Chapter 9
Biomass and CO_2-Derived Fuels Through Carbon-Based Catalysis. Recent Advances and Future Challenges

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Abstract Liquid transportation fuels from biomass and CO_2 are considered a promising strategic alternative to simultaneously reduce greenhouse gas emissions and fulfill the massive energy demands. Pyrolysis allows the transformation of lignocellulosic biomass into bio-oil (liquid fraction) which can be further upgraded to hydrocarbon fuels by well-known methodologies including catalytic hydrodeoxygenation (HDO) and steam or aqueous phase reforming to transform bio-oil into hydrocarbons and H_2 as promising alternatives to fossil fuels in forthcoming future. The efficient conversion of CO_2 to fuels and useful chemicals is an essential step toward reducing the atmospheric concentration of CO_2. (Electro)chemical catalytic CO_2 reduction is a promising route to convert CO_2 back into valuable chemicals and fuels. The use of carbon materials for biomass and CO_2 transformation has gained impact as an alternative to conventional oxides due to their excellent features including high surface area, electroconductivity, and low cost. This chapter describes the recent works reported in the literature on the use of carbon-based catalysts to convert biomass and CO_2 into sustainable biofuels. An overview of the most promising carbon-based catalysts and processes will be presented, including the main

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challenges to improve carbon-based catalysts' performance and to reduce costs to make biomass and CO_2-derived fuels an effective alternative for future mobility.

Keywords Biomass valorization · CO_2 conversion · Carbon-based catalysts · Renewable fuels

9.1 Introduction

Alternative fuels are extremely important to the future of energy and transportation sectors which play an important role in today's economy and society with a huge impact on growth and employment. Modern industry depends on fossil resources for producing fuels and chemicals and the forecasts for 2050 rely on emissions of about 200 million tons of CO_2 produced from the massive used of these fossil feedstocks contributing to cumulative greenhouse gas emissions and environmental issues (De Luna et al. 2019). Concerning this topic, the production of renewable fuels from alternative resources is an extremely important request and, the growing interest in new technologies for the valorization of renewable biomass and CO_2, in the last 10 years is well documented in literature reviews (Sudarsanam et al. 2018; Kondratenko et al. 2013; Lu et al. 2021). Biomass is not only the major carbon-containing sustainable resource for supporting the exponentially growing energy demand but also prompts less greenhouse gas emissions. The best policy to compete with fossil-based fuel refineries is the integration and upgrading of biomass-derived feedstocks in a similar (bio)refinery approach. Biorefineries use several technologies to convert different biomass feedstock into biofuels and bio-based chemicals, able to replace a large fraction of industrial chemicals and materials currently derived from fossil resources (Ruiz et al. 2013).

There is a large number of technologies to convert biomass into chemicals and fuels including biological, thermal, and chemical processes (Sudarsanam et al. 2018). Pyrolysis is a widely used process to sustainably convert biomass into liquid fuels. The search for advanced fast pyrolysis processes has grown in the last years in order to convert low-value biomass materials into bio-oil and numerous useful products (Amenaghawon et al. 2021). However, bio-oil is a complex mixture of numerous oxygenated compounds with a significant content of water, depending on the biomass source.

Compared with traditional fossil energy sources, bio-oil presents unstable physical–chemical characteristics and low calorific value. In order to make bio-oil a vital part of energy infrastructures, as a future transportation fuel, their upgrading through oxygen removal and molecular weight reduction is imperative in order to simultaneously increase thermal stability and reduce volatility and viscosity (Jacobson et al. 2013). There are several examples of bio-oil upgrading methods, Fig. 9.1, although they present limitations to their large-scale application (Qu et al. 2021). The hydrodeoxygenation (HDO) process is considered a fundamental strategy of biomass upgrading to produce transportation fuels. The main challenge of HDO technology

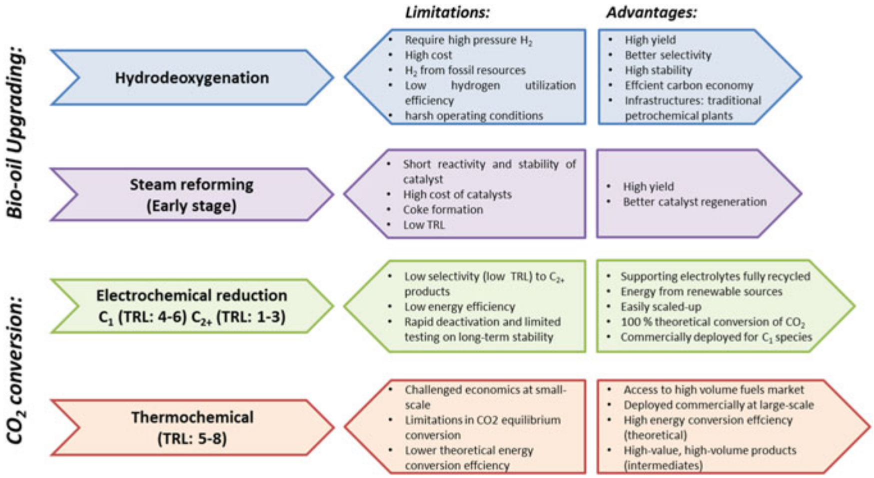

Fig. 9.1 Limitations and advantages of promising routes for (biomass) bio-oil upgrading and CO_2 conversion. Adapted from (Grim et al. 2020; Panwar and Paul 2021)

implementation at the commercial scale is its dependence on high-pressure hydrogen, expensive and mainly obtained from fossil resources and, the safety issues of the high H_2 pressure. The use of hydrogen-free alternatives such as in-situ production using bio-oil derivatives is an attractive option (Jin et al. 2019a).

Indeed, steam reforming allows converting the oxygenated and non-oxygenated hydrocarbons from bio-oil by reaction with steam at high temperatures, to obtain syngas (a mixture of hydrogen and carbon monoxide) and CO_2. This route to bio-oil upgrading has been extensively studied as illustrated in Fig. 9.1 (Tan et al. 2020), where the main advantages and limitations are highlighted.

The quest for a more sustainable society and a cleaner environment grounded based on green chemistry and engineering principles has prompted the development of new studies combining CO_2 capture and its transformation into high-added-value chemicals through catalytic or electrocatalytic reactions (Rafiee et al. 2018; Roy et al. 2018; Wu et al. 2017), Fig. 9.1. Currently, the typical thermochemical routes of CO_2 conversion produce methanol, CO, dimethyl ether (DME), etc., (Rafiee et al. 2018) and, even more advantageous, the electrochemical processes can provide valuable or energy-dense chemicals such as formic acid and ethanol (Kumar et al. 2017). CO_2 electrochemical reduction (CO_2RR) has recently attracted huge attention as a promising and clean technology to convert CO_2 into useful chemicals and low-carbon fuels using electrons as reductants at mild conditions.

Lu et al. (2021) have published recently a review about the use of efficient single-atom catalysts to convert biomass and CO_2 into renewable fuels and chemicals and presented a scheme illustrating the integrated carbon cycle of both biomass and CO_2 simultaneous conversion, Fig. 9.2 has a strategy to minimize CO_2 emissions and to find alternative renewable feedstocks for the intensive future demands of renewable energy and chemicals.

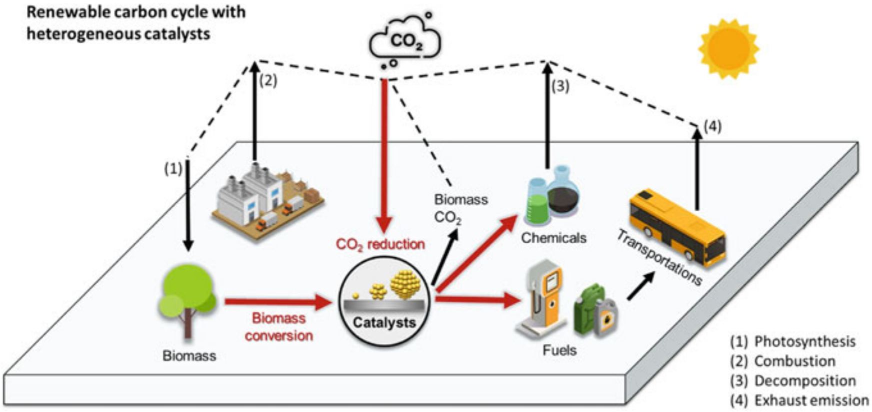

Fig. 9.2 Proposed renewable carbon cycle with heterogeneous catalysts to convert biomass and CO_2 into renewable fuels and chemicals simultaneously. Reproduced with copyright from (Lu et al. 2021)

The choice of the catalyst is a fundamental role in the upscaling and industrialization of biomass and CO_2 process conversion. Efficient catalysts have been designed and used for both biomass and CO_2 valorization, although a technology at commercial maturation is still a challenge due to the high costs of currently developed catalysts; the low selectivity control toward the target products; and most importantly, the low stability of the catalysts. The development of cost-efficient, highly active, and selective catalytic systems is essential to a significant step forward in this research topic, Table 9.1.

Carbon-based (nano)materials are important building blocks for a multitude of advanced applications including catalysis and energy conversion. Carbon materials have been widely used as catalysts or catalyst support in several liquid and gas phase reactions. Generally, carbon materials possess distinctive physicochemical properties including high specific surface area, variable porosity, excellent stability and superior electronic conductivity, and interesting tunable surface functional groups for incorporation of additional moieties. Also, the combination of these features with their structure, interconnected pores, and heat stability make them key materials to be used as catalysts or catalyst support for the conversion of biomass and CO_2 into fuels (Gawande et al. 2020; Fernandes et al. 2019).

Carbon-based materials exist in different allotropic forms such as carbon black (CB) and activated carbon (AC, including the biomass-derived materials), carbon aerogel, diamond, fullerene, carbon nanofibers (CNF), carbon nanotubes (CNT), graphite and graphene (Seelam et al. 2010; Lam and Luong 2014). The high surface area, low cost, and availability of AC and CB make them the materials of choice to support catalysts. Advanced engineering synthesis of various nanostructured carbon materials including nanoparticles, nanotubes (one-dimensional materials), graphene sheets (2D), and mesoporous carbons (3D) provide new opportunities for the development of advanced carbon-based catalysts not only for fuel production but also

Table 9.1 An overview of different technologies to convert bio-oil and CO_2 into derived fuels. The typical catalysts and supports and the future challenges for commercialization

Method	Catalysts/supports	Future challenges for commercialization
Hydrodeoxygenation • *Increases the heating value, reduces the viscosity of bio-oil*	• Sulphide transition metals (W, Co, Ni, Mo); • Reduced metals: Noble (Pd, Pt, Rh, Ru); and transition metals (Ni, Co, Mo, W); bimetallic (PtSn, Pt-Pd, RhPd, NiW, NiMo, Co-Mo; • Supports: SiO_2, SiO_2–Al_2O_3, TiO_2, ZrO_2, zeolites and carbon-based materials	• studies use model compounds; bio-oil stability is an issue • Catalysts are prone to deactivation in bio-oils • Economic viability is still a problem: the cost of noble metals prevents the large-scale application • Alternatives to current harsh conditions
Steam reforming • *Produces hydrogen by steam reforming of bio-oil*	• Metal catalysts (base and noble)-Ni, Rh, Pt, Pd, Co, Cu, Ir, Fe • Supports: MgO, MgO–Al_2O_3, CeO_2, ZrO_2, Calcite, Dolomite, Al_2O_3 Zeolites-Y, ZnO and carbon-based materials	• Use low-cost metals • Improve water tolerance of the low-cost active phase (Ni, Co, Fe) • Reduce reaction temperature to reduce thermal requirement by for example operating in the liquid phase • Improve TRL (currently at stage 1–2)
Thermochemical reduction • *Produces low-carbon fuels and methanol by* CO_2 hydrogenation	• Metal and metal oxide-based catalysts: Cu/ZnO/Al_2O_3, Fe_3O_4, Co/Al_2O_3; • Metal promoter molecules such as K, Mn, Na, and Cu	• Develop multifunctional water and CO_2 tolerant catalysts • Improve product selectivity • Improve catalysts performance
Electrochemical reduction • *Produces chemicals and low-carbon fuels using electrons as reductants under mild conditions*	• Noble metals: Pd, Pt, Ru • Transition metal elements and related compounds (metal oxides/metal complexes): Cu, Fe, Co, Ni, Cr, Mn	• Economic viability is still a problem: the cost of noble metals prevents the large-scale application • Electrocatalysts improve performance: high activity and stability • Reduce energy consumption and increase the energy efficiency of the process

for fine chemistry applications (Pérez-Mayoral et al. 2020). Graphene, one of the most promising carbon-based materials, offers high stability in water media, in both acid and basic conditions, which are typical conditions found in biomass feedstocks. Moreover, their high surface area also allows better dispersion of the active phases improving the efficiency of the catalysts in biomass and CO_2 upgrading and other catalytic applications. For instance, surface functionalized of carbon support could dramatically increase selectivity in HDO and significantly boost Faradaic efficiency toward CO and other valuable chemicals, such as CH_3OH, during electrochemical CO_2 reduction (CO_2RR). Carbon-based materials are also excellent hosts for metal-nanoparticles, working as hybrid catalysts with multifunctionalities to be used in biomass and CO_2 conversion.

