CARBON 85 (2015) 119–134

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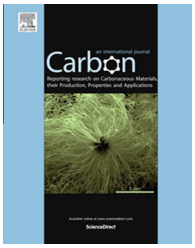

A multi-method study of the transformation of the carbonaceous skeleton of a polymer-based nanoporous carbon along the activation pathway

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ARTICLE INFO

Article history:
Received 28 September 2014
Accepted 16 December 2014
Available online 22 December 2014

ABSTRACT

The change in the carbonaceous skeleton of nanoporous carbons during their activation has received limited attention, unlike its counterpart process in the presence of an inert atmosphere. Here we adopt a multi-method approach to elucidate this change in a poly(furfuryl alcohol)-derived carbon activated using cyclic application of oxygen saturation at 250 °C before its removal (with carbon) at 800 °C in argon. The methods used include helium pycnometry, synchrotron-based X-ray diffraction (XRD) and associated radial distribution function (RDF) analysis, transmission electron microscopy (TEM) and, uniquely, electron energy-loss spectroscopy spectrum-imaging (EELS-SI), electron nanodiffraction and fluctuation electron microscopy (FEM). Helium pycnometry indicates the solid skeleton of the carbon densifies during activation from 78% to 93% of graphite. RDF analysis, EELS-SI, and FEM all suggest this densification comes through an in-plane growth of sp^2 carbon out to the medium range without commensurate increase in order normal to the plane. This process could be termed ‘graphenization’. The exact way in which this process occurs is not clear, but TEM images of the carbon before and after activation suggest it may come through removal of the more reactive carbon, breaking constraining cross-links and creating space that allows the remaining carbon material to migrate in an annealing-like process.

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http://dx.doi.org/10.1016/j.carbon.2014.12.051
0008-6223/

1. Introduction

The study of the solid skeleton of carbonaceous materials is as long standing as X-ray diffraction (XRD) [1]. Whilst the study of the evolution of the carbonaceous skeleton during processing has a somewhat shorter history [1], it is still well developed for the case where the carbons and their precursors are heated in an inert atmosphere (*i.e.* in pyrolysis/carbonization and graphitization) (*e.g.* [2–17]). Far less effort has, however, been directed towards elucidating the evolution of the skeleton when heating occurs in the presence of oxidising gases (*i.e.* during gasification/activation processes), in stark contrast to the accompanying porosity change. There is now a growing realisation that there are two sides to the gasification/activation story [18–22]: one must consider the evolution of the carbonaceous skeleton as well as the porosity that it defines in order to have a complete picture.

The earliest work concerned with elucidating the change in the solid skeleton of carbonaceous materials when heated under an oxidative environment appears to be that of Noda and Inagaki [23], who compared XRD-derived quantities for carbons obtained from heating under inert and oxidative environments. Based on the graphitic crystallite model of Biscoe and Warren [2], for the same heat treatment temperature, they found oxidative environments yielded crystallites with a greater number of layers and a smaller inter-layer spacing. They hypothesised this oxidative enhancement of ‘graphitization’ came from the oxygen removing more reactive cross-links between the graphitic crystallites in preference to the less reactive crystallites themselves, allowing them to then go on and grow, presumably through some re-arrangement and fusion process akin to annealing. Behaviour similar to that seen by Noda and Inagaki was observed 25 years later by Levendis and Flagan [24] for a glassy carbon derived from furfuryl alcohol (FA), the material of particular focus in the study reported here. Although they offer up nothing new on the possible origins of this behaviour, they do proffer support for it in the form of transmission electron microscopy (TEM) images of the carbon heat treated in nitrogen and air.

The next body of work in the field appears to have centred on understanding gasification-induced densification, which was first posited when char particles were observed to shrink whilst being gasified under kinetically controlled conditions. This phenomenon was first alluded to by Johnson [18] (see also pg. 1524 of [25]), who considered gasification of various 400–800 μm sized coal chars in hydrogen and steam at 35 bar and 1200 K. Hurt and co-workers [19] undertook a more comprehensive study a decade later by studying the gasification of a variety of fine (less than 38 μm) chars, including Spherocarb, under kinetic control. Johnson attributed densification during gasification to ‘reorientation of individual carbon crystallites’ (there is also mention of growth in the crystallite dimensions in the context of surface area decrease with conversion in one coal char). Hurt and co-workers went further, however, by hypothesising atomic-scale re-arrangement of the solid atoms following removal by gasification of some atoms and cross-links between sections of the skeleton. Indirect support for this hypothesis was provided subsequently by the work of Kantorovich and Bar-Ziv in which a model that appears to capture the essentials of the hypothesis was able to reproduce experimentally observed changes in porosity [21], reactivity [26] and thermal conductivity [27] with char conversion during gasification.

Further understanding of the change in the carbonaceous skeleton under oxidative conditions has come from some of the work focused on elucidating the underlying causes of char reactivity variation during coal gasification and combustion [28–36]. This work clearly shows that the nature of the change in extent of order in the skeleton with conversion is dependent on the char and the conditions it experiences: most of the studies demonstrated an increase in extent of order with conversion [28–36], but others also saw a decrease [28,35] or no change at all [34,35]. The more recent work of Feng et al. [22], however, raises the prospect that conclusions drawn from this prior work may be open to question if based solely on XRD analysis. As an indirect method, XRD is also not generally well placed to elucidate the underlying mechanism of the change in the carbonaceous skeleton. The use of multiple techniques together and/or more direct methods such as TEM is likely to be more fruitful.

A small number of the studies that have adopted a multi-technique or direct analysis approach to studying change in the carbonaceous skeleton with conversion have proposed mechanisms for the change. Based on the Oberlin basic structural unit (BSU) model [37], which is akin to the graphitic microcrystallite model [2], and their assembly into regions of local molecular orientation (LMO) [6], Rouzaud et al. [20] used quantitative TEM of petroleum coke at various levels of conversion from steam gasification at 950 °C to propose that, except at high conversions, regions of LMO of intermediate size (10–100 nm) were preferentially consumed over the larger and smaller regions of LMO. They attributed this behaviour to a balance between the accessibility of the oxidant to the solid atoms, which increases with the extent of LMO, and their reactivity, which decreases with the LMO extent. However, more recent studies involving coal chars [36] and coke [38] argue that the smallest graphitic crystallites are preferentially consumed, leaving behind the larger crystallites, which can be equated to all but the smallest of Oberlin’s regions of LMO. Beyond this earlier work, some studies [33,36,38] support the earlier hypothesis [19,21,23] that disordered carbon is preferentially consumed. They, on the other hand, offer mixed support for the previously hypothesised notion [18,19,21,23] that removal of the more reactive carbon allows the remainder to go on and anneal – Tran et al. [38] ruled this possibility out, claiming that the more ordered carbon already existed in their precursor (coke), whilst Sharma et al. [33] argued that the ordered structures did not initially exist in their coal char but formed through an oxidative-assisted annealing process.

To a significant extent, the current modest understanding of the fundamentals of carbon skeleton evolution under oxidative environments arises out of the limitations of the various experimental techniques and approaches used to date. In the case of the most common XRD-based analysis, the most fundamental concern is its reliance on the view that carbons