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Review

Porous carbon-supported catalysts for energy and environmental applications: A short review

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Porous carbon materials including traditional activated carbons, carbon nanotubes and nanofibres, and recently emerged novel structured carbons synthesised by hard and soft templating methods have been widely used in a variety of applications. This review examines the extent to which these carbons have been used as catalyst support materials in the fields of energy and environmental chemistry. Catalyst preparation and synthesis methods are briefly summarised. Applications of carbon supported catalysts to energy related applications such as Fischer Tropsch Synthesis, Biomass-To-Liquid processes and environmental applications are reviewed with an aim to elucidate: the performance of these supported carbon catalysts; their issues and challenges; and identify potential research applications and directions.

Contents

1. Introduction

Carbon has long been deemed a good catalyst support material because of its diverse porous structure, resistance to acidic and basic environments, low cost, easy accessibility, good recycling characteristics, low density, and amenability to synthesise variants or post-synthetically engineer traits using a wide range of manufacturing, activation and carbonisation methods [1]. The extraordinary versatility of the core chemical element carbon has given rise to a wide diversity of structural forms of solid carbon, known as polymorphs which are composed entirely of carbon but have different physical structures. Two variants are amorphous carbons and crystalline carbons (Fig. 1).

Graphite and diamond are the two best known crystalline carbon forms and have been widely used in lubricants, electrodes, jewellery and for other industrial applications. Fullerenes and carbon nanofibres started emerging in 1960s and 1970s. But only since the formal discovery of carbon nanotubes by Iijima in 1991 [2], have these tubular/fibre structured carbon materials stimulated research in wider areas of application including semiconducting, aerospace, catalysis and gas storage. Debate as to the benefits and drawbacks of these crystalline carbon materials continue.

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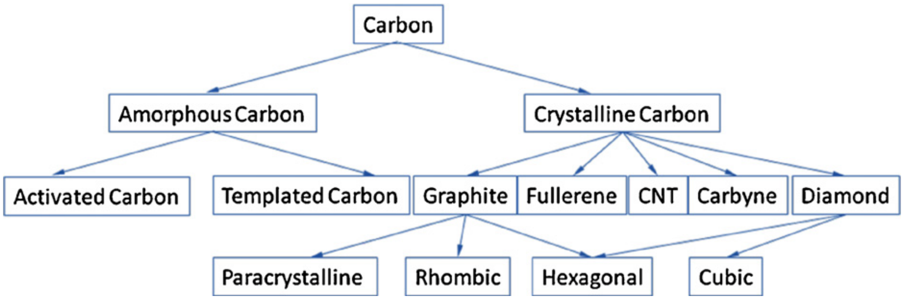

Fig. 1. Polymorphs of carbon.

Nevertheless, some of these materials have found industrial application and show superior performance for applications such as fuel cell electrodes and catalysis [3,4].

As the other major form of carbon, amorphous carbon is primarily made of graphitic sheetlets with no regular order which are characterised by strong covalent bonding in the basal plane. Activated carbon is one of the most common amorphous carbons. Its manufacture and use date back to the 19th century [5]. Comprehensive reviews on activated carbon are available elsewhere [6–9]. The usefulness of activated carbon mainly derives from its high micropore and mesopore volumes and the resulting high surface area. Modern manufacturing processes basically involve three main steps, namely: raw material preparation, low-temperature carbonisation, and activation. The raw materials are carbonaceous matter such as wood, peat, coals (with anthracite and bituminous coals being the main source), petroleum coke, coconut shell, fruit nuts, and other biomass derived sources [6–9]. Due to the presence of favourable pore geometries and volumes, activated carbons have been used in the areas of gas separation and storage [10–20], water purification [21], catalysis [22–28], and electrochemistry [29].

In recent years, templated carbons have emerged as a type of ‘amorphous’ carbon with well controlled pore size and structures. They are synthesised by using hard and soft templating approaches [30,31] and possess extremely high surface areas (as high as $4100\,m^2/g$) [32] and large pore volumes (as large as $2.25\,cm^3\,g^{-1}$) which make them extremely promising candidates for applications such as catalyst supports and adsorbents [33–38].

Reviews on each of the carbon forms mentioned above can be found elsewhere [6–9,39–42]. In the current review, we focus on the most recent developments in the use of these materials as catalyst supports in energy and environmental applications. We will briefly overview the current synthesis and preparation techniques used to produce carbon catalyst supports and will discuss the specific applications in each of the fields of energy and the environment. We will assess the potential benefits of carbons over existing technologies in order to address the major concerns of energy supply and climate change. We will also identify challenges and problems and highlight some potential applications for these carbon nanomaterials.