There are several reviews recently published reporting the advances in biomass conversion/bio-oil upgrading (Khosravanipour Mostafazadeh et al. 2018; Cordero-Lanzac et al. 2021; Pujro et al. 2021; Attia et al. 2020) and on thermochemical conversion/electrochemical reduction of CO_2 (Fernandes et al. 2019; Qiao et al. 2014; Feng et al. 2019; Wang et al. 2017; Xie et al. 2018; Zhu et al. 2016; Khezri et al. 2017; Abdelkader-Fernandez et al. 2020; Handoko et al. 2018; Roy et al. 2018; Esteve-Adell et al. 2017b); with a few examples focusing on the of using carbon-based materials as catalyst support (Cordero-Lanzac et al. 2021; Lam and Luong 2014) and several examples exploring the physico-chemical and textural properties and surface functionalization methodologies and this is why we will not focus this topic in the present chapter (Lam and Luong 2014; Benzigar et al. 2018; Pérez-Mayoral et al. 2020).

However in this chapter, we present the recent advances in the application of carbon-based materials (including the ones prepared from biomass) to covert biomass/bio-oil into fuels giving special emphasis to the most promising technologies developed regarding their potential of industrialization as an alternative to the current unsustainable fossil fuels energetic scenario. Considerable attention has focused on the main technical challenges and future opportunities of bio-oil upgrading using HDO and steam reforming (hydrogen production); and, electro-or thermo-catalytic reduction of CO_2, Fig. 9.3. The design of promising catalysts and their structure-performance relationship are important points for future sustainable processes with the main goal of lowering the production costs providing a viable alternative to future mobility. The combination of carbon materials features with more sustainable processes can be the key to revolutionize the production of fuels from biomass and CO_2 although the limitations presented in Fig. 9.1 are still significant and struggle the large-scale application. We will make an overview of the future challenges to overcome these problems in the next sections.

9.2 Catalytic Carbon-Based Processes to Biomass-Derived Fuels

Conversion of biomass into liquids fuels and chemicals has attracted considerable interest in the last years. Several routes have been developed including pyrolysis as a typical sustainable process to convert biomass into liquid fuels and one of the most promising attempts to develop alternatives to energy production (Jin et al. 2019b; Carrasco et al. 2017). Fast pyrolysis is by far the most interesting industrial approach (Amenaghawon et al. 2021). The resulting oil also called bio-oil is produced under typical heating of 450–600 °C in the absence of oxygen (Dhyani and Bhaskar

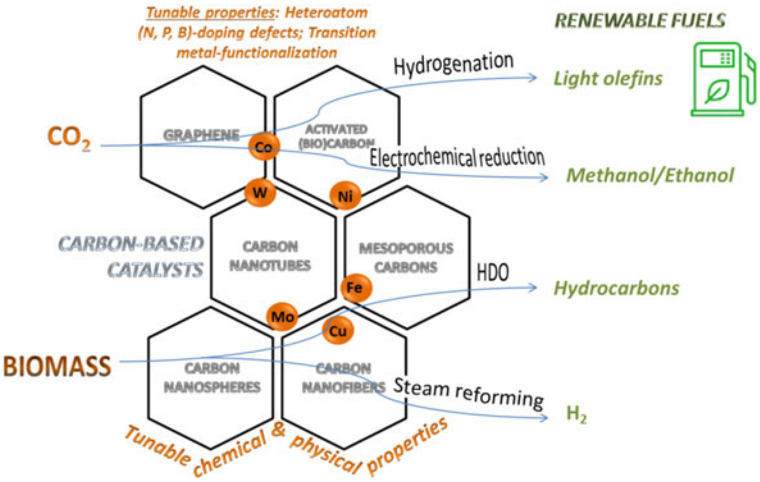

Fig. 9.3 Schematic representation of carbon-based catalysts' role in the future of biomass and CO_2-derived fuels

2018). Bio-oil is a complex mixture of compounds comprising sugars, carboxylic acids, hydroxyaldehydes, hydroxyketones, and phenolics. The presence of oxygen (typically 40–50%) is one of the key differences between bio-oils and other hydrocarbon fuels, causing lower heating value, thermal and chemical stability, higher viscosity and immiscibility, higher acidity, and coke formation during processing when compared with conventional fuels (Guo et al. 2018; Pang 2019). HDO and steam reforming are examples of downstream bio-oil upgrading, Fig. 9.1. In the next section special emphasis will be given to HDO reactions as the most promising and effective method for bio-oil upgrading to hydrocarbons. The focus will be given on the recent works employing carbon-based materials as a catalyst or catalyst support and alternatives to the conventional H_2 from fossil fuels, the "H_2-free" HDO reactions, as a sustainable strategy for HDO industrial application. An overview of the state of the art of HDO of real bio-oil upgrading will also be addressed. Furthermore, due to the importance of H_2 production from alternative sources the steam reforming of bio-oil to syngas (a mixture of hydrogen and carbon monoxide) will also discuss as other interesting routes to bio-oil upgrading.

9.2.1 Hydrodeoxygenation of Bio-Oil

Hydrodeoxygenation is an important catalytic reaction to transform biomass derivatives into potential fuels (De et al. 2015). During HDO process bio-oil C–O bonds are broken and by hydrogenation and/or dehydration eliminated decreasing the oxygen content. The catalysts should be carefully designed to meet the key challenge of

HDO processes and promote a high degree of oxygen removal under minimum hydrogen consumption. Several processes have been intensively studied for the selective removal of oxygen from bio-oil, lignin, and other substrate models under high pressure of hydrogen in the presence of a heterogeneous catalyst (Jacobson et al. 2013; Mortensen et al. 2011). In fact, and due to the complexity of the bio-oil molecules, the use of model compounds is typically used to discern mechanistic information, useful guidelines for the catalysts, and process design (Arora et al. 2020; Bjelic et al. 2019). The typical reaction routes for HDO of various model compounds are summarized in Fig. 9.4 (Qu et al. 2021).

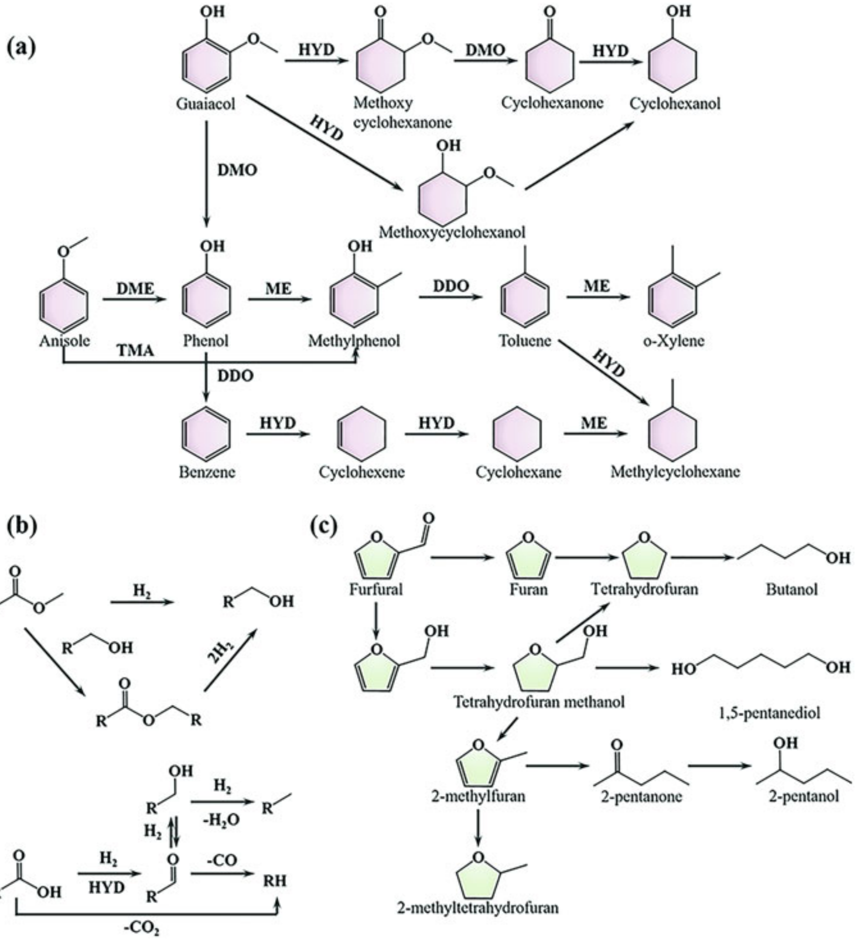

Fig. 9.4 Reaction routes for HDO of various model compounds: **a** containing phenol, guaiacol, and anisole; **b** acids and esters; and **c** furan and furfural. DDO: deoxygenation; HYD: hydrogenation; DME: demethylation; TMA: methyl transfer; ME: methylation. Reproduced from (Qu et al. 2021) with permission from the Royal Society of Chemistry

The HDO efficiency can be accessed by several reaction parameters including temperature, hydrogen pressure, type of reactor, solvent, time, catalyst selection, weight hourly space velocities (WHSV), etc. Among those, catalyst selection plays a central role and typically a good HDO catalyst must have appropriate surface oxophilicity to promote C–O bond cleavage, combined with moderate hydrogenation ability and to reach a selective hydrogenation of the bio-oil derivatives to the target products (Hita et al. 2020). The synergistic effect of support and the active phase (metal) can be crucial to the efficiency of HDO catalysts playing a role in the stabilization and dispersion of metallic particles. Moreover, the supports can also have activity, can mediate reactants activation, and can facilitate the active phase-reactant encounter enhancing metal-support interaction (Jin et al. 2019a). Carbon materials arise in several biomass conversion processes, including in HDO reactions, not only as promising catalyst supports, but also as a metal-free active phase catalyst, due to their distinctive physicochemical, low cost, and lower affinity for coke deposition compared to acidic supports (Mukundan et al. 2015).

The use of alternative HDO methodologies for bio-oil upgrade avoiding, for example, the use of external H_2, is attaining a significant interest as a potential economic approach to transform biomass into biofuels (Jin et al. 2019a). Due to the growing interest in more sustainable processes, this discussion will be centered on the performance of the use of carbon-based materials as catalyst support and the use of H_2 alternative sources in an attempt to serve as a helpful guide toward the development of efficient carbon-based catalysts and sustainable HDO processes and their potential of industrialization. To date, the HDO processes use mainly external H_2 and guaiacol is the mostly studied biomass derivative model. Noble metals (Pt, Pd, Rh, Ru) (Santos et al. 2018; Thompson and Lamb 2018), transition metals (Ni, Fe) (Guo et al. 2018) and metal sulfides, molybdenum carbides (Cai et al. 2017; Blanco et al. 2020c) and rhenium carbides (Blanco et al. 2020b, 2021) are usually used as metal active phases. Bimetallic multifunctional catalysts (Pd/Fe, Ru/Re) (Lee et al. 2020; Arora et al. 2020) and additive promotors can also act as an efficient catalyst for HDO catalysis. CB and AC have been used as carbon-based supports for the synthesis of efficient heterogeneous catalysts due to their low production cost and high specific surface area. Nevertheless, the use of CNT, CNF and GO provide new opportunities for the development of more efficient and stable catalysts. The use of commercial carbon-supported noble metal catalysts for HDO reactions have also been extensively explored (Bjelic et al. 2019; Thompson and Lamb 2018; Guo et al. 2018).

