https://dx.doi.org/10.1016/j.biortech.2017.06.163

A Review of Biochar-Based Catalysts for Chemical Synthesis, Biofuel Production, and Pollution Control

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Abstract

This review addresses the use of biochar as a green and versatile catalyst support for emerging high-end applications beyond soil remediation, including chemical synthesis and biodiesel production from biomass, and pollutant degradation in the environment. Their catalytic performances are comparable or even superior to the conventional resin-, silica-, or carbon-based catalysts, owing to the favourable intrinsic features of biochar (various functional groups, intricate network of structures, etc.). Yet, distinctive active sites are needed for different applications. It is highlighted that the active site accessibility for substrates critically determines the performance, which is associated with the biochar physicochemical characteristics (-SO_3H site density, pore size distribution, surface area, etc.). They show varying significance depending on the catalytic sites on biochar, which may be controlled via novel pre-/post-synthesis modifications. This review elucidates the links among catalytic performances, physicochemical properties, and pyrolysis/modification-induced features, advising the tailored production of application-oriented biochar-based catalyst in the future.

Keywords: biochar; solid catalyst; acid-catalyzed conversion; biorefinery; waste valorization.

1. Introduction

Biochar is a low-cost carbon-rich material derived from a wide variety of waste biomass, such as sludge/manure, food waste, and agricultural residues, via pyrolysis with limited oxygen or hydrothermal carbonization under high pressure (Tang et al., 2013). The advantageous properties

including relatively large surface area, high pore volume, long-term stability, and enriched surface functional groups have rendered biochar a broad spectrum of potential applications. It has played an important role in: (i) soil improvement by increasing the nutrient interactions, soil fertility, and crop productivity; (ii) carbon sequestration by suppressing the greenhouse gas emissions (Lehmann et al., 2015; Hussain et al., 2017); (iii) soil remediation by immobilizing various contaminants through sorption, precipitation, etc. (Ahmad et al., 2014; Rizwan et al., 2016); as well as (iv) wastewater treatment based on its effective removal of heavy metals, organic chemicals, and microbial contaminants from the aqueous system (Mohan et al., 2014; Tan et al., 2015; Inyang et al., 2016). Its contaminant removal efficiency can be further improved upon engineering modifications such as magnetization, carboxylation, and amination (Rajapaksha et al., 2016a). In recent years, the applications of biochar have been extending to the high-end fields such as energy and healthcare industry, in view of its economical synthesis, sustainability merits, and manoeuvrable characteristics (Ok et al., 2015).

The conversion of biomass to value-added chemicals is one of the emerging applications of biochar (Liu et al., 2015a, Zhang et al., 2017). For instance, hydroxymethylfurfural (HMF) arises as one of the attractive products with high market value, which is a versatile platform chemical for the synthesis of medicines, solvents, polymer, surfactants, and biofuels (Yu et al., 2017a&b; Yu and Tsang, 2017). While acid site-bearing resins/polymers or zeolites are widely investigated for HMF synthesis, biochar upon functionalization shows a great potential in serving as a sustainable alternative. Therefore, it is highly desirable to expand the existing literature for boosting the development of application-oriented biochar-based catalyst in the area of biorefinery.

According to the latest reviews on conventional catalytic systems (i.e., mineral acids, commercial catalysts, etc.), the biomass valorization is often impeded by the low reactivity of sugar-involved reactions and low selectivity of target products due to the side reactions (Zhang et al., 2016; Chen

et al., 2017a; Yu and Tsang, 2017). To overcome these challenges, it is necessary to tailor the catalyst characteristics such as channel size, Brønsted-to-Lewis acid ratio, and hydrophobicity for controlling the reaction kinetics. Hence, there is a need to elucidate the significance and possible means to manipulate these properties for biochar catalyst-mediated biomass valorization.

Recently, biochar-based materials have been studied for the catalysis of refinery processes (e.g., syngas cleaning and syngas conversion), biodiesel production, as well as air pollution control (Qian et al., 2015; Cha et al., 2016; Lee et al., 2017a). While the current reviews summarize the reported performances of different biochars, information on the roles of their physicochemical properties remains scattered and diverse. It has been suggested that the surface functionality, for example, the -SO_3H groups as the Brønsted acid sites and dispersed metal nanoparticles, governs the catalyst efficiency (Liu et al., 2015b). Other properties such as particle strength, hydrophobicity, surface area, porosity, and mineral content also emerge as important factors depending on the particular applications (Qian et al., 2015). Such divergent knowledge needs to be systematically organized and critically reviewed to offer insights for the advancement on biochar-based catalysts. It remains uncertain how and to what extent these parameters determine the catalytic performances in wide-ranging reactions. Therefore, in-depth understanding on the interrelations between the catalytic activity and physicochemical properties is required for synthesizing purpose-driven biochar by novel pre- or post-synthesis methods.

This review summarizes the innovative applications of biochars as catalysts in: (i) chemical synthesis from biomass, (ii) biodiesel production, and (iii) air and water pollution control. For each application, the catalytic performances are scrutinized to elucidate the critical physicochemical properties via comparison to carbon-based alternatives and conventional solid catalysts. Existing and potential methods for biochar synthesis and tailoring to serve different catalytic applications are discussed.

2. Tailoring biochar properties for catalytic application

The physicochemical properties of biochar, including acid density (-SO_3H in particular), surface area, pore size and volume, surface oxygen functional groups, and metal dispersion and speciation, are conducive to the performance of biochar-based catalysts (will be discussed in **Section 3-5**). Therefore, it is important to control these properties by manoeuvring the protocol of catalyst preparation.

2.1 Thermochemical production of biochar

Biochar is usually produced via pyrolysis of biomass under limited oxygen supply at the temperature ranging from 300 to 800°C. Conventional carbonization, i.e., slow pyrolysis, produces biochar as the major product along with a small amount of syngas including CO, CH_4, and H_2, and condensed bio-oil (Liu et al., 2015b). It requires a relatively long residence time (> 1 h) and low heating rate (5-7°C/min). Comparatively, fast pyrolysis favours the production of bio-oil, of which the heating rate is over 200°C/min and the residence time is less than 10 s (Qian et al., 2015). The solid residue, i.e., biochar, may display relatively small surface area due to incomplete pyrolysis and tar-like materials entrapped in the pores (Lobos et al., 2016).

Gasification is the thermochemical process that produces biochar as the solid co-product and syngas as the main product at > 700°C in the presence of oxidizing agent (O_2 or steam). Tar reforming that shares a similar operation mechanism also gives biochar as a secondary product.

Hydrothermal carbonization of biomass resulted in hydrochar as the biochar analogue at low temperatures (180-250°C) under pressure in water, which eliminates the energy-intensive drying of feedstock (Libra et al., 2011). It therefore appears as a cost-effective approach to generate biochar for catalytic applications.