2. Preparation and synthesis of carbon-supported catalysts

2.1. Commercial carbon materials

Commercial carbons are defined here as those that can be purchased off the shelf as-is and used as a support for the dispersion of catalytic components. Commercial carbon materials such as activated carbons, carbon nanotubes and nanofibres, and fullerenes are the most widely reported catalyst support materials in the literature [6–9,39–42]. To improve their catalytic properties and stability, the active metal component of the catalyst is usually dispersed by impregnation or by precipitation-deposition.

Impregnation is a simple technique for insertion of metals into the pore network of the carbon support. In most cases, the precursor metal solution is mixed together with the support carbon materials, and is allowed to enrich the surface with metal centres through contact and evaporation. The mixed solution can be subjected to mixing by methods such as sonication or stirring to ensure maximum metal dispersion in the solution [44]. Next, the material is dried and subsequent heat treatment under inert gas is usually performed to further stabilise the metal catalyst [45,46]. Because of its simplicity and ease of metal loading control, this is a well-established catalyst preparation procedure, which has been widely reported in the literature. In this method, support materials can be any type of carbon such as carbon nanotubes/nanofibres [45–51], carbon spheres [52,53], activated carbons [44,54,55], or structured carbons [56]. However, the poor metal dispersion and pore blocking of the support can be a problem, especially when the metal loading is high [57–66].

The precipitation–deposition method is another simple catalyst preparation pathway. Generally, it involves mixing of two chemical reagents the precipitant of which contains the core catalyst element. Sometimes a hydrolysing reagent is used to facilitate the precipitation [44]. As with the impregnation preparation technique, pore blocking and poor metal dispersion are undesirable.

There are ways to improve the catalyst dispersion by surface functionalisation such as doping [53], introducing oxygen groups by acid treatment or by surface grafting [44,67–71]. These introduced functional groups act as anchoring sites during metal impregnation–deposition, leading to improved metal dispersion and size control of the resultant metal nanoparticles. Other methods such as micro-emulsion preparation using a surfactant have also been attempted in an effort to improve the metal dispersion, with limited success [49].

2.2. Ordered porous carbon materials

Ordered porous carbon materials have very well controlled porosities and structures. Until now, a variety of approaches have been developed for the preparation of ordered microporous, mesoporous, or macroporous carbons as reviewed by Hyeon [71], Stein [70], Ryoo [72] and Kyotani [73]. For example, by using zeolites as templates, researchers successfully synthesised three-dimensional (3-D) ordered microporous carbon materials with uniform pores using various carbon precursors via infiltration and chemical vapour deposition (CVD) [32] and lefaching of the zeolite to leave a templated carbon. Using a nanocasting (hard templating) approach combined with various ordered mesoporous silica particles as templates or a direct templating preparation (soft templating) using supramolecular aggregates as templates, ordered mesoporous carbons with tuneable pore sizes and structures have been successfully synthesised [30,74–76]. By using inverse silica opal or colloidal crystals of polystyrene microspheres as templates,