In a recent review, Sharma et al. (2020) presented a variety of carbon catalysts to convert lignin and its derivatives models by HDO reaction as a powerful tool for the generation of non-petroleum chemicals and fuels. The authors presented structurally different carbon-supported metal catalysts and discussed the effect of surface properties in mechanistic insights. Li and co-authors (2021) also focus their studies on the progress effects of the microenvironment of carbon-based catalysts on the HDO of biomass. The authors focus the review on the effects of the surface of carbon support microenvironment (structure and functionalization) in the catalytic performance and the mechanism of HDO reactions and concluded that carbon-based catalysts with mesoporous structure and high surface area favors the formation of small particle size and consequently higher dispersion and distribution of metallic active sites leading to high catalytic activity. They also found an effect of pore size distribution on the adsorption of reactants and transport of products which also affects the activity and selectivity of HDO reaction. These reviews represent a very good overview of the work done in the last years in HDO reactions using carbon-based materials and are important future guidance to the design and development of efficient carbon-based catalysts for this type of reaction. However, must of the published works use harsh reaction conditions, including (200–400 °C) and high H_2 pressure (4–20 MPa) in batch or fixed-bed reactors which means high energy consumption. Furthermore, the current commercialize H_2 gas is typically produced from fossil fuels which is an expensive and non-renewable source. Therefore, the use of milder HDO processes is invariably desirable to design an economic way to biomass conversion to fuels. Noble metal-supported carbon-based materials are the mostly used in the works presented in the literature, although significant efforts are being made to increase the economics of HDO technology motivating the transition to non-noble metal catalysts and mild reaction conditions (low H_2 pressure and temperature) to reach high selectivity for the desired products. The demonstrated evidence of comparable catalytic activities to noble metal-based catalysts obtained with some non-noble (Cu, Co, and Ni) metal-based catalysts is a promising signal to the economic scale-up of this process (Kordouli et al. 2017; Guo et al. 2018; Feitosa et al. 2019; Bjelic et al. 2019; Mendes et al. 2020; Lopez et al. 2020; Jin et al. 2021; Blanco et al. 2020a).

In general, the surface area and the pore size distribution of carbon materials play an important role in the particle size, dispersion, and distribution of metal active phases increasing the accessibility to the reactants and consequently the HDO conversion and selectivity.

9.2.1.1 “H_2-Free” Alternatives

Jin et al. (2019a) presented novel approaches to avoid the external H_2 supply, discussing the challenges and research trends of novel HDO technologies including catalytic transfer hydrogenation (CTH) and the combination of reforming and HDO. The development of hydrogen-free alternatives has been attracting the interest of the catalysis community and, although a challenge, a variety of alternatives are available at different degrees of maturity. Attempts to perform HDO at atmospheric H_2 pressure afforded excellent results for the production of aromatic compounds (Wu et al. 2021). Nevertheless, the design of highly active and stable catalysts remains a challenge and a significant drawback to the implementation of biorefinery schemes. Other “*H_2-free*” HDO strategies use as an alternative to hydrogen sources alcohols, formic acid (FA), and water-assisted in-situ HDO which is perhaps the most promising from an economic point-of-view, due to the possibility of using the water content of bio-oil as a source to generate the hydrogen in-situ. Seeking for economically viable biomass upgrading alternatives, Reina and co-authors (Jin et al. 2019b, 2021;

Parrilla-Lahoz et al. 2021) developed a novel in-situ HDO strategy using H_2O as a hydrogen source suppressing the external high-pressure hydrogen. The first approach (Jin et al. 2019b) used a series of Ni-based catalysts supported on CeO_2 with/without AC for the guaiacol HDO. The catalyst Ni/CeO_2–C showed to be the most promising reaching more than 20% conversion using only water as an H_2 source. Although the low conversion, the suppression of the high-pressure H_2 evidenced the importance to further optimize the design of the catalysts, reactor and operating conditions to improve the results and develop a new and economically advantageous route for HDO reactions.

More recently the same authors (Jin et al. 2021) used Ni supported nitrogen-doped AC catalysts (Ni/N-AC) and water as a hydrogen donor for the in-situ HDO of guaiacol. Nitrogen-doped carbons were more active than the undoped carbons in the "H_2-free" HDO process. The conversion of guaiacol increases by 8% when Ni/N-AC was used (prepared using polyaniline as a nitrogen source) comparing with non-doped Ni/AC catalysts. Therefore the excellent performance of Ni/N-AC was ascribed by the authors to the acid-base properties and to the modified electronic properties of the carbon support which favors the C–O cleavage, the water activation, and the dispersion of Ni particles on the catalysts' surface. In order to develop multifunctional catalysts able to activate water and the subsequent use of the in-situ generated hydrogen, the authors also presented a sequence of efficient Pt and Ni-based catalysts supported on N-doped graphene combined with ceria (Parrilla-Lahoz et al. 2021). NiCeO_2/GOr-N presented the best activity/selectivity balance and it was elected as the most promising catalyst to conduct the "H_2-free" HDO reaction. The as-prepared non-activated Pt-based catalysts showed superior performance than the Ni ones, although the reductive pre-treatment of the catalysts resulted in a superior performance for NiCeO_2/GOr-N with up to 30% conversion which was attributed to the optimal properties and better metal dispersion obtained with N-doped systems. Previously Yang et al. prepared a Co supported in an N-doped carbon catalyst (Co@NC) (Yang et al. 2017) by one-pot carbonization of biomass-derived glucose in the presence of melamine, as nitrogen source, and $CoCl_2$ as the catalyst precursor. The optimized Co@NC-700 (pyrolyzed at 700 °C) shows the best activity for vanillin HDO exhibiting 15.4 times higher activity than the non-doped Co/AC with >95% vanillin conversion and 100% selectivity to 2-methoxy-4-methylphenol (MMP) at 180 °C. The authors also compared the efficiency of Co@NC-700 catalyst under molecular hydrogen concluding that this catalyst is more active and selective for MMP under FA than under H_2. The superior performance of Co@NC-700 under H_2-free (external) conditions could be assigned to N-derived defective sites on carbon-based support, which potentially play a relevant role as base additive in FA dehydrogenation and metal like active center for the hydrodeoxygenation of vanillin.

Although the use of noble metals is not very attractive from an economic point of view, the fact of using milder conditions and other alternatives to molecular hydrogen can be advantageous. Emphasizing the work done by Nie et al. (2017) which prepared by one-pot carbonization of biomass-derived glucose, melamine as nitrogen source and $ZnCl_2$ as porogen nitrogen-enriched highly mesoporous carbons

(NMCs), with a specific surface area of 1017 $m^2\ g^{-1}$ and mesopore volume proportion of 92.1%. This NMC allowed a well-dispersed Pd catalyst and consequently high activity (100% conversion), stability, and selectivity for HDO of vanillin to MMP (>99%) in water phase with formic acid (FA) as hydrogen donor, at 150 °C and 0.5 MPa N_2. The excellent results were ascribed to the high mesostructure, N-doped species on the surface of NMC, and their relationship with Pd particles. Pu et al. (2020) prepared for the first time N-doped hierarchically porous carbons (HPC) using MOF as a sacrificial template to control the material morphology and composition. The authors observed that by just varying the nitrogen precursors the HPC morphology, hydrophilicity, and nitrogen configuration can be fine-tuned. Particularly, a honeycomb-like morphology was obtained using dicyandiamide (DCD) as a nitrogen source. The resulted Pd@HPC-DCD catalyst showed excellent activity and stability to the HDO of vanillin in aqueous solution, using FA as hydrogen source under 0.5 MPa N_2 at 140 °C with >99% yield of unsaturated hydrocarbons. The significant catalytic activity of Pd@HPC-DCD in water was attributed not only to its hierarchical structure, but also to the well-dispersion of Pd species, even to the favorable hydrophilicity. De Luna et al. (2019) have previously presented a bimetallic catalyst Pd–Ag supported on Fe_3O_4/nitrogen-doped reduced graphene oxide (N-rGO) for HDO of lignin-derived compounds including vanillin with 100% conversion and 99% selectivity for MMP at 130 °C, using FA as a hydrogen source in water.

These published works showed that N-doped carbon materials are promising supports to enhance the catalytic performance of HDO due to: Basicity and hydrophilicity of the carbon-based supports which could improve the interaction between substrate and support under the aqueous reaction conditions; N-dopants on carbon matrix can be assumed as defects and anchoring sites favoring the particle formation and to the reduction of their size (Jin et al. 2021).

9.2.1.2 Toward Real Biofuels

The economic limitations are the main drawbacks to the industrialization of HDO and, in fact, HDO is only considered viable when renewable hydrogen is accessible and cheap enough to be used in large quantities or when alternative H_2 sources are employed. Recent publications have been using real bio-oil as feedstock and carbon-based supports taking advantage of their physicochemical features in HDO reactions, particularly on the conversion of bulkier and highly refractory components (Hita et al. 2020; Cordero-Lanzac et al. 2020). Noble metal catalysts, such as Ru, Rh, Pd, and Pt, showed high efficiency in the HDO of pyrolysis oil producing upgraded oil with higher yield and quality. Carbon surface functionalization can also improve the catalyst acidity contributing to their stability (Cordero-Lanzac et al. 2017, 2020). Cordero-Lanzac and co-authors promoted the HDO of real bio-oil using a phosphorous-functionalized activated carbon (ACP) bifunctional Pt–Pd catalyst. The authors observed that the presence of hydrothermally resistant acidic sites allowed for high selectivity to aromatics yields, maintaining the catalyst stability

(Cordero-Lanzac et al. 2020). However, the noble metal catalysts' high prices and their short-live when used for treating bio-oils due to sulfur poisoning (bio-oil generally contains sulfur) are unattractive for industrialization and clearly demonstrate the importance to develop inexpensive and highly active non-noble catalysts for HDO.

Inexpensive activated carbon-supported nickel and cobalt phosphide catalysts (varying the metal/P molar ratio) were prepared and applied in the HDO reaction of wood-derived pyrolysis oil (Guo et al. 2018). The effect of phosphorus content on HDO performance was investigated under 300 °C and 50 bar of H_2 for 3 h and it was possible to observe that the properties of the upgraded bio-oils were significantly affected. Both Ni and Co-based catalysts allow obtaining of upgraded bio-oils with lower O/C and H/C ratios increasing P content (up to $M/P = 3/2$) suggesting that the increasing of HDO activity is associated with the hydrogenation activity deterioration. High-quality bio-oil products (similar to the obtained with the commercial 5 wt% Ru/C) were achieved with the addition of the small amount of Ru as a co-catalyst. AC-supported NiP was selected as the most promising inexpensive catalyst allowing comparable activities to the expensive Ru/C catalyst. The same authors compared previously the activity of different catalysts under the same conditions presented above and concluded that AC-supported NiP was the most promising regarding the yields, the composition of upgraded oil, and the prices of the catalysts (Guo et al. 2016).

Mendes et al. (2020) prepared nickel phosphides supported in AC and mineral charcoal and compared the effect of using these two types of carbon with carbon-covered alumina (CCA) support (Mendes et al. 2020). HDO reactions were performed using a commercial bio-oil under 150 and 250 °C and H_2 pressures between 50 and 100 bar. The effect of temperature and H_2 pressure on the efficiency of deoxygenation and quality of bio-oil were evaluated. Ni_2P-AC showed better performance at 150 °C than Ni_2P on mineral charcoal and CCA, giving bio-oils with lower oxygen content and consequently higher heating value. On other hand, at higher temperatures (250 °C) Ni_2P/CCA showed the best results compared with the other carbon-based materials giving bio-oils with a lower O/C molar ratio and higher H/C molar ratio. These differences were justified by a pore blocking of the non-covered carbon supports. For the first time, Remon et al. (2021) evaluated the effect of the initial H_2 pressure and temperature, reaction time, and catalyst/bio-oil ratio in the HDO of bio-oil (lignocellulosic) using a Mo_2C/CNF catalyst to produce liquid biofuels and value-added chemicals. Process optimization revealed that using an initial H_2 pressure of 40 bar and temperature of 350 Remon et al., and 0.19 $g_{cat}\ g^{-1}{}_{bio\text{-}oil}$ for 1 h, allowed to convert 65% of the organic content of the bio-oil into a liquid bio-fuel which represents a deoxygenation degree of 70% and an energy efficiency of 62%. The authors proposed a schematic representation for the composition of the upgraded bio-oil and the potential reactions that contribute to the formation of solids (mainly char), aqueous, and gaseous species through the upgrading process, Fig. 9.5.