2.1.1 Feedstock

Biomass with varying contents of hemicellulose, cellulose, and lignin may yield biochars with distinctive physicochemical properties under the same temperature (Keiluweit et al., 2010). This

4

is because the three types of polysaccharides show different thermal liability, e.g., hemicellulose, cellulose, and lignin decomposes at 220-315°C, 315-400°C, and 160-900°C, respectively, as a result of their difference in structural features such as crystallinity, cross linking, and branching (Yang et al., 2007; Keiluweit et al., 2010). Therefore, the composition of biomass feedstock may determine the heating temperature required to obtain the desirable porous structure. For example, the microcrystalline cellulose without lignin gave graphitic structure at 350°C, which was much lower than the temperature of 700-900°C employed for lignocellulosic biomass (Lobos et al., 2016). The matrix of raw biomass also affects the biochar micro-structure. For instance, wood biochar showed intricate network of fibrous ridged surfaces, pores, and channels resembling the structure of raw wood, which vastly differed from the planar structure of the sugar-derived carbon (Dehkhoda et al., 2010; Dong et al., 2015).

Ash content in the feedstock is important for the biochar properties and catalytic performance. Inorganic elements (Ca, K, Na, P, Si, Mg) were concentrated in the char after pyrolysis, which may play as the active sites for catalysis of, for example, methane decomposition (Klinghoffer et al., 2015) and hydrogen production (Yao et al., 2016) (**Section 4.2**). Therefore, it is important to select appropriate feedstock for the corresponding application, modulating the extent of biochar modification or even dispensing with it. Nevertheless, high ash content in biomass feedstock could retard the formation of stable polycyclic aromatic carbon (SPAC) fraction that determined the biochar stability (McBeath et al., 2015). In particular, high concentration of Si would affect the efficiency of metal impregnation (a type of modification; **Section 2.2**) because it promoted metal sintering upon melting at high temperature and reduced the degree of metal dispersion (Yao et al., 2016).

2.1.2 Temperature

The temperature of the thermochemical treatment is critical for the biochar properties. In general, the fixed carbon content, surface area, and pore volume increase with the temperature as more

volatile matters are released from the biomass, despite the reduction of biochar yield as a trade-off (Yuan et al., 2013; McBeath et al., 2015; Lobos et al., 2016). As the temperature rises, the microcrystalline cellulose in biomass gradually transforms in five phases: unaltered material, transition char, amorphous char, composite char, and turbostratic char (Keiluweit et al. 2010). The last stage is achieved at 600-700°C. Such transformation is associated with the gradual loss of oxygen functional groups and aliphatic groups such as cutans and lipids (400°C), as well as the formation of polycyclic aromatic structures via dehydration reactions (Keiluweit et al. 2010; McBeath et al., 2015). The temperatures of 500-700°C were revealed as the optimal in terms of the SPAC content and biochar yield for the commonly used feedstock (e.g., wood, agricultural/forestry residue, manure, and macroalgae). At higher temperature, condensation of volatiles may block the pores, and gasification of char may lead to increased macropore volume at the expense of the microporosity (Muradov et al., 2012).

2.2 Activation of biochar

A wide range of activation methods were used to modify the biochar properties and functionalities, such as chemical treatment, gas activation, and metal impregnation, which can be conducted before, during, or after biochar synthesis (**Table 1**).

2.2.1 Pre-synthesis treatment

5.3.1.1 Metal impregnation

Metal impregnation aims to attach metals as the active sites on biochar, such as Lewis acid sites that facilitate glucose isomerization as well as fructose dehydration for HMF/levulinic acid production (Liu et al., 2015a; Yu et al., 2016**; Section 3**). This can be achieved by co-calcination of biomass with metal compounds. For example, the mixture of pre-hydrolyzed corncob comprising sugars and solid residue, and $Sn(OH)_4$ and $Co(OH)_2$ were carbonized in a tube-carbide furnace under N_2 in two stages (i.e., 100°C for 10 h and 200°C for 38 h) (Liu et al., 2015a; **Table 1**). The resultant catalyst had the surface area of 6.34 m^2/g, pore volume of 0.003 cm^3/g,

and acid density of 0.542 mmol/g. Metallic Ni as a common catalyst can be loaded in a similar manner. Biomass was impregnated with $Ni(NO_3)_2 \cdot 6H_2O$ solution and subsequently pyrolyzed at 700°C in N_2 after drying (Shen and Yoshikawa, 2014). Treating the Ni-containing biomass with a strong reducing agent, i.e., $NaBH_4$, before pyrolysis further enhanced the catalytic performance (for tar reforming; **Section 4.2.1**), because the formation of active metallic Ni^0 from cation was effectively promoted. Besides, the hydrolysis of $NaBH_4$ in the Ni^{2+} solution facilitated the development of porosity and surface area in biochar. Metal impregnation can be also achieved in a post-synthesis manner, which will be discussed in **Section 2.2.2.2**.

5.3.1.2 Phosphoric acid treatment

Phosphoric acid treatment of raw biomass could enhance the physical properties of biochar. The microcrystalline cellulose was treated with 5% H_3PO_4 at 70-80°C for 2 h under stirring prior to pyrolysis (Lobos et al., 2016; **Table 1**). This could increase the surface area from 199 to 557 m^2/g (electroactive surface area: from 18 to 38 m^2/g) and pore volume from 0.026 to 0.22 cm^3/g as a result of H_3PO_4-mediated dehydration of the cellulose. More structural defects such as terraces, steps, and kinks were also created on the surface to benefit the subsequent metal impregnation step, resulting in the catalyst with electrocatalytic activity four times higher than that without H_3PO_4 treatment. Such acid treatment also favoured the formation of biochar over liquid products during fast pyrolysis. Similar observations were remarked in another recent study, which demonstrated the activation of raw biomass via H_3PO_4 pretreatment followed by carbonization under steam/N_2 mixture (Shen et al., 2015a). This biochar possessed high surface area (1955 m^2/g) and porosity (0.48 ml/g), which may favour homogeneous dispersion of metals ($Mn\text{-}CeO_x$) during the subsequent impregnation, compared to the post-pyrolysis steam-activated biochar and activated carbon.

2.2.2 Post-synthesis treatment

5.3.1.3 Sulfonation

Sulfonated biochar is an effective catalyst for acid-driven reactions. Not only the strong sulfonic acid groups are introduced, but the weak acid groups are also created including carboxyl and phenolic hydroxyl groups (Kastner et al., 2012; Deng et al., 2016). They can serve as the Brønsted acid sites to catalyze hydrolysis and dehydration process (Osatiashtiani et al., 2014; Yu et al., 2016; **Section 3**), as well as esterification and transesterification (Dehkhoda et al., 2010; **Section 4.1.1**). In addition, H_2SO_4 can enlarge the surface area and pore structure of biochar that are conducive to better catalytic performances in general (Kastner et al., 2012). Yet, the opposite may occur under excessive sulfonation, for example, up to 98% decrease in surface area as reported in the literature (Dehkhoda et al., 2010).

Typical sulfonation reagents include concentrated sulphuric acid (~98%), fuming sulphuric acid, and gaseous SO_3. It was reported that biochar modified by concentrated sulphuric acid showed a lower catalytic activity for transesterification (**Section 4.1.1**) in comparison to that sulfonated by fuming sulphuric acid (Dehkhoda et al., 2010). Another study also suggested that the concentrated acid-sulfonated biochar (99% H_2SO_4) displayed lower $–SO_3H$ group density than the gaseous SO_3-sulfonated carbons as the SO_3 gas was more reactive and selective (Kastner et al., 2012). Moreover, the former carried weaker acids as the hydrogen bonding sites, which promoted water adsorption on the catalyst that hindered the catalytic activity for esterification.