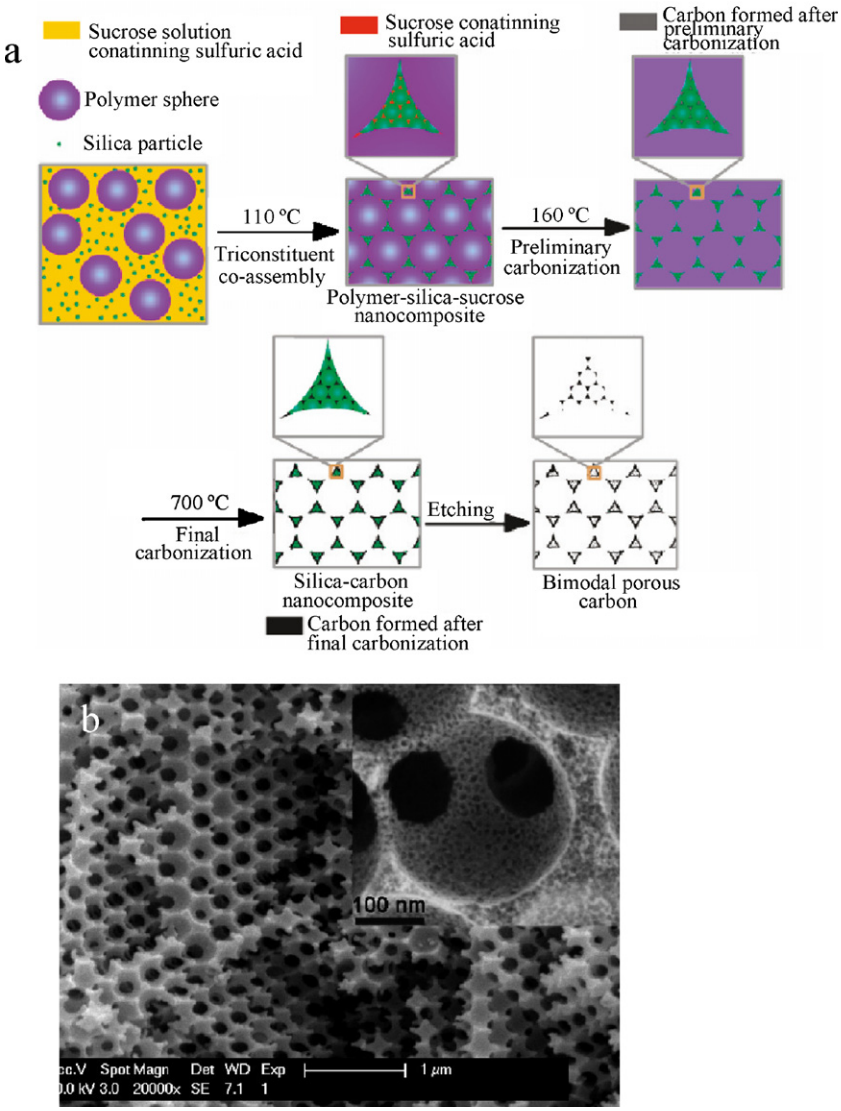

Fig. 2. Synthesis of hierarchical carbon [75].

3-D ordered macroporous carbons could also be successfully synthesised through infiltration or CVD [31,77]. Recently a highly efficient approach of employing multiple templates of different chemical properties and sizes has been developed by Zhao's group to produce hierarchically structured carbons (Fig. 2) [76]. With these special types of hierarchical carbons, micro-, meso- and macro-pores exist in the same structure and are not only tuneable but are also interconnected through the small window pores on the pore walls. These materials show improved diffusion characteristics compared to traditional carbons. Traditionally synthesised carbons generally have dead-end pores and consequently can have diffusion limitations.

Fig. 2a shows schematically how hierarchically structured carbon materials can be synthesised from templates of polymer spheres, silica particles and sucrose. Fig. 2b is a typical structure of the hierarchical carbon produced using this procedure.

Catalyst loading onto structured carbons can proceed either by traditional impregnation or precipitation methods [33,78–80] or in situ during the carbon synthesis [18,22,77,81,82]. Stein's group invented an electrochemical approach to coat ordered porous carbons by utilising their unique pore connectivity properties. Uniform coatings of metal particles were obtained when this technique was used (Fig. 3) [3]. Most of these ordered porous carbon-supported materials are used as electrodes in fuel cell applications [33–37,28,83].

It has been demonstrated that carbons with appropriate geometries for catalytic applications can be synthesised. In the next section we will review the use of carbon as a catalytic support material in fuel production applications.

3. Use of carbon as catalyst supports in synthetic fuel production

As has been mentioned previously, porous carbon materials have found applications in separation processes as adsorbents, in catalytic processes as supports and in electrochemical systems as electrode materials because of its unique physical and chemical properties. Generally, glassy carbon (or vitreous carbon) and graphitic carbon are used for electrodes because of their electron conducting properties. Carbon nanotubes/nanofibres and activated carbons are applied in catalysis and sorption fields because of their porous nature. Carbon materials used in fuel cell and adsorption applications have been reviewed extensively [39,40,79,83–86]. Therefore this section will focus on applications of porous carbons with a particular emphasis on their use in synthetic fuels

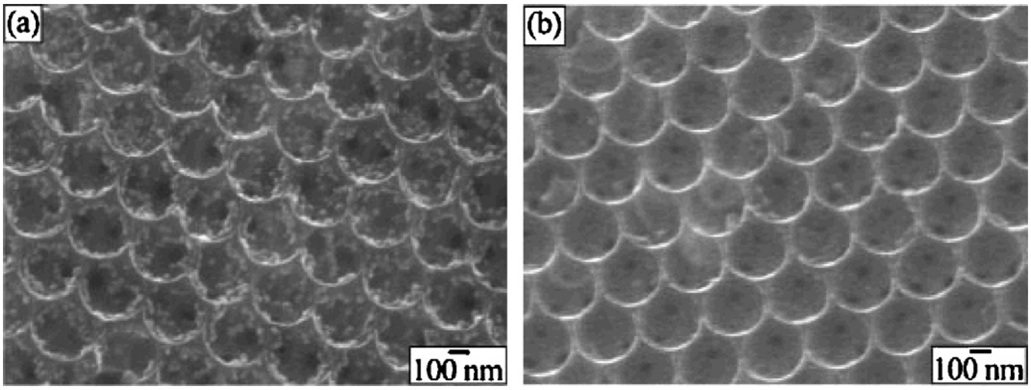

Fig. 3. (a) Precipitated tin sulphate nanoparticles on a 3D carbon; (b) tin oxide nanoparticles coated on a 3D carbon after thermal decomposition of the tin sulphate at 400 °C [3].

production from via Fischer Tropsch Synthesis (FTS), biomass conversion, methanation, fuel upgrading and hydrogen production.