It is noteworthy to mention the great progress already made in the area of bio-oil upgrading contributing to enhance the knowledge about the potential use of biomass/waste biomass as an energy source, in future bio-refineries. The use of

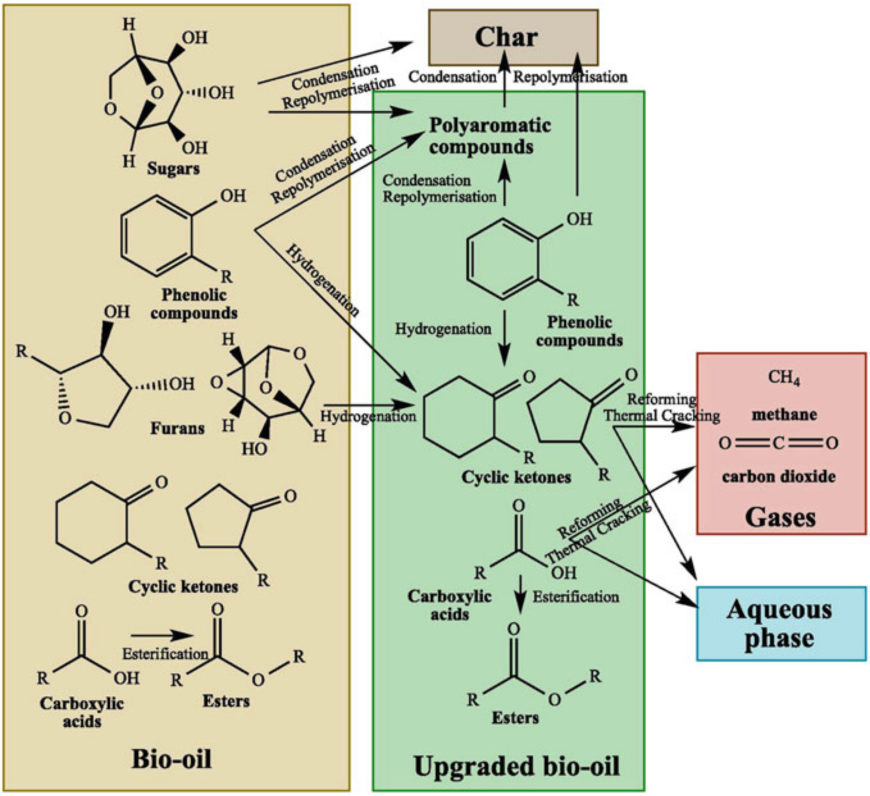

Fig. 9.5 Schematic pathway showing the chemical transformations of the bio-oil during the HDO process. Reproduced with copyright from (Remon et al. 2021)

“H_2-free” processes combined with high efficient (non-noble)-carbon-based catalysts with balanced acidity and basicity should be considered a key step to improve HDO catalytic performance and a strategy to achieve the economic viability of the industrial production of fuels from biomass. The use of low cost and renewable precursors to prepare the carbon-based catalysts is also highly recommended (Santos et al. 2020). Alcohols consider attractive alternatives to replace external H_2 supply since they can act as hydrogen donor by releasing H_2 via reforming reactions. The potential of H_2 production from steam reforming (SR) and aqueous phase reforming (APR) of bio-oil will be discussed in Sect. 2.2.

9.2.2 Steam Reforming of Bio-Oil for Hydrogen Production

Hydrogen (H_2) can be generated from biomass according to several processes that involve thermochemical or biological processes. Among the thermochemical processes, pyrolysis, liquefaction, and gasification are the main routes considered. All these processes transform biomass into a mixture of gas containing H_2, CO, CH_4, and other products. The gas phase can generally be enriched in H_2 using common processes like methane steam reforming or decomposition, water gas-shift reaction, or partial oxidation reaction. During pyrolysis, the bio-oil produced contains a fraction of heavy aromatics, namely tar, which must be removed as they are quite problematic for downstream equipment, causing clogging and blockage. Typically, tar can be removed by reforming over biochar-based materials and has been widely discussed in several reviews (Xu et al. 2020; Ren et al. 2021; Tan et al. 2020). On the other hand, in hydrothermal liquefaction, a bio-oil is also produced together with an aqueous phase that can be further upgraded by steam or aqueous phase reforming to H_2.

The general bottleneck of those processes is catalyst deactivation. The present part will give a sample of several recent studies where carbon materials can be employed to improve the H_2 production and/or catalyst stability from the bio-oil fraction depending on the process considered.

Steam reforming is mainly employed in small oxygenates easily vaporizable like methanol, ethanol, acetic acid, or glycerol. Methanol is not currently a bio-based product, and thus, it will be omitted in this part.

Steam reforming generally involves metal-supported catalysts, and there are only a few reports where carbon materials are employed as support (Özkan et al. 2011; Janas et al. 2015; Augusto et al. 2020; Seelam et al. 2010). The literature review displays that one of the critical factors for hydrogen production is the metallic particle size. Indeed, Silva et al. have reported that the turnover frequency (TOF) of H_2 production was improved by decreasing the particle size of Co in the case of ethanol steam reforming (ESR) (da Silva et al. 2014). Such behavior was explained by the presence of the lower amount of terraces responsible for the coke deposition. Hence reducing the particle size limited carbon deposition over the metal particle, enhancing the ESR activity. Based on this study, Augusto et al. have evaluated the effect of the carbon support for ESR in the case of Co-based catalysts (Augusto et al. 2020) and found that the carbon support affects the dispersion of Co. The better dispersion was obtained on carbon nanofibers (CNF) and AC, however, the latter suffer strong deactivation due to particle sintering, while over CNF the particle size was maintained with a slight deactivation due to partial oxidation of Co.

On the other hand, the use of carbon nanotube (CNT) as support was compared to more traditional support, Al_2O_3 by Seelam et al. (2010) and found that higher activity for ESR could be reached (Seelam et al. 2010).On the other hand, CNT was compared to graphite carbon as a support for Ni in the SRE, and results have shown that the CNT was the best support for the generation of H_2 (Rautio et al. 2015). However, the post-reaction analysis showed a significant carbon content increase after the reaction ascribed to CNF and CNT formation. Recently, a composite of CNT-silica fiber (SF) was also evaluated in ESR (Prasongthum et al. 2017). The combination of the fibrous structure of silica and the high surface area of CNT has been shown to significantly improve Ni's stability and metal dispersion, probably due to the presence of oxygen-functional groups (OFG). Another strategy employed to prevent Ni from sintering/oxidation was an encapsulation of the metal by a graphene shell (Chen et al. 2019). In this study, the thickness of the graphene shell was optimized and the resulting catalyst showed to enhance the H_2 yield product compared to a classical Ni/Al_2O_3 catalyst, with no deactivation reported during the experiment.

In the case of acetic acid steam reforming (ASR), similar fibrous composite platelet CNF-silica fiber (SF) was used as a support for Co and reported a higher ASR activity and better long-term stability compared to Co/SF and Co/Q10 that was ascribed to better metal dispersion and the unique structure (Natewong et al. 2018).

The effect of biochar activation was also evaluated in the case ASR over Ni catalyst (Chen et al. 2018b; Wang et al. 2020c; Stasi et al. 2020; Di Stasi et al. 2021). Indeed, it was reported that in the case of Ni supported over biochar, the activation using KOH-HNO_3 provided the highest specific surface area, and therefore, the Ni dispersion was enhanced (Chen et al. 2018b).

Interestingly authors also found that the activity could be improved by increasing the sulfur content. Recently, activation of biochar by HNO_3 using different concentrations has been carried out and showed to affect the hydrophilicity of the resulting support and the pore structure and the OFG, leading to a different particle size of Ni. Among these aspects, hydrophobicity is the most relevant parameter for ASR. Indeed, high hydrophobicity results in low activity and high coke formation while moderated hydrophobicity improved adsorption of the reaction intermediate on C–O–C-aliphatic OFG. In contrast, the gasification of reaction intermediates was proposed to occur over carbonyl OFG (Wang et al. 2020c). Di Stasi et al. have activated biochar using pure CO_2 at 700 °C and screened several metals in ASR and reported low deactivation of the metal phase during the reaction (Stasi et al. 2020). However, in a more recent study, they found that using a mixture of several pyrolysis bio-oil model compound deactivation was observed due to metal poisoning of heavy products, nevertheless such deactivation could be inhibited using bimetallic (Di Stasi et al. 2021). As far as glycerol steam reforming (GSR) is concerned, only a few reports are using carbon-based materials (Veiga and Bussi 2017; Liu et al. 2018c; Chen et al. 2020b). Again it appears that the use of carbon material improves the metal dispersion essentially. For instance, in the case of Ni supported over AC) oxidation of the support has been shown to enhance the Ni anchoring into smaller particle size (Veiga and Bussi 2017), while in the case of CNT support, the well-dispersed metallic Ni showed to promote the consecutive glycerol decomposition and the water gas-shift reactions to hydrogen production (Liu et al. 2018c). Recently, the same strategy to encapsulate Ni into a graphene shell and attached to a skeleton of SiO_2 was also investigated for GSR protecting Ni from oxidation and sintering with a high yield of H_2 (*ca.* 5.09 mol H_2/mol glycerol) and stability (Chen et al. 2020b). Glycerol reforming can take place in an aqueous phase and is generally a preferred process as it occurs at a lower temperature (Fasolini et al. 2019).

9.2.2.1 Aqueous Phase Reforming (APR)

APR was first introduced by Dumesic et al. as a promising process for producing H_2 in an aqueous phase under moderated conditions compared to the gas phase (Davda et al. 2005). In this respect, model compounds were often considered like glycerol, acetic acid, ethylene glycol, etc. Carbon materials were mainly considered support due to their high surface, variety of textural and structural properties, and good stability in the aqueous phase. Furthermore, their surface chemistry can be easily modified by introducing functional groups at the surface that can introduce hydrophilic properties to the hydrophobic carbon (Lam and Luong 2014). For instance, it has been reported that in the case of several ordered-mesoporous carbons (OMCs), the APR activity of ethylene glycol was directly correlated to the metal dispersion (Pt), which was affected by the different pore structures of the OMCs (Jeong et al. 2014). In this sense, nano-sized OMCs displayed higher Pt dispersion than micro-sized OMCs, and among the nano-sized OMCs, hollow-type framework configurations were better than rod-type. On the other hand, recently, Ru-supported over N-doped mesoporous carbon was investigated for glycerol APR (Gogoi et al. 2020). It was found that the incorporation of N into the carbon could significantly enhance the catalytic properties. Indeed N creates some basic sites over the support and improves anchoring over the support preventing it from sintering. Recently, the use of graphene as a support to Pt has shown to also allows narrow distribution of Pt particle size (1–5 nm) (Elias Bamaca Saquic et al. 2021).

Over CNT, superior yields toward H_2 in glycerol APR compared to oxide supports and associated with higher metal-support interactions (Rahman 2015). On the other hand, the introduction of OFG by acidic treatment can improve Pt dispersion; however, a lower TOF was reported but could be recovered by annealing the remaining OFG. Hence, it was proposed that OCG was detrimental when the reaction occurs in a binary mixture with different hydrophilicity due to competitive adsorption (Wang et al. 2010b). Similar conclusions could be obtained using bimetallic Pt–Co supported on single-wall CNT (Wang et al. 2010a).