There is a high potential of sulfonated biochar in wider applications such as organic chemical synthesis. Acetanilide, N-butylacetamide, and nitroacetanilide can be produced via the N-, O-, and S- acylation processes over the sulfonated amorphous carbon-silica composite (Gupta and Paul, 2011). The latter may be replaced by sulfonated biochar that shares the same active sites.

5.3.1.4 Metal impregnation

Incipient wetness impregnation is a common technique to load metal nanoparticles on the biochar support. The Ni-containing biochar (for catalytic hydrogen production) was produced by immersion in the aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ for 4 h, followed by drying and calcination

at 800°C (Yao et al., 2016). Similarly, Ni-based biochar was produced for catalytic tar conversion (Shen and Yoshikawa, 2014). It is interesting to note that biochar impregnated before pyrolysis (**Section 2.2.1.1**) showed higher tar conversion efficiency than the one impregnated after pyrolysis, possibly due to the higher surface area of the former (135-218 vs 62-87 m^2/g). For iron nanoparticles, impregnation was conducted with iron nitrate solution followed by 1-h calcination at 1000°C (for syngas conversion; Yan et al., 2013) or 300°C (for tar reforming; Kastner et al., 2015), which may result in metallic iron and iron carbide as the major species. The metal particles were effectively anchored upon the decomposition of surface oxygen functional groups during impregnation. The synergy between stable carbonaceous shell and strong iron core prevented the sintering of metals and collapse of catalyst structure during application.

Platinum, ruthenium, and copper particles can be loaded in a similar manner. The biochar dispersed in the buffer solution (pH 3) containing $CuSO_4$ and $RuCl_3$ was sonicated for 30 min, followed by the addition of the reducing agent $NaBH_4$ to yield Cu-Ru nanoparticles (Lobos et al., 2016). The intermediate product was further dispersed in the H_2PtCl_6 solution to give the Cu-Ru@Pt core-shell nanoparticles on biochar, which exhibited high catalytic activity for electro-oxidation of methanol (**Section 4.3.1**). For synthesis of catalyst containing Pt only, the last step using H_2PtCl_6 solution was appropriate (Fan et al., 2015). It is noteworthy that calcination was not required in these protocols (Fan et al., 2015; Lobos et al., 2016). Nevertheless, metal impregnation may partially block the pores according to a recent study on biochar-supported Mn-CeO_x (Shen et al., 2015a).

Sol-gel method is an alternative metal impregnation technique for synthesis of TiO_2-loaded biochar. This process involves the sequential addition of TiO_2 precursor (e.g., titanium isopropoxide and tetrabutylorthotitanate), ethanol, and other additives (e.g., diethanolamine and HCl), with calcination serving as the last step (Li et al., 2007; Kim and Kan, 2016). The calcination temperature ranging from 300-700°C may exert marginal effect on the surface area

(237-293 m^2/g) (Li et al., 2007). The resultant biochar/TiO_2 catalyst was shown effective for photocatalytic degradation of antibiotics (Kim and Kan, 2016) and dye (Li et al., 2007) (**Section 5.2**).

The application of metal-impregnated biochar may extend to chemical production from biomass in a way similar to other carbonaceous materials, such as Ni/Zn-activated carbon catalysts for the conversion of cellulose to lactic acid (Zhang et al., 2011b) and Ru-mesoporous carbon catalysts for the hydrolysis of cellulose to glucose (Kobayashi et al., 2010).

5.3.1.5 Gas activation

Biochar can be activated via steam treatment under heating (700-850°C, 1-7 h) (Cha et al., 2010; Iwazaki et al., 2010; Shen et al., 2015a; Rajapaksha et al., 2016b). Steam activation successfully increased the surface area of silk biochar by 122-196 times and enlarged the mesopore volume for efficient mass transport during catalytic application, with minor effect on surface morphology (Iwazaki et al., 2010). Compared to the commercial activated carbon, the steam-activated cotton biochar showed a comparable surface area (496 and 516 m^2/g) but lower pore volume (0.27 vs 0.08 ml/g) after metal impregnation (Shen et al., 2015a). It was outcompeted by the biochar co-activated by H_3PO_4 and steam, which exhibited the outstanding surface area of 1955 m^2/g and large pore volume of 0.48 ml/g (**Table 1**). In general, the steam-activated biochar did not perform as well as the commercial catalysts (e.g., Pt/C catalyst for oxygen reduction reaction; Iwazaki et al., 2010; **Section 4.3.2**) or biochar activated by acid/base (e.g., H_3PO_4/steam- and KOH-activated biochar for NO conversion; Cha et al., 2010; Shen et al., 2015a; **Section 5.1**).

It has been reported that CO_2 treatment coupled with heating (850°C, 15 min) significantly increased the surface area of duckweed biochar from 5-12 to 60 m^2/g (Muradov et al., 2012). Such treatment also enhanced the microporosity by creating new pores via CO_2 gasification reaction, while the pore structure remained nearly unchanged. Apart from activation, CO_2 was also employed for supercritical drying of aerocellulose precursors before pyrolysis to ensure the

nanostructure of the pyrolytic carbon (Guilminot et al., 2008). This may apply to biochar production for preserving the original (or pre-modified) structure of the biomass feedstock.

Ozone treatment of biochar (23°C, 6 h) can introduce weak acidic groups on the surface, for example, carboxylic, phenolic, and lactonic groups (Kastner et al., 2012). However, these weak acids neither promoted esterification nor assisted the strong $–SO_3H$ groups in a synergistic manner.

5.3.1.6 Base treatment and ionic liquid grafting

Treatment with base such as KOH has been commonly adopted to increase the surface area and porosity of biochar (Dehkhoda et al., 2010; Jin et al., 2014; Fan et al., 2015). The activation of rice straw and sewage sludge derived biochar in KOH (KOH:biochar = 1:1, 60°C, 2 h) followed by calcination (700°C, 1 h) successfully expanded the surface area from 140 to 772 m^2/g and from 18 to 783 m^2/g, respectively, in association with the increased pore volume (Cha et al., 2010). Such results also indicated the feedstock-dependent efficiency of chemical activation. The ultrasound-assisted KOH treatment may further enhance the properties according to an earlier study, which demonstrated significant increase in the surface area (from 16.7 to 702 m^2/g) and pore volume (from 0.01 to 0.39 cc/g) of switch grass biochar (Bhandari et al., 2014). The improvement may be ascribed to the ability of KOH to facilitate hydrolysis reaction on the biochar surface and dissociation of tar-like materials entrapped in the pores (Lin et al., 2012).

