**Study of glucose isomerisation to fructose over three heterogeneous carbon-based Aluminium-impregnated catalysts**

Xinni Xionga, Iris K.M. Yua,b, Daniel C.W. Tsanga,\*, Liang Chena, Zhishan Suc, Changwei Huc, Gang Luod, Shicheng Zhangd, Yong Sik Oke, James H. Clarkb,d

a Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

b Green Chemistry Centre of Excellence, Department of Chemistry, University of York, York, YO10 5DD, UK

c Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China

d Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP3), Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, China

e Korea Biochar Research Center, Division of Environmental Science and Ecological Engineering, Korea University, Seoul 02841, Republic of Korea

*\*Corresponding author:* *dan.tsang@polyu.edu.hk*

**Abstract**

Driven by the worldwide demand for sustainable resources and renewable energy, the synthesis of bio-based platform chemicals has attracted broad interest. The isomerisation of glucose to fructose acts as a critical intermediate step among many chemical synthesis routes. In this study, biochar (BC), graphitic oxide (GIO), and graphene oxide (GO) were used as carbon supports to synthesize Al-impregnated heterogeneous catalysts, which were then used for glucose isomerisation under microwave heating in the water at 140 oC. The kinetics model with parameters was used to reveal the interplay of the active sites and compare the activity of the three carbon-based catalysis systems. Catalyst characterisation results showed effective aluminium (Al) impregnation onto the three types of catalysts, and it was found that GIO-Al200 and GO-Al200 showed comparable catalytic activity (fructose yield of 34.3-35.0%) for glucose isomerisation. At the same time, BC-Al200 exhibited slightly lower catalytic activity (fructose yield of 29.4%). The conversion kinetics suggested similar catalytic mechanisms on the three catalysts while BC-Al200 manifested slower kinetics, possibly implying higher activation energy. The fructose selectivity decreased with increasing time due to the formation of side products, yet BC-Al200 resulted in less carbon loss than GIO-Al200 and GO-Al200, probably attributed to its lower catalytic activity and higher pH buffering capacity. A green synthesis route of this study promotes biomass valorisation and makes engineered biochar a promising carbon-based catalyst for sustainable biorefinery.

**Keywords:** engineered biochar, biomass valorisation, sustainable biorefinery, graphene oxide, glucose isomerisation; waste management.

**1. Introduction**

The biorefinery based on biomass valorisation is currently drawing significant attention among the scientific community as a strategy for the manufacture of a new generation of various value-added chemicals and fuels with limited environmental footprints (Sudarsanam et al., 2018; Clark, 2019). Cellulose- and starch-rich biomass can go through a range of chemical processes including hydrolysis, isomerisation, dehydration, and rehydration to generate various platform chemicals (Xiong et al., 2019), including 5-hydroxymethylfurfural (5-HMF) (Yu and Tsang, 2017), levulinic acid (LA) (Chen et al., 2017; Chen et al., 2018), and γ-valerolactone (GVL) (Dutta et al., 2019). These chemicals can play significant roles in future industrial productions of many products such as pharmaceuticals, polymers, resins, solvents, fungicides, and biodiesel. Fructose (ketohexose), is a crucial precursor in such processes as well as a valuable product in its own right. It can be produced by the isomerisation of biomass-derived glucose (aldohexose) (Delidovich and Palkovits, 2016) using Lewis acid (through the intramolecular 1,2-hydride shift from the C2 to C1 position) (Li et al., 2017) or Brønsted base (through hydrogen transfer from O2 to O1 position) (Chen et al., 2018b) catalysis although yields are generally poor. The conventional biocatalytic process requires strict control of temperature (40−80 °C) and pH (5.8-8.0) as well as expensive enzymes (i.e., glucose isomerase) (Li et al., 2017). The synthesis of cost-effective and recyclable chemical catalysts that operate under mild conditions for this process is an important goal.

