

## OVERVIEW ON POROUS CARBON-SUPPORTED CATALYSTS FOR SYNTHETIC FUEL PRODUCTION AND ENVIRONMENTAL APPLICATIONS

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### ABSTRACT

Porous carbon materials including traditional activated carbons, carbon nanotubes and nanofibres, have been widely used in a variety of applications. This paper 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, 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.

### 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).

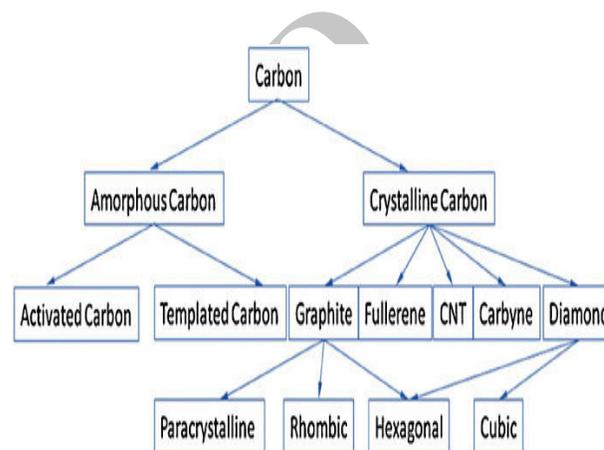


Fig. 1. Polymorphs of carbon.

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.

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.

Due to the presence of favourable pore geometries and volumes, activated carbons have been used in the areas of gas separation and storage [2–5], water purification [6], catalysis [7], and electrochemistry [8]. 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 [9] and possess extremely high surface areas (as high as 4100 m<sup>2</sup>/g) [10] and large pore volumes (as large as 2.25 cm<sup>3</sup> g<sup>-1</sup>) which make them extremely promising candidates for applications such as catalyst supports and adsorbents [11–15]. In the current paper 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 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.

## PREPARATION AND SYNTHESIS OF CARBON-SUPPORTED CATALYSTS

**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. 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 [16]. Next, the material is dried and subsequent heat treatment under inert gas is usually performed to further stabilise the metal catalyst [17,18]. 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 [17–23], carbon spheres [24,25], activated carbons [16,26,27], or structured carbons [28]. However, the poor metal dispersion and pore blocking of the support can be a problem, especially when the metal loading is high [29–31]. 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 [16]. 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 [25], introducing oxygen groups by acid treatment or by surface grafting [16,32–35]. 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 [21].

## USE OF CARBON AS CATALYST SUPPORTS IN SYNTHETIC FUEL PRODUCTION

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. Therefore this section will focus on applications of porous carbons with a particular emphasis on their use in synthetic fuels production from via Fischer Tropsch Synthesis (FTS).

**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 [36]. 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 [37]. More recently, efforts have focused on Co because of its superior activity, its higher chain growth probability, and its lower WGS activity [38].

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 [16,27,39,40] 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 C5+ 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 [41]. 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 [21,23,41]. The optimum size of Co crystals for FTS is around 8 nm [40]. 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 [16,32–35]. 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 [24,39].

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 [26].

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 stabilization of Fe. Improvements in activity with the addition of Mo were small (<1%). 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. 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<sub>4</sub> selectivity and therefore an increased selectivity to higher molecular weight products [17]. 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. 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 [42]. 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 [28].

## CARBON CATALYSTS FOR ENVIRONMENTAL APPLICATIONS

**CO Removal:** One major problem encountered in fuel cell (FC) applications is the requirement for very low CO containing feed gas, especially when H<sub>2</sub> is generated from fuels [43,44]. Some FC anodes can be poisoned by trace amounts of CO, so there is a requirement to remove CO [45]. CO is also a notorious catalyst poison in such reactions as the Haber process for ammonia synthesis [46]. CO can be removed by a membrane in theory, but the membrane is expensive and it usually requires a compressor to improve flux [47]. 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<sub>2</sub>-rich atmosphere (PROX:  $2\text{CO} + \text{O}_2 \leftrightarrow 2\text{CO}_2$ ). PROX can lower CO concentrations to around 10 ppm [48], but oxygen is required for the reaction, which adds to process complexity and cost. CO methanation ( $\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}$ ) is another practical alternative because this reaction has all its reagents in the gases and no extra gas source is needed [49]. The most widely used means for reducing CO in gaseous streams industrially is the WGS reaction ( $\text{CO}_{(g)} + \text{H}_2\text{O}_{(v)} \leftrightarrow \text{CO}_{2(g)} + \text{H}_{2(g)}$ ). 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. [46,50]. Compared to metal oxide supported Ru catalysts, the carbon supported catalysts show lower temperature



activity and also show lower overall rates of conversion [45,49].

### **Nitrogen oxide (NO<sub>x</sub>) and sulphur oxide (SO<sub>x</sub>) removal:**

Nitrogen oxides (NO<sub>x</sub>) 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, and even cancer [51]. Extensive research on selective catalytic reduction (SCR) of NO<sub>x</sub> has been conducted for many decades [52,53]. One of the major sources for NO<sub>x</sub> is from internal combustion engines.

Different groups of catalysts have been tested for the conversion of NO<sub>x</sub> conversion. Combinations of a number of metals (Pt, Pd, Rh, Au, Ag, Cu, Co, Fe, In, and Ga) with different supports (zeolites, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and activated carbons) have been reported to produce active catalysts for the SCR of NO<sub>x</sub> reaction. Pt supported on activated carbons has shown higher NO<sub>x</sub> conversion than conventional Pt supported on Al<sub>2</sub>O<sub>3</sub> and has been actively used for hydrocarbon facilitated SCR catalysts [54].

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. 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. Like NO<sub>x</sub>, SO<sub>x</sub> is another major pollutant, often accompanying NO<sub>x</sub> in combustion flue gas and inducing environmental and health issues, which require the simultaneous removal of both noxious gases. Typically, CuO/Al<sub>2</sub>O<sub>3</sub> catalysts are used for the catalytic removal of SO<sub>x</sub> and NO<sub>x</sub>. These materials can readily adsorb SO<sub>2</sub> and selectively reduce NO<sub>x</sub> to N<sub>2</sub> with NH<sub>3</sub> as a reducing agent. However, this system suffers severely from sulphation, resulting in irreversible damage of the catalyst support. Activated carbon supported Cu catalysts show improved activity for SO<sub>2</sub> removal than the conventional ones supported on alumina because the porous carbon support was able to adsorb significant amounts of SO<sub>2</sub> without deactivation of the catalyst [55,56]. 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 [55]. Stability remains a challenge for many of these carbon-supported catalysts.

### **CONCLUSIONS**

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. 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. 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.

### KEYWORDS

Carbon, Catalyst, support, Fischer Tropsch, Nitrogen oxide, sulphur oxide

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