Metal-free carbon materials have also been considered for the production of H_2 by APR (Esteve-Adell et al. 2017b, 2017a). Indeed a series of boron-doped graphene has been active for glycerol and glucose APR (Esteve-Adell et al. 2017b). The same group has also reported that ethylene glycol could be successfully decomposed into H_2 and CO_2 over metal-free graphene obtained from alginate pyrolysis and proposed that acid-base Lewis pairs act as the dehydrogenative center (Esteve-Adell et al. 2017a).

To summarize, the use of carbon-based material for improving the H_2 production has been shown to be effective especially in limiting the deactivation of the metallic site. In this respect, several strategies could be employed offering a myriad of possibilities to limit the deactivation. For instance, in the case of deactivation by particle sintering, the use of carbons with high surface area or specific morphology (e.g., CNF) enhances the metal dispersion thus, delaying the deactivation, while in some other cases, a graphitic shell prevents particles from sintering (Karapinar et al. 2019). On the other hand, the surface chemistry of the carbon is of great importance and can be easily tuned by for example acidic-treatment (Jeong et al. 2014), thermal treatment, or doping with heteroatoms like N (Kibria et al. 2019), or B (Kumar et al. 2017). In this sense, the hydrophobicity can be adjusted as well as the acid-base properties. All these parameters are essential in preventing deactivation.

9.2.3 Economic Analysis of Bio-Oil-Derived Fuels

The main challenge of bio-oil upgrading is to produce economical alternatives to light/heavy fuels for transport or heat generation. Recent tests on bio-oil combustion at an industrial scale demonstrated that bio-oil is a suitable alternative to conventional heavy fuel oil. The major issues affecting the bio-oil production/upgrading costs are the low product yield and the feedstock/equipment (upgrading) high costs, suggesting an expensive final upgraded bio-oil is still unable to be competitive as a commercial liquid fuel (Kumar and Strezov 2021). The application of alternative hydrogen sources is an effective strategy to decrease the high cost of HDO processes since generally this process occurs at less severe operation conditions (Kumar and Strezov 2021). H_2 produced from steam reforming of bio-oil is a clean and sustainable fuel as its combustion produces water and no harmful gases. In addition, it can be also used in HDO of bio-oil, as an alternative to H_2 from fossil derivatives in a biorefinery approach. Syngas can be further converted via Fischer-Tropsch process for the production of hydrocarbons.

9.3 Catalytic Carbon-Based Processes to CO_2-Derived Fuels

9.3.1 Thermochemical CO_2 Hydrogenation Using a Carbon-Based Catalyst

According to recent reports, around 50% of anthropogenic emissions can be absorbed by oceans, land, and forests and close to 85% of the remaining 50% could be used to obtain fuels and chemicals, the production of fuels being the main market (De et al. 2020). The following subchapter summarizes the research published in the last years, 2017–2021, on CO_2 hydrogenation using carbon-based catalysts through thermocatalysis. Although CO_2 can be transformed into several useful products such as CO, methane, formic acid, methanol, dimethyl ether, carbonates, lower olefins, etc., the majority of the literature is found for methanol and formic acid given their current interest as a hydrogen carrier. The information has been divided based on the target product, namely, CO_2 to methanol/formic acid, CO, and hydrocarbons (CH_4, CO_2^+, , and olefins). Transformations involving CO_2 hydrogenation are highly important especially for H_2 transportation and storage. However, the conversion of CO_2 has some thermodynamic challenges. On the one hand, C–O bonds are more stable than C–H bonds and, on the other hand, the hydrogenation products are normally liquids and, hence, entropically unfavored, since the transition from gas to liquid decreases the entropy.

9.3.1.1 Hydrogenation to Methanol and Formic Acid

Hydrogenation of CO to methanol is a well-known process for which commercial catalysts consist of Cu/ZnO. Based on this system, several research works have appeared regarding CO_2 hydrogenation to methanol using Cu/ZnO or Cu/ZnO/ZrO_2 in combination with different carbon structures. For example, Din et al. (2018) reported the use of Cu/ZrO_2 supported on carbon nanofibers with several Cu loadings (5–25 wt.%) prepared by deposition precipitation. The best catalytic results in the liquid phase hydrogenation using a CO_2/H_2 feed volume ratio of 1:3 was obtained with a Cu loading of 15 wt.% reaching a methanol yield of 20 g kg^{-1}cat h^{-1} at 180 °C and 30 bar. The catalytic performance was correlated with the concentration of basic sites and copper exposed area. The authors also studied CO_2 hydrogenation in the liquid phase at 30 bar and 180 °C using Cu–ZrO_2-carbon nanofibers-based catalysts prepared by deposition precipitation (Din et al. 2019). The catalysts were promoted with 1–4 wt.% ZnO which improved the activity and selectivity up to an optimal value of 3 wt.%, for which the measured yield to methanol was 45 kg^{-1}cat. h^{-1} with a methanol selectivity of 92% (vs. 78% without promoter). The increased yield to methanol was due to the better selectivity compared to the unpromoted catalysts, since the activity was indeed lower due to the worse dispersion of copper on the ZnO-promoted sample.

Also, Witoon et al. (2018) studied the effect of adding graphene oxide into CuO–ZnO–ZrO_2. Increasing GO loadings of 0.5–2.5 wt.% improved the yield of methanol. However, higher loadings hampered the co-precipitation of mixed metal oxides, this leading to the formation of isolated oxides nanoparticles and higher CuO particle size, and lower yield to methanol compared to the catalyst without GO. Nevertheless, the selectivity was still higher compared to the GO-free catalyst. The optimum GO loading was found to be 1 wt.% at 200 °C and 20 bars. The positive effect of GO was ascribed to the higher amount of active sites for CO_2 activation and to the hydrogen spillover promoted by GO from the copper nanoparticles to the metal oxide particles.

Deerattrakul et al. (2018) employed a different synthetic method to prepare Cu–Zn/reduced graphene oxide catalysts by impregnation of Cu and Zn on hydrothermal reduced graphene oxide. The researchers assessed the effect of the hydrothermal reduction temperature and found that 140 °C provided the highest surface area (458 m^2g^{-1}) among the tested temperatures. The catalysts with 15% weight loading of Cu–Zn afforded the highest yield to methanol (94.53 mgMeOHgcat–1 h^{-1}) at 250 °C and 15 bar.

The role of nitrogen doped on carbon supports has been also addressed by several authors on CO_2 hydrogenation to methanol and formic acid. For example, 10%Cu/Zn catalysts were prepared over an N-doped reduced graphene oxide (N-rGO) previously prepared by chemical exfoliation of graphite with hydrazine (Deerattrakul et al.

2017). Using in-situ X-ray absorption near-edge spectroscopy, the authors described the influence of the reduction time which was found to be optimal, among the materials tested, at 90 min and 350 °C. The best methanol yield at 250 °C and 15 bar was 591 mg MeOH/g cat/h.

More recently, Deerattrakul et al. (2019) reported that pyridinic nitrogen was relevant on the system CuZn/graphene to improve the metal dispersion, H_2 dissociation, as well as the activation of CO_2 to produce methanol. Also, the synthesis using urea as a nitrogen source provided the highest N-pyridinic among other N precursors tested such as ammonia and hydrazine hydrate.

Using a different experimental approach Ma et al. (2019b) also evaluated the effect of nitrogen-doped graphene. In this work, the authors synthetized several catalysts by co-precipitation of nitrogen-doped graphene (NG) and Cu/ZnO/Al_2O_3 with a different weight percentage of NG. The results showed that the addition of NG improved both CO_2 conversion and CH_3OH selectivity up to an optimal NG loading of 10 wt.%. The results were correlated with the better CO_2 and H_2 adsorption promoted by NG. Apparently, at low NG loading the system Cu/ZnO/Al_2O_3 is not well dispersed, the dispersion improving upon increasing the NG content. Also, the graphene is capable of transferring hydrogen to the copper particles forming copper hydride, this being relevant in the hydrogen spillover mechanism which may occur between the oxides and copper.

Additional theoretical calculations were performed by Esrafili et al. (2017) for the CO_2 hydrogenation with Pt- and Ni-doped graphene for which a termolecular mechanism was proposed. According to this mechanism, the H_2 molecule could be activated by two preadsorbed CO_2 molecules, one H atom is then transferred to one CO_2 molecule forming a −OCOH intermediate which would be then converted into HCOOH. The formation of formic acid would be the rate-determining step, which is more energetically favored over Pt than Ni. On the contrary, the bimolecular mechanism is described by two steps, which start with the co-adsorption of both reactants on the surface. Then, also a −OCOH intermediate is formed which finally is transformed into formic acid through the creation of a C–H bond.

More recently, Gao et al. also studied the CO_2 hydrogenation to formic acid by DFT, on Pt_4 cluster doped single-vacancy graphene (Xu et al. 2020). Among the reactions mechanism studied, Langmuir-Hinshelwood, Eley-Rideal, and termolecular Eley-Rideal, the activation energy results also suggested that the most favored reaction path was the termolecular Eley-Rideal.

Also by DFT, Yodsin et al. (2019) investigated the platinum supported on defective carbon nanocones (Pt/dCNC) during CO_2 hydrogenation to formic acid. The calculations suggested that formic acid yield depended on the concentration of H_2, and that dissociation of H_2 followed by H spillover is more energetically favorable, while the desorption of formic acid is the rate-determining step.

Some investigations evaluated the potential of Cu single metal atoms on C_2N monolayer for the CO_2 hydrogenation to formic acid using first-principles calculations (Ma et al. 2019a). The results indicated that two main mechanisms can take place. While the path I start with the co-adsorption of H_2 and CO_2, path II is initiated by the adsorption of H_2. The latter path is more energetically favored and the reaction could even take place at room temperature.

Sredojević et al. (2018) also studied CO_2 hydrogenation to formic acid by DFT using Ru and Cu single atoms trapped in graphene sheets. The calculations showed that a high activation energy is required to transfer hydrogen atoms to CO_2. Alternatively, the pre-dissociation of H_2 may occur on the metal surface before CO_2 adsorption, this being preferred energetically for Ru catalyst. For this system, the formic acid desorption is the rate-limiting step. However, for the Cu-based catalyst the strong affinity of H atoms for defective graphene hinders the transfer of the H atom to CO_2.

Molybdenum carbide supported on carbon materials has also been tested in CO_2 hydrogenation to formic acid and methanol as a low-cost catalyst with similar properties to noble metals. Examples in the liquid and gas phases can be found. Both theoretical and experimental results showed that the use of nitrogen-doped carbon creates an interface between molybdenum carbide and the support which enhances the adsorption and activation of CO_2 and H_2 (Wang et al. 2020a). The best system of those reported that MoC@N5.6C provided a turnover frequency of 8.20 molFAmolMoC^{-1} h^{-1} at 140 °C and 20 bar, in the liquid phase hydrogenation.

More recently, Dongil et al. (2021) evaluated Cu-molybdenum carbide systems supported on commercial high surface area graphite. The authors reported the synthesis of molybdenum carbide through the carbothermal method using the support as the hydrogen source. The formation of both molybdenum oxycarbide and carbide was confirmed by X-ray absorption near-edge spectroscopy. Deuterium desorption thermal experiments also showed that molybdenum hydride species were formed. The formed hydride species were suggested to be the reason for transformations involving $MoO_xC_yH_z \leftrightarrow \beta\text{-}Mo_2C$. Also, the formation of metallic Mo when the synthesis was performed at 70 °C under H_2, resulting in less active and selective catalysts. The addition of copper improved the catalytic performance, acting as a promoter since monometallic Cu was not active in the studied system.

9.3.1.2 RWGS and Methanation (or Hydrogenation to C2$^+$)

Ni and Ru single metal atoms supported on carbon nanotubes have also been tested by Rivera-Cárcamo et al. (2020) for CO_2 hydrogenation at atmospheric pressure and 340 °C. The results indicated that while nickel-based catalysts were selective to CO, ruthenium-based catalysts were more selective to CH_4. In addition, for ruthenium catalysts a relationship between selectivity and electronic properties was observed, so that electron-rich particles were more selective to CH_4, while electron-deficient were more selective to CO.

