyst had a high surface area of up to 809.2 m^2/g, and the impregnated nitrogen and Pt contents were 5.6 and 1.12%, respectively. Owing to these excellent physicochemical parameters, the Pt/NC-800 catalyst exhibited

Table 2 Amorphous carbon and carbon nanofiber supported catalysts for biomass-related conversion in academic literature (*NAC* nitrogen-doped activated carbon; *NC* nitrogen-doped carbon, *AC* activated carbon; *CNF* carbon nanofiber)

Nano-catalysts	Biomass	Products	Conditions	Conversion	Selectivity	Ref
Ni/NAC-1–1073	Furfural	Tetrahydrofurfuryl alcohol	353 K, 3 h	100%	~100%	Gong et al. (2017)
Pt/NC-800	5-hydroxymethylfurfural	2,5-furandicarboxylic acid	110 °C, 0.5 MPa O_2, 24 h, Na_2CO_3	100%	83.9%	Yang et al. (2020a)
MCo@C	Vanillyl alcohol	Vanillin	85 °C, H_2O_2 as oxidants	96.97%	99%	Lai et al. (2018)
CuO/N–C-HNSs	5-hydroxymethylfurfural	Furan-2,5-dimethyl-carboxylate	100 °C, tert-butyl hydroperoxide as an oxidizing	100%	93%	Gupta et al. (2021)
Fe_2O_3@NC-800	Aromatic aldehydes	Benzonitriles	60 °C, 24 h	–	99.45%	Wang et al. (2021b)
Ni-Cu/AC	Canola stalks	H_2	440 °C, 20 min, 2.5 wt% catalysts	20.96 mmol gas g_{CS}^{-1}	–	Salimi et al. (2018)
Pd/CNF	Vanillin	2-methoxy-4-methyl-phenol	100 °C, 5 bar H_2, 5 h	100%	> 90%	Espinosa et al. (2019)
Co_3O_4/CNF	Cinnamaldehyde	Cinnamyl alcohol	160 °C, 7 h, 2-propanol	100%	95%	Zhou and Qi (2020)
Fe-Mo_2C/CNF	Biomass	Hydrogen rich syngas	1.5 MPa, 850 °C	–	> 60%	Lalsare et al. (2021b)

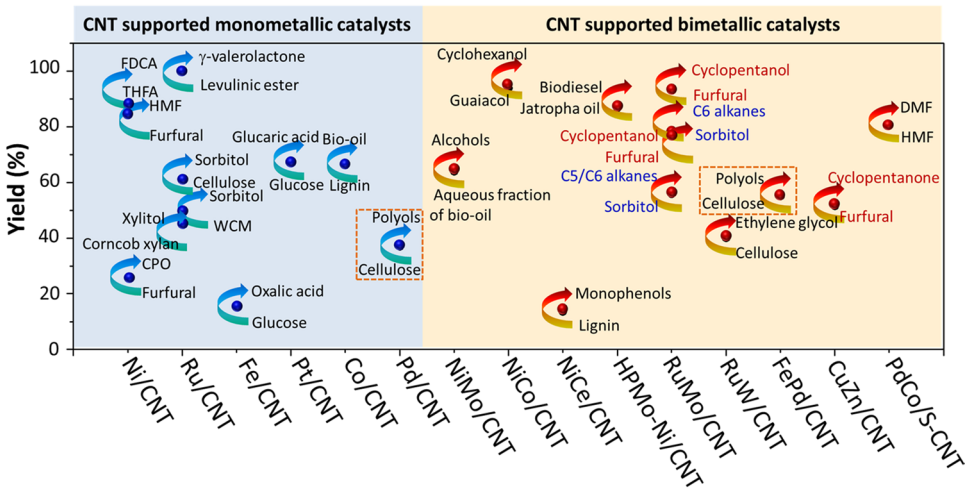

Fig. 5 Carbon nanotube supported monometallic and bimetallic catalysts for biomass-related conversion from the reported literature (*CNT* carbon nanotube; *THFA* tetrahydrofurfuryl alcohol; *HMF* 5-hydroxymethylfurfural; *FDCA* 2,5-furandicarboxylic acid; *WCM* waste cellulosic materials; *DMF* 2,5-dimethylfuran)

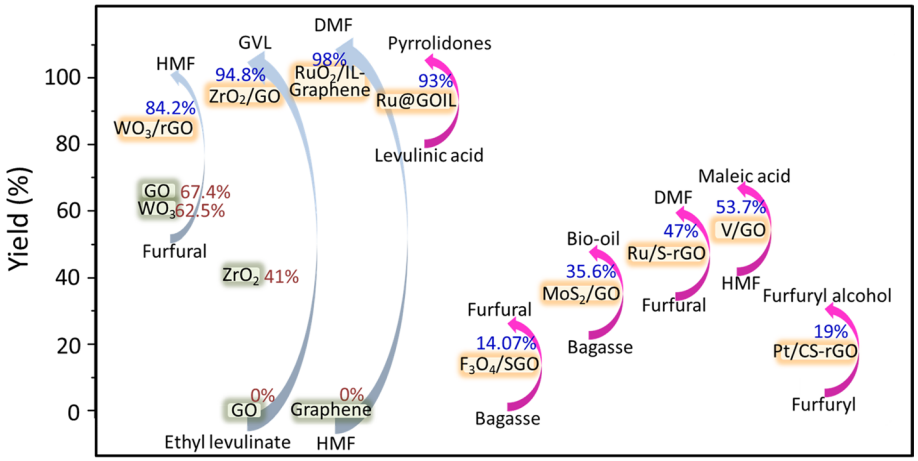

Fig. 6 Graphene supported monometallic catalysts for biomass-related conversion the in previously reported literature (*HMF* 5-hydroxymethylfurfural; *DMF* 2,5-dimethylfuran; *GVL* γ-valerolactone; *GO* graphene oxide; *rGO* reduced graphene oxide)

