CARBON 78 (2014) 113–120

Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/carbon

Control of the pore size distribution and its spatial homogeneity in particulate activated carbon

Cheng Hu [a], Saeid Sedghi [a], S. Hadi Madani [b], Ana Silvestre-Albero [c], Hirotoshi Sakamoto [d], Philip Kwong [a], Phillip Pendleton [b,e], Ronald J. Smernik [f], Francisco Rodríguez-Reinoso [c], Katsumi Kaneko [g], Mark J. Biggs [a,]*

[a] *School of Chemical Engineering, The University of Adelaide, SA 5005, Australia*
[b] *Ian Wark Research Institute, University of South Australia, SA 5095, Australia*
[c] *Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica, Universidad de Alicante, Apartado 99, E-03080, Spain*
[d] *Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan*
[e] *Sansom Institute, University of South Australia, SA 5001, Australia*
[f] *School of Agriculture, Food and Wine, The University of Adelaide, SA 5005, Australia*
[g] *Center for Energy and Environmental Science, Shinshu University, Wakasato 4-17-1, Nagano 380-8553, Japan*

ARTICLE INFO

Article history:
Received 27 April 2014
Accepted 21 June 2014
Available online 30 June 2014

ABSTRACT

There are circumstances where it is desirable to achieve a particular, optimal, pore size distribution (PSD) in a carbon, including in the molecular sieving, gas storage, CO_2-capture and electrochemical energy storage. Activation protocols that cycle a carbon a number of times between a low-temperature oxygen chemisorption process and a higher temperature pyrolysis process have been proposed as a means of yielding such desired PSDs. However, it is shown here that for PFA-based char particles of ~100 μm in size, only the super-micropores are substantially developed under such an activation protocol, with the ultra-micropores being substantially un-touched. It is also shown that a typical CO_2-activation process yields similar control over PSD development. As this process is nearly 15 times faster than the cyclic-O_2 protocol and yields larger pore volumes and areas for a given level of conversion, it is to be preferred unless spatial homogeneous porosity within the particles is also desired. If such homogeneity is desired, it is shown here that CO_2 activation should continue to be used but at a rate of around one-tenth the typical; this slow rate also has the advantage of producing pore volumes and areas substantially greater than those obtained using the other activation protocols.

1. Introduction

Whilst activated carbons are well known to be highly disordered across multiple length scales, there are situations where it is highly desirable to control the pore characteristics. For example, confining the pore size distribution (PSD) tightly around an optimal pore size is advantageous for carbons used in molecular sieving [1], natural gas storage [2], CO_2 capture [3], and supercapacitor electrodes [4]. Similarly, it is also sometimes desirable to co-develop both micro and mesopores so as to enhance transport to the micropores [5,6].

The need in some activated carbon applications to have a desired PSD has led to the development of a number of activation protocols that claim to provide a high degree of control

---

* *Corresponding author*: Fax: +61 8 8303 4373.
E-mail address: mark.biggs@adelaide.edu.au (M.J. Biggs).

http://dx.doi.org/10.1016/j.carbon.2014.06.054

over the distribution (*e.g.* [7–10]). Whilst each of these appears to deliver some degree of control, they are complex and time-consuming compared to the more routinely used methods. Additionally, there is no proof that these more complex protocols yield spatially uniform carbons, an absence of which would not only run counter to the driver for their use, but may also bring other disadvantages. For example, if the desired PSD is localized only to the periphery of a carbon particle [11,12], a rapid degradation in its performance would be likely as it wears during use. Molecular and other models derived from properties of macroscopic volumes of a carbon [13,14] are also less meaningful if spatial variation in the pore structure exists.

In the contribution here, we contrast the control over the PSD and degree of spatial heterogeneity in activated carbon particles obtained from three activation protocols. The first is the controlled activation protocol of Py et al. [8] that involves repeated application of a cycle in which oxygen is first chemisorbed onto the carbon at a moderate temperature (*e.g.* 250 °C) and then removed along with some of the carbon at a higher temperature (*e.g.* 800 °C) in an inert atmosphere. The second is based on the CO_2 activation protocol of Qajar et al. [15], which is typical of industrial practise [16]. The final protocol is the same as the second except at a tenth of the activation rate, which has been used by Molina-Sabio et al. [17]. The degree of spatial heterogeneity was assessed using a modified form of the procedure developed by Buczek et al. [11,12], who examined the radial variation of porosity in activated carbon granules. All the activated carbons were derived from a carefully prepared poly(furfuryl alcohol) (PFA) precursor. This precursor was primarily adopted to avoid heterogeneities that would arise from natural precursors such as coal and wood, and because carbons derived from PFA possess broadly similar pore system characteristics of many other polymer-based carbons of increasing interest, including those obtained from phenolic resin and poly(vinylidene chloride) (PVDC) [18].