The effect of nitrogen has been studied by some authors. For example, Liu et al. (2018b) used zeolitic imidazolate frame-works (ZIFs) as precursors to obtain N-doped carbon supports. Two catalysts were prepared by pyrolyzing Fe and Fe/K modified ZIF and they were employed on the hydrogenation of CO_2 at 320 °C and 30 bar with an H_2/CO_2 ratio of 3. Results were also compared with carbon spheres

(CS) and AC. While conversion was just slightly higher on the Fe-ZIF catalysts (26.8–29.3%) and higher for the K-doped Fe(K) (34%), the selectivity obtained with the Fe/Zn-NC and Fe(K)Zn-NC was remarkable, reaching 22.1–27.4% to C5+ (compared to just 0.4–5.4% obtained with CS and AC) and 30–32% to C_2–C_4 olefins (compared to <3% reached with CS and AC).

Potassium-doped iron catalysts supported on SWCNT and MWCNT were also tested for CO_2 hydrogenation to hydrocarbons at 613 K, 20 bar, and $H_2/CO_2 = 3$ (Wang et al. 2020b). The different results with both types of CNT highlight the importance of the electronic properties of carbon materials. The authors reported high selectivity to olefins (C5+) being 39.8% and 21.8% for SWCNT and MWCNT respectively. However, the different conversions reported should also be considered when comparing the data since the value obtained with SWCNT was also higher (52.7%) compared to MWCNT (43.6%). The authors also reported that FeK/MWNTs catalyst favored the formation of light olefins (C2–C4 = selectivity, 30.7%) and that FeK/SWNTs catalyst led to low concentration of the unwanted products CO and CH_4 which resulted in an outstanding yield to of heavy olefins of 27.6 μmolCO$_2$ gFe^{-1} s^{-1}. The better selectivity of FeK/SWCNTs to heavy olefins (C5+ selectivity = 39.8%) was explained by the effect of the higher electron concentration on the outer surface of SWCNT, larger proportion of Hägg carbide and the ability to interact strongly with light olefins. Apparently, the electron donation of SWCNT due to their larger curvature, given by the lower diameter of SWCNT compared to MWNTs, i.e., 0.47 versus 2.2 nm, favors the scission of the C–O bond, this also promoting the formation of carbon monomers and the optimal carbon to hydrogen surface ratio to obtain olefins.

On the other hand, Wu et al. (2018) have investigated FeK supported over novel honeycomb-structure graphene and have observed that the support was able to confine the Fe particle preventing them from agglomerates, while the mesoporous-microporous architecture could reduce effectively mass transfer limitation achieving 73 μ mol CO_2 g^{-1} s^{-1} yield of light olefins (C2–C4 selectivity = 59%).

N-doped graphene synthetized by pyrolysis in argon of chitosan at 900 °C proved to be active and selective to methane at temperatures of about 500 °C with estimated turnover frequencies of 73.17 s^{-1} (Jurca et al. 2018). The better catalytic performance of this system compared to other doped graphenes catalysts seem to be related to the presence of N-pyridinic atoms which are able to adsorb CO_2 forming carbamate adsorbed species.

Also, Wang et al. (2018a) studied Ni supported on nitrogen-doped carbon nanotubes for CO_2 methanation at atmospheric pressure and several temperatures. The catalyst offered around 80% conversion and 100% selectivity to CH_4 at 360 °C using an H_2:CO_2 ratio of 4 and proved to be stable for more than 24 h.

Li et al. (2018) studied the promotion of Ni/CNT catalysts with manganese on CO_2 methanation and the effect of oxygen surface functionalization. The experimental and theoretical results indicated that, as calcination temperature increased from 350 to 550 °C, the amount of oxygen groups and, hence, the strength of interaction with metallic nanoparticles decreased.

The increase of calcination temperature from 350 to 550 °C had a negative impact on activity and was even more pronounced on the selectivity to CH_4. The presence of a larger proportion of defects (corner, edge, or terrace) on the catalyst prepared at 550 °C was given as an explanation for the less significant effect on the activity since these sites contribute to the activity.

Also, the addition of Mn as a promoter improved activity due to the better CO_2 adsorption as also confirmed by the CO_2-temperature programmed desorption and transient response experiment. The best catalysts of those tested were those promoted with Mn and calcined at the lowest temperature, 350 °C, which also proved to be stable during 140 h of operation.

Nitrogen doping carbon materials have also been tested on CO_2 hydrogenation to CO and CH_4. Unfortunately, it is difficult to find a comparison with analogous undoped systems or different carbon nanostructures.

Sikora et al. (2018) synthetized bamboo-like carbon nanotubes (BCNTs) by catalytic chemical vapor deposition which were oxidized by acid treatment to prepare calcium alginate-gelled BCNT spheres. After thermal treatment, Pd, Rh, and Ni nanoparticles supported on BCNT spheres were tested in CO_2 hydrogenation at 200–600 °C. Pd supported BCNT was more selective to CO while Ni favored the formation of CH_4.

Cobalt (1.5–35 wt%) supported on different carbon structures, i.e., nanotubes, nanofibers, low-layered graphite (LGF) as well as carbon nanotube-Nb_2O_5 composites were evaluated and compared with Nb_2O_5 (Tursunov and Tilyabaev 2019). The CNT-Nb_2O_5 composites were synthetized by decomposing methane at 650 °C for 5 h in the presence of Nb_2O_5 which had been previously impregnated with a solution of cobalt nitrate. Overall, the catalysts are 100% selective to CH_4 and CO, the selectivity is dependent on the metal loading. At 3 wt.% Co loading CNT, CNF, and LGF were selective to CO reaching 78%, 23%, and 64%, respectively, while at higher loadings the catalysts offered exclusively CH_4. Also, using specific Co loadings on CNT (3 wt% of Co) and LGF (1.5 wt% of Co), resulted in inactive catalysts apparently due to the amorphous nature of the cobalt particles of those samples. The stability and catalytic performance of the catalysts could be enhanced by incorporation nitrogen atoms into graphene sheets through reaction with the oxygen surface groups of the carbon structures.

The hydrogenation of CO_2 has also been tested under supercritical conditions, enhancing mass transfer and H_2 solubility. For example, Bogdan et al. (2019) evaluated Co and Ni supported on CNT which showed great activity on CO_2 hydrogenation, cobalt being the most active and selective catalyst with 25–26% conversion and 100% selectivity to CH_4 at 300–450 °C. The authors also reported that under supercritical conditions the space–time yield to the product increases significantly (by 5–8 times) compared with the reaction in the gas phase.

Chernyak et al. (2020) used spark plasma sintered Fe/CNT catalysts and evaluated the effect of the sintering temperature on the structure and performance of the catalysts as well as the stability of the materials during supercritical conditions (85 bar and 350 °C) and different CO_2:H_2 ratio. Spark plasma sintering (SPS) is one of the techniques to obtain bulk CNT materials along with hot pressing or pressing with binder. SPS consists of applying high pressure and pulsed current, leading to fast sample heating (up to 1000 °C/min) which allows to preserve the CNT structure. In this work the synthesis starts by producing the multi-walled CNTs by chemical vapor deposition of hexane over the Co–Mo/MgO catalyst at 750 °C. Then a specific equipment for SPS is employed in which the samples were sintered under the pressure of 30 MPa at 800 and 1200 °C under vacuum for 5 min. The activity was similar at both tested sintering temperatures and similar to a catalyst prepared by impregnation and reduction in H_2. Also, the catalysts displayed a quite similar selectivity using a CO_2:H_2 ratio of 1:2, to CO (18–22%) CH_4 (34–36%), C_2–C_4 (33–35%), and C_5 + (9–12%).

The effect of nitrogen doping in CNT on the RWGS and FT synthesis has been reported by Williamson et al. (Williamson et al. 2019) and described that the C–N dipoles in the support when CO_2 and CO were adsorbed were more relevant than the particle-support interactions.

9.3.2 Electrocatalytic CO$_2$ Reduction Using Carbon-Based Catalysts

The CO_2RR has been attracting considerable attention over the last years as it provides a valuable pathway for renewable production of fuels as well as renewable energy storage. Additionally, it offers further advantages, like fully controlled electrochemical process by applying external electrolytes and potentials, the possibility to reduce the whole cost and the consumption of chemicals through the reuse of the electrolytes, and the operation under ambient conditions. In addition, the numerous possibilities for the selection of components of electrocatalytic reaction system combined with the multiple assemblage combinations and the fact that electrochemical setups are generally modular and compact and the scale-up can be simpler (Fernandes et al. 2019).

As for all reactions related to energy like oxygen and hydrogen reactions, here electrocatalysts (ECs) play a critical role in the electro-kinetics, mechanism, and product distribution. The major challenge is the design and successful preparation of highly efficient, low-cost, selective, and stable Ecs capable of addressing the kinetically slow CO_2 process. Various review papers have been published regarding the application of homogeneous and heterogeneous Ecs for the CO_2 electroreduction (Qiao et al. 2014; Kuhl et al. 2012; Feng et al. 2019; Liu et al. 2018a; Zhu et al. 2016; Wang et al. 2017; Xie et al. 2018; Khezri et al. 2017; Abdelkader-Fernandez et al. 2020; Fernandes et al. 2019). Exhaustive reviews addressing the electroreduction of CO_2 from a mechanistic/theoretical perspective have been published recently (Kibria et al. 2019; Handoko et al. 2018; Zhang et al. 2017), even though the CO_2RR complexity involving multiple possible pathways surely will continue to stimulate scientists to look for further insights on this topic.

Nonetheless, here we present an up-to-date review of the recent advances in the last 5 years involving carbon-based materials for the electrochemical transformation of CO_2 into selected fuels (methane, methanol, ethanol, and syngas).

Carbon-based materials are interesting materials for electrocatalysis, mainly owing to their mechanical and physicochemical properties which include electron conductivity, thermal stability, large surface area, and corrosion resistance. Owing to its surface chemistries and tailorable porous structures apart from the properties already referred to above, carbon-based materials have been largely applied both as a support for metal-based electrocatalysts as well as versatile heterogeneous metal-free electrocatalysts itself. Carbon-based materials' electrocatalytic activity is intrinsically related to their structures, chemical surfaces, and defects. Porous carbons display large porous structures, leading to a high transfer of mass and larger surface areas with a greater concentration of active sites per mass of catalyst. Additionally, the incorporation of heteroatoms, in particular nitrogen, portrays a valuable functionalization at a molecular level modulating the electronic and physicochemical for targeted purposes like CO_2 electroreduction.

9.3.2.1 About CO_2 Reduction Reaction (CO_2RR)

The CO_2 molecule is a chemically inert and thermodynamically stable molecule that presents low electron affinity and consists of 2 C=O bonds, each with a bond dissociation energy of 750 kJ mol^{-1} (Ma et al. 2019c). Considering other bond dissociation energy values namely of C–C (336 kJ mol^{-1}), C–H (441 kJ mol^{-1}), and C–O (327 kJ mol^{-1}) is clear why CO_2RR reduction is more difficult to occur compared to the reduction of other organic molecules (Fan et al. 2018; Ma et al. 2019c). In addition, the CO_2RR is more challenging when the electrolyte is water due to the fact that CO_2 is weakly dissolved ($\approx$ 0.33 mol dm^{-3} at 25 °C, 1 atm), (Fan et al. 2018) in acidic and neutral solutions and due to possible occurrence of the hydrogen evolution reaction (HER).

The CO_2RR happens at electrode/electrolyte boundaries and the process involves three main steps. The first comprises the CO_2 chemical adsorption on the surface of the electrocatalyst, and the second is the electron transfer and/or proton migration to break C–O bonds and/or form C–H bonds. The third and last one involves the rearrangement of product species, their desorption from the electrode, and diffusion into the electrolyte.

CO_2RR is a thermodynamically challenging process but it also presents innumerable kinetic problems. Generally, the CO_2RR proceeds thru distinct multi-step paths with the involvement of electrons (2–18) resulting in various products. Parameters like the type of ECs, electrolytes, pH, pressure, temperature, and CO_2 concentration greatly influence the number and type of paths (Mao and Hatton 2015). Various reduction products can be formed such as formic acid (HCOOH, acid medium), carbon monoxide (CO), formate ($HCOO^-$, basic medium), methane (CH_4), methanol (CH_3OH), ethanol (C_2H_5OH), formaldehyde (CH_2O), oxalic acid ($H_2C_2O_4$, acid medium), oxalate (${C_2O_4}^{2-}$, basic medium), and ethylene (C_2H_4) among others.