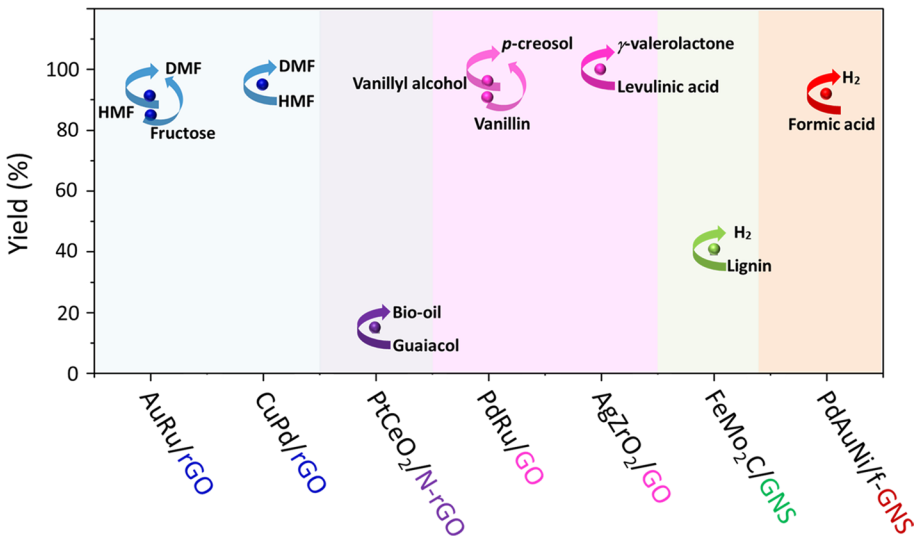

Fig. 7 Graphene supported multimetallic catalysts for biomass-related conversion in academic literature (*HMF* 5-hydroxymethylfurfural; *DMF* 2,5-dimethylfuran; *rGO* reduced graphene oxide; *N-rGO* nitrogen-doped reduced graphene oxide; *GO* graphene oxide; *GNS* graphene nanosheet)

a 100% conversion of 5-hydroxymethylfurfural and a high yield of 83.9% for 2,5-furandicarboxylic acid. The above results point out that amorphous carbon-supported metallic nanoparticulate catalysts show both high conversion and yield in the conversion of biomass-related compounds.

Nanomaterials decorated amorphous carbon hybrid catalysts with strong magnetic properties were also applied for catalytic biomass conversion. Lai and co-workers (2018) designed a magnetic hybrid carbon catalyst, MCo@C, by embedding Co_3O_4 and Co^0 nanoparticles. By decorating fine catalytic nanoparticulate components onto the nitrogen-doped hollow carbon nanospheres structures, namely HNSs catalysts, Gupta et al. (2021) recently synthesized a CuO/N–C-HNSs catalyst for catalytic oxidative esterification. Both amorphous carbon hybrid catalysts showed excellent catalytic conversion performance, as listed in Table 2.

The nitrogen-doped carbons prepared from biomass are also commonly exploited in supporting nanoparticulate catalysts, such as iron oxides and bimetallic Ni-based catalysts. Specifically, Wang et al. (2021b) fabricated a nitrogen-doped carbon of NC-800 and used it to support iron oxide nanoparticles to obtain the Fe_2O_3@NC-800 catalysts, which showed up to 99.45% catalytic ammoxidation performance of converting aromatic aldehydes to benzonitriles. Canola stalks have also been chosen as the starting materials for producing activated carbon, abbreviated as AC. In this study, bimetallic Ni-Ru, Ni-Co and Ni-Cu nanoparticles were impregnated onto the as-synthesized activated carbon to obtain the corresponding hybridized catalysts, which were then utilized to hydrothermally catalyze the canola stalks to acquire H_2-rich gas (Salimi et al. 2018). After careful experimental optimization and performance tests, the Ni-Cu/AC was screened as the best catalyst with a high yield of H_2 generation (20.96 mmol/gas per gram canola stalk). These recent studies elucidate that the amorphous carbons as supporting materials are beneficial to improve the catalytic performances and capacities in upgrading both the conversion of biomass-derived compounds and original biomass as the starting materials.

The excellent physicochemical properties of amorphous carbon show great suitability in working as supporting frameworks. New types of metallic catalysts are emerging each year, consequently, novel methods for combining and impregnating these catalysts with amorphous carbon without compromising their catalytic capacities would significantly advance the field.

Carbon nanofiber-supported catalysts

Compared to other carbon supports, research on biomass-related conversion using carbon nanofiber-based catalysts is scarcely exploited. Typically, the carbon nanofiber supports were employed to decorate monometallic Pd nanoparticles to synthesise the Pd/CNF catalysts, which demonstrated higher catalytic activity towards the production of 2-methoxy-4-methyl-phenol from vanillin than the Pd/CNT catalysts counterparts (Espinosa et al. 2019). On the other hand, the carbon nanofiber supports were also utilized to incorporate ultrafine Co_3O_4 nanocatalysts for the catalytic hydrogenation of biomass-related aldehydes (Zhou and Qi 2020). The as-prepared Co_3O_4/CNF catalysts featured a high surface area of 106.7 m^2/g, excellent mesoporous pores of ~ 11.6 nm, uniformly distributed and ultrasmall Co_3O_4 nanoparticles of ~ 1.57 nm. Owing to these features, the catalysts showed complete conversion of cinnamaldehyde and 95% selectivity for cinnamyl alcohol in the presence of 2-propanol. By contrast, both the pure carbon nanofiber and Co_3O_4 nanocatalysts exhibited negligible catalytic functionalities. A bimetallic Fe-Mo_2C/CNF hybrid catalyst was synthesized by Lalsare et al. (2021b) for applications in biomass reforming, in which the Fe-Mo_2C/CNF catalysts contained the two important active and stable Mo_2C and Fe_3C_x nanoparticles. Greater than 60% concentrated H_2 gas was generated in the reforming of hardwood biomass with excellent repeatability. Additionally, the Fe–Mo_2C, Ni–Mo_2C and Pd–Mo_2C nanoparticulate catalysts were loaded onto graphene nanosheets to understand their performances in hardwood biomass reforming, which followed the order of Fe > Ni > Pd, indicating that the Fe–Mo_2C was the most active. This case demonstrated that different metal species exhibited highly differed catalytic performances in catalytic hardwood biomass reforming.