3.1. Fischer Tropsch Synthesis (FTS)

Fischer Tropsch Synthesis (or FTS) converts a mixture of carbon monoxide and hydrogen into liquid hydrocarbons. The process is a key component of gas-to-liquids technology and produces a petroleum substitute, typically from coal, natural gas, or biomass for use as synthetic fuel. FTS has received attention as a source of low-sulphur diesel fuel and to address the supply or cost of oil-derived hydrocarbons.

Cobalt-based catalysts have been found to be very effective for the FTS provided the H_2:CO ratio is approximately 2:1 [87]. Syngas produced from sources such as coal or biomass usually results in H_2:CO ratios lower than 2:1. For these lower H_2:CO ratios, iron is often advocated, particularly due to its activity towards the water-gas-shift (WGS) reaction which can alter the H_2:CO ratio favourably towards the 2:1 ratio required for FT synthesis [57,88]. More recently, efforts have focused on Co because of its superior activity, its higher chain growth probability, and its lower WGS activity [57,89,90]. However, Co is much more expensive with its relative cost being approximately 1000 times higher than Fe [91]. Accordingly, optimal design of Co FTS catalysts is essential for efficient use of the metal.

The tunable pore sizes and surface areas of carbon materials have made them attractive supports for FT catalysts. For example, cobalt supported on activated carbons, carbon nanotubes/nanofibres, and carbon spheres [44,55,92–94] has been tested for its efficacy for FTS. Research revealed that at the same amount of metal loading, CNT supported Co catalysts showed comparable selectivity for C_{5+} hydrocarbons and a CO conversion of more than 80% compared to the conventional alumina supported Co catalysts. This is thought to be due to the CNT support aiding in the dispersion of metal clusters and therefore increasing active metal surface area [95]. It has also been shown that for carbon supported cobalt catalysts, as for metal oxide supported cobalt catalysts, the size of the cobalt particle is the most important factor in determining FTS activity [49,51,95]. The optimum size of Co crystals for FTS is around 8 nm [94]. In order to control the metal particle size, surface functionalisation by acid treatments or grafting has been attempted so that anchoring sites might be introduced, leading to better metal dispersion and more uniform cobalt particle distribution [44,67–71,91]. Zhang et al. reported a CNT supported cobalt catalyst that exhibited a much improved metal dispersion after nitric acid pre-treatment and gave a 25% higher hydrocarbon yield than the CNT without acid pre-treatment [44].

In order to improve the catalytic properties of these carbon supported cobalt catalysts, researchers have introduced precious metals such as Pt, Ir and Ru. Because of their active outer shell electrons, precious metals have different oxidation states and therefore facilitate electron transfer during reaction. Their presence in the catalyst has been shown to promote the catalytic activity and selectivity of cobalt catalysts [45,92,93]. However, the cost of these metals generally outweighs the observed improvement in FTS activity. Rare earth metals such as La and Zr are also reported to be able to promote the cobalt catalyst supported on activated carbon. However, it was found that the improvement both in catalytic activity and selectivity to C_{5+} hydrocarbons is limited (<5%) with the addition of the promoting metals. Above a certain concentration (0.3% for La and Zr) these metals are seen to reduce activity [96].

Supported iron catalysts are also one of the most common types of catalysts used in the FTS processes. Similar to cobalt FTS catalysts, iron supported on activated carbon, carbon nanotubes/nanofibres and carbon spheres have been the most frequently studied carbon-supported catalysts. Investigation of the carbon support materials has suggested that the FTS activity of these iron based catalysts can be directly related to the surface area of the carbon support, which in turn is related to the relative ease of mass transfer and the relative fraction of metal crystallites present in the pores, and is inversely related to the metal crystallite size [54]. Both Bao's and Abbaslou's groups have shown that tubular carbon supports can prolong the life of Fe FTS catalysts. This is thought to be the result of deposition of catalytic sites on interior surfaces of the nanotubes resulting in decreased sintering of the metal particles and therefore a more stable catalyst [48,97]. Slightly improved conversion is also observed. Abbaslou et al. studied the effects of pore size on a Fe/CNT catalyst for FTS. The work revealed that most of the metal particles were deposited inside the tubes. The pore diameter of the CNT material had a significant effect on activity, with the wider pore material showing lower activity than the narrower pore material. It is thought that this was due to the Fe particle size effect, with the smaller Fe particles existing in the narrower CNT pores. Bao's work suggested that the presence of metal particles inside the tubes may have led to the confinement of reaction intermediates inside the channels, which increased the contact time with active metal sites and resulted in the production of heavier hydrocarbons [46,47,97]. However, having metal particles situated inside the tubes could possibly lead to an increase in diffusional resistance and could also affect the long term effectiveness of these CNT supported Fe catalysts. The recent work of Davis et al. has aimed to elucidate the position of these metal catalyst particles [98]. In this study, they observed reduced surface area and pore volume when the Fe particles deposited on the inside walls of the CNTs. This

Table 1
Operating conditions of FTS.

