Preparation of functionalized and metal-impregnated activated carbon by a single-step activation method

Seyed A. Dastgheib [a,*], Jianli Ren [a,1], Massoud Rostam-Abadi [a], Ramsay Chang [b]

[a] Illinois State Geological Survey, Prairie Research Institute, University of Illinois, 615 East Peabody Dr., Champaign, IL 61820, United States
[b] Electric Power Research Institute, 3412 Hillview Avenue, Palo Alto, CA 94304, United States

ARTICLE INFO

ABSTRACT

A rapid method to prepare functionalized and metal-impregnated activated carbon from coal is described in this paper. A mixture of ferric chloride and a sub-bituminous coal was used to demonstrate simultaneous coal activation, chlorine functionalization, and iron/iron oxides impregnation in the resulting porous carbon products. The $FeCl_3$ concentration in the mixture, the method to prepare the $FeCl_3$-coal mixture (solid mixing or liquid impregnation), and activation atmosphere and temperature impacted the surface area and porosity development, Cl functionalization, and iron species impregnation and dispersion in the carbon products. Samples activated in nitrogen or a simulated flue gas at 600 or $1000\,°C$ for 1–2 min had surface areas up to $\sim 800\,m^2/g$, bulk iron contents up to 18 wt%, and surface chlorine contents up to 27 wt%. Potential catalytic and adsorption application of the carbon materials was explored in catalytic wet air oxidation (CWAO) of phenol and adsorption of ionic mercury from aqueous solutions. Results indicated that impregnated activated carbons outperformed their non-impregnated counterparts in both the CWAO and adsorption tests.

1. Introduction

Functionalized and/or metal impregnated activated carbons (ACs) are promising catalysts and sorbents for various industrial applications. For example, iron-impregnated ACs are effective catalysts for Fischer–Tropsch synthesis, water–gas-shift reaction, hydrocracking of heavy oil, removal of trace metals from water, remediation of chlorinated pollutants, catalytic wet air oxidation (CWAO) of phenol and other refractory compounds, and removal of bacteria from water [1–12]. Activated carbons functionalized with halogens (including chlorine) enhance the removal of mercury from coal combustion flue gases [13].

Adsorption affinity and catalytic performance of activated carbon is tailored by surface functionalization or metal impregnation with proper chemical agents [e.g., 14–17]. Functionalized and/or impregnated porous carbon materials are conventionally prepared through separate post-activation stages. Porosity in carbon is first developed by a physical or chemical activation process of a feed material such as coal or biomass. The porous carbon is then functionalized by treating it with a proper chemical agent, either a

gaseous or a liquid phase, in a post activation process [e.g., 14–17]. Metal impregnation of a porous carbon is performed by excess solution, incipient wetness, ion exchange, or chemical vapor deposition techniques followed by a calcination/reduction step [14]. For example, iron-impregnated activated carbons were prepared by a wet impregnation method using ferric chloride solution followed by heat treatment in nitrogen [16]. In an alternative approach, iron-impregnated carbon catalysts were produced by stirring coal powder in $FeCl_3$ solution for 24 h under a controlled pH condition. The slurry then was filtered, washed, and pyrolyzed at $798\,°C$ for 6–60 min in steam [3,4]. In another similar approach, iron-loaded carbon catalysts were prepared by precipitating iron species onto coal followed by devolatalization at $500–950\,°C$ for 30 min and activation in CO_2 at $900–950\,°C$ for 10–30 min [18].

Combining the activation, functionalization, and metal impregnation processes into a single-step process offers a simple and fast method to prepare functionalized carbon sorbents/catalysts in a more cost-effective manner than conventional methods. Single-step methods for activation and metal impregnation of carbon materials include spray pyrolysis (SP) and hydro-thermal treatment (HTT) [5,19–23]. In the SP method, including ultrasonic spray pyrolysis (USP), an aerosol stream containing a mixture of a carbonaceous precursor and a metal catalyst precursor is generated and pyrolyzed at temperatures above $500\,°C$ in <20 s. Porous carbon materials containing well-dispersed iron nanoparticles were prepared by SP methods [19–22]; however, the yield of the carbon product was low because a substantial amount of the carbonaceous

precursor was gasified during the pyrolysis/activation step. In addition, the SP process is energy intensive because a large amount of water associated with aerosol particles must be evaporated during the pyrolysis/activation step.

In single-stage HTT methods, a solution/slurry containing a carbonaceous and a metal precursor is heated to temperatures above the thermal decomposition of precursors to form well-dispersed nano-sized metal species in the composite product. The HTT method requires a long reaction time (e.g., 2 h) and a high-pressure equipment. Furthermore, an additional heat treatment step is needed to increase the product's surface area [5,23].

In this paper, a rapid method to prepare functionalized and impregnated activated carbon from coal is described. This method offers carbon activation, carbon surface functionalization and metal impregnation (AFI) in a single-step process in 1–2 min. Ferric chloride and a sub-bituminous coal were selected as precursor materials to demonstrate porosity development, chlorine functionalization, and iron/iron oxides impregnation of the porous carbon product. Results from this work reveal that porosity development, chlorine functionalization, and iron impregnation can be tailored by adjusting the activation atmosphere and temperature, and precursor composition. Furthermore, potential catalytic and adsorption applications of the carbon materials were explored in wet air oxidation of phenol and adsorption of ionic mercury from aqueous solutions. Results indicated that impregnated/functionalized activated carbons outperformed their non-impregnated counterparts in both the wet air oxidation and adsorption tests.

