



# Pore enlargement of carbonaceous materials by metal oxide catalysts in the presence of steam: Influence of metal oxide size and porosity of starting material



Vicente Montes, 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 15 June 2017

Received in revised form

28 July 2017

Accepted 2 August 2017

Available online 3 August 2017

### Keywords:

Mesoporous activated carbon

Enlargement of pore size

Metal catalyzed steam activation

## ABSTRACT

Porous carbon materials are produced in large amounts but are generally microporous and, thus, may have diffusion limitations for reactions with larger molecules. In this study, iron, lanthanum, cerium, nickel and cobalt oxides were studied as catalysts to enlarge or create mesopores in carbonaceous materials through metal-catalyzed steam activation. The carbonaceous materials were impregnated with 25 wt% metal nitrate salts and exposed to humidified N<sub>2</sub> (steam, 50 cm<sup>3</sup>/min N<sub>2</sub> plus 5 cm<sup>3</sup>/h liquid water) at 1073 K. The metal precursors were converted to metal oxides, and produced carbon samples with pore sizes between 2 and 60 nm and mesopore volumes up to 0.65 cm<sup>3</sup>/g. The size of the pores created was determined by the metal oxide size. Cobalt oxide produced the largest pores followed by nickel, cerium, lanthanum and iron oxide. For materials with mainly micropores, activation proceeded by gasification and collapse of pore walls, while for materials with larger pores, pore widening occurred. Catalyst recycling was achieved by acid leaching after activation, and no differences in the produced materials were found using fresh or recovered cerium nitrate.

© 2017 Elsevier Inc. All rights reserved.

## 1. Introduction

Porous carbon is produced in large amounts by carbonization, pyrolysis, physical activation, and chemical activation and used extensively as an adsorbent, catalyst support, gas storage medium, and electrode material [1–3]. These production methods mainly lead to microporous carbon [1,4,5], which is suitable for many applications but may present diffusion limitations for applications with larger molecules. As such, researchers have developed several techniques to synthesize mesoporous carbonaceous materials [2,6–8]. For example, chemical activation with ZnCl<sub>2</sub> or H<sub>3</sub>PO<sub>4</sub> has produced mesoporous carbon from biomass waste but with long processing times [9]. Another technique involves the use of templates that are removed after carbonization or polymerization. Hard templates are mainly inorganic materials, while soft templates are organic materials or surfactants [2,10,11]. One of the main problems with templating is the complicated synthesis of the solid and the relatively pure reagents required. Instead, it may be possible to take advantage of

existing technologies, facilities and sources that produce microporous carbon in large scale, by developing a method to enlarge micropores.

One approach is partial gasification of the material, releasing carbon as gases (CO or CO<sub>2</sub>), increasing the pore size but decreasing the yield of product. Over 40 years ago, metal impurities in a carbon feed were shown to catalyze the gasification and promote mesopore volume creation [12]. Several subsequent studies have demonstrated the possibility of promoting the formation of mesopore volume with the addition of metals using steam and/or CO<sub>2</sub> activation of coal or biomass [2,13,14]. The additives promote carbon gasification, and include alkalis such as K, Na, Ca and some metals such as Ni or Fe [13,15,16].

Alkali promotion normally leads to mesopores of size 2–4 nm. For example, Cazorla-Amorós et al. studied the steam activation of a char from almond shell in the presence of Ca, with pore enlargement close to the particle size of CaO, i.e., 2 nm [17]. Some transition metals can also create mesopores. For example, Tomita et al. reported the creation of mesopores of size 10 nm using Ni catalysts during the gasification of char [18]. They observed that the Ni particle size was very similar to the mesopore size created so they suggested that a pitting action of the catalyst during

\* Corresponding author.

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

gasification created mesopores. Similar effects have been reported by Xuejing et al. during the synthesis of nickel catalysts supported on activated carbon [19]. Oya et al. prepared fiber from phenol resin and cobalt acetylacetonate by carbonization at 1173 K followed by steam activation at the same temperature. The resulting activated carbon had some mesopores of size 10–50 nm [20]. Shen et al. have described the incorporation of 3 wt% cerium and/or yttrium to increase the mesopore volume of activated carbon from peach shells by steam activation [21,22]. They reported a mesopore volume increase of 0.46 cm<sup>3</sup>/g with a loading of 1 wt% Ce at an activation temperature of 1143 K. Despite the increase in volume, the pore size distribution was not significantly different from the original material with most mesopores in the range of 4–10 nm.

The work to date has generally focused on the role of metal oxides in gasification, with loadings of 0.1 mol metal oxide per mole carbon, and not on activated carbon production, per se. Higher metal loadings may be required to create larger pores throughout the carbon particles as the metals can become coated with carbon or agglomerated during activation [23,24]. As the metals are expensive, recycling is required to make the process economic. This study describes pore enlargement in several carbonaceous materials by metal catalyzed steam activation. The starting materials had different levels of porosity and included various activated carbon materials and biochar. The initial experiments were performed with ceria to demonstrate that cerium can be recovered and reused, and to determine the effect of the properties of the starting materials on the pore development. Then other metal oxides (Co, Ni, La, and Fe) were tested.

## 2. Material and methods

### 2.1. Materials

The following chemicals were used in this study. KOH flakes (85%) and lanthanum (III) nitrate hexahydrate (99.9%) were purchased from Alfa Aesar (Heysham, United Kingdom). HNO<sub>3</sub> (68–70%) and HCl (36.5–38%) were purchased from VWR International (Pennsylvania, USA). NaOH pellets (97%), hydrogen peroxide solution (30% in water), cerium nitrate hexahydrate (99%), iron nitrate nonahydrate (99.5%), nickel nitrate hexahydrate (98%) and cobalt nitrate hexahydrate (98%) were purchased from Sigma Aldrich (Missouri, USA).