 Biochar, a waste-derived carbonaceous material with relatively high surface area, porous structure, and stable characteristics, is prospective materials for catalyst synthesis (Li et al., 2020) and material engineering (Wang et al., 2019). Serving as a catalyst support (Lam et al., 2017), biochar can be functionalised by metallic pyrolysis (Lam et al., 2015) and physical and chemical activation (Liew et al., 2018). By the introduction of Brønsted or Lewis acidity into biochar (Xiong et al., 2018), the surface physicochemical properties can be tailored to manipulate the catalytic activity for various biomass valorisation reactions (Xiong et al., 2017). In recent studies, glucose isomerisation was shown to be catalysed by wood biochar impregnated with aluminium (Al) and tin (Sn) (Yu et al., 2019a; Yang et al., 2019). Besides, chemical oxidation of natural graphite powder can generate graphite oxide (GIO) with a layered structure. GIO could be exfoliated via ultrasonication, producing graphene oxide (GO) with one or a few layers of carbon atoms (Ray, 2015). GO and their derived materials are another group of promising carbon-based catalysts because of their superior properties such as two-dimensional hexagonal lattice structure, high stability, and large surface areas (Bottari et al., 2017). The basal planes and hole defects of GO structure contain numerous epoxides, hydroxyl groups, and carboxyl oxygen-bearing moieties, which may act as hydrogen-bond donor and acceptor moieties (Georgakilas et al., 2016). These oxygen-containing functional groups also account for the oxidative and weakly acidic properties of GO (Antunes et al., 2014). Recent studies have intensively studied GO as a catalyst for biomass conversion (Zhu et al., 2015), for example, GO without modification catalyses fructose conversion to 5-HMF (Wang et al., 2014; Shaikh et al., 2018) and cellulose into glucose (Mission et al., 2017). Metal modified GO such as graphene oxide–ferric oxide (GO-Fe2O3) exhibited great catalytic activity in converting glucose into 5-HMF with 86% yield (Zhang et al., 2015). Sulfonated graphene oxide achieved 94% 5-HMF yield from fructose dehydration (Hou et al., 2016), whereas sulphur-modified GO acted as a catalyst for the conversion of cellobiose to 5-HMF (Wang et al., 2016a).

Functionalization of these carbon materials with tailorable morphology and good chemical stability shows great potential for catalyst synthesis. Aluminium is a promising Lewis acid dopant for heterogeneous catalysis (Yu et al., 2016). It has been demonstrated that Al-biochar composites, graphite oxide- and graphene oxide-supported catalysts are promising materials for catalytic glucose isomerisation (Yu et al., 2019a; Yu et al., 2019b). Aluminium oxide-silica/carbon composites (Al-Amsyar et al., 2017), N-graphene-modified Al2O3 (Guo et al., 2016), graphene oxide/aluminium (GO/Al) mixed powders (Zhou et al., 2018) were previously shown to be effective for catalysing biomass conversion and value-added chemicals synthesis. However, different dosages and experimental conditions were often employed in previous studies, making it difficult to compare the effectiveness directly. A proper comparison of the different heterogeneous carbon-based catalysts under the same condition is needed to provide insights into the future design of sustainable and cost-effective catalysts for glucose isomerisation.

In this study aluminium-doped carbon supports (i.e., biochar, graphite oxide, and graphene oxide) are studied for green catalyst preparation to compare and explore the interplay as well as the effect of the carbon on glucose isomerisation. The conversions were carried out via microwave heating in the water at 140 oC (i.e., green solvent and moderate temperature), which helps ensure the environmental suitability of the process for biorefineries. We then compared the catalytic performance of three different carbon materials as support of Al catalysts and addressed the kinetics of catalytic glucose isomerisation chemistry in water. This work aims to explore the catalytic performances and interplays on different catalysts and provide scientific insights into the design of engineered materials for biorefinery processes and biomass valorisation.

**2. Materials and Methods**

* 1. Raw materials and chemical reagents

Graphite powder (AR, Accuchem) served as the precursor of synthesizing GIO and GO. Sawdust collected from the Industrial Centre of the Hong Kong Polytechnic University was the feedstock for producing wood biochar. The AlCl3∙6H2O (ACS grade) purchased from Anaqua is the impregnation agent in this study. Standard compounds used in conversion experiments as well as calibration of the analytical instrument were glucose (≥99.5%), 5-HMF (≥99%), and furfural (99%) from Sigma Aldrich; cellobiose (≥98%), levulinic acid (98%), and formic acid (98%) from Alfa Aesar; levoglucosan from Fluorochem; and fructose (≥ 99%) and maltose monohydrate (≥98%) from Wako.