Carbon supports	Mean pore size nm	Catalysts	Operating conditions	CO conversion %	C5 + selectivity %	Ref.
AC from peat	–	Fe, K and Cu	260 °C, 20 bar	51	50	[7]
AC from peat	–	Fe, K and Cu	280 °C, 20 bar	86	56	[7]
CNT	11	Fe	275 °C, 20 bar	25–30	48	[8]
CNT	17	Fe	275 °C, 20 bar	10–12	12	
CNT	–	Fe	220 °C, 25 bar	45.3	–	[2]
CNT	–	Fe	270 °C, 51 bar	79–85	24–36	[5]
CNT	10, 50	Co	220 °C, 20 bar	27–33	75–87	[4]
AC	–	Co	220 °C, –	12.6	17.9	[9]
AC (peat, pecan, wood, walnut)	–	Fe Mo Cu K	310 °C, 20 bar	38–90	30–50	[10]

observation could well explain the pore blockage and the lower CO rate as reported in Abbaslou's work [99]. Instead of depositing Fe metal particles inside the tubes, Davis et al. harboured the Fe nanoparticles in three dimensional surface structures such as nanoscale ridges and valleys, or wells on CNT supports and tried to avoid the blockage of the main channels. Meanwhile, these surface structures, referred as 'docking stations', restricted the surface movement of the catalysts and minimise the potential energy of particles, and improve the stability of the catalysts [98].

The promoting effects of other metals on carbon supports have also been investigated. Mo is reported to be able to promote iron catalysts supported on carbon nanotubes through the stabilisation of Fe. Improvements in activity with the addition of Mo were small (<1%). As was shown to be the case for La and Zr promotion of Co FTS catalysts by Wang et al. [96], there is a concentration above which Mo shows a deleterious effect on FTS activity. In the case of Mo Fe catalysts, this is reported to be 5 wt% and higher and is due to the blockage of active metal sites [91,92]. Potassium (K) was found to inhibit the reduction of the iron catalysts and therefore, the addition of K decreased the catalytic activity. But the presence of K is found to increase the olefin selectivity [51]. Promotion with copper was also reported to have improved the reduction of the iron catalyst but no significant FTS activity improvement was observed. However the use of copper did suppress the gasification of the carbon sphere support, resulting in a decreased CH_4 selectivity and therefore an increased selectivity to higher molecular weight products [51]. An extensive study of FTS on CNT-supported bimetallic cobalt/iron catalysts was also reported [49]. It showed that the monometallic cobalt catalyst still exhibited high selectivity (85.1%) towards C_{5+} liquid hydrocarbons. The addition of small amounts of iron did not significantly change the product selectivity. However, the bimetallic Co–Fe/CNT catalysts proved to be attractive in terms of alcohol formation.

In summary, compared to the metal oxide supported FT catalysts, carbon supported FT catalysts generally have reduced metal–support interaction and therefore a significantly improved reducibility and a higher catalytic activity. The reaction conditions of selected experiments using different catalysts are presented in Table 1. As reflected in the literature, the attractive properties of using carbon supports are their porous structure, resistance to acidic and basic media, and thermal stability under non-oxidative environments [100,101]. Moreover, the functional groups, in particular acidic functional groups, present on the carbon surface are excellent sites for obtaining a good dispersion of metal catalysts and for cracking higher hydrocarbons [102]. A comparison between activated carbon and carbon nanotube supports revealed that the former candidate generally has a dominant microporous structure which often imposed additional transport resistances and hindered mass transfer processes [43,101]. Carbon nanotubes possess similar properties as activated carbons but in most cases outperform activated carbon in terms of their higher thermal stability. Most importantly, carbon nanotubes have predominantly mesoporous structures which could help to facilitate transport processes within these materials [101]. Some studies have shown that because of their unique tubular structure, a confinement effect observed in CNTs was observed. CNTs have been shown to promote the transformation of metals into metal carbides. This could be related to higher activities and C_{5+} selectivity in FT synthesis [97]. Kong et al. reported that highly conductive CNTs were able to promote hydrogen spill-over from the CNTs to the catalyst sites [103]. The unique hydrogen species over the CNT-supported catalyst together with the acidic functional groups played significant roles in the selective cracking of heavier hydrocarbons to C_{10}–C_{20}, leading to lower C_{21+} selectivities [102]. However, due to the reduced metal–support interaction and increased reducibility of the carbon-supported catalysts, it is suspected that sintering will be a concern for these materials, as it is for metal oxide supported FTS catalysts. With the advanced porous carbon fabrication technologies developed in recent decades, structured carbons containing tuneable pore sizes or hierarchical pore structures have emerged as a new type of potential catalyst support materials, which will widen the areas of application for these new materials.