The relatively scarce research on carbon nanofiber implies great opportunities to be exploited as supporting substrates for different metallic catalysts. The metallic species decorated carbon nanofiber hybrid catalysts can be applied to a variety of biomass conversion reactions. Alternatively, carbon nanofiber can be modified or tailored by nitrogen and sulfur atoms to work as a catalyst on its own, therefore narrowing research gaps in the field of biomass conversion.

Carbon nanotube-supported monometallic catalysts

Supporting monometallic and bimetallic nanoparticulate catalysts onto carbon nanotube surfaces as highly efficient hybrids have been extensively researched. In this section, different types of metallic catalysts and bimetallic catalysts combined with carbon nanotube for biomass-based conversion reported in the last five years will be specifically reviewed, as presented in Fig. 5.

Carbon nanotube-supported nickel-based catalysts for biomass conversion

The hydrogenative transformation of furfural into tetrahydrofurfuryl alcohol was also exploited by using Ni nanoparticles loaded carbon nanotube catalysts, namely Ni-CNT. Liu et al. (2016) decorated Ni nanoparticles onto carbon nanotube supports with different loadings, in which the 10% Ni/CNT with an average particle size of 5.9 nm exhibited the best performance under the optimized conditions, with a 99.1% conversion of furfural and an 85.1% selectivity to tetrahydrofurfuryl alcohol. As for the hydrogenation of furfural, Herrera et al. (2020) also decorated Ni nanoparticles onto functionalized carbon nanotube to obtain the hybrid Ni/CNTox catalysts, which exhibited unique amphiphilic characteristics to stabilize the catalysts between the water/oil interface for improving the catalytic activity, hence leading to the formation of the major components consisting of cyclopentanone, levulinic acid, and tetrahydrofurfuryl alcohol. Sharma et al. (2019) carried out aerobic oxidation of biomass-derived 5-hydroxymethylfurfural using the nickel-functionalized carbon nanotube catalysts, which showed a 94.5% conversion of 5-hydroxymethylfurfural and a 92.4% selectivity of 2,5-diformylfurane when using water as a solvent. In specified catalytic reactions, nickel-based catalysts exhibited great catalytic functionalities in converting biomass.

Carbon nanotube-supported ruthenium-based catalysts for biomass conversion

The Ru-based catalysts are widely studied in upgrading biomass and its-derived molecules. For biomass hydrolysis, Ribeiro et al. (2016) prepared a Ru/CNT catalyst, namely carbon nanotube supports impregnated with Ru nanoparticles, for direct converting corncob xylan, hemicellulose, into xylitol in a water solvent. Experimental results showed that the Ru/CNT was able to yield 45.4% of xylitol compared with only 11.8% of the un-impregnated carbon nanotube catalyst. The results demonstrated the importance of the introduction of Ru nanoparticulate catalyst for enhancing catalytic selectivity. Although only 50% the target product is yielded, the catalyst is easy to recycle due to its solid phase properties. Additionally, the Ru/CNT catalysts were also exploited for aerobic oxidation of 5-hydroxymethylfurfural to acquire 2,5-diformylfurane, with a high yield of 92.4% under optimal conditions (Sharma et al. 2019). This research demonstrates the merits of using nanocarbons as supports for nanoparticle catalysts. Another example concerning producing sorbitol from direct cellulose conversion employing Ru-based catalyst was reported by Rey-Raap et al. (2019), who decorated Ru nanoparticles onto mixed carbon supports via the hybridization of glucose-derived carbon and carbon nanotube (Fig. 5). Ru-functionalized carbon nanotube catalysts also emerged for the transformation of biomass-based chemicals into high-value products. For instance, Zhang et al. (2017a) functionalized carbon nanotube with polymeric ruthenium porphyrin for catalytic hydrogenation of biomass-derived levulinic ester, in which the catalysts showed a very high catalytic selectivity of 99% towards the production of γ-valerolactone, with a full conversion of levulinic ester. These cases validated that carbon nanotube exhibited poor catalytic ability, but was able to enhance the catalytic capability after incorporation with ruthenium-based catalysts.

Other carbon nanotube-supported metallic catalysts for biomass conversion

The other carbon nanotube supported metallic nanoparticulate catalysts, including Fe-(Ventura et al. 2018), Pt-(Deng et al. 2021), Co-(Jia et al. 2021) and Pd-(Espinosa et al. 2019) related nanoparticles, are also investigated to upgrade the catalytic conversion of biomass (Fig. 5). Recently, Deng et al. (2021) found that pure carbon nanotube failed to generate glucaric acid from the cellulose-derived glucose. However, a relatively high yield of 67% glucaric acid was achievable when using the Pt nanoparticles decorated carbon nanotube catalysts in an aqueous medium. Ventura et al. (2018) investigated the catalytic performances of aerobic oxidative cleavage of C6 polyols by decorating them onto carbon nanotube and N-doped carbon nanotube supports, respectively. The Fe-decorated carbon nanotube catalyst exhibited varied yields of oxalic acid (up to 48.4%) and succinic acid (up to 17.6%) from oxidative cleavage of 5-hydroxymethylfurfural (up to 99% conversion) under different conditions. When fructose was used as a substrate, the Fe-decorated carbon nanotube catalyst also showed an overall 99% conversion ratio of fructose at 140 °C, with the selectivity of 46.8% and 21%, respectively, for oxalic acid and succinic acid. The Fe-decorated carbon nanotube showed no catalytic capacity for the cleavage of glucose, but the N-doped Fe-decorated carbon nanotube catalysts displayed a 41.8% conversion of glucose and a 37.1% selectivity towards oxalic acid at 150 °C in an oxygen atmosphere for 6 h, owing to strongly enhanced acidic sites. Non-metal atom doping played important role in further enhancing catalytic functionality in biomass conversion.

Carbon nanotube as support for single metal species in valorizing biomass presents higher catalytic capability, durability, selectivity, stability, recyclability, and less leaching character than that of the carbon nanotube counterparts. However, many reports exhibited low catalytic conversion efficiencies below 50%, which could be greatly improved in future studies. Follow-up research should focus on reducing

the metallic nanoparticle size (i.e. increasing active sites), anchoring strength with carbon supports (i.e. high durability in cycling measurements and harsh conditions), combing with multiple non-metal elements (i.e. altering local catalytic environments and adding new catalytic abilities).

