



Synthesis of porous carbon from petroleum coke using steam, potassium and sodium: Combining treatments to create mesoporosity



Luis D. Virla, Vicente Montes, Jingfeng Wu, Stephanie F. Ketep, Josephine M. Hill*

Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Dr NW, Calgary, Alberta, T2N 1N4, Canada

ARTICLE INFO

Article history:

Received 24 February 2016

Received in revised form

20 June 2016

Accepted 12 July 2016

Available online 14 July 2016

Keywords:

Petroleum coke

Activated carbon

Mesopores

Chemical activation

Steam activation

Asphaltene adsorption

ABSTRACT

Bitumen upgrading involves the hydroconversion of larger molecules that require catalyst supports with meso- and/or macropores for access to the active sites. In this study, various activation processes were studied to activate delayed petroleum coke, which is a by-product of oil sands bitumen upgrading and an inexpensive source of carbon. The petroleum coke was subjected to steam, chemical (KOH, NaOH) and combined activation methods at 973 K and 1073 K. The produced materials were characterized with nitrogen physisorption at 77 K and scanning electron microscopy. Combined with the yields, the results suggested that the combination of steam with sodium or potassium increased the mesoporosity of the carbon samples possibly by a catalytic gasification mechanism. A mesopore volume of 0.39 cm³/g with a yield of 27% was achieved by simultaneously activating with sodium and steam. Washing the material after activation with sodium and before introducing steam produced the same mesoporosity but doubled the yield, confirming that steam alone is not effective at creating porosity. The accessibility of the larger pores was confirmed with the adsorption of asphaltenes from Athabasca extra-heavy crude oil. The capacity for asphaltene adsorption increased with increasing mesopore volume.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

Activated carbon (AC) is used for many applications and made from a variety of materials including wood [1], lignocellulosic biomass [2], peat [3], lignite [4], coconut shells [5], and bituminous coal [6]. These feeds can be physically or chemically activated to produce a product with the desired properties for the application. Pore size in particular must be tailored so that reactants and/or adsorbents can access the internal surface of the AC. As of yet, however, there is no standard method to produce AC and a procedure must be developed for each specific feed.

Petroleum coke (petcoke), which is a carbon-rich (80–85 wt%) byproduct of oil sands bitumen upgrading, has been explored as an inexpensive feed for AC production [7–20]. Activation using methods employed for coal generally results in microporous AC [12,13,16–19] that may be suitable as gas adsorbents and as catalyst supports for reactions with smaller molecules [11–13,20]. For reactions with larger molecules, such as molecules in bitumen with highly aromatic polycondensed asphaltenic structures, AC with

meso- and/or macropores is required. Mesoporous AC has been obtained from lignocellulosic materials by physical, and/or chemical activation [21–24] but similar preparation methods do not produce mesopores when petcoke is the precursor. For example, Otowa et al. [8] obtained microporous AC with a surface area >3000 m²/g by reacting petcoke and KOH in a mass ratio of 1:4 at 1073 K for 2 h. Other authors obtained similar results in terms of pore size when alkali metal hydroxides and carbonates were used as activation agents [7,11,16–18]. Other activation agents such as ZnCl₂ or H₃PO₄ [9] or the combination of two different activation agents such as KOH and steam in the same activation process [10] have been investigated but also resulted in microporous products.

Small et al. [25] compared different physical methods for the activation of delayed and fluid petcoke feeds including reaction with CO₂, steam, CO₂ with steam and N₂ with steam at two different activation temperatures (1073 K and 1173 K) and activation times between 2 h and 6 h. The authors obtained the highest mesopore volumes – 0.15 cm³/g with delayed coke and 0.17 cm³/g with fluid coke – using CO₂ with steam activation (steam rate of 0.5 cm³/min) at 1173 K for 6 h. Rambabu et al. [19] compared physical (steam or CO₂ at 1173 K for 9 h) and chemical (KOH or H₃PO₄ at 773 K for 1 h) methods for fluid petcoke activation. The authors found that among the activation agents tested, steam produced reasonable mesopore

* Corresponding author.

E-mail address: jhill@ucalgary.ca (J.M. Hill).

volume ($0.10 \text{ cm}^3/\text{g}$ with a surface area of $482 \text{ m}^2/\text{g}$) while KOH produced the highest surface area ($692 \text{ m}^2/\text{g}$ with a mesopore volume of $0.038 \text{ cm}^3/\text{g}$). The highest mesopore volume of $0.13 \text{ cm}^3/\text{g}$ was obtained by using a combination of steam followed by treatment with 70% HNO_3 .

In our own group, we have previously used CO_2 [15,16] and KOH [13,26] to produce AC from delayed petcoke. Consistent with the literature, mainly microporosity was developed by these activation agents. Based on experiments with different sized particles, flow rates, and pretreatments [15], the reaction with CO_2 is diffusion limited. Steam activation of petcoke has been shown to be diffusion limited also [10,25]. Potassium, however, is highly mobile and, thus, has been used as a catalyst for gasification [26–28]. Potentially a combination of chemical and steam activation will be successful in creating mesoporosity. When micropores are created by chemical activation, the subsequent addition of steam could promote the formation of new pores and the widening of existing pores. This hypothesis was the basis of the current study. To further investigate the accessibility and morphology of the pores developed, asphaltene adsorption was evaluated on some of the prepared materials as well as on a commercially available AC.