It is also worth mentioning that FTS catalysts are susceptible to poisoning by sulphur-containing compounds. Highly porous carbon support materials display good adsorption characteristics for sulphur, therefore reducing the effects of poisoning of the active sites [104]. However, more work on the stability of carbon supported FT catalysts is still required. Deactivation of carbon-supported FTS catalysts is generally associated with different carbon phases formed during the reaction, including re-oxidation and carbides. Control of these phase transformations is crucial to maintaining catalytic activity and preventing breakdown of the catalyst particles [56].

3.2. *Biomass conversion processes*

Catalytic conversion of biomass to fuels and chemicals has attracted great attention as a possible means for reducing the carbon burden on the environment [105]. Some predict that a shift to a carbohydrate-based economy will result in 20% of transportation fuels and 25% of chemicals in the U.S. being derived from biomass by 2030 [106].

Research is being conducted worldwide to develop new technologies for the generation of energy from biomass. Current technologies to produce liquid fuels from biomass typically involve multiple steps and are energy-intensive processes. These include, but are not restricted to, the production of ethanol by fermentation of biomass derived glucose [107], bio-oils by pyrolysis or high pressure liquefaction of biomass, polyols from hydrogenolysis of biomass derived sorbitol [108], biomass gasification [109,110] and biodiesel from vegetable oils [6].

With the increased attention on fuel from biomass, concerns have been raised about competition for biomass for food and energy [109]. An extensive number of works have been devoted to the degradation of the non-edible parts of biomass, e.g. cellulose. Traditional means of converting cellulose using enzymes,

Table 2
Operating conditions of biomass conversion.

Supports	Catalysts	Feedstock	Operating conditions	Conversion %	Sorbitol yield %	Ref.
XC72	Pt	Cellulose		88	44	[11]
AC	Pt	Cellulose		86	16.8	
Carbon black	Ru	Cellulose		86.4	37	
	Ir	Cellulose	190 °C, 50 bar	77.3	21	
	Pd	Cellulose		76.7	0.3	
	Rh	Cellulose		86.8	5.2	
Carbon black	Pt	Cellulose		80–100	53	
CNT	Ru	Cellulose	185 °C, 50 bar	–	61	[12]
CNT	Ru	3-β-D-Glucopyranosyl-D-glucitol	185 °C, 50 bar	78	38	[13]

mineral acids and supercritical water have drawbacks such as slow reaction rate, difficult separation of products and catalysts, corrosion hazards, harsh conditions and generation of large amounts of waste requiring neutralisation [111]. Heterogeneous catalysis has advantages over more established methods for cellulose extraction in that liquid separation is not required. Several authors have reported the conversion of cellulose to sugar alcohols by zeolite or alumina-supported Pt and Ru catalysts [111–113]. Precious metal supported carbon catalysts have also been investigated [114–117]. In Kobayashi's work, the authors compared 23 inorganic oxides and carbon supported catalysts, and tested their activity and selectivity before and after the reaction. They found that when the alumina was used as a support, the selectivity for the sugar alcohols decreased from 70% to 53%, indicating reduced hydrogenation activity of the catalyst. In their corresponding XRD measurement of the spent catalyst after the first reaction, diffraction patterns of γ-Al_2O_3 completely disappeared, and sharp peaks of AlO(OH) (boehmite) were observed, suggesting the deteriorated catalytic activity is caused by the hydration of the support.

They also carried out the screening of water-tolerant supports such as carbons, TiO_2 and ZrO_2. Among these supports, a carbon black BP2000 was found to provide the highest catalytic activity and good durability; the yields of the sugar alcohols in the reuse tests were 58%, 64% and 65%, respectively, and the total TON of Pt was 175. Furthermore, no change was seen for the XRD patterns of Pt/BP2000 catalyst before and after the reaction. The mean Pt diameters calculated with Scherrer's equation were both 2.6 nm before and after the reaction. These results indicated the water-tolerant property of this catalyst.

In short, the effect seems to be a chemical phenomenon but cannot be generalised to all carbons. The authors sited in Ref. [11] refer to one type of carbon only as being more resistant to water for the conversion of biomass [114,117].