An innovative surface modification using ionic liquid has been recently reported to produce biochar catalyst for HMF production (Zhang et al., 2017). The ionic liquid was grafted on the sulfonated biochar first. The chloride from the ionic liquid was then substituted by fluorine via ionic exchange using F-containing acids. Such modification improved the substrate accessibility to $–SO_3H$ sites by loosening the carbon sheets, and augmented the acidity and thermal stability of the $–SO_3H$ groups via the intramolecular electrostatic interaction with the ionic liquid (Zhang et al., 2017).

3. Emerging applications of biochar-based catalysts for chemicals production

3.1 Pathways of catalytic biomass conversion into versatile chemicals

Lignocellulosic biomass is a renewable raw material for synthesis of various platform chemicals and biofuels (**Fig. 1**). It comprises carbohydrate polymers (cellulose and hemicellulose) and aromatic polymers (lignin) interacting via intra- and inter-molecular hydrogen bonds. Valorization of these biopolymers involves extensive breakdown and transformation reactions, among which hydrolysis, isomerisation, dehydration, and rehydration have been demonstrated to be facile over biochar-based catalysts.

Hydrolysis involves the breakage of glycosidic bonds in polysaccharides to release monosaccharides, for example, converting xylan and glucan to xylose and glucose, respectively. In general, the hydrolysis of lignocellulosic biomass is initiated by Brønsted acid (proton) at the temperature range of 90-260^{o}C under atmospheric or pressurized conditions (Zhou et al., 2011). Proton attacks the oxygen atom in glycosidic linkages to form a cyclic carbonium ion, which subsequently accepts a hydroxide ion to yield the monosaccharide (Zhou et al., 2011; Zhang et al., 2016). Lewis acid (electron pair acceptor) may also weaken glycosidic bond by coordinating with the glycosidic oxygen in a similar fashion (Tao et al., 2011).

The released monomeric aldoses (glucose and xylose) can be isomerized into ketoses (fructose and xylulose, respectively), of which the carbonyl functional groups (C=O) exhibit higher reactivity to facilitate further reactions for upgrading. Activation barrier for the dehydration of glucose and xylose are higher than that of fructose and xylulose, respectively (Choudhary et al., 2012; Enslow and Bell, 2015), due to the stable ring structure of aldoses. Isomerization usually occurs at the temperature ranges of 90-110^{o}C over Lewis acid or Brønsted base catalysts, which promotes the critical hydrogen transfer from C2 to C1 (Zhang et al., 2016).

Fructose and xylulose undergo dehydration to produce HMF and furfural, respectively. The

process is mediated by Brønsted acid catalyst at a temperature range of 120-200°C (Zhang et al., 2016). These chemicals containing a furan ring, aldehyde group, and alcohol group (in HMF) are high-value precursors of medicines, polymers, and biofuels, which could substitute the petrol-derived commodities as well as relieve the stress on fossil energy and burden of greenhouse gas emissions. Levulinic acid and formic acid as the products of the acid-catalyzed rehydration of HMF are also versatile platform chemicals.

Polymerization as an irreversible side reaction becomes significant at high temperatures and prolonged reaction time during the catalytic conversion (Chen et al., 2017b; Yu et al., 2017a). It occurs among the substrates, intermediates, and products to form the carbonaceous humins, which lowers the yield and selectivity of desirable products. In case of heterogeneous catalysis, humins may block the active sites and hence undermine the performance of solid catalyst after repeated use (Deng et al., 2016; Chen et al., 2017a). Previous studies suggested that both Brønsted acid and Lewis acid play a role in promoting polymerization, depending on the acid strength and acid site number (Li et al., 2016; Tsilomelekis et al., 2016; Yu and Tsang, 2017). Therefore, active sites and Brønsted-to-Lewis acid ratio of biochar-based catalyst should be carefully designed to strike a balance between promoting the desired pathways and the unavoidable side reactions.

Other reactions including epimerization of xylose to lyxose and glucose to mannose, retroaldolization of fructose to glyceraldehyde and dihydroxyacetone, as well as glucose to glycolaldehyde and erythrose would take place simultaneously during the HMF or furfural production (Zhang et al., 2016). However, these pathways are not covered in this review because they have not yet been demonstrated over biochar-based catalysts to our best knowledge.

3.2 Biochar catalyst for biomass valorization into chemicals

3.2.1 Biochar catalyst for hydrolysis

In the presence of sulfonated corn stover-derived biochar, the lignocellulosic biomass, i.e., corn

stover, switch grass, and prairie cord grass, yielded glucose of 8-10% (19-22% conversion) and xylose of 23-41% (68-81% conversion) with respect to the corresponding polysaccharide (Li et al., 2013; **Table 2**). The results were comparable to the hydrolysis of model compounds over the same catalyst: cellulose gave 3% glucose (24% conversion) and xylan produced 40% xylose (100% conversion). This demonstrated that the biochar-based catalyst maintained high performance confronting the impurities and complex matrix in biomass. A similar conversion of 85% of model xylan was achieved using sulfonated biochar derived from wood and peanut hulls (Ormsby et al., 2012; **Table 2**). Interestingly, this biochar had greater surface area (365 vs 10 m^2/g), larger pore volume (0.2 vs 0.05 cm^2/g), and higher acid density (3.66 vs 0.95 mmol/g) compared to the abovementioned corn stover biochar, while the density of $–SO_3H$ group as the strong Brønsted acid in both catalysts are 0.7. This comparison implies that the strong active sites may play an important role besides the total acidity, surface area, and pore volume.

The biochar catalyst showed faster xylan hydrolysis rates than the commercial sulfonated macroreticular resin (Amberlyst 15) at 90-110^{o}C, with the turnover frequency (TOF) 15 times higher (Ormsby et al., 2012). Although the acid density of Amberlyst 15 was much higher than the biochar catalyst (4.71 vs 0.69 mmol/g), its far smaller surface area and pore volume restricted the accessibility to active sites as well as adsorption capacity for the substrates. Therefore, we may expect a threshold for these physical parameters, below which the accessibility and contact between substrate and catalytic site appears as the limiting factor regardless of the acid site density. Apart from improving the surface area and porosity, it is also desirable to manipulate the position of active sites (i.e., within mesopores or on the exterior surface) via surface modification for managing the catalytic reactions in biochar. Nevertheless, the difference in hydrolysis rates became less apparent when the temperature increased to 120^{o}C (Ormsby et al., 2012), probably due to the enhanced mass transfer. Higher energy input also favoured the kinetics of xylan hydrolysis (2 h at 120^{o}C vs 24 h at 93^{o}C to obtain ~90% xylan conversion). Likewise, for

cellulose hydrolysis, high temperature of 275°C allowed 100% conversion of cellulose within a short reaction time of 15 min over a sulfonated biochar catalyst in methanol as the medium (Dora et al., 2012).

Biochar exhibited significantly higher hydrolysis activity than activated carbon in terms of xylan conversion (85 vs 57%), initial reaction rate (30 times), and TOF (9 times) at the same temperature, despite its lower surface area (365 vs 1391 m^2/g) (Ormsby et al., 2012). This was because the activated carbon may not be effectively sulfonated due to the considerable cross linking and polymerization as a result of energy-intensive activation process (900-1000°C). In addition, while the micro-/mesopores harboured the acid sites within activated carbon, the acid groups on the biochar surface were more accessible to the large substrates such as cellulose and hemicellulose (Li et al., 2013). Besides, the hydrophobicity of biochar prevented the sulfonic groups from hydration, upon which they were easily leached as sulphuric acids in the aqueous system (Li et al., 2013; Gallo et al., 2016).