Porous carbonaceous materials with different physical properties and ash contents were chosen for this study. The microporous carbonaceous materials include: 1. delayed petroleum coke (P, Suncor Energy Inc., Alberta, Canada) activated with 1:1, 1:2 or 1:3 KOH:coke mass ratio (PK, P2K, P3K, respectively) at 1023 K for 30 min under 250 cm<sup>3</sup>/min of flowing N<sub>2</sub> (detailed description in Ref. [25]); 2. activated charcoal (Norit, Norit Row 0.8 SUPRA Pellets, Sigma Aldrich, Missouri, USA), and 3. biochar prepared through pyrolysis of Aspen Wood Chips (AW, Alberta-Pacific Forest Industries Inc., Alberta, Canada) at 873 K for 2 h under 200 cm<sup>3</sup>/min flowing N<sub>2</sub> (detailed description in Ref. [26]). The mesoporous carbonaceous materials are 1. commercial activated carbon from lignite coal Colorsorb<sup>®</sup> G5 (G5, Jacobi Carbons Inc., Kamlar, Sweden), 2. delayed petroleum coke (P, Suncor Energy Inc., Alberta, Canada) activated with 1:1 NaOH mass ratio (PNa), and 3. Carbon Black Monarch 120 (CB, Cabot Corp., Massachusetts, USA). All samples were ground and sieved within a range of 150–63 μm and dried at 423 K overnight before use to remove any adsorbed moisture and other volatile species. This particle size was chosen to balance diffusion limitations and complete gasification of the particles.

### 2.2. Metal-catalyzed steam activation

The carbonaceous materials were impregnated with cerium (Ce), iron (Fe), lanthanum (La), nickel (Ni) or cobalt (Co) using metal nitrate salts dissolved in a 50:50 vol% mixture of isopropanol and acetone by wet impregnation. In a typical activation, 1 g of carbonaceous material was loaded with 0.25 g of nitrate salt to give target metal loadings of 8.1–3.5% depending on the metal. A mass (0.25 g) of nitrate salt was dissolved in a volume equal to 150% of the total pore volume of each material, using a 50:50 vol% mixture of isopropanol and acetone. Once the metal salt nitrate was dissolved, the carbon materials were added. The slurries were shaken for 12 h at 250 rpm in an incubating shaker (VWR symphony 5000I, Henry Troemner LLC, USA) and then dried at 350 K for 12 h. For the metal-catalyzed steam activation, the impregnated samples were exposed to steam, which consisted of 5 cm<sup>3</sup>/h liquid water carried by 50 cm<sup>3</sup>/min N<sub>2</sub>. Normally 2.5 g of sample was placed in a ceramic boat within a horizontal tube furnace and heated at 5 K/min to 1073 K under N<sub>2</sub> flow (250 cm<sup>3</sup>/min). Steam was then introduced for 30 min followed by cooling under N<sub>2</sub> flow (50 cm<sup>3</sup>/min) to room temperature (typically 2 h). Experiments with different cerium loadings (3, 8.1 and 16.2 wt%) and different steam exposure times (0, 60, 90 or 120 min) were also performed.

After metal-catalyzed steam activation, an acid washing step was done to leach out the metal. Specifically, 0.5 g of solid was washed with 4 cm<sup>3</sup> of HNO<sub>3</sub> and 2 cm<sup>3</sup> of H<sub>2</sub>O<sub>2</sub> (added dropwise) at 323 K under stirring for 60 min. Then the sample was centrifuged to separate the solid from the liquid, which was kept for recycle experiments. The washing step was repeated several times, in order to leach out all the metal used for activation. Finally, the solids were washed with deionized water until neutral pH, and dried at 323 K overnight. The names of the prepared solids include the name of the carbonaceous material followed by the activation procedure with St for steam activation, and M/St for metal-catalyzed steam activation, where M corresponds to the metal used. For example, sample PK loaded with 8.1 wt% cerium, steam activated and washed is named PK\_Ce/St. If no time is specified with the name, the sample was activated for 30 min. If the sample is followed by “no wash”, then the acid washing step was not done.

The yield was calculated by dividing the mass of product by the initial mass of feed:

$$\text{Yield (\%)} = \frac{\text{Mass of Product}}{\text{Initial mass of feed}} \times 100\% \quad (1)$$

The recycling studies were done with cerium and material PK. The acid solution containing the cerium recovered from the washing process was placed in a beaker and the liquid phase was evaporated under stirring at 293 K. The remaining solid was used for subsequent catalyzed metal steam activation experiments. The resulting samples will be identified as samples activated with recovered cerium.

### 2.3. Sample characterization

N<sub>2</sub> physisorption (TriStar 3000, Micromeritics Instrument, Norcross, USA) at 77 K was used to determine the pore structure of the samples. Before analysis, all samples were degassed at 423 K for 5 h. Pore size distribution (PSD), micropore volume (accumulated volume between 0 and 2 nm) and mesopore volume (accumulated volume between 2 and 50 nm) were calculated using a Non Local Density Functional Theory (NLDFT) Independent Weights method provided by Micromeritics. Using other theories - NLDFT-Dependent weights and 2D-NLDFT - gave similar trends with a difference in pore volumes of less than 10%. The specific surface

Download English Version:

<https://daneshyari.com/en/article/4758053>

Download Persian Version:

<https://daneshyari.com/article/4758053>

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