* 1. Production of Al-impregnated catalysts

The GIO was prepared from graphite powder in accordance with the Hummers’ method (Hummers et al., 1958). Specifically, 10 g of graphite (G) and 5 g of sodium nitrate (NaNO3) were mixed with concentrated sulphuric acid (H2SO4) (98 wt%, 230 mL) in an ice bath with stirring and subsequently added 30 g of potassium permanganate (KMnO4) slowly. After agitated at ca. 35 oC for 30 min, 460 mL water was added to the mixture, followed by continuous stirring at 98 oC for 15 min. At the end of thermal treatment, water was added for dilution, and residual KMnO4 was reduced using hydrogen peroxide (H2O2). Afterwards, repetitive centrifugation and decantation by deionised water were conducted to wash and collect the solid residue. The washed residue after drying in an oven was collected as GIO. For the production of GO, the dried GIO was suspended in deionised water and was subjected to sonication for 5 h. The mixture was dried in an oven to collect all the solids as the GO. Sawdust was used as the raw material to synthesize biochar (BC)-based catalysts directly.

For the Al modification, GIO, GO, and sawdust were placed in aqueous AlCl3 (200 mL) for 4-h stirring, followed by oven-drying. The elemental Al loading, i.e., the mass ratio of Al to the carbon supports, was 10 wt%. The AlCl3-treated carbon supports were then activated in a muffle furnace (Carbolite) with a heating rate of 10 oC min-1. The target temperature (200 or 500 oC) was maintained for 2 h. The calcined materials are denoted as GIO-Al200, GO-Al200, and BC-Al200 (i.e., the loading of Al species onto and the formation of biochar took place simultaneously in a single step), in which 200 refers to the temperature of thermal activation.

* 1. Characterisation of the synthesized catalyst

The surface morphology was studied using scanning electron microscopy (SEM; TESCAN VEGA3). Brunauer-Emmett-Teller (BET) surface areas, pore volumes, and pore diameters were measured by nitrogen adsorption−desorption isotherm measurements at -196 °C with a gas sorption analyser (Micromeritics Accelerated Surface Area and Porosimetry system, ASAP 2020). Micro-Raman spectroscopy (Renishaw) of the biochar-based catalyst was performed with a 532 nm laser and 50× objective. Solid-state 27Al nuclear magnetic resonance (NMR) spectroscopy was conducted using a 500 MHz JNM-ECZ500R (JEOL) with a scan number of 1301 and relaxation delay of 5 s.

* 1. Glucose conversion

The isomerisation of glucose to fructose was conducted in an Ethos Up Microwave Reactor (Milestone), according to the protocol in Yu et al. (2019b). Specifically, catalyst (0.25 g) and glucose (0.5 g) in deionised water (10 mL) were subjected to heating to 140 oC in a sealed Teflon vessel. The ramp time was 5 min and the temperature holding time was 1, 3, 5, 10, 15, 20, 30, or 40 min. Magnetic stirring was maintained throughout the heating. After that, the system was cool to room temperature by forced ventilation inside the reactor.

To evaluate the leaching of active sites, supplementary tests were carried out where the selected carbon samples were heated following the protocol as mentioned above except the addition of glucose. After heating, the solid and liquid phases were separated by centrifugation and decantation, and their respective catalytic performance was investigated by repeating the same thermal process adding glucose as the substrate. Water was also added as the reaction medium for the catalytic conversion over the solid phase.

* 1. Catalysis sample analysis

After dilution with deionised water (1:3 v/v) and filtration through a mixed cellulose ester filter (0.22 µm), the liquid samples were analysed via high-performance liquid chromatography (HPLC). A Chromaster instrument coupled with a refractive index detector (Hitachi, Japan) and an Aminex HPX-87H column (Bio-Rad) was used. The temperature was set at 50 oC, whereas 0.01 M H2SO4 served as the mobile phase (0.5 mL min-1). The product yield and selectivity on a carbon mole basis were calculated using the equations (1) and (2).