More specifically, delayed petcoke was activated at 1073 K with physical activation using steam, chemical activation using KOH or NaOH, and combined chemical and steam activation. Based on the initial results, additional experiments were done at 973 K and different activation times to further increase the mesopore volume and better understand the process. The surface area, pore volume, and pore size distribution of the produced samples were determined using nitrogen physisorption, while the particle size was determined with scanning electron microscopy. The accessibility of the created porosity was tested with asphaltene adsorption at room temperature using ultraviolet/visible (UV–Vis) spectroscopy to analyze the toluene solution concentrations.

2. Experimental

2.1. Materials

Delayed petcoke from oil sands bitumen upgrading (Suncor Energy Inc., Alberta, Canada) was ground and sieved to obtain particle sizes in the range of 150–300 μm , and these particles were dried overnight at 383 K before further use. The petcoke contains 3.1 wt% (dry-basis) ash, 9.8 wt% volatile matter, and 86.8 wt% fixed carbon, and has a surface area of $0.5 \text{ m}^2/\text{g}$ with a total pore volume of $0.012 \text{ cm}^3/\text{g}$ as determined by N_2 adsorption [13,29]. Detailed information can be found in the Supplementary Information, Table S-1. Analytical grade chemicals KOH (85%, Alfa Aesar, Heysham, United Kingdom) or NaOH (97%, Sigma-Aldrich Inc., St. Louis, USA) were used for the chemical activation. N_2 (99.999%, Praxair Canada Inc, Mississauga, ON, Canada) gas was used without further purification. A commercially available AC, Colorsorb® G5 (Jacobi Carbons Inc., Kamlar, Sweden) made from hardwood from Malaysia was used for comparison in the asphaltene adsorption studies.

2.2. Preparation of activated carbon

As every lab set-up is different, treatments that have been shown to produce micropores were repeated to provide baseline values. The feed, $\sim 2.5 \text{ g}$ of ground and dried petcoke, was placed in a ceramic boat within a horizontal tube furnace, heated at 5 K/min under flowing nitrogen ($250 \text{ cm}^3/\text{min}$, as controlled by a mass flow controller - Brooks Instrument 0254, Hatfield, USA) to 393 K, and held at this temperature for 60 min to remove any moisture. After the drying step, the temperature was raised to 1073 K at 5 K/min, and held at this temperature for the desired activation time with

the desired atmosphere. The product was cooled to room temperature under flowing N_2 ($50 \text{ cm}^3/\text{min}$). For simplicity, all materials after treatment will be referred to as AC regardless of actual surface areas and porosities. All data presented was determined by averaging values for at least two batches of AC. The variability of the surface areas, pore volumes and yields were generally less than 10% between batches. Temperature control is critical in obtaining good reproducibility. Specifically, care was taken to always place the mixtures in the same location in the furnace. The specific activation treatments are described in the following sections.

2.2.1. Physical activation

Physical activation consisted of exposing the petcoke to humidified N_2 (steam). Humidification of the N_2 stream was achieved by flowing $50 \text{ cm}^3/\text{min}$ of N_2 over a column packed with quartz wool that was saturated with water using a syringe pump (Cole Parmer 17867, Vernon Hills, USA) feeding $5 \text{ cm}^3/\text{h}$ of liquid water. The packed column was kept at $\sim 423 \text{ K}$ using heating tape controlled by a variable transformer (Variac 3PN1010B, Staco Energy products Co., Dayton, USA). The samples were activated at 1073 K for 120 min.

2.2.2. Chemical activation

For chemical activation, ground and dried petcoke was physically mixed in a mortar and pestle with a chemical agent – KOH or NaOH, in a mass ratio of 1:3 (i.e., 1 part petcoke with 3 parts chemical agent) – and activated in flowing nitrogen at 1073 K for 0 or 120 min. After cooling to room temperature in flowing nitrogen, the product was washed with 1 M HCl followed by de-ionized water until the pH of the rinsing water was neutral. Washing has been shown to remove metal salts formed during activation [7,30]. EDX analysis confirmed the removal of ash and remaining alkali from carbon samples after washing. The samples were then dried overnight at 383 K.

2.2.3. Combined chemical and steam activation

Three different procedures were used for combining chemical and steam activation in an effort to increase the pore sizes and yields, and also better understand the activation processes. In all procedures, the mixture of petcoke and chemical agent - KOH or NaOH at 1:3 mass ratio – was prepared and heated in flowing N_2 to 1073 K as previously described for the chemical activation procedure. In the first procedure, steam was introduced to the reactor when the mixture reached 1073 K and held at this temperature for 30 or 120 min. These samples are named K/St and Na/St. In the second procedure, the sample was chemically activated for 120 min at 1073 K and then steam was introduced to the reactor for 30 or 120 min at 973 or 1073 K. These samples are identified as K_St and Na_St. For these two procedures, the samples were cooled to room temperature after activation, washed with acid as described previously, and dried overnight at 383 K. In the third procedure, chemical activation was performed first as described in Section 2.2.2. After being washed and dried overnight at 383 K, the sample was placed back in the furnace for steam activation for 30 or 120 min at 973 or 1073 K, and then cooled to room temperature. Samples that were washed between chemical and steam activation are identified as K_w_St and Na_w_St. A summary of all samples prepared and their preparation methods are presented in Table 1. If not specified in the name, the base conditions for activation temperature (1073 K) and activation time (120 min) were used. For example, the sample named Na was activated at 1073 K for 120 min, while the sample named Na0 was heated to 1073 K and then cooled (i.e., held at 1073 K for 0 min).

Download English Version:

<https://daneshyari.com/en/article/71934>

Download Persian Version:

<https://daneshyari.com/article/71934>

[Daneshyari.com](https://daneshyari.com)