Carbon nanotube-supported bimetallic catalysts

Different kinds of bimetallic catalysts supported by carbon nanotube have been intensively studied for biomass-related applications, such as Ni-based bimetallic catalysts, Ru-based bimetallic catalysts, less-frequently employed Cu-based bimetallic catalysts, Fe-based bimetallic catalysts and other combinations (Feng et al. 2021; Lei et al. 2020; Sudarsanam et al. 2020). This section will review the carbon nanotube supported bimetallic nanoparticulate catalysts for biomass-related utilizations.

Carbon nanotube-supported nickel-based bimetallic catalysts for biomass conversion

For research involving multiple bimetallic nanoparticles, Zhou et al. (2016) synthesized NiCu/CNT, NiCo/CNT and NiMo/CNT catalysts by using HNO_3-functionalized carbon nanotube to catalyze wheat-pyrolyzed bio-oil into alcohols. To reach the highest yield, the ratio between the two adopted metals were tuned as well as the reaction parameters, including catalyst loading, temperature, water/bio-oil ratio and hydrogen pressure. The results showed that the NiMo/CNT exhibited the highest yield of up to 61.8%, while the NiCu/CNT reached the alcohols yield of 59.3%. Considering application in catalytic hydrogenation of furfural, Liu et al. (2016) tried the Ni/CNT and bimetallic NiCu/CNT catalysts. In this study, both carbon nanotube supported catalysts with 10 wt% loadings demonstrated the optimal selectivity towards tetrahydrofurfuryl alcohol. Under the optimal condition, the bimetallic NiCu/CNT catalyst achieved 100% conversion of furfural with a 90.3% selectivity towards tetrahydrofurfuryl alcohol. The improvement in the conversion and yield were stemmed from the synergy between Ni and Cu.

The combination of bimetallic NiCe catalysts and carbon nanotube supports for catalytic depolymerization of biomass-based lignin has been investigated by Ma and co-workers (2018b). The prepared NiCe/CNT catalysts showed excellent cycling capacities, and the yield of monophenols was 21.4% at a 63.9% conversion of lignin. Yang et al. (Yang et al. 2019) initially impregnated Ni nanoparticles onto the surface of carbon nanotube supports, followed by introducing phosphomolybdic acid, namely HPMo, inside or outside the carbon nanotube walls, to form the Ni-modified HPMo loaded carbon nanotube catalysts, abbreviated as HPMo-Ni/CNT. Then, the HPMo-Ni/CNT catalyst was applied for catalytically cracking Jatropha oil to produce biodiesel, which showed a high conversion ratio of 98.2% and a yield of 86.7%. These studies implied the strong advantages of metallic synergisms.

Carbon nanotube-supported ruthenium-based bimetallic catalysts for biomass conversion

The biomass-related conversions using Ru-based bimetallic catalysts supported by carbon nanotube are also essential to broaden the catalytic categories and to enlarge the commercial potentials. To obtain hydrocarbon fuels of C5 and C6 alkanes, Sun et al. (2017) incorporated the bimetallic RuMo catalysts onto the carbon nanotube supports with an aim for the hydrodeoxygenation of sorbitol. The results showed a complete conversion and a 55.8% yield of the C5 and C6 alkanes. For the hydrodeoxygenation of sorbitol, Weng et al. (2018) adopted the phosphoric acid-treated carbon nanotube as supporting microstructure to decorate the bimetallic RuMo catalysts. The obtained selectivity values for the C6 alkanes in the gas phase was 74.7% and the alkane/alcohols in the liquid phase was 87.8%. Focussing on the synergistic effects between Ru and Mo to strengthen catalytic activities, Wang et al. (2019a) also designed the bimetallic RuMo/CNT catalysts with remarkable catalytic activities, for catalytic rearrangement of biomass-derived furfural. This study indicated that the RuMo/CNT catalysts showed a 100% capacity of rearranging furfural to yield a 74.3% high selectivity to cyclopentanol under optimized conditions. For the same purposes, the selectivity of cyclopentanol from catalytic rearrangement of furfural was further improved to 89.1% by employing the RuMo/CNT catalysts (Meng et al. 2020b). The compositional ratios between Ru and Mo were carefully adjusted to reach the highest selectivity, and the best ratio for Ru and Mo was found to be 1%: 2.5%. The above examples indicated the importance of finding suitable combinations between heterogenous metallic species.

Direct hydrolytic catalysis of cellulose for manufacturing ethylene glycol using RuW/CNT catalysts was illustrated by Ribeiro et al. (2018), who impregnated the metal precursors onto carbon nanotube supports in an aqueous medium followed by thermal reduction to obtain the bimetallic RuW/CNT catalysts. In the presence of water, the RuW/CNT catalysts exhibited a full conversion of cellulose with a 40% yield of ethylene glycol. To further improve the yield of ethylene glycol from cellulose, optimization of RuW/CNT catalysts should be applied.

Carbon nanotube-supported ion-based bimetallic catalysts for biomass conversion

Following up on the hydrolytic catalysis of cellulose, the bimetallic FePd/CNT catalysts was further exploited (Xu et al. 2017). The as-prepared FePd/CNT catalyst with the metal mole ratio of 1:1 displayed the highest yield in hydrogenolytically transforming cellulose into polyols, reaching up to 55%. The monometallic Pd/CNT catalyst only exhibited a yield of 37%, therefore the ~ 50% increase is originated from the synergism between the two metals. Ventura et al. (2018) discussed the performance of converting biomass-related fructose into formic acid over the bimetallic FeV/CNT catalysts, which was able to reach a conversion of 98% to fructose) and a selectivity of 76% to formic acid. The above studies verified that the carbon nanotube supported bimetallic ion-based catalysts were superior to monometallic counterpart catalysts.