2. Experimental details

2.1. Carbon preparation

2.1.1. Synthesis of PFA char

All the carbons considered here were derived from a PFA precursor. To eliminate possible sources of variability in the samples, as-received FA (98%; Sigma–Aldrich, USA) was vacuum-distilled to remove any stabilizers and oxidized and partially-polymerized FA (see the Supplementary Information for further details). To ensure the distillate did not undergo further partial-polymerization or oxidation, it was stored at −20 °C under an argon (99.5%, Coregas, Australia) atmosphere until used.

The FA distillate was mixed with as received oxalic acid dihydrate (>99.5%; Ajax, USA) as a polymerization catalyst at 100:3 weight ratio. Mixing was done by careful stirring for 15 min under argon at 25 °C. Following mixing, 5 mL of the mixture was transferred to a high-alumina content pyrolysis boat (Coors, USA) of dimensions 90 mm long by 17 mm wide by 11.5 mm high. The boat was then loaded into the 200 mm long midway zone of a horizontal, quartz tube-furnace (Lindberg, USA), where the temperature was constant to within ±1 °C. The contents of the boat were then polymerized and cured to form a thermosetting mass by heating to 150 °C at a constant rate of 5 °C min^{-1} under a 500 mL min^{-1} continuous argon flow before being soaked for 1 h. Carbonization was then done under the same argon flow conditions by further increasing the temperature to 800 °C at a constant rate of 5 °C min^{-1} before being soaked for 2 h. The sample was then finally cooled to room temperature by switching off the furnace whilst continuing the argon flow. The yield of all batches obtained from this carbonization procedure was 33.5% ± 0.2%, whilst elemental analysis (TruSpec CHN analyzer, Leco, US) of the batches revealed the composition of the batches of char to be consistently (on an atomic-% basis) 90.8% carbon, 8.6% hydrogen and, by difference, 0.6% oxygen.

The cooled char was broken up into chunks of around 2–5 mm in size using a clean zirconia press and then immediately ball-milled (P23, Fritsch, Germany) and sieved (Cole-Parmer, USA) to obtain a powder with a particle size distribution of 38–106 μm. The powder samples were kept in glass vials under an argon atmosphere until used.

2.1.2. PFA char activation

Three different activated carbons were considered. The first were derived by applying the cyclic O_2-activation protocol of Py et al. [8] to mixed batches of the PFA-based char produced by the process described above. The remaining two activated carbons were obtained by applying CO_2 activation to the char at two different rates: that used by Qajar et al. [15], which we estimate to be 9% conversion *per* hour (henceforth referred to as fast-CO_2 activation), and one-tenth of this rate (henceforth referred to as slow-CO_2 activation), which has been used by Molina-Sabio et al. [17]. The activation processes were all undertaken in the same furnace and boat configuration used to make the PFA char. Samples at both low- and medium-conversion – defined as 25% and 45% mass loss after activation respectively – were produced for all the activation protocols so as to elucidate conversion-dependence.

For the cyclic O_2-activation protocol, the char was exposed to repeated cycles involving first chemisorption under a 100 mL min^{-1} flow of O_2 (99.5%, Coregas, Australia) at 250 °C for 8 h (see Supplementary Information for an explanation of why this period was used) followed by pyrolysis under a 100 mL min^{-1} flow of argon (99.5%, Coregas) at 800 °C for 2 h. The low-conversion (*i.e.* 25%) and medium-conversion (*i.e.* 45%) carbons, denoted here as $C25O_2$ and $C45O_2$, were obtained by undertaking 5 and 9 cycles respectively. The resultant activated carbons were kept in glass vials under an argon atmosphere until used.

Low- and medium-conversion activated carbons from the fast-CO_2 activation protocol were obtained by exposing the char to 500 mL min^{-1} CO_2 (99.5%, Coregas, Australia) at 900 °C for 3 and 5 h, respectively, after initially heating to that temperature from ambient at a rate of 5 °C min^{-1}; in line with the labeling used for the cyclic-oxidation chars, the low- and medium-conversion samples obtained from this fast-CO_2 activation protocol are denoted here as $C25FCO_2$ and $C45FCO_2$ respectively. The same basic procedure was adopted