The recyclability of biochar-based catalyst should be considered. It was reported that the catalytic activity of reused sulfonated biochar declined by ~14% in the second run, and it was completely deactivated after the fourth run due to acid site leaching and mass loss (Ormsby et al., 2012). Comparatively, the mesoporous carbon-supported Ru nanoparticles maintained steady cellulose hydrolysis (20-21% glucose) over five runs, during which metal leaching was not detected (Komanoya et al., 2011). Therefore, metal impregnation may be a viable alternative to sulfonation to modify biochar for catalytic hydrolysis of glucans (glucose-based polymers).

3.2.2 Biochar catalyst for isomerization and dehydration

Functionalized biochar are also able to facilitate isomerization of glucose to fructose and/or dehydration of glucose to HMF. Biochar-based sulfonic acids modified by ionic liquid achieved HMF yield of 27.94% from cellulose with a moderate selectivity of 62% within 3 h at 80°C in water (Zhang et al., 2017; **Table 2**). The promising performance was ascribed to the grafted ionic

15

liquid that enhanced the accessibility, acidity, and thermal stability of $–SO_3H$ sites. The performance may be improved by changing the solvent. For example, 65% HMF at maximum was yielded from inulin (a glucan) in ionic liquid at 100°C for 60 min over the model lignin-derived sulfonated hydrochar, of which the performance was competitive with the common solid catalysts (e.g., Amberlyst and sulphated zirconia) (Kang et al., 2013). Similarly, sulfonated biochar achieved a furfural yield of 81.1% (83% selectivity) from the pre-hydrolyzed corncob at 170°C in 60 min under the biphasic co-solvent (Deng et al., 2016; **Table 2**). The latter system allowed rapid and continuous extraction of furfural to the organic phase upon production in the aqueous phase, reducing the off-path humins formation for high furfural yield. The reclaimed biochar catalyst (subsequently washed by hot water, ethanol, and acetone) showed a decrease in the furfural yield from 81 to 24.6% after five runs, which was associated with 91.4% reduction in the $–SO_3H$ group density and 94% increase in the humins-to-catalyst ratio. Thus, regeneration of the catalyst at 150°C in sulphuric acid (98%) was required after each run to maintain the performance.

Besides sulfonated biochar, mineral-impregnated (SnO_2-Co_3O_4) biochar catalyst yielded 30% of furfural from corncob in water at maximum (Liu et al., 2015a). The multivalent metal functioned as Lewis acid sites to facilitate the isomerization of xylose to the more reactive xylulose for facile dehydration reaction afterwards. The metals also reacted with hydroxyl ion from water to generate Brønsted acid density (0.538 mmol/g), promoting the hydrolysis of glycosidic bond as well as dehydration of xylulose. Therefore, the Brønsted acid and Lewis acid facilitated the tandem reactions in a cooperative manner to produce furfural effectively. Similar synergistic effect was also remarked for the HMF production from food waste over homogenous metal chloride catalysts (Yu et al., 2016; Yu et al., 2017b) as well as from standard glucose over the heterogeneous SO_4/ZrO_2 catalyst (Osatiashtiani et al., 2014). In the latter case, Lewis acid sites may be assisted by the coexisting Brønsted base to facilitate isomerization, according to the

mechanistic studies on $CrCl_3$-mediated glucose transformation (Choudhary et al., 2013a; Choudhary et al., 2013b). The basic -OH group in the active species $[Cr(H_2O)_5OH]^{2+}$, which was formed upon the partial hydrolysis of Cr^{3+} in water, activated the critical Cr-catalyzed hydride shift within glucose by initiating a proton transfer.

Therefore, introducing both Brønsted and Lewis acidity to biochar by acidification and/or mineralization is favourable and pivotal for the catalytic valorization of biomass. The ratio of the dual functions is critical for high product yield and selectivity. A recent review has illustrated that the optimum Brønsted-to-Lewis acid ratio varies for glucose conversion to HMF over zeolites and niobium oxides, depending on the system components such as solvent and temperature (Yu and Tsang, 2017). The acid-to-base ratio may also play a role in case of acid- and base-carrying bifunctional candidate such as SO_4/ZrO_2 catalyst (Osatiashtiani et al., 2014). In addition, the acid/base strength may arise as another important parameter that tunes the system selectivity towards the favourable reactions relative to the side reactions, according to the recent studies on model compound conversion over mineral catalysts (Kreissl et al., 2016; Li et al., 2016). These considerations should be taken into account when tailoring the active sites on biochar-based catalysts.

Pore structure that determines the accessibility for substrate to the active catalytic sites should also be carefully designed. Sulfonated carbons with hierarchically ordered macropores (220 nm) and mesopores (4.8 nm) (SCHOP) synthesized using a template showed significantly higher fructose conversion (100%) than the regular mesopore (71.9%) and micropore (52.4%) sulfonated carbons within 18 min (Wang et al., 2016). Contrasting with the surface catalysis on micro- and mesoporous carbon, SCHOP enabled diffusion within the macro-channels, favouring contact between fructose and internal active sites as well as separation of products from the active sites. The authors also proposed the hierarchically ordered pore structure enhanced the resistance of active sites against blocking by humins, although the mechanism was not elucidated.

Interestingly, acidic mesoporous carbon (CMK-5) with a smaller pore size (2.67 & 3.38 nm vs 7.5 nm) and lesser acid sites (0.9 vs 2.3 mmol/g) gave a higher TOF of 0.069 min^{-1} for fructose dehydration to HMF, compared to the silica-based catalyst (TOF = 0.048 min^{-1}) (Crisci et al., 2010; Gallo et al., 2016). We infer that the better performance and low deactivation rate of CMK-5 may pertain to its higher surface area (616 vs 218 m^2/g) and bimodal pore structure. These findings may highlight the significance of porous structure and location of catalytic sites of biochar for sustainable biomass valorization processes.

3.2.3 Biochar catalyst for rehydration

Levulinic acid (LA) is also a key platform chemical of polymers and fuels. There is no study on the production of LA over biochar-based catalysts to our best knowledge. However, a great potential is anticipated as mineral acids (e.g., HCl, H_2SO_4, H_3PO_4), solid acid, inorganic salts (e.g., $FeCl_3$), and zeolite have been demonstrated as effective catalysts to give promising yield of LA (Morone et al., 2015; Wei and Wu, 2017; Chen et al., 2017b). Modification towards these functionalities could realize the application of biochar for facile LA production from biomass. It was reported that LA was detected as a by-product under prolonged reaction time and increased temperature during biomass valorization mediated by functionalized biochar (Zhang et al., 2017).