In order to transform sorbitol into fuels such as hydrogen, light alkanes and liquid alkanes, aqueous-phase reforming is normally conducted that using heterogeneous catalysis. Nickel oxide has been found to be very effective in hydrogenolysis. However, metal dispersion of these catalysts is poor and sintering is a problem due to the way the catalyst are prepared using high temperature calcination. Since carbon materials generally have large, inert and tailorable surfaces, which facilitate metal dispersion, they have been studied widely as catalyst supports [112,118]. Li et al. have found that NiO supported on carbon has shown enhanced sorbitol conversion (3–40% depending on the preparation method) compared to unsupported NiO catalysts. They also found that the preparation method employed significantly affected the metal dispersion in the carbon supported catalysts. A co-precipitation method using a reducing agent was shown to have better catalytic properties than impregnation. They also found that different reducing agents used in the catalyst preparation step had a significant impact on the catalytic properties. There was no attempt from the authors to explain their results in more detail. We believe the results are supported by the findings of other work that relate preparation of the carbon support to its observed properties [43–45,48]. Impregnation with precursor salts fills the pores of the carbon support. These salts are reduced locally during the catalyst reduction. This generally leads to poor metal dispersion, and generally poorer catalytic activity. However, with co-precipitation, the metal precursor either co-precipitates with the reducing agent inside the pores, or the reducing agent alters the surface functional groups. During reduction, the reducing agent is removed, which allows access to a larger proportion of the pore volume for surface functional groups that act as anchoring sites for metal clusters, resulting in improved metal dispersion and therefore better catalytic performance.

Novel structured carbons have also attracted interest as catalyst supports for biomass conversion. Zhang et al. prepared structured carbon-supported tungsten carbide (WC) catalysts by using self-developed mesoporous carbons (3-D MC and CMK-3) as supports, and used them for converting cellulose into ethylene glycol (EG) [119]. They found that both of these structured carbon supported WC catalysts showed improved selectivity to EG (~70%, which is about 30% higher than the activated carbon supported catalyst). The 3-D MC supported WC not only showed high conversion (100%) and high selectivity to EG (72.9%) but also showed little deactivation over the time period tested. Zhang et al. also investigated Ni supported on three types of carbon support including self-developed structured carbons and one microporous activated carbon. Their results again revealed that the structured carbon supported Ni catalysts exhibited enhanced selectivity compared to the activated carbon by approximately 10%, suggesting the structured carbon support played a role in enhancing the performance of the catalyst.

Biomass can also be gasified to produce CO and H_2 (synthesis gas), which can be further processed to produce methanol or liquid alkanes by FTS. This process is known as Biomass To Liquids (BTL). Feasibility studies published in the open literature typically consider all the carbon supported FT catalysts mentioned in Section 3.1 as suitable catalysts for the BTL process via FTS [56]. However, it is argued that the iron-based catalyst may be a more attractive option for the BTL process because its syngas has lower H_2:CO ratio and iron more effective for Water Gas Shift (WGS), is much cheaper, and is more resilient to poisoning than Co [90].

In summary, carbon-supported catalysts have shown promise for biomass conversion due to their water tolerance, large and tailorable surface areas that enhance the catalyst dispersion and the ability to selectively position catalytic metals. Selected studies involving biomass conversions using different types of carbon as catalyst supports is summarised in Table 2. With recent developments in synthesis of 3-D carbons with versatile and accessible pore structures, carbon will play an increasingly important role as a catalyst support for biomass conversion.

4. Carbon catalysts for environmental applications

4.1. CO removal

One major problem encountered in fuel cell (FC) applications is the requirement for very low CO containing feed gas, especially when H_2 is generated from fuels [120,121]. Some FC anodes can be poisoned by trace amounts of CO, so there is a requirement to remove CO [122]. CO is also a notorious catalyst poison in such reactions as the Haber process for ammonia synthesis [123,124]. CO can be removed by a membrane in theory, but the membrane is expensive and it usually requires a compressor to improve flux [125]. One of the most studied systems for the removal of final traces of CO in recent years has been the preferential oxidation of CO in a H_2-rich atmosphere (PROX: $2CO + O_2 \leftrightarrows 2CO_2$). PROX can lower CO concentrations to around 10 ppm [126,127], but oxygen is required for the reaction, which adds to process complexity and cost. CO methanation ($CO + 3H_2 \leftrightarrows CH_4 + H_2O$) is another practical alternative because this reaction has all its reagents in the gases and no extra gas source is needed [128]. The most widely used means for reducing CO in gaseous streams industrially is the WGS reaction ($CO_{(g)} + H_2O_{(v)} \leftrightarrows CO_{2(g)} + H_{2(g)}$).

Ru catalysts supported on metal oxides are the most common catalysts used in the methanation reaction. In recent years, new carbon structures such as carbon nanotubes and nanofibres have been tested for their efficacy for methanation. Different types of Carbon Nanofibres (CNFs) have been studied as supports for methanation catalysts by Jimenez et al. [123,129]. Compared to metal oxide supported Ru catalysts, the carbon supported catalysts show lower temperature activity and also show lower overall rates of conversion [122,128].