Other carbon nanotube-supported bimetallic catalysts for biomass conversion

Less-frequently reported bimetallic CuZn/CNT catalysts for converting furfural into cyclopentanone were fabricated by Zhou et al. (2017), who also investigated the monometallic catalysts, e.g. Cu/CNT, Co/CNT, Ni/CNT, and other bimetallic Cu-based catalysts, e.g. CuCo/CNT, CuMo/CNT and CuNi/CNT. Under the optimal conditions, the CuZn/CNT catalysts presented an 83.4% conversion of furfural and a 61.7% selectivity of cyclopentanone, which was the best amongst all the carbon nanotube supported catalysts. For the utilization of sulfur-modified carbon nanotube, namely S-CNT, as supports for bimetallic catalysts, Liao et al. (2020a) initially dispersed the carbon nanotube in a sulfur-containing organic solution, followed by an evaporation step to produce the S-CNT. Then, the PdCo/S-CNT catalysts, fabricated by conventional impregnation and thermal reduction, gave rise to an overall 96% conversion of 5-hydroxymethylfurfural and an 83.7% selectivity of 2,5-dimethylfuran. The superb performance was accredited to the highly active Pd nanoparticles and the formed Co_9S_8 nanoparticles in the PdCo/S-CNT catalysts. The above results show the high potentials of bimetallic catalysts supported by carbon nanotube to be applied in biomass-related upgrading.

Currently, most studies are focused on attempting various combinations of binary metal species for the optimisation of the highest catalytic yields. In these studies, a large number of precious metals have been utilised, which should be replaced by earth-abundant metal species from an environmental perspective. Although in-depth research on bimetallic catalysts supported onto carbon nanotube has been conducted, the formation of alloyed catalysts is rarely mentioned or published with respect to biomass valorization. Consequently, future exploitations on creating carbon nanotube supported alloy catalysts would be highly promising.

Supported graphene catalysts

Graphene-based materials are not only excellent catalysts, their pronounced physical, chemical and mechanical properties also make them essential supporting or grafting frameworks for multifunctional substances in myriad applications (Xia et al. 2020a, b), including either solid particles or molecular catalysts. As the most studied materials, graphene and its derivatives exhibit their exceptional performances in combination with different types of nanomaterials, especially particulate nanocatalysts. Owing to a broad scope of metallic nanocatalysts that can be loaded onto graphene-based microstructures, hence three separate subsections are reviewed, including graphene supported monometallic catalysts, graphene supported multimetallic catalysts and graphene-related hybrid catalysts.

Graphene-supported monometallic catalysts for biomass conversion

A variety of monometallic catalysts have been decorated onto graphene-based supports, targeting for specific catalytic conversion of biomass. Han et al. (2017) synthesized WO_3/rGO catalysts, namely reduced graphene oxide supported tungsten trioxide nanoparticles, via a facile hydrothermal approach for the catalytic conversion of fructose, which exhibited a full conversion of fructose and yielded an 84.2% production of 5-hydroxymethylfurfural. The WO_3/rGO catalysts also displayed high catalytic repeatability and convertibility in transforming other biomass-derived compounds into 5-hydroxymethylfurfural, e.g. glucose, sucrose, and cellulose. The overall enhanced performance was caused by the enlarged contact surface area between the WO_3 and the hydroxyl group-contained reduced graphene oxide. Impregnation of zirconia nanoparticles with graphene oxide supports has been demonstrated by Lai et al. (2019). The research showed that the ZrO_2/GO catalysts exhibited high efficiency in catalyzing biomass-derived ethyl levulinate into γ-valerolactone in the presence of *iso*-propanol, with a corresponding conversion ratio of 96.2% and a yield of 91.7%. Both the unsupported zirconium dioxide and graphene oxide supports presented very poor catalytic activities. Another type of metal oxide nanoparticle, i.e. RuO_2, was decorated onto graphene nanosheets in the ionic liquid (IL) solution to form the final RuO_2/IL-graphene catalysts, which showed a broad spectrum of high catalytic conversion capacities ranging from 60 to 100% in oxidizing acholic compounds, such as biomass-derived 5-hydroxymethylfurfural, furfuryl alcohol, and benzyl alcohol. Similarly, the graphene nanosheet exhibited no catalytic capabilities on its own (Jeong et al.

2019). Graphene materials can be combined with WO_3, RuO_2 and ionic liquid to enhance biomass conversion.

Ionic liquid as a stabilizer for stabilizing metal ions in the ionic environment was studied by Raut et al. (2020), who prepared a Ru@GOIL catalyst in which the Ru ion was immobilized tightly on the surface of graphene oxide. The Ru@GOIL catalyst not only showed high activity in the reductive amination of pure levulinic acid to 96% yield of 1-benzyl-5-methylpyrrolidin-2-one, but also demonstrated promising capacity in transforming biomass-derived levulinic acid to a 41% yield of 1-benzyl-5-methylpyrrolidin-2-one. Besides, the production of pyrrolidone with a high yield of 93% was achievable using the Ru@GOIL catalyst. Other graphene supported monometallic catalysts, such as F_3O_4/SGO (Trung et al. 2020), MoS_2/GO (Khodafarin et al. 2020), Ru/S-rGO (Chen et al. 2020), V/GO (Chai et al. 2020), and CS-rGO (Morales-Torres et al. 2021) were also used for the catalytic conversion of biomass. Owing to the introduced Ru nanoparticles that were of high selectivity towards furan derivatives and sulfonic groups that were of high activity in dehydration of fructose, the Ru/S-rGO catalysts enabled a full conversion of fructose with a ~ 47% yield of 2,5-diformylfuran, see Fig. 6 (Chen et al. 2020). Stabilizer and sulfur atom doping are important to impart graphene materials with high catalytic capacities.

Graphene-supported multimetallic catalysts for biomass conversion

Considering the synergistic effects between different metallic nanocatalysts help to improve catalytic performances, many studies have focused on fabricating graphene supported bimetallic nanocatalysts (as summarized in Fig. 7). As such, syntheses of 2,5-diformylfuran from 5-hydroxymethylfurfural by different kinds of bimetallic nanocatalysts supported on reduced graphene oxide nanosheets were also being implemented. Ma et al. (2018a) fabricated the bimetallic AuRu nanoparticles supported on reduced graphene oxide (AuRu/rGO) catalysts with improved capacity for transferring photo-excited electrons, which yielded 91%/86% 2,5-diformylfuran from 5-hydroxymethylfurfural/fructose, much higher than the monometallic Au/rGO and Ru/rGO catalysts. Mhadmhan et al. (2019) used the bimetallic CuPd/rGO catalysts for conducting catalytic hydrogenation of 5-hydroxymethylfurfural, where the catalysts showed remarkable high converting capacity towards 5-hydroxymethylfurfural in the presence of 2-propanol, with the yield of 2,5-dimethylfuran reaching up to 95%. By contrast, the monometallic Cu/rGO and Pd/rGO catalysts presented poor catalytic activities. As discussed, reduced graphene oxide as support can enhance the catalytic performance of bimetallic AuRu and CuPd catalysts.