4. Emerging application of biochar–based catalysts for energy production

4.1 Bio-oil production

4.1.1 Esterification/ transesterification

Biochar-based catalysts have been applied for biodiesel production. The free fatty acid (FFA), from vegetable oil and animal fats, and low-molecular-weight alcohol undergo esterification to give esters as the biofuel (**Fig. 2**). Sulfonated biochar maintained high FFA conversion of 97-98% from refined microalgal oil in methanol for three runs at 100°C (Dong et al., 2015; **Table 3A**). Using waste vegetable oil as the FFA source, 77-89% FFA conversion can be achieved over an analogous sulfonated biochar at 60°C in the presence of ethanol (Dehkhoda et al., 2010). These

results are comparable to the esterification of model FFAs, for example, 70-100% conversion of pure palmitic and stearic acids at 55-60^{o}C, depending on the amount of methanol (Kastner et al. 2012). This strongly evidenced the applicability of biochar catalyst for biofuel production via esterification. However, significant chlorophyll and phospholipids in particular biomass, e.g., microalgae, may inhibit the catalyst and lower the biodiesel quality, which should be removed upfront (Dong et al., 2015; **Table 3A**).

In comparison to the commercial Amberlyst 15, biochar achieved a higher conversion of FFA from microalgal oil (99 vs 94%) under the same reaction condition, which may be attributed to the better dispersion of biochar in the medium (Dong et al., 2015). Another study showed that after sulfonation (99% H_2SO_4), the activated carbon exhibited higher esterification activity than the biochar catalysts (97 vs 70% conversion) due to the larger pore volume (0.76 vs 0.13-0.2 cm^3/g) and pore radius (1.1 vs ~1.06 nm) (Kastner et al. 2012). These favourable properties facilitated the access of the substrates to the active sites, which may compensate for the shortcomings of lower $–SO_3H$ density in the activated carbon (0.2 vs 0.61-0.69 mmol/g).

Biochar catalyst also applies to transesterification, during which glyceride in vegetable oil and animal fat reacts with low-molecular-weight alcohol to produce esters (biodiesel) and glycerol. The process shows a higher dependence than esterification on strong Brønsted acidity. Fuming H_2SO_4-modified biochar that possessed more $–SO_3H$ groups (~1 mmol/g) gave noticeable amounts of products, i.e., 47-64% methyl oleate and 13-20% methyl linoleate from canola oil and methanol, equivalent to a maximum biodiesel yield of 10% (Dehkhoda et al., 2010; **Table 3A**). It can be also observed that the production increased as a function of the surface area of catalyst. In contrast, the hydrothermally sulfonated biochar using concentrated H_2SO_4 did not catalyze transesterification probably due to the relatively low content of $–SO_3H$ sites (~0.6 mmol/g) (Dehkhoda et al., 2010). However, using the hydrothermally sulfonated biochar, Dong et al. (2015) reported about 5% higher yield of fatty acid methyl ester (FAME) from microalgal oil at

120°C compared to 100°C. This suggested that the transesterification activity can be increased by energy supply, which may pertain to the enhanced miscibility of triglyceride in methanol at high temperatures.

It was demonstrated that after pre-esterification of microalgal oil by sulfonated biochar, CaO was added for the subsequent transesterification, attaining 99% FAME yield (Dong et al., 2015). It is more sustainable to apply CaO-containing biochar derived from $CaCO_3$-rich biomass, e.g., palm kernel shell. The latter can achieve nearly 100% FAME production under optimal conditions according to an optimization and kinetic study (Kostić et al., 2016). Other Ca-rich waste materials such as waste egg shell (Chakraborty et al., 2010), bovine bone waste (Smith et al., 2013), and crab shell (Madhu et al., 2016) may be considered as additives to biomass feedstock for co-pyrolysis, manufacturing cost-effective transesterification biochar-based catalyst (Chen et al., 2017a).

4.1.2 Hydrogenation

Syngas derived from thermochemical conversion of biomass contains CO, H_2, CO_2, and volatile hydrocarbons, which can be upgraded into fuels through different processes. The biochar-based carbon-encapsulated iron nanoparticle catalyst promoted Fischer-Tropsch synthesis (FTS) effectively, achieving 95% CO conversion and 68% liquid hydrocarbons selectivity (Yan et al., 2013; **Table 3B**). Besides, activated biochar loaded with ruthenium facilitated methanation, in which 97% CO and 55% CO_2 in syngas were converted to give a CH_4 yield of 54% (92% selectivity) under sufficient H_2 supplement (Wang et al., 2014). The large surface area (728-757 m^2/g) of activated biochar favoured a higher dispersity of Ru (> 70%) compared to other conventional support such as Al_2O_3 (43%) and SiO_2 (17%), which may account for the effective catalytic performance.

In addition to syngas conversion, the application of modified biochar may extend to other

chemical synthesis that involves hydrogenation. For example, coconut shell activated carbon incorporated with Pd-Ni-B amorphous alloy achieved nearly 100% conversion of the nitroaromatic compounds (Chen et al., 2015). This illustrates the great potential of metal-impregnated biochar as a solid catalyst for other analogous industrial processes.

4.2 Biogas production

4.2.1 Tar reforming

Tar reforming is referred to turning the hydrocarbon mixture (e.g., phenolic, olefin, and polycyclic aromatic compounds) that is unavoidably formed during biomass gasification and pyrolysis into valuable syngas. Biochar containing catalytic sites in common with the conventional catalysts could be effective for tar reforming, including dolomites (calcium magnesium carbonate), olivine (magnesium iron silicate), and nickel- and alkali metal-based catalysts (Anis and Zainal, 2011). A recent study showed that 95% removal of the alkali and alkaline earth metals (Ca, K, Mg, P, and Na) from biochar led to 18% decrease in the decomposition of methane, illustrating the significance of these elements for the catalytic tar reforming despite their small quantity (2%) (Klinghoffer et al., 2015). Similarly, K- and Ca-containing switchgrass biochar achieved high removal efficiency, although their roles were not discussed (Bhandari et al., 2014). The switchgrass biochar activated by KOH gave the best performance, i.e., about 90% removal of toluene possibly due to the high surface area (~900 m^2/g) (**Table 4A**). In addition, iron calcined biochar (Kastner et al., 2015) and silica-based nickel nanoparticle-embedded biochar (Shen and Yoshikawa, 2014) also proved effective.

Biochar as the catalyst support was critical. The activity of mineral ash was about 90% lower than the biochar-based catalyst, probably due to the inefficient metal dispersion (Klinghoffer et al., 2015). The metal dispersion depended on the biochar formation environment, for instance, biochar produced from gasification in CO_2 showed higher metal dispersion, while a steam-containing atmosphere led to agglomeration of the metal species. The authors also remarked the

21

potential catalytic activity of the carbon support. The basic oxygen groups (carbonylic, quinonic, and pyrone structures) might play an important role as they remained attached at the cracking temperature of 700-900°C, while acidic groups (lactones or carboxylic groups) underwent desorption at 350°C.