2. Methodology

2.1. Material preparation

A pulverized sub-bituminous coal (mass mean diameter = ~10 μm) from the Powder River Basin (PRB) in the U.S. and anhydrous iron (III) chloride (Fisher, 97%), as the chemical agent for chlorine functionalization and iron impregnation, were used in this work. Mixtures of coal and ferric chloride were prepared by two methods: solid mixing and solution (liquid) impregnation. In the solid mixing method, a mixture of 1.5 g of the coal and either 0.22 or 0.88 g of ferric chloride was ground together in a grinder for ~2 min. In the solution impregnation method, 1.5 g of the coal was dispersed in 10 mL ethanol, and then either 0.22 or 0.88 g of ferric chloride dissolved in 20 mL deionized water was added. The slurry was dried in air at 105 °C overnight to obtain coal/FeCl$_3$ mixtures containing 12.8% or 37.0% (dry basis) FeCl$_3$.

2.1.1. Pyrolysis and activation experiments

As-received coal sample and coal/FeCl$_3$ mixtures were heated to either 600 or 1000 °C under 500 mL/min of nitrogen or a simulated flue gas (SFG: 10% CO$_2$, 6% O$_2$, 5% H$_2$O, and 79% N$_2$) and held at this temperature for 1 min before cooling under the same atmosphere to room temperature (Fig. 1). Carbon products from the PRB coal were prepared in both nitrogen and SFG atmospheres. In a typical activation/pyrolysis experiment, about 1 g of the coal/FeCl$_3$ mixture was loaded in a Hastelloy boat (25 mm × 125 mm) and kept outside the heating zone (80–120 °C) of a preheated quartz tube (inside diameter = 50 mm, length = 120 cm) for ~50 min while the furnace was heated to either 600 or 1000 °C and the quartz tube was purged with N$_2$ or simulated flue gas. The sample was then pushed to the center of the heating zone of a tubular furnace (length = 60 cm). It generally took about 2 min for the sample's temperature to reach either 600 or 1000 °C (Fig. 2). The sample boat was kept at either 600 or 1000 °C for an additional 1 min before it was pulled out of the heating zone to the cool section of the quartz tube. Cooling time to ~300 °C typically took about 2–4 min (Fig. 2). Both ends
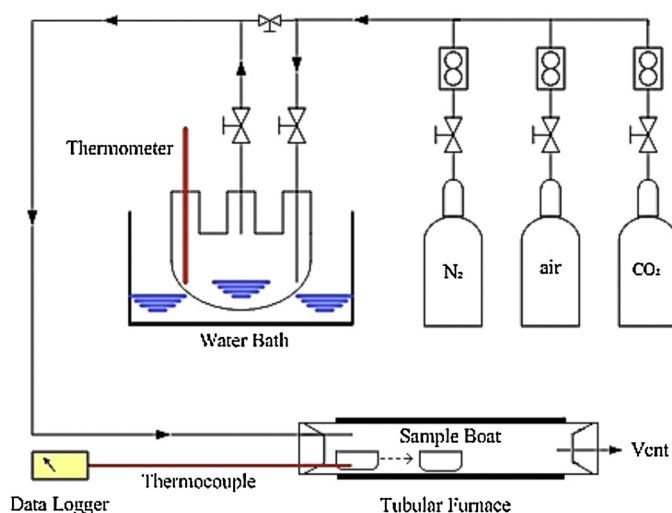

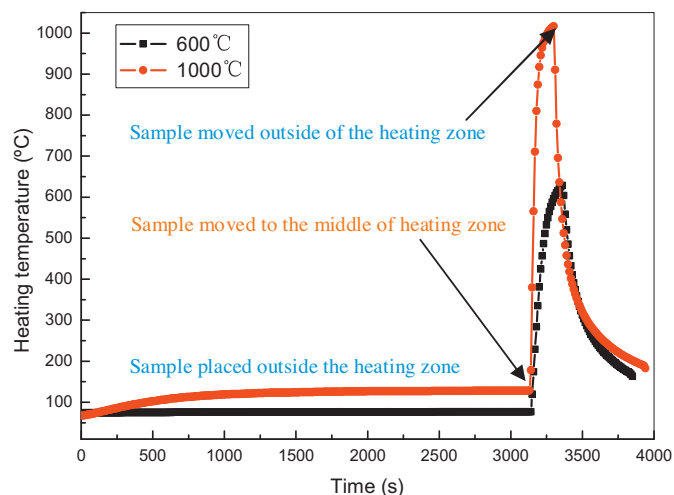**Fig. 1.** Diagrammatic experimental setup for pyrolysis/activation experiments.

Fig. 2. Heating and cooling temperature profiles of the samples for experiments performed at 600 and 1000 °C.

of the quartz tube were covered by rubber stoppers. Teflon tubing inserted in the stoppers allowed the activation/pyrolysis gas enter and exit the quartz tube. A type K thermocouple probe that was touching the sample boat measured the sample temperature. The thermocouple also served to push the sample boat to the middle of the quartz tube, after the initial purge and temperature stabilization period. To avoid air leaks into the quartz tube, the thermocouple probe passed through rubber septa and several fittings connected to the inlet port. A data logger recorded temperatures during the activation/pyrolysis experiments (Fig. 1). Product yield was estimated from the weight of the samples, before and after the pyrolysis. Based on the replicate runs of four different samples, the average relative standard error in the yield data was 3.4%.

2.1.2. Sample identification codes

Samples are identified according to their precursors and preparation methods. PRB precursor is designated as P, solid and liquid mixing/impregnation methods as S and L, 12.8% and 37.0% (wt%) initial FeCl$_3$ content in the PRB coal as 1 and 2, SFG atmosphere as F, and 600 and 1000 °C activation/pyrolysis temperatures as 600 and 1000. For example, sample PFe-S2-600F refers to a sample prepared from a mixture of PRB coal and FeCl$_3$ powders containing 37.0 wt% FeCl$_3$, and activated in the SFG atmosphere at 600 °C; or sample