Nitrogen-doped reduced graphene oxide (N-rGO) was also exploited as a supporting nanosheet for Ni- and Pt-based nanocatalysts in biomass conversion. Parrilla-Lahoz et al. (2021) impregnated bimetallic $NiCeO_2$ and $PtCeO_2$ nanoparticles with N-rGO to obtain the respective $NiCeO_2$/N-rGO and $PtCeO_2$/N-rGO catalysts for upgrading guaiacol under a hydrogen-free atmosphere. Both the catalysts exhibited remarkable catalytic hydrodeoxygenation activities, with the fresh $PtCeO_2$/N-rGO showing a ~ 45% selectivity towards catechol and good selectivity towards phenol as well as o-cresol. After thermal reduction, the $NiCeO_2$/N-rGO catalyst was preferable in guaiacol hydrodeoxygenation, making it the only catalyst that could produce anisole. The hydrodeoxygenation of biomass-related compounds (e.g. lignin, vanillyl alcohol, and vanillin) has also been conducted using the bimetallic PdRu/GO catalysts by Arora et al. (2020). The results showed distinctive activity and selectivity towards the production of *p*-creosol. For the conversion of vanillyl alcohol and vanillin, both the converting efficiencies reached 100% with high *p*-creosol selectivity of 96% and 92.3%, respectively. Additionally, the PdRu/GO also exhibited multi-catalytic hydrodeoxygenation abilities and versatilities in transforming lignin into phenolic products via photo-catalytic fragmentation. To avoid the metal leaching issues, Bai et al. (Bai et al. 2020) combined silver and zirconium dioxide nanoparticulate catalysts with graphene oxide to form highly structurally stable $AgZrO_2$/GO catalysts, which possessed pronounced catalytic capabilities in transforming biomass-derived levulinic acid into γ-valerolactone. A 100% high selectivity towards γ-valerolactone at the complete conversion of levulinic acid was reached in a water medium under hydrogen. In general, doping reduced graphene oxide with nitrogen and introducing metal oxide in bimetallic nanoparticle catalysts help to enhance catalytic biomass transformation capabilities.

The formation of graphene nanosheets (GNS) directly from pyrolyzing economically viable hardwood pellet biomass was exploited by Lalsare et al. (2021a). They synthesized the Mo_2C/GNS, $FeMo_2C$/GNS, $NiMo_2C$/GNS and Pd-Mo_2C/GNS catalysts, in an attempt to reform lignin-rich biomass, e.g. *p*-cresol, lignin and hardwood, to obtain a high H_2:CO ratio syngas with the assistance of methane. Among all the prepared catalysts, the $FeMo_2C$/GNS exhibited the best catalytic hydrodeoxygenation conversion of 99% lignin, owing to its high activity for methane activation and weakly surface adsorbed hydrogen that was easily desorbed into the gas phase. Multimetallic catalysts have also been surveyed frequently. For example, Bulut et al. (2018) incorporated trimetallic PdAuNi alloy nanoparticles onto amine-functionalized graphene nanosheets (PdAuNi/f-GNS) for the dehydrogenation of formic acid to acquire hydrogen. The resultant hybrid catalysts exhibited a broad spectrum of merits, including high catalytic conversion of at least 92%, superior structural stabilities with no metal leaching, excellent

recyclability, an ~ 100% H_2 selectivity, and most importantly without the needs of additives. Graphene nanosheets are capable of decorating different multimetallic catalysts for improving their capacities in different biomass conversion systems.

Other graphene-related hybrid catalysts for biomass conversion

Another type of nanomaterials was also decorated onto the surface of graphene-related materials for biomass-related conversion. The well-known metal–organic frameworks (MOF) in combination with graphene oxide was reported by Wei et al. (2020), who conducted the catalytic production of 5-hydroxymethylfurfural from glucose over the catalyst. The UiO-66-SO_3H-NH_2/PDA@GO catalyst possessed an ultrahigh surface area of 1135 m^2/g, mesoporous size of 2.3 nm and a large amount of acid–base contents. Owing to these outstanding properties, the catalyst showed a 55.8% yield of 5-hydroxymethylfurfural. Strong solid base catalysts (Cs@GO/UiO-N_2) were fabricated for aldol condensation of furfural and methyl isobutyl ketone for the formation of an important bio-jet-fuel precursor (Zhao et al. 2020b). As expected, the resultant catalysts showed a yield of 88.6% at 130 °C in 6 h, owing to the strong basic sites from Cs. The Cs@GO/UiO-N_2 was imparted with high hydrophobicity by introducing octyl groups in n-octyltrimethoxysilane solution to form the hydrophobic Cs@GO/UiO-N_2-C8 catalysts, which were more active, stable, and recyclable. Combining metal–organic frameworks with graphene materials shows various unique physiochemical features, which enable them to be simply tuned for new types of catalytic biomass conversion.

As graphene shares similar physical and chemical properties to carbon nanotube, therefore all attempts or studies experimented on carbon nanotube supports can be seamlessly applied to graphene-related materials, including new metal species hybridization and performance optimization. Further, graphene-relevant materials can be easily modified and impregnated, thus opening up manifold options to create new supported catalysts. Graphene as a superior supporting medium has seen numerous studies related to multimetallic hybrid catalysts, but nearly no alloy catalysts or high-entropy alloy catalysts had been reported. While high-entropy alloy catalysts have been extensively used in various catalysis scenarios, nearly no study has been found in biomass conversion, which is worth to be exploited in future studies. The catalytic matrix of excellent multimetallic catalysts consists of high activity, selectivity, durability, stability, renewability and recyclability. Therefore, how to efficiently anchor or combine them with graphene supports to achieve high catalytic efficiencies are the main challenge. Efforts to elucidate the interactions between the metal species and the graphene supports on affecting catalytic performance in the complicated biomass conversion process should also be pursued.