9.3.2.2 Production of Methane

Currently, few examples can be found in the literature regarding electrocatalysts that can maintain high and stable methane selectivity. Among them, transition metals, particularly Cu, exhibit the most excellent catalytic performance on the selectivity of methane (Guo 2021). The protonation of adsorbed CO is the most decisive step considering the overpotential. Therefore, strong bonding with CHO or COH intermediate is critical for the electrocatalyst surface to increase the potential of the protonate CO. Additionally, the competition of HER is a tricky problem due to the similarity of standard potential.

Sun et al. (2016) reported the CO_2RR to methane by N-doped carbon (graphene-like) material (NGMs) coated onto carbon paper electrodes and using ionic liquids as the electrolyte. The authors used distinct bases containing nitrogen (3-pyridinecarbonitrile, 3-hydroxypyridine, 4-dimethylaminopyridine, benzimidazole, and 1-vinylimidazole) to prepare them, which resulted in different percentages of nitrogen species ranging from 4.8 to 1.8%. The $FE_{methane}$ decreased from 93.5% to 20.8% from 3-pyridinecarbonitrile to 1-vinylimidazole. According to the authors, the active sites were pyridinic-N and pyridinic-/pyrrolic N species. The strong interaction between the electrode and the adsorbed CO prevents its escape, facilitating the hydrogenation reaction to yield CH_4. Wang et al. (2018b) developed perfluorinated covalent triazine framework (CTF) derived hybrids and applied them as CO_2RR electrocatalysts. Their studies suggested that the edge-gN and edge-2gN on the CTF hybrid acted as the electrocatalytic sites to obtain CH_4 with a FE of 99.3%. When both F and N-dopants were introduced, F regulated the N to enhance the adsorption of the key intermediate $^*CO$ and $^*CH_2$.

Following their primary studies on CO_2RR on N-doped graphene quantum dots (NGQDs) (Wu et al. 2016), Yakobson and co-workers reported a vast work on computational simulations to identify the underlying mechanisms regulating the process of CO_2RR using this type of materials (Zou et al. 2017). In previous works, the same authors have shown that NGQDs are able to convert electrochemically the CO_2 molecule into different hydrocarbons and oxygenates, like CH_4, C_2H_4, and C_2H_5OH, making them valuable alternatives to Cu for CO_2RR (Wu et al. 2016). The reduction of CO_2–CO is promoted by the N-doped edges on NGQDs which results in the enhancement of their bonding with *COOH (Zou et al. 2017).

9.3.2.3 Production of Methanol

Methanol generation using CO_2RR is tricky due to its 6e- and $6H^+$ transfer processes which require higher selectivity (Fernandes et al. 2019). First, CO_2 is reduced to CO which is adsorbed on the electrocatalyst surface then, the CO is then reduced to CHO^*, CH_2O^*, and CH_3O^*. Finally, the products are eventually desorbed from the electrocatalysts surface to produce methanol (Liang et al. 2021; Yang et al. 2019; Zhao and Lu 2019). Theoretical calculations have suggested that surface geometry could modulate the total energy of metal-free sites via strain effects (Zhou et al.

2019), thus possibly tuning the production of methanol by CO_2RR on curvature carbon-based catalyst surfaces. In fact, Chai and Guo (2016) demonstrated that N-doped CNT with a certain degree of curvature (6.0) could produce methanol whereas the graphene electrocatalysts without curvature produced CO/HCOOH.

Mou et al. (2019) suggested that an increasing difficulty in CH_2O and CO production would lead to CH_3OH production using boron phosphide nanoparticles as electrocatalysts. This catalyst achieved a high $FE_{methanol}$ of 92.0% at −0.5 V versus RHE. DFT calculations disclosed that P and B promote the binding and activation of CO_2 molecules, and the $^*CO + {}^*OH$ to $^*CO + {}^*H_2O$ process is the rate-determining step ($\Delta G = 1.36$ eV). Additionally, CO and CH_2O products are not easily generated on the boron phosphide (111) surface, which is responsible for the high selectivity and activity for methanol production. These studies emphasized that the production of methanol depends on the chemical state of the reactant and on the electrocatalyst surface properties. A proper surface curvature combined with an optimized heteroatom doping configuration will be favorable as the metal-free site for CO_2RR–CH_3OH conversion. Partially oxidized Co nanoparticles on a single-layer nitrogen-doped graphene were reported by Wang and co-workers (Huang et al. 2018a) with a $FE_{methanol}$ of 71.4% at −0.90 V versus. SCE with a current density of 4 mA cm^{-2} and high yield of 1.10 mmol dm^{-3} h^{-1}. Higher faradaic efficiency of 97.0% at −0.98 V versus. SCE was obtained over urchin-like $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ (Huang et al. 2018b). Yang et al. (2019) described the preparation and application of CO_2RR–CH_3OH electrocatalyst of N-doped carbon nanofibers involving Cu single atoms. The electrocatalyst was produced by a scalable 3-step strategy involving the pyrolysis of polyacrylonitrile (PAN) fibers-integrated Cu^{2+}/ZIF-8 nanoparticles. To guarantee only the presence of Cu single atoms (Cu–N_4 moieties) as the main active sites, the material was washed with H_2SO_4 solution after carbonization. This step was important to remove residual Zn atoms and Cu aggregates. The final electrocatalyst was capable of producing methanol with an outstanding FE of 44% at −0.9 V versus RHE. Another MOF-derived carbon obtained thru the carbonization of HKUST-1 ($[Cu_3(BTC)_2(H_2O)_3]_n$, BTC = trimesic acid) was applied as CO_2RR electrocatalyst with high methanol selectivity (Zhao et al. 2017). The oxidation degree and size of carbon-embedded Cu-containing NPs were controlled using different pyrolysis temperatures (900, 1000, and 1100 °C). The authors noticed that the carbon produced at 1000 °C, exhibited the highest proportion of Cu^+ in form of Cu_2O, the lowest average NP size, and the optimal relation between charge and mass transfer resistances, showing the best selectivity toward methanol with FE = 43.2% at −0.3 V versus. RHE and even formed ethanol ($FE_{ethanol} = 34.8\%$ at −0.5 V vs. RHE).

9.3.2.4 Production of Ethanol

The reduction of CO_2 to ethanol is highly desirable due to its considerable industrial applications but its 12-electron process, with the equilibrium potential of 0.084 V versus. RHE requires higher selectivity to be achieved (Mohamed et al. 2020). Similar to other multi-carbon (C^{2+}) products, the majority of electrocatalysts reported for the production of C_2H_5OH are based on copper since Cu metal allows the dimerization of CO, which is a vital step for the production of molecules with more than one carbon. However, only a small number of examples can be found in the literature regarding electrocatalysts that are able to produce ethanol with FE > 30%, as other competing C^{2+} products, especially ethylene, are also formed (Hoang et al. 2018; Chen et al. 2018a; Mi et al. 2019; Kim et al. 2021).

Non-metal electrocatalysts have also been reported, with outstanding selectivity for C_2H_5OH production (FE > 90%) when a B and N co-doped nanodiamond (BND) was used (Liu et al. 2017b). B and N-dopants induced reactive sites by regulating the electronic state of the BND. Moreover, the B or N-doped BND presented higher overpotential for HER than graphitic carbon materials, so the dopant-induced active sites can favor CO_2RR over HER in a broader potential window. However, this high selectivity was achieved at a low current density of less than 2 mA cm^{-2} which limits its practical applications. Lu and co-workers (Yuan et al. 2018) have also reported the application of several functionalized graphene oxide (GO) surfaces with different pyridine derivatives (pyridoxine, 4-hydroxypyridine, 4-aminopyridine, 8-hydroxyquionoline, and 5-amino-1,10-phenanthroline) as CO_2RR electrocatalysts. The best results were achieved with GO sheets modified with pyridoxine (GO-VB6) with a 2.32% N-pyridinic content. The GO-VB6 showed optimum CO_2 electrocatalytic activity with an overall faradaic efficiency of 45.8% and a $FE_{ethanol}$ of 37%.

Nitrogen-doped ordered cylindrical mesoporous carbon (c-NC) has also been reported by Song et al. (2017) as a robust metal-free EC for CO_2RR to ethanol. The c-NC (Fig. 9.6a) was prepared by a soft template method via the self-assembly of resol (C precursor), F127 (soft template), and dicyandiamide (N precursor). The c-NC electrocatalyst has distinctive cylindrical channels embedded in the carbon bulk. The authors also prepared the inverse mesoporous N-doped carbon (i-NC) that preserves similar pore parameters and tested it in the same conditions to highlight the advantage of the cylindrical mesoporous structure. It is important to refer that the N content of both materials was strictly controlled to be the same. The c-NC showed 100% selectivity and a high faradaic efficiency of 77% at −0.56 V versus RHE (Fig. 9.6). The HER side reaction was greatly hindered, and CO generation was completely suppressed during CO_2RR in an aqueous solution. Both experimental and theoretical studies demonstrated that the dimerization of key CO^* intermediates and the subsequent proton–electron transfers that led to the superior electrocatalytic performance was facilitated by the synergetic effect of the nitrogen heteroatoms and the cylindrical channel.

Later, the same group reported a hierarchical medium micropore-embedded ordered cylindrical nitrogen-doped mesoporous carbon (MNC) prepared by a similar method (Song et al. 2020). The desolvation induced by the medium micropores uniformly embedded in the mesopore channel wall, led to the accumulation of electrolyte ions, and enabled high local electric potentials. Consequently, the activation of CO_2 molecules and the C–C coupling of the key intermediates were facilitated by surface-active pyridinic and pyrrolic N sites with high electron density. As a result,

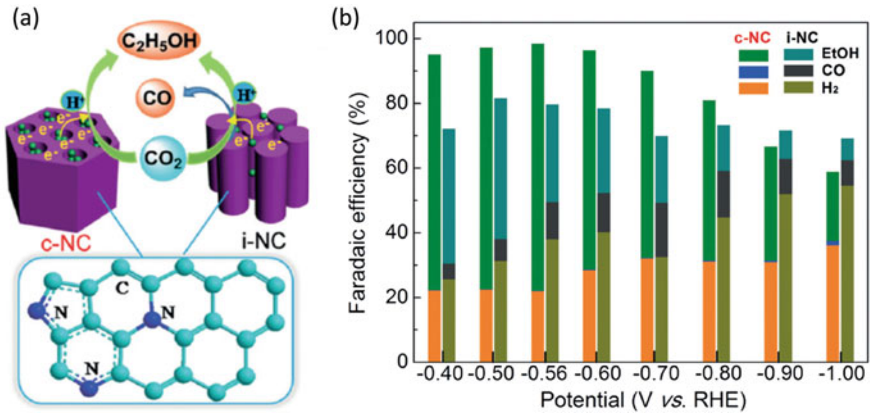

Fig. 9.6 Illustration of c-NC and i-NC for CO_2 electroreduction (**a**) and FEs of CO_2 electroreduction products over c-NC and i-NC electrocatalysts at various applied potentials (**b**). Reproduced with permission from (Song et al. 2017). Copyright 2017 Wiley-VCH

an ethanol production rate as high as 2.3 mmol $gcat^{-1}$ h^{-1} was achieved as well as a FE of 78%.

Recently, Cu single atoms/nanoparticles/clusters have been combined with various carbon matrixes to prepare CO_2RR electrocatalysts. The most commonly used strategy is to use N-doped carbon materials to improve the interactions with the metal ECs. For example, Karapinar et al. (2019) showed that Cu0.5NC produced ethanol with high selectivity of 43% and with a current density of 16.2 mA cm^{-2} at −1.2 V versus RHE if the single-atom Cu sites on N-doped graphene were reversibly converted into Cu nanoparticles. Chen et al. (2020a) have also observed that N-doped graphene quantum dots modified with Cu nanorods (Cu-nr) (NGQ/Cu-nr composite) were able to produce C^{2+} alcohols with FE of 52.4% a partial current density of 147.8 mA cm^{-2} at −0.9 V versus RHE (Chen et al. 2020a). Zhan et al. (2020b) have also reported the CO_2 conversion to ethanol using Cu_2O/Cu nanoparticles supported on vertically ZIF-L coated N-doped graphene. The authors grew the 2D pseudopolymorph of ZIF-8 (ZIF-L), on graphene sheets, introduced a Cu precursor on this nanocomposite and finally, pyrolyzed for 2 h at 1000 °C. The final electrocatalysts resulted in a $FE_{ethanol}$ of 70.52% at −0.87 V versus RHE.