As the reforming process prolonged, ring condensation in the biochar resulted in loss of oxygen functional groups as well as relocation and agglomeration of the metal species, of which the dispersion and catalytic activity decreased (Min et al., 2013). Another cause of catalyst deactivation was the coke deposition on biochar associated with pore blockage and surface area reduction (Bhandari et al., 2014; Shen and Yoshikawa, 2014), which is similar to the adverse impact of humins on biomass conversion to chemicals (**Section 3**). Nevertheless, compared to the conventional tar reforming techniques (dry/wet gas cleaning, thermal cracking, and plasma cracking) (Anis and Zainal, 2011), catalytic cracking over biochar presents a more cost-effective and green option due to the lower energy consumption. It deserves more research efforts to develop resilience against the undesirable reactions that deactivate the catalyst.

4.2.2 Hydrogen production

Hydrogen is another sustainable alternative to fossil fuels in view of its low emissions, which can be produced via biogas reforming. Wood biochar achieved 70% CH_4 conversion within 120 ms at 1000°C in the presence of CO_2 and steam as the pyrolysis gas (Dufour et al., 2008; **Table 4B**). In such case, biochar was continuously regenerated to maintain high surface area and accessible pore structure via the oxidation of carbon by CO_2 and H_2O at high temperature. Similarly, the CO_2-treated duckweed-derived biochar obtained 82% and 25% conversion of CO_2 and CH_4 at the early stage of biogas reforming, respectively (Muradov et al., 2012). The results outcompeted the untreated biochar (42% and 10% conversion of CO_2 and CH_4, respectively), which had significantly lower surface area compared to the CO_2-treated one (5-12 vs 60 m^2/g). Nevertheless, the latter lost its initial activity of ~90% due to blockage of the active sites by carbon deposition.

22

It was suggested that the unsaturated carbon atoms, which originated from the thermally decomposed surface oxygen functional groups, served as the active sites for the chemisorption and decomposition of CH_4 (Dufour et al., 2008). The biochar catalyst gave similar performance before and after demineralization in the same study, suggesting the negligible role of ashes for promoting methane decomposition. Interestingly, this contrasted the result of methane decomposition process for tar reforming (Klinghoffer et al., 2015; **Section 4.2.1**). In addition, pyrolytic waste tire biochar achieved 95% conversion of methylcyclohexane to hydrogen upon wetness impregnation of Pt nanoparticles in the micro regions (Zhang et al., 2011a), which may apply to catalytic methane-to-hydrogen process. More investigations are required to rationalize the divergent findings over the active sites on biochar for biogas reforming.

Biochar enhances the hydrogen production during biomass pyrolysis/gasification. During the pyrolysis of microalgae, the addition of unmodified biochar as the catalyst promoted hydrogen production and selectivity by the factor of 1.37 and 1.59, respectively (Norouzi et al., 2016). Besides, the Ni-loaded biochar catalyst resulted in 64.02 vol% hydrogen in wheat straw gasification at 800°C (Yao et al., 2016). The best performing biochar catalyst (derived from cotton stalk) contained high contents of K and Ca as revealed by elemental analysis. Similar to tar reforming (**Section 4.2.1**), these alkali and alkaline earth metals were significant in promoting biomass reforming reactions, possibly through direct catalytic effect and enhanced water adsorption (Yao et al., 2016). In contrast, high Si content would result in agglomeration and sintering of metals, which reduced the dispersion of catalytic active sites. Other biochar properties (external surface area and Ni loading) and gasification conditions (steam-to-biomass ratio and temperature) also governed the catalytic performance.

4.3 Electrochemical energy utilization

4.3.1 Methanol electro-oxidation

Biochar has been also employed for fuel cell production to generate clean and renewable energy.

23

Conventionally, carbon-supported Pt-based electrocatalysts, such as carbon-silica composite aerogels and carbon-supported Pt nanoparticles (Pt/C), are used to promote methanol electro-oxidation in direct methanol fuel cells (Johnson et al., 2011). Biochar-supported Cu-Ru@Pt nanoparticles (derived from acid-treated cellulose) exhibited promising catalytic activity for electro-oxidation of methanol in terms of the high turnover number (TON) of 0.151 molecule (sites s)$^{-1}$ and a low poisoning rate at 0.026% s^{-1} (Lobos et al., 2016; **Table 4C**). Its catalytic activity was 3-9 times higher than the commercial Pt-Ru/C catalyst, which was attributed to the electronic and strain effect induced by the interaction between the nanoparticle shells and the highly defective surface of biochar support. The latter (as a result of acid treatment of the biochar precursor, i.e., cellulose) was further highlighted as the key to the fast turnover rate and high poisoning tolerance, which facilitated the oxidation of the poisoning species adsorbed on the nanoparticles. Similarly, the okara-based mesoporous biochar supporting Pt nanoparticles displayed higher electrocatalytic activity than the conventional carbon black-based Pt/C catalyst, generating a higher peak current density (12.2 mA/cm) as well as higher poison resistance (Zhou et al., 2014). The okara biochar showed a high degree of graphitization that favoured the composite conductivity. It also induced abundant grain-interfaces among the loaded Pt particles as the active sites, leading to a higher electrochemical active surface area compared to Pt/C (58.2 vs 30.6 m^2/g).

The KOH-activated pectin hydrochar (hydrothermally carbonized at 200^{o}C for 12 h) was a promising support for Pt nanowires to catalyze methanol electro-oxidation, achieving higher mass current density than Pt/C (450 vs 194 mA/mg) (Fan et al., 2015). The high performance may be related to the preferential exposure of Pt crystal facets and enhanced electron and mass transport at the electrode/electrolyte interfaces. Meanwhile, the surface hydroxyl and carboxyl groups on biochar promoted the formation of hydroxyl species (Pt-OH) in the presence of water, hence accelerating oxidation of poisons such as CO intermediates. Such poison tolerance may resemble the function of defective surface of biochar synthesized from acid-treated cellulose mentioned

24

above (Lobos et al., 2016). On the other hand, unmodified hydrochar can also be used as a supercapacitor owing to its large specific surface area (2440 m^2/g) and balanced micro- and mesoporosity that enabled charge accumulation (Fan et al., 2015).

4.3.2 Oxygen reduction reaction

Steam-activated silk fibroin-derived biochar without metallic elements presented certain electrocatalytic activity for oxygen reduction reactions in fuel cell, giving a power density of 142 mW/cm^2 (1.42 x 10^6 mW/m^2) operated at 80ºC, which was lower than that of the typical Pt/C catalyst as the authors remarked (Iwazaki et al., 2010; **Table 4C**). The quaternary nitrogen atoms were suggested as the active sites in biochar, while the activity could be further improved by incorporating zirconium oxides particles, increasing the average number of electron transferred from 3.5 to 3.9.

Likewise, nanocomposites of iron oxide and biochar (derived from cornstalks and pomelo skins) were promising for promoting oxygen reduction reaction in microbial fuel cells (Ma et al., 2014). The mixed composites exhibited a power density of 1502 mW/m^2 at 30ºC, which was 26% greater than the Pt/C catalyst and was maintained for 18 cycles with small decline (7.12%). The uniformly dispersed Fe species on the large surface area (476.5-547.7 m^2/g) improved the electrical conductivity and density of catalytic active sites. In another study, cellulose-based biochar impregnated with Pt showed electrocatalytic activity comparable to Pt/C (-85 to -74 vs -79 mV/dec) despite the lower Pt active area due to agglomeration (<10 vs 72 m^2/g) (Guilminot et al., 2008). Promising results may be obtained by careful selection of the feedstock. For example, biochar derived from nitrogen- and iron-rich sludge gave a power density of 500 mW/m^2 at maximum, which was slightly lower than that of Pt/C (625 mW/m^2) but greater than bamboo biochar (272 mW/m^2) and activated carbon (308 mW/m^2) (Yuan et al., 2013).

5. Emerging application of biochar-based catalysts for pollution control

5.1 NO_X reduction and ammonia ozonation

25

Selective catalytic reaction is an effective measure to control NO_x emission, as indicated in Eq. 1. The KOH-activated biochar derived from rice straw and sewage sludge attained 86% and 46% NO_x removal at 50°C, respectively, which was ascribed to the abundance of oxygen functional groups, high surface area, large pore volume, and thus high NH_3 and NO adsorption capacity (Cha et al., 2010; **Table 5**). However, it is interesting to note that the activated rice straw biochar and sewage sludge biochar had comparable surface area (772 and 783 m^2/g) and pore volume (0.42 and 0.61 cm^3/g), implying that they may not be the most critical factors for high catalytic activity. Instead, the higher content of nitrogen and alkali metals (K and Na) in raw rice straw may make a more significant contribution, which needs further assessment.

$$O_2 + NO_x + NH_3 \rightarrow N_2 + H_2O \quad \text{(Eq. 1)}$$

Transitional metal oxides can enhance the NO_x removal. For instance, impregnating 3 wt% MnO_x to rice straw biochar resulted in an outstanding NO_x removal efficiency of 84% at 50°C (Cha et al., 2010). Similarly, Mn/Ce-impregnated cotton stalk biochar (co-activated by H_3PO_4 and steam) presented higher N_2 selectivity and catalytic activity in comparison to activated carbon and steam-activated biochar (Shen et al., 2015a). This was associated with the favourable physicochemical properties as a result of co-activation process, including specific surface area for catalytic sites (1614 m^2/g), surface acidity (71.38 μmol/g), porosity (0.481 ml/g), active site dispersion, metal speciation (Mn^{4+}/Mn^{3+} = 2.25; Ce^{4+}/Ce^{3+} >> 1), and surface oxygen functional groups (P-O-C, P-O-P, C=O, C-NO_2, etc.). In particular, the latter two facilitated oxygen transfer and hence the oxidation of NO to NO_2, which improved NO conversion to N_2 via an alternative catalytic pathway.

Activated biochar has been applied for catalytic ozonation of gaseous ammonia (Eq. 2), which was produced from pyrolysis of pelletized peanut hulls under steam (Kastner et al., 2009; **Table 5**). It achieved a high NH_3 conversion of about 65% under the maximum O_3 supply (~900 ppm_v) at 23°C. Carbon surface and water vapour promoted ·OH free radical formation for catalytic ozonation, underscoring the significance of the biochar support. However, at a low O_3

26

concentration (62 ppm_v), its performance was less satisfactory and outcompeted by wood fly ash under the same condition (~18 vs 45% NH_3 conversion), probably due to the relatively low surface area and insufficient active metal oxide species (e.g., Cu, Mn, Ni, and Co).

$$O_3 + NH_3 \rightarrow NO_2 + H_2O \quad \text{(Eq. 2)}$$

5.2 Photocatalytic degradation of organics

Modified biochar is a potential photocatalyst for degradation of organic pollutants. For example, sulfamethoxazole (SMX, antibiotics) can be effectively degraded (91% at maximum) over biochar-supported well-dispersed TiO_2 granules under ultraviolet irradiation, which was prepared by treatment with acid and titanium isopropoxide (Kim and Kan, 2016; **Table 5**). The carbon sites enabled adsorption of SMX via the π-π interaction, while excellent conductivity of carbon suppressed the recombination of electrons and electron holes, which often occurred in the case of commercial TiO_2 lowering the photocatalytic activity. In addition, it was easier to separate the biochar-supported catalyst compared to TiO_2 powder that aggregated after use and required energy-intensive recovery. Likewise, for the removal of methylene blue (MB) as a dye, the vapour-activated coconut shell biochar exhibited higher photocatalytic activity than the TiO_2 powder (100 vs 61%) possibly due to favourable adsorption of MB and evenly dispersed TiO_2 on the biochar support, as well as the large surface area (293 m^2/g) (Li et al., 2007). These results demonstrated the significance of the accessibility and distribution of catalytic sites, particularly for the metal-mediated processes (e.g., biofuel production in **Section 4**), which could be significantly enhanced by using biochar as the support.

Artificial photosynthesis and solar energy conversion may appear as potential applications of biochar-based catalyst upon modification to resemble the structure and photoelectrical properties of nanostructured carbon allotropes (fullerenes, carbon nanotubes, and grapheme), which were effective candidates according to the previous study (Umeyama and Imahori, 2013).

6. Prospect

In summary, the biochar-based catalyst is promising because of its tuneable surface chemistry and porosity that can be engineered to mimic the conventional catalysts. The biochar support exhibits intrinsic advantages, e.g., the reserved channel structure and high metal content from particular biomass feedstock and abundant carbon-induced interactions with the substrates, which present technological merits in addition to sustainability concerns.

Despite successful demonstration of biochar application as catalysts, there is plenty of room for improvement in its catalytic activity and selectivity towards the desirable products. In particular, the production of high-value chemicals from biomass is very challenging, of which the complexity and recalcitrance often limits the product yield to only 30-40% (**Table 2**). Advancement requires the paradigm shift towards “application-oriented” or “reaction-oriented” biochar synthesis, as there is no universal conclusion over the most important parameters. Therefore, future biochar synthesis should take into account the reaction characteristics upfront (e.g., hydrophobicity and molecular size of reactants, intermediates, and products) to inform the desirable parameters, thereby designing the production/modification protocol with a bottom-up approach.

We should also reckon the significance of the catalytic site location. For example, when the active sites are dispersed within the biochar channels, the pore size governs the catalytic efficiency by controlling the reactant diffusion. It exerts trivial impact when the active sites are located on the exterior surface. Future investigations are needed to examine the benefits and feasibility of impregnating the active sites at designated locations of biochar to control the desirable/undesirable reactions for highly efficient and sustainable applications.

7. Conclusions

Biochar emerges as a sustainable and low-cost catalyst support for chemical synthesis, biofuel production, and pollution control, giving performance comparable or superior to

conventional/commercial catalysts. This review highlights the substrate access to active sites as the key to promising catalysis, which counts on the physicochemical properties (-SO_3H density, surface area, porosity, metal dispersion, etc.). Their relative significance varies depending on where catalysis occurs over biochar, which may be manoeuvred through innovative synthesis/modification. By improving the understanding on the effects of existing modifications on biochar features, this review advises protocol development to engineer high-performance biochar-based catalyst for emerging applications.

7. Acknowledgement

The authors appreciate the financial support from the Environment and Conservation Fund (K-ZB78) and the Hong Kong International Airport Environmental Fund (K-ZJKC).

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29

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34