3D graphene-related hybrid catalysts

Nanocarbon-assembled 3D structures as intact and highly interconnected materials have been used in a large number of applications in different domains, such as catalysis, sorption, sensing, environmental remediation, solar-thermal evaporation, thermoelectric generator, energy storage and conversion (Anjali et al. 2019; Kharissova et al. 2019; Mao et al. 2018; Nardecchia et al. 2013; Qiu et al. 2018). Nanocarbon-assembled 3D structures can inherit excellent physical, chemical and mechanical properties from their nanocarbon building blocks, therefore they also have been extensively exploited in the above-mentioned research areas. Compared to nanocarbon-based powdery catalysts, the nanocarbon-assembled 3D structures are less reported in the field of biomass utilization.

Nakhate et al. (2016) adopted the mixed biomass-derived glucose and graphene oxide powder as starting materials to construct a carbon-based graphene oxide (CGO) monolith via a hydrothermal carbonization technique. The carbon-based graphene oxide monolith was then sulfated using chlorosulfonic acid to form the monolithic SO_3H@CGO catalysts for the esterification of levulinic acid and the etherification of benzyl alcohol with a different types of alcohol compounds, respectively. Results showed superior performances: for esterification, the conversion of levulinic acid ranged from at least 84–100%; similarly, the etherification of benzyl alcohol reached an excellent conversion of 80–97% and remarkable product selectivity of 86–96%. This study also revealed that all the graphene oxide powder, sulfated graphene oxide powder and non-sulfated carbon-based graphene oxide monolith exhibited very poor catalytic conversion capacity of levulinic acid compared with the SO_3H@CGO monolith, with corresponding selectivity of only 29, 68, 14%. For degrading cellulose, Huang et al. (2016) synthesized a 3D ZIF-8/rGO hydrogel catalyst by a combination of reduced graphene oxide hydrogel and metal–organic framework ZIF-8 nanoparticles. The ZIF-8/rGO hydrogel catalyst maintained outstanding catalytic activities with five catalytic runs in an aqueous solution, yielding 93.66% of formic acid at a full conversion of cellulose. Another case of biomass conversion over graphene oxide-based hydrogel catalysts was studied by Ariaeenejad et al. (2020). Graphene oxide nanosheets were imbedded into a 3D polymer hydrogel, then the new GO-embedded hydrogel was conjugated with an enzyme (PersiCel1) to form the hydrogel-enzyme bioconjugate catalysts for sugar beet pulp hydrolysis. Experimental results indicated that the hydrogel-enzyme bioconjugate catalysts displayed considerably higher catalytic

activity than that of the pure enzyme, with a saccharification increase of 154.8%.

Constructing 3D reduced graphene oxide nanostructures as supports for metallic nanoparticles was attempted by Hirano et al. using the freeze-drying method (Hirano et al. 2020). The as-synthesized Pt/rGO, Ni/rGO, Fe/rGO and Co/rGO catalysts were utilized for catalytic conversion of glucose to produce 5-hydroxymethylfurfural via a microwave-assisted reaction. Amongst all the catalysts, the Ni/rGO exhibited the best catalytic activity, with the conversion of glucose and the yield of 5-hydroxymethylfurfural reaching up to 100 and 95%, respectively. Importantly, the 3D nanostructures of Ni/rGO showed a much higher yield of 5-hydroxymethylfurfural than its conventional 2D counterpart that was only 75%. The enhancement was attributed to the large surface area and porosity of freeze-dried 3D catalysts which resulted in the exposure of more oxygen groups, and therefore significantly improved surface acidity. In a different strategy to convert biomass, Joule-heating of resistive 3D reduced graphene oxide-based films was attempted. Jiang et al. (2019) dispersed graphene oxide and lignin in solution to fabricate a graphene oxide-lignin film, followed by calcination in an argon atmosphere to afford the reduced-graphene-oxide-lignin with electrical conductivity of 6.4 S/cm. After Joule-heating of up to ~ 2500 K for 1 h, the amorphous reduced-graphene-oxide-lignin film became a highly crystalline and graphitic carbon film, possessing an ultrahigh electrical conductivity of 4500 S/cm. This application offers new routes for transforming biomass into other forms of high-value products, though no catalytic process is involved.

From the above examples, the employment of 3D carbon structures for catalyzing biomass and biomass-derived chemicals are drawing more and more attention, therefore plenty of novel 3D carbon structures as nanomaterials with high catalytic activities and selectivity should be exploited in the future, as illustrated in Fig. 8.

3D carbon structure derived from biomass is another popular approach to utilize and reuse earth-abundant substances (Wu et al. 2016; Zhou et al. 2019). For instance, lotus pollen was fabricated into 3D hierarchical carbon skeleton for use as a supercapacitor (Li et al. 2015). Protein-rich fish-scale as waste biomass was transformed into 3D porous carbon nanonetwork for the oxygen reduction reaction (Guo et al. 2017). G*elidium amansii* biomass was converted into a 3D carbon nanofiber aerogel aiming for energy storage applications (Li et al. 2018a). Therefore, the utilization of biomass and its new derivatives will be expanded into more broad areas to realize and speed up industrialization. On the other hand, the catalytic conversion of different biomass mixtures to produce new substances are rarely reported, hence developing new catalytic nanomaterials to advance this field is urgent.

3D graphene-based macrostructures for biomass conversion have the potential to be a popular research topic despite being reported less frequently in recent literature. These studies were generally focused on employing single metal species, which can draw on existing multimetallic catalysts, namely forming 3D graphene macrostructures supported multimetallic catalysts to multi functionally catalyze various biomass. Doping of nitrogen and sulfonation can also be implemented in 3D graphene macrostructures.

