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Performance of Fe/AC catalyst prepared from demineralized pine bark particles in a microwave reactor

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ABSTRACT

Activated carbon supported iron catalysts derived from pine bark were prepared by different methods using a microwave reactor. The catalyst samples were characterized by physical adsorption of N_2, Fourier Transform Infrared (FTIR) spectroscopy, and Transmission Electron Microscopy (TEM). The catalyst activity was evaluated for catalytic wet peroxide oxidation of phenol at 50 °C. The results showed that the catalyst prepared by preloading the metal precursor to deashed biomass before carbonization and activation in a microwave reactor possessed much higher reactivity than catalyst prepared from other methods. The acid washing to remove ash from biomass eliminated the adverse effect of metals contained in the ash on catalyst, modified the biomass tissue which favored the catalyst dispersion on the biomass. The metal pre-loading to biomass led to a more uniform dispersion of catalyst on activated carbon. The microwave treatment saved energy, shortened preparation time. High catalytic activity for the catalytic wet peroxide oxidation of phenol was observed for catalyst samples prepared from pre-loading the active metal to pre-deashed bark samples.

1. Introduction

Microwave heating, which uses electromagnetic energy with wavelengths between 1 mm and 1 m with corresponding frequencies from 300 MHz to 300 GHz, can be used to heat many dielectric materials. Two frequencies, namely 915 MHz and 2450 MHz, reserved by the Federal Communications Commission (FCC) for industrial, scientific and medical purposes, are commonly used. Microwave heating has some unique characteristics and is quite different in many ways from conventional convective and radiative heating because the heat is generated directly inside the materials through molecular interaction with the electromagnetic field. The advantages of microwave heating include [1]:

(1) Fast and uniform heating. Because microwave can penetrate materials, heat can be generated throughout the volume of the materials. The transfer of energy does not rely on diffusion of heat from the surfaces.
(2) Selective heating. The molecular structure determines its ability to interact with microwaves and thus energy transfer, leading to different microwave absorption rate for different materials.
(3) Improvement of product quality due to avoided degradation of product strength and surface properties caused by exposure to high temperatures.

In the past 30 years, microwave heating, has been used successfully in many chemical industrial processes, such as organic, polymer synthesis [2] and biomass pyrolysis for the production of bio-oil and bio-char [3–5] due to its advantages over conventional heating method.

Recently, the use of microwave for production, regeneration and surface modification of activated carbon has received some attention. Yagmur et al. prepared activated carbon from waste tea by phosphoric acid activation with and without microwave treatment, the results showed that the microwave induced activation method provided time and energy savings, and the surface area and pore volume were improved by the microwave treatment [6]. Ania et al. compared the regeneration of activated carbon by two different heating methods (a single mode microwave oven and a conventional electric furnace), and found the microwave treatment shortened the regeneration time considerably and preserved the porous structure of regenerated activated carbon more effectively than conventional electric furnace [7]. The study of Nabais et al. showed that microwave thermal treatment caused a reduction in both the size and volume of micropores, and, more importantly, it modified the surface chemistry of the Activated Carbon Fibers (ACFs) with the production of pyrone groups [8]. There

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has not been reported study on microwave-assisted preparation of catalysts supported on Activated Carbon (AC). In addition, activated carbon supported catalysts are usually prepared by impregnating the carbon support with metal salt solution followed by calcinations, with little research on directly using biomass as the support matrix to prepare activated carbon supported catalyst [9]. Sakata et al. prepared activated carbon supported copper and zinc catalysts by preloading catalyst precursors onto the sawdust particles, and the results showed that catalyst particles can be better dispersed on the activated carbon surface which led to higher catalytic activity compared to conventional method by loading catalyst to the activated carbon particles [9].

Heterogeneous Catalytic Wet Peroxide Oxidation (CWPO) is one of the most promising technologies for the remediation of concentrated and biotoxic wastewater [10,11]. Novel materials such as iron containing zeolitic materials [12] or SBA-15 based nanocomposites [13] have shown a great potential for the CWPO of phenolic aqueous solutions. In this process, once added to the solution, H_2O_2 is believed to decompose thermally by the breakdown of the oxygen—oxygen bond, resulting in the generation of two hydroxyl radicals. This results in the availability of free radicals at the very beginning of the process, thereby enhancing the degradation of the parent compound and eliminating the induction period.

The work carried out by Zazo et al. showed that around 85% of TOC removal efficiency was achieved when Fe/AC catalyst was used in the CWPO process [14]. Rey et al. showed that catalysts with a more uniform Fe distribution had a higher oxidation activity than those with an internal (egg-yolk type) or external (egg-shell type) distribution [15]. The influence of AC surface characteristics on phenol degradation in this process makes it difficult to predict the behavior of a given activated carbon, because the decomposition of H_2O_2 into undesirable O_2 instead of reactive $\cdot OH$ radicals strongly depends on the catalyst surface structure and accessibility of the oxygen groups [16]. Recently nano metal particles have been applied as a high efficiency catalyst to CWPO process by many researchers, as reviewed in detail by Amarajothi Dhakshinamoorthy et al. [17].

We have been exploring the utilization of pine bark, a waste forest byproduct abundantly available in Canada, and demonstrated that bark could be upgraded to high quality biomass by lowering the ash content. In this paper, we explored the use of demineralized Mountain Pine Beetle (MPB) killed pine bark as the support precursor to prepare Fe/AC catalyst in a microwave reactor, combining the unique features of microwave heating and preloading catalyst precursors to biomass. The catalytic activity of these catalysts was then evaluated using Catalytic Wet Peroxide Oxidation (CWPO) of phenol as a model reaction and compared with the catalysts prepared by conventional heating and metal impregnation methods.

2. Materials and methods

2.1. Sample preparation

2.1.1. Raw materials preparation

The raw material of Pine Bark (PB) used in this study was collected in British Columbia, Canada. All samples were washed to have soil removed, followed by oven dried at 378 K to a constant weight and then ground in a hammer mill. The fraction of particle size between 0