$Product yield \left(mol\%\right)=\frac{P\_{f}(mg/ml)×n\_{p}/MW\_{P}}{Glu\_{i} (mg/ml)×n\_{Glu}/MW\_{Glu}}×100$ (1)

$Product selectivity \left(mol\%\right)=\frac{P\_{f}(mg/ ml)×n\_{p}/MW\_{P}}{(Glu\_{i}-Glu\_{f})(mg/ml)×n\_{Glu}/MW\_{Glu}}×100$ (2)

where *Pf* stands for the concentration of the products; *np* and *nGlu* means the number of carbons in the corresponding product and glucose, respectively; *MWp* and *MWGlu* represent the molecular mass of the corresponding product and glucose, respectively; and *Glui* and *Gluf* stand for the initial and final concentration of glucose, respectively.

The initial rate (*r*) of glucose conversion is based on the concentration change of glucose during the first 1-min reaction. According to Khajavi et al. (2005), degradation processes of monosaccharides (e.g., glucose) is following the Weibull equation (3), where *k* and *n* stand for rate constant and shape constant, respectively. These kinetic parameters were obtained by nonlinear regression analysis using the Solver of Microsoft Excel.

*C/C0 =exp[(-kt)n] (n<1)*  (3)

The parameter n stands for the kinetic order of the reaction and describes the shape of kinetic curves in this model. In particular, when *n* > 1, it exhibits a sigmoidal pattern; when *n* = 1, the model represents simple first-order kinetics; when *n* < 1, the value of C/C0 steeply drops during the early stage, and with time increasing, it presents a steady decrease (Khajavi et al., 2005).

**3. Results and Discussion**

3.1 Fructose yield change with time

All of the synthesized BC-Al200, GIO-Al200, and GO-Al200 materials showed useful catalytic activity in the isomerisation of glucose in the water with maximum fructose yields of 29%-35% after microwave heating at 140 oC. The product profiles of the catalytic conversion with increasing time over the three Al-impregnated carbon catalysts showed a similar trend (Figure 1a-c) in terms of fructose yields, where the curves rose steadily at the expense of glucose and then levelled off after approximately 20 min.

For both GIO-Al200 and GO-Al200 catalysts, fructose yields increased to ~35% after 20 min of reaction. The carbon support GO was derived from GIO by ultrasonic exfoliation. As indicated by Table 1, the surface area (13.2 m2/g) and total pore volume (0.064 cm3/g) of GO-Al200 were higher than that of GIO-Al200 (3.38 m2/g; 0.015 cm3/g). In the SEM image (Figure 2a), the surface of GIO-Al200 shows a multi-layer stacking structure, which is absent from the surface morphology of GO-Al200 (Figure 2b). The rough surfaces with more porous structures were possibly beneficial to the adsorption of fructose for catalysis. Although ultrasonication exfoliated the carbon structure by increasing the surface area and enlarging the pores, changes in these physical properties did not induce noticeable differences in catalytic activities between GIO- and GO-Al200 catalysts. Although the enhanced physical structure assisted the bonding of AlCl3 onto the surface of carbon supports in this study (surface Al content increasing from 5.9% of GIO-Al200 to 12.5% of GO-Al200, based on previous XPS results (Yu et al., 2019b)), such improvement did not increase the catalytic activity. The critical determinant of catalytic activity is probably related to the distribution and speciation of Al on the surface, which vary with the conditions of synthesis and modification processes.

In comparison, when using BC as the support material (BC-Al200), the maximum fructose yield reached 29.4% after 40 min, which was slightly lower than that of GIO-Al200 (35.0%) and GO-Al200 (34.3%) under the same conditions (Figure 1). Less glucose (49.3%) was consumed after 40 min in the BC-Al200 system than that for GIO-Al200 and GO-Al200 (67.6% and 66.3%, respectively), suggesting higher catalytic activities of the graphene-based catalysts than the biochar-based one (the corresponding selectivity will be further discussed in Section 3.3). BC-Al200 was derived from wood waste, in which lignin and cellulose could have retained their structure and crystallinity at the relatively low pyrolysis temperature adopted in this study (200 oC) (Keiluweit et al., 2010). The graphitisation of materials was examined by calculating the ratio of D peak to G peak (ID/IG) in Raman spectra. The ID/IG ratio for BC-Al200 was 0.52 (Figure 8a), which was lower than that for GIO-Al200 and GO-Al200 at 0.95 and 0.93, respectively (Yu et al., 2019b). The discrepancy in surface morphology of carbon support may lead to the varying extent of Al bonding during impregnation and heating processes, which subsequently resulted in the observed difference in the structures of materials. The GIO and GO catalysts tended to be more disordered, which could be favourable to their catalytic activities. In comparison, there was no clear trend in the fructose yield with the different surface areas and surface Al contents of BC-, GIO-, and GO-Al200, suggesting that these properties were not the most critical determinant of catalytic activity (Figures 1&2; Table 1).