9.3.2.5 Production of Syngas

Syngas (synthesis gas), a highly desirable feedstock for the production of value-added chemicals by post-thermochemical processes, is a gas mixture of carbon monoxide (CO) and hydrogen (H_2). Since the CO_2RR is usually performed in aqueous media, the hydrogen evolution reaction (HER) from the reduction of water or protons (H^+) is a competitive reaction of CO_2RR (Hernandez et al. 2017). A considerable number of attempts have been conducted to design electrocatalysts able to produce syngas with a controllable and specific H_2/CO ratio which is crucial for maximizing the product yield. However, obtaining a high activity while maintaining a desirable H_2/CO ratio (0.5–2) is not trivial. If the CO_2 supply rate does not reach the consumption rate due to diffusion limitations, there is CO_2 deficient environment near the electrocatalytically active sites. This results in unsatisfactory *COOH intermediates, leading to a dominant HER. Thus, the HER and CO_2RR reaction rates must be adjusted and balanced for the efficient production of syngas (Ramirez-Valencia et al. 2021; Zhang et al. 2020a). This ratio is dependent on different parameters, like temperature, pH, electrolyte feed rate, current density (applied potential), and the electrocatalyst composition or particle size. Here we will focus on the electrocatalysts, namely, the carbon-based ones.

In 2017, Liu et al. (2017a) grew N-CNTs in-situ on stainless steel under an inert atmosphere, using melamine as both the nitrogen and carbon sources and applied it as an electrocatalyst for the conversion of CO_2 into syngas. The integrated electrode displayed efficient, robust, and controllable clean syngas production with a FE_{CO} of 75%. More importantly, the authors were able to tailor the H_2/CO ratio in the clean syngas products in the range between 1:3 and 3:1 by tuning the applied potential or the pyrolysis temperature. Nitrogen-doped tubular carbon foam electrodes were reported by Li et al. (2019) as both, gas diffusers and self-supported electrocatalysts for CO_2 transformation into syngas. The monolithic tubular electrodes were capable of producing syngas over a wide potential range (−0.5 to −1.3 V vs. RHE) and its ratio was tunable from 1:3 to 2:1 through the control of the N defect enrichment being independent of the applied potential. Metal-free porous N-doped carbon prepared using melamine and pentaerythritol as the N and C sources, respectively have also been successfully applied for the production of syngas through CO_2RR showing good selectivity ($FE_{CO} = 74\%$, $FE_{H2} = 18\%$, at −0.6 V) (Chen et al. 2021). More importantly, the authors were able to adjust the syngas ratio from 0.24 to 5.25 with good product selectivity by varying the applied potential from −0.4 to −1.0 V.

Apart from heteroatom-doped a considerable number of noble metal-free carbon-based electrocatalysts have been reported for the syngas production from CO_2RR in the last 5 years. For example, Zhao et al. (2020) reported the generation of syngas through CO_2RR for a sequence of Fe–N–C ECs. These were prepared by calcination at high temperature utilizing transition metal Fe incorporated into urea-formaldehyde resin precursor. The best Fe–N–C electrocatalyst (3%, 950 °C) exhibited a FE close to 100% with no liquid phase product with an attractive activity of CO and H_2 generation ($FE_{CO} = 74\%$, $FE_{H2} = 25\%$) at a low overpotential of −0.6 V. More importantly, the syngas (H_2/CO) ratio from 4:1 to 1:3 can be controlled by adjusting the applied potential with good long-term stability. Zhang et al. (2020a) prepared a series of Ni_xFe_{1-x}–NC single-atom catalysts (SACs), which enabled syngas production with a wide range of CO/H_2 ratio (0.14–10.86). The authors concluded that Fe sites play a crucial role in HER reaction, while the Ni sites in the CO_2RR and that the fine tuning of the Ni/Fe ratio they were able to control the product composition in a large window from high CO end to high H_2 end.

Recently, Atanassov and co-workers (Delafontaine et al. 2020) published an excellent review on the metal-nitrogen-carbon EC for CO_2 reduction toward syngas generation. The authors highlighted the high potential of MNC electrocatalysts due to (i) their versatility and tunable selectivity toward H_2 and CO generation by applying distinct moieties and metal elements, and (ii) their carbonaceous nature which allows a high degree of control of key parameters like hydrophilicity and porosity distributions. Furthermore, they pointed out the durability/robustness under operation as an important aspect of real-like implementation.

9.3.3 Economic Analysis of CO_2-Derived Fuels

Given the early stage of the CO_2 to fuels technology, it is difficult to estimate the future market. Nevertheless, the market will remain low in the short term.

In order to use CO_2, it has to be captured, purified, and transported. Hence, the cost of CO_2-derived fuels will depend on the price of the energy, the technology, as well as that of CO_2 and H_2 and other required materials such as catalysts. Also, while CO_2 supply shortages can increase the costs of CO_2, carbon taxes can encourage the producers of CO_2 to use conversion technologies.

The prices of CO2 capture and purification are different depending on the source of CO_2, fluctuating from 15 to 60 \$/tCO_2 for concentrated CO_2 streams, 40–80 \$/tCO_2 for coal and gas-fired power plants, or above 100 \$/tCO_2 for dilute point sources (e.g., industrial furnaces). Obviously, direct CO_2 capture from the air is the most expensive method, ranging from 94 to 232 \$/tCO_2, due to the required energy to concentrate the stream sources (Keith et al. 2018). Nevertheless, technical developments are expected to reduce costs.

It is also intuitive that the proximity between the source of CO_2 and the point of use of the derived fuels would drastically decrease the costs, however, this is not possible in every situation.

Some techno-economic analyses have been reported. For example, it is estimated that the production costs of methanol and methane from CO_2 are 2–7 times higher compared to fossil sources, electricity being the main associated cost, which represents 40–70% of the total expenses (Agency 2019). Under these conditions, the production of methanol and its derivatives from CO_2 hydrogenation might be realized in areas with low-cost renewable energy and available CO_2, such as in North Africa, Chile, or Iceland where there is already a facility, George Olah, that processes over 5 k ton of CO_2 per year into methanol employing H_2 obtained using renewable electricity.

There have been some recent publications that evaluate the costs of producing gasoline from CO_2. For example, Caballero et al. simulated a capture and one-stage conversion system for CO_2 through Fischer Tropsch (Fernández-Torres et al. 2022). The authors considered different carbon capture (either directly from the air or from other concentrated sources) as well as different hydrogen sources from methane reforming to that renewable wind or solar. The associated costs of the produced gasoline varied from 1.8 to 2 $/l for gas natural derived H_2 to 6–8 $/l for electrolysis derived H_2 using wind or solar renewable energy.

Also, Marchese et al. (2021) evaluated a system consisting of direct air capture and then the conversion of CO_2 through the Fischer-Tropsch mechanism. The authors considered different scenarios where the energy was supplied either by natural gas or renewable sources. The estimated costs were 5–6.3 €/kg of wax depending on the interests rate.

It is expected that production costs of CO_2-derived fuels will decrease in the future mainly due to the availability of low-cost renewable electricity. Nevertheless, in the near future CO_2-derived methane and CO_2-derived liquid fuels will be too expensive unless public taxes are applied. On the contrary CO_2-derived methanol may be competitive depending on the region (Marchese et al. 2021). The main advantages are the climate benefits, hence the price can be linked to it provided public policies are set.

9.4 Conclusion, Future Challenges, and Perspectives

The current challenges and research trends toward efficient carbon-based catalysts for renewable fuels production from biomass/CO_2 were addressed in this review aiming to inspire the broad community of scientists working toward a low-carbon society where biomass renewable resources are the best choice. This review showed the potential of biomass (bio-oil upgrading) and CO_2 conversion as a very promising strategy to produce sustainable and cleaner fuels to reduce the massive dependence on fuel from fossil resources. From this review paper it is possible to conclude that:

- In terms of the use of carbon-based catalysts, the published studies use commonly activated carbon and biochar as support. These carbon materials and specially biochar are easily tunable allowing materials with different physical and chemical properties and exceptional pore structure and specific surface area which results in catalyst better dispersion. Carbon nanotubes and graphene are also interesting materials due to their unique structures (nanomaterials) providing a larger reaction area and excellent electrical and thermal conductivity. In the future, the application of modification methods will improve even more the pore structure and mechanical strength of carbon-based catalysts and their ability to gradually become the protagonist of biomass and CO_2 conversion into fuels. Low-cost carbon supports are key factors to the potential of industrial scale bio-oil/CO_2-based energy in the future. The mechanical strength and the regeneration and recycling capabilities of the catalysts are fundamental requirements for industrialization.
- N-dopants on carbon matrix can be assumed as crucial anchoring sites or defects for particle formation and size reduction.
- HDO is one of the most extensively studied processes for the catalytic upgrading of bio-oil to remove oxygen containing functional groups improving the bio-oil quality including heating value and process efficiency. The development of

cost-competitive non-noble metal catalysts, with high selectivity for C–O bonds cleavage preserving simultaneously the C–C bonds at low H_2 pressures, remains a major challenge. Therefore, novel catalysts, sustainable solvents, and especially the adoption of an "H_2-free" HDO process are key factors to overcome the economic barriers of a potential commercial scale. Future work should also focus on improving the understanding of bio-oil HDO reaction pathways. The commercialization of bio-oil is not yet viable but can be in the near future, after reducing the upgrading costs of bio-oil. Furthermore, some studies have prompted HDO as a versatile route to produce jet fuel hydrocarbons from bio-oil. The development of catalysts to efficiently eliminate oxygen under low levels of H_2/mild conditions avoiding coke formation/catalyst deactivation is crucial to the sustainability of bio-jet fuel production from bio-oil.

- The steam reforming of bio-oil is an environmentally friendly route to produce H_2 or syngas and can be considered an important process in the future although the major challenge of these processes is catalyst deactivation. Carbon materials have been shown to efficiently improve metal dispersion, and water resistance, and limit metal sintering enhancing H_2 production and/or catalyst stability from the bio-oil fraction depending on the process employed.
- CO_2 thermochemical and electrochemical reduction has not only an economic potential due to low-cost feedstocks but also contributes to the mitigation of CO_2 emissions through its utilization. The catalyst and the support play an important role in this conversion. Carbon-based materials as a catalyst or catalyst support showed to be efficient demonstrating that: the N-doped carbon materials favor the CO_2 activation and the electronic properties of graphenic structures may influence by changing the electronic properties of the metal-nanoparticles promoting hydrogen transfer. While there are several works on CO_2 hydrogenation to methanol and hydrocarbons, there is still much work to do on the transformation to formic acid which is relevant to be coupled with intermittent renewable energy generation sites. In a similar way, the CO_2 transformation through electrochemical processes is favored by the presence of nitrogen in the electrocatalysts structure regardless of the presence of metals. Results have shown that N-doping boosts the electrocatalytic activity and that most likely the pyridinic-N sites represent a key factor for this enhanced activity.
- Despite significant advances in CO_2 and biomass conversion into fuels, the low yields, the complexity (multi-step; difficulties in purification) of the processes, the high costs, and the catalysts' deactivation are hurdling the large-scale production and the competitiveness of a CO_2/biomass biorefinery.
- From an overall view of these biomass/CO_2 conversion methodologies, it is clear that a cost-effective and efficient catalytic process has not been developed so far, so there are several opportunities for researchers to develop new catalysts and catalysts supports, design reactors, and find alternative reaction conditions (single-step catalytic conversions) to produce bio-oil biofuels from biomass and CO_2.

- Life cycle assessment of bio-oil production and upgrading technologies and CO_2 (electro)catalytic conversion is essential to bring the vision of the sustainability of the processes and target products at an industry level.

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