4.2. Nitrogen oxide (NO_x) and sulphur oxide (SO_x) removal

Nitrogen oxides (NO_x) are one type of the major contaminants emitted from high temperature combustion process and are associated with environmental problems such as acid rain, urban smog, ozone depletion and health related issues such as bronchitis, pneumonia, immunodeficiency and even cancer [130]. Extensive research on selective catalytic reduction (SCR) of NO_x has been conducted for many decades [131,132]. One of the major sources for NO_x is from internal combustion engines. Three Way Catalysts (TWCs) are used in vehicles to reduce tailpipe emissions of NO_x as well as CO and unburnt hydrocarbons [130,133]. Different groups of catalysts have been tested for the conversion of NO_x conversion. Combinations of a number of metals (Pt, Pd, Rh, Au, Ag, Cu, Co, Fe, In, and Ga) with different supports (zeolites, Al_2O_3, SiO_2, and activated carbons) have been reported to produce active catalysts for the SCR of NO_x reaction [134–137]. Pt supported on activated carbons has shown higher NO_x conversion than conventional Pt supported on Al_2O_3 and has been actively used for hydrocarbon facilitated SCR catalysts [136,138]. Lecea et al. showed that a Y zeolite supported Pt showed better performance than carbon supported Pt. However, the carbon supported catalysts maintained their catalytic activity over time because of their better high temperature stability compared to zeolites [130]. Unfortunately, activated carbon supports tend to combust in oxidising environments at unacceptably low temperatures. In order to address this, multi-walled carbon nanotubes have been used because of their higher thermal stability and better resistance to oxidation than activated carbons. Santillan-Jimenez has confirmed that Multi Walled Carbon Nanotube (MWCNT) supported Pt catalysts exhibited superior NO_x reduction activity in comparison with Pt/Al_2O_3 [138]. Also, their results showed improvement in resistance to oxidation compared to activated carbon.

Like NO_x, SO_x is another major pollutant, often accompanying NO_x in combustion flue gas and inducing environmental and health issues, which require the simultaneous removal of both noxious gases [139]. Typically, CuO/Al_2O_3 catalysts are used for the catalytic removal of SO_x and NO_x. These materials can readily adsorb SO_2 and selectively reduce NO_x to N_2 with NH_3 as a reducing agent. However, this system suffers severely from sulphation, resulting in irreversible damage of the catalyst support. Tseng et al. have found that activated carbon supported Cu catalysts show improved activity for SO_2 removal than the conventional ones supported on alumina because the porous carbon support was able to adsorb significant amounts of SO_2 without deactivation of the catalyst [140,141]. It has also been shown that acid treatments of activated carbons further improved their activity. This was due to the improved metal dispersion resulting from the functional groups introduced by the acid treatments [140]. Stability remains a challenge for many of these carbon-supported catalysts.

5. Conclusion, challenges and outlook

Porous carbon materials, including traditional activated carbons, carbon nanotubes and nanofibres have been shown to be useful catalyst support materials by many researchers. Their pore structure and surface chemistry can be easily controlled by different activation and treatment procedures which can either alter the pore structure or create surface functional groups. They act as anchoring sites for metal precursors and therefore give better catalyst dispersion and particle size control. These advantages are well recognised in the research community. Despite the fact that CNT-supported metals have been widely investigated and have shown potential applications in catalysis, catalyst nanoparticles (NPs) deposited on nanotubes are unstable due to their high surface energies and the weak interaction between CNTs and NPs. Thus they tend to coalesce or sinter to minimise their chemical potential even at moderate temperatures. In essence, particle growth accompanied by a corresponding loss of active surface areas often leads to the deterioration of catalytic activity, and thermal stability is still an important factor to study in carbon-based catalysts.

Moreover, some of the activated carbons tend to have pores only in the micro-range, thus limiting their usefulness as catalyst support materials, particularly when conventional metal loading techniques are applied. Mesopores are needed to facilitate mass transfer and surface reaction so combinations of meso- and micropores in a support material are preferred. Carbon nanotubes and nanofibres contain mesopores but their efficacy for catalytic reactions has not been conclusively proven.

Ordered porous carbons have emerged as novel types of structured carbons in recent years. These carbons have pores structures tuneable in the micro- and meso-ranges. Some carbon materials can even be constructed by connecting the micropores to macropores, thus forming hierarchical structures. These types of structures are extremely useful in terms of mass transfer and enhancing reaction pathways and are anticipated to be very effective catalyst media. However, these materials have not been tested thoroughly as catalyst support materials. Research using these materials in energy related applications such as FTS and biomass conversion is limited, but work reported so far shows promise. Current research efforts are mainly concentrated on synthesis of these materials and research into applications is less well advanced. Therefore, systematic research studies for the application of these materials as catalyst supports will provide interesting opportunities for researchers in this field.

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