The highest fructose yield (29.4-35.0 mol%) of glucose isomerisation over the three synthesized carbonaceous catalysts in the current study showed greater catalytic activities than the other biochar-based catalysts reported in the recent literature. For example, 10 wt% Al impregnated biochars pyrolysed at 500, 600, and 700 oC as catalysts for glucose isomerisation achieved 14–16 mol% fructose yields at 160 oC (Yu et al., 2019a) and tin-modified biochar catalyst obtained 12.1 mol% fructose yield at 150 oC (Yang et al., 2019), although the temperature used in this study was lower (140 oC).

3.2 Conversion kinetics and rate comparison

The kinetics parameters (n and k) of the three catalysts are shown in Table 2. The Weibull equation was employed in this study to fit the kinetics of glucose isomerisation (Figure 3). As for GIO-Al200, GO-Al200, and BC-Al200 in the current research, the order constants (n) were in the narrow range of 0.57-0.73 under the studied condition, indicating similar catalytic mechanisms despite using different carbon supports. The other constant k in the kinetic model characterises the reaction rate. According to the Arrhenius equation, k= k0 exp (-E/RT), the variation in k value at constant temperature (140 oC) indicates the difference in activation energies in the catalytic systems studied. As shown in Figure 3 and Table 2, the GIO-Al200 and GO-Al200 presented very similar kinetic parameters, e.g., initial rate (r) = 30.99 mmol/L-min for GIO-Al200 and 28.47 mmol/L-min for GO-Al200). Given their comparable catalytic activities, GIO was more advantageous in terms of its simpler synthesis procedure compared to GO. In comparison, BC-Al200 displayed lower activity than the GIO/GO-based catalysts, as the initial rate of BC-Al200 (14.49 mmol/L-min) was also lower than that of GIO-Al200 and GO-Al200. The faster kinetics of the latter were probably due to the more amorphous structures as discussed above. The aqueous AlCl3-catalysed glucose isomerisation at 140 oC (Choudhary et al., 2013; Tang et al., 2016) has been shown to mostly follow the first-order reaction (n = 1), and the reaction rates of 0.014 min-1 and 0.0048 min-1 were respectively reported in these studies. The rate constant of glucose to fructose in a subcritical aqueous ethanol system at 180 oC was observed to be less than 0.06 min-1 (Gao et al., 2015), while another Brønsted base-catalysed (triethylamine) glucose isomerisation at 60 oC achieved the rate constant at 0.0096 min-1 (Carraher et al., 2015). Currently, available kinetics studies on glucose conversion over heterogeneous catalysis are limited. The comparable kinetic constants of the carbon-supported GIO-Al200, GO-Al200, and BC-Al200 catalysed systems in the current research prove the effectiveness and competitive advantages of the heterogeneous catalysts.

3.3 Fructose selectivity and side reactions

Fructose selectivity varying with time on the three catalysts showed a similar trend (Figure 4a), where fructose selectivity decreased from 87-97% at 1 min to 51-50% at 40 min. It implied that the highest selectivity appeared within 1 min. While fructose was the main product from glucose in this Lewis-acid catalysed system, a small amount of 5-HMF (up to 6.38% yield) was formed by dehydration of fructose under the Al-impregnated catalysts (Figure 1a-c). When the fructose selectivity is plotted against the glucose conversion (Figure 4b), the relative positions among the three curves of GIO-Al200, GO-Al200, and BC-Al200 were quite close, implying similar balance between the desirable fructose formation and side reactions. Besides, the three catalysts exhibited an almost identical selectivity pattern to fructose, suggesting a similar nature of active sites. Differences in the reaction rates were probably due to the numbers and forms of accessible Al sites on the carbon supports.