Perspective

As biomass conversion shows great industrial and commercial prospects, more efforts should endeavour from the below aspects in future studies:

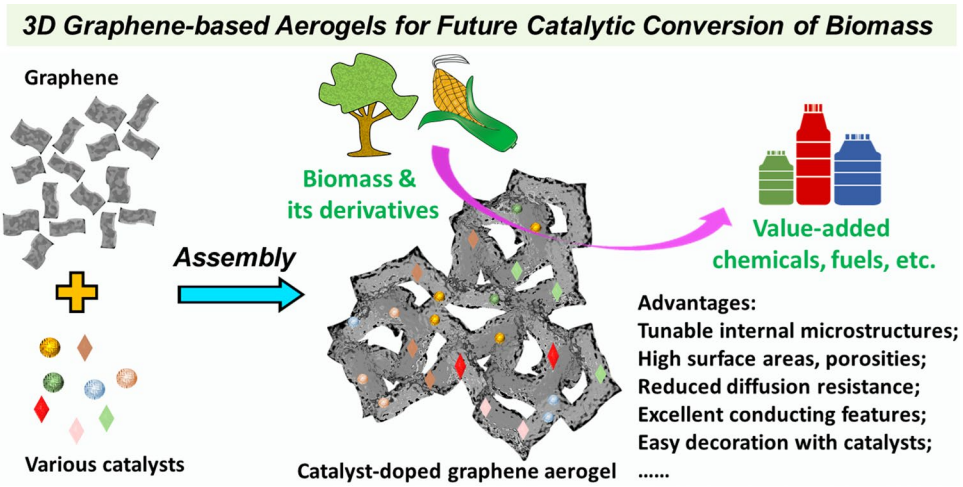

Fig. 8 3D graphene-based aerogels for future catalytic conversion of biomass and biomass-derived compounds into value-added products. Assembling graphene materials and various catalysts to form graphene aerogels supported catalysts is advantageous for biomass conversion, due to the remarkable advantages of graphene aerogels, such as tuneable internal microstructures, high surface areas, controllable porosities for reducing diffusion-related resistance, excellent conducting features and easy decoration with catalyst

(i) developing new types of durable, multifunctional and hybridized nanomaterial catalysts to improve the catalytic performance of biomass-related applications is urgent because the achievements of high conversion efficiency of biomass-derived molecules and high yield of value-added products are the main themes.
(ii) biomass shows characteristics of high abundance, inexpensiveness and is also renewable. Therefore, direct conversion of biomass into multifunctional catalysts is also an essential field to be deeply excavated. Additionally, transforming various biomass-related wastes into inexpensive and effective catalysts, such as biogas residues that contain high contents of metals, is also an important research route to achieve resource re-utilization.
(iii) nanocarbons can be assembled into different forms (e.g. powder, film, foam, aerogel), which therefore can be incorporated with the well-known high-performance nanomaterial catalysts to further improve their catalytic capacities or reduce costs and energy consumptions (i.e. reaction temperatures and durations, catalyst loadings). The pronounced physicochemical properties of 3D nanocarbon aerogel materials are important to be exploited in the catalytic conversion of biomass-related substances.
(iv) the combination of one-dimensional carbon nanotube and two-dimensional graphene as nanocatalysts or supporting frameworks will offer more aspects in biomass-related conversion. Studies should focus on nanocarbon ratios, graphitic defects, oxygenic functional groups, doping to internal microstructures, porosities, and conducting properties.

Despite great advancements in this field, performance-marked catalysts for varied biomass valorization were produced only on a laboratory scale with relative high preparation costs. Scaling up the catalyst production whilst still exhibiting uncompromised catalytic performance is a long-standing challenge. Based on this, some outlooks regarding future industrialization of catalytic biomass valorization are proposed here to expedite its progress:

(i) The essential prerequisites to industrialize biomass conversion are correlated with low-cost and high-performance catalysts that should embrace a simplified preparation process. Particularly, improving the product selectivity and lowering subsequent separation/purification costs are the major concerns. With the great advancement of computer science, innovation in creating novel catalysts can originate from machine learning, neural network algorithm, artificial intelligence and density functional theory. These methods have been successfully employed in designing complex and efficient catalysts, which will improve the success rate and in turn avoid unnecessary experimental steps and waste materials.
(ii) The catalytic conversion of biomass mainly centres on biomass-derived compounds, whereas direct transformation of pure biomass is rarely investigated. Typically, the products display undesirable yield and selectivity. Hence, designing and creating new catalysts for directly catalyzing pure biomass into fuels or chemicals will unveil high industrial ability. Additionally, the catalytic transformation of different biomass mixtures deserves future exploitations, for which new types of products may be produced via commonly reported nanomaterial catalysts.
(iii) Currently, the conversion of biomass and its derivatives is largely dependent on traditional thermocatalysis. However, photocatalysis and electrocatalysis approaches can perform the experiments under mild reaction temperatures, with high selectivity of targeted products, clean and high efficiency, therefore showing great potential to be used in industry.
(iv) Different types of high-quality chemicals can be achieved through renewable energy approaches, e.g. electrocatalytic and photocatalytic synthesis of biomass-derived compounds. The physicochemical properties of the targeted chemicals in the complex biomass catalysis regimes should be well understood. Low-cost separation approaches should be devised to effectively separate these high-value commercial chemicals.
(v) Developing specific carbon-supported catalysts for targeting only high-valuable and high-end chemicals is also a promising area to advance the industrialization of biomass valorization.
(vi) Single-atom catalysts have shown the greatest metal utilization advantages and unprecedented catalytic multi-functionalities. Therefore, single-atom catalysts should be fabricated and exploited in valorizing biomass. Additionally, various non-precious metal species can be utilized to replace the current noble metal powder catalysts.

Conclusion

This review summarizes the recent advances in nanomaterial-related catalysts for catalyzing biomass-correlated substances into high-quality fuels, fine chemicals, and commercial products. All common starting materials, e.g. varied biomass, biomass-derived compounds, platform molecules, and nanomaterial catalyst types, e.g. metallic nanoparticles,

carbon-based catalysts, carbon-supported hybrid nanomaterials, and metal–organic frameworks, were elaborately exemplified and discussed to offer the researchers the existing circumstances of biomass-related upgrading and conversion and to accelerate the investigations in carbon-based 3D macroscopic structures in this filed.

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Declarations

Conflict of interest The authors declare no conflict of interest.

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