Prolonged reaction time promoted the formation of other side products, which was revealed by the increasing loss of total carbon over time (Figure 5). For example, a small amount (less than 1.25%) of levoglucosan (LG) was observed over the reaction time of 40 min. When reaction time reached 40 min, the carbon loss to unidentified products was 22.9%, 21.3%, and 11.8% for GIO-Al200, GO-Al200, and BC-Al200, respectively. BC-Al200 produced fewer side products and carbon loss than GIO-Al200 and GO-Al200, probably attributed to its lower catalytic activity. The unavoidable carbon loss may be due to undesirable reactions such as polymerization and hexose internal condensation (Yu et al., 2016). After glucose is converted to fructose, it can further dehydrate to 5-HMF if there is an acid environment. Carbohydrate products and other intermediates that formed from this reaction system may polymerise through aldol addition and condensation, thus forming oligosaccharides, which more easily occurs under Lewis acidity than Brønsted acidity (Yu et al., 2016; Yu et al., 2017).

3.4 Roles of active sites and leaching

Additional tests on glucose conversion over solid and liquid phases separately at 140 oC for 20 min were performed by hydrothermal treatment of the original catalyst. As illustrated in Figure 6, the catalytic activity of both liquid and solid phase after hydrothermal treatment of GIO-Al200 and BC-Al200 implied that active species leached from the solid catalyst to the solution to some extent during heating. To explore the potential role of pyrolysis temperature on the active sites of the catalysis, we produced GIO-Al at 500 oC (GIO-Al500) and evaluated its catalytic performance in supplementary tests. The fructose yield from the solid phase of GIO-Al500 after hydrothermal treatment was approximately twice higher than that from the liquid phase. The substantially lower contribution of liquid fraction than solid phase suggested that a higher activation temperature of catalyst production would stabilise the active sites and allow less subsequent leaching. However, GIOAl-500 achieved a lower overall fructose yield compared to its counterpart calcinated at 200 oC.

The final pH of the solution decreased over time (Figure 7), ranging from 3.89 to 2.68 between 1 and 40 min. This observation is probably because acid products (e.g., formic acid) formed over time and the leaching of active Al species from the carbon support. Leaching of Al decreased the solution pH with time thus increasing the number of protons that could promote side reactions such as dehydration and polymerization, which accounted for the observed decrease of fructose selectivity over time (Figure 4). This phenomenon became less significant when BC-Al200 was applied, as the final pH was higher than with GIO-Al200 and GO-Al200. As mentioned in Section 3.3, BC-Al200 gave fewer side products with higher fructose selectivity (60.4%) than GIO-Al200 and GO-Al200 (51.0% and 51.8%) at 40 min. For instance, the 5-HMF yield from using BC-Al200 at 40 min was 3.48%, which was lower than 6.38% and 5.97% of GIO-Al200 and GO-Al200. This result can be explained by the presence of alkali minerals in sawdust and its derived biochar (Wang et al., 2016b), which buffered the decrease of solution pH. Therefore, the pH buffering capacity of biochar catalyst can help to moderate the catalytic activity and reduce the undesirable side reactions.

3.5 Active sites of BC-Al200

In the Al-impregnated carbon catalysis system, aluminium species coordinated in the carbon support catalyse glucose isomerisation in a Lewis acid-driven pathway, where hydride shift occurred in different carbon positions of glucose in conjunction with an electron pair acceptor. It has been reported that the Lewis acidic active sites for glucose isomerisation might be Al species in the amorphous phase including aluminium carbide (Al4C3) and four-, five-, six- coordinated Al species (e.g., β-Al(OH)3, γ-Al(OH)3, Al-O-C, AlO(OH), and γ-AlO(OH)) that are impregnated on the carbon supports (Yu et al., 2019a, Yu et al., 2019b), and also probably from hydrolysed Al(III) complex [Al(H2O)4(OH)2]1+ / [Al(OH)2(aq)]+ (Tang et al., 2015; Norton et al., 2018; Cao et al., 2019). Such Al-coordinated complexes played an active role in shortening the hydrogen transfer distance during glucose isomerisation, thus overcoming the energy barrier and facilitating the rate-determining hydride shift (Ju et al., 2019). Moreover, the oxygen-containing functionalities can further facilitate glucose isomerisation by enhancing reflection, transmission, and absorption of microwave in the oxygen moieties intensified hotspots (Yu et al., 2019b).

As for biochar catalyst in the current study, the amorphous phase of BC-Al200 was shown in the Raman spectra with ID/IG at 0.52 (Figure 8a). Effective impregnation of Al species was confirmed by XPS (Figure 8b) and NMR spectra (Figure 8c). According to XPS fitting, it can be seen that β-Al(OH)3, γ-Al(OH)3 / Al-O-C, and γ-AlO(OH) are the main Al components in the BC-Al200 catalyst, constituting approximately 67.8%, 15.3%, and 17% of the total Al species. These species might be present in the configurations of four-, five-, and six-coordinated aluminium, (Al[4], Al[5], and Al[6]) as shown in Figure 8c. Diverse oxygen-containing groups on the biochar surface, such as hydroxyl and epoxy groups can facilitate the impregnation of Al and promote the formation of an Al-O matrix (Yu et al., 2019a). Similar chemical features of BC-Al200 suggested similar pathways when using graphite-derived and biomass-derived materials as carbon support to synthesize active catalysts for glucose isomerisation. Nevertheless, when comparing the Al species of the three catalysts, Al4C3 was present in GIO-Al200 but was absent from GO-Al200 and BC-Al200. The contents of Al[6] (including Al[6]\* and Al[6]#) of all the three catalysts were between 70% and 80%, while Al[4] of BC-Al200 was only slightly lower than those of GIO-Al200 and GO-Al200 (8.8% and 10.5%) (Yu et al., 2019b). The Al[5] (five-coordination) content constituted 16.8% of BC-Al200, while the corresponding figures in GIO-Al200 and GO-Al200 were only 5.9% and 1.1% (Yu et al., 2019b). Such differences of Al species may act as significant factors in determining the active site distributions, the roles of which are expected to be further explored with computational simulation of molecular geometry and energy barriers. The more amorphous surface of graphite and graphene oxide may present more abundant and evenly distributed microwave-sensitive functionalities and active sites rendering faster kinetics as well as greater catalytic activities than the biochar support.

These findings provide key information about conversion kinetics and catalytic activity, and hence contribute to further optimising the synthesis process of carbon-based catalysts for sustainable biorefinery. As summarised in Figure 9, the synthesis method of metal-doped carbonaceous catalysts was facile and green, which reduced the use of costly and potentially hazardous chemicals as well as minimised the release of secondary pollutants into the environment. The carbon supports acted as the skeleton with diverse functionalised moieties, while the metal doping introduced the active species with catalytic sites. Comparatively, biochar-based catalysts showed a similar catalytic performance and kinetics mode with graphite/graphene oxide-based catalysts. Biochar derived from waste biomass is a renewable and sustainable material, and its simple one-step production process through pyrolysis with metal doping seems economically competitive for large-scale production. The utilisation of engineered biochar can relieve greenhouse gas emissions and waste disposal burdens. Further optimisation of synthesis design can improve the catalytic performance of engineered biochar for producing valuable platform chemicals in a cost-effective and environmentally friendly way.

**4. Conclusions and future prospects**

This study compared the performances of three carbon materials (GIO, GO, and BC) as supports to synthesize heterogeneous catalysts by impregnation with 10 wt% Al for the catalytic isomerisation of glucose to fructose for sustainable biorefinery. By using microwave heating at 140 oC in water as a green solvent, Al-impregnated carbon-based catalysts showed considerable catalytic activities for glucose isomerisation with maximum fructose yields of 29-35%. GIO-Al200 showed similar catalytic activities as GO-Al200, while BC-Al200 presented slightly slower kinetics with less carbon loss as side products. Engineered biochar catalyst could be synthesized in a low-cost and sustainable manner with less resource consumption and carbon emission to the environment. From the results of this study, the design of cost-effective and environment-friendly carbon-based catalysts to optimise the catalytic activity could be further investigated. For example, adjusting the pyrolysis temperature or purging gas to tailor the oxygenated functionality of biochar surface, and changing the concentration or speciation of impregnation agent to improve the dispersion of active sites, are promising directions for future design of catalysts for sustainable biorefinery. More explorations on integrated biorefinery to make full use of the biomass feedstock and exploit the chain reactions with various value-added products are expected to achieve high carbon efficiency. The insights revealed in this work contribute to the green design of Al-impregnated biochar catalyst for biorefinery process and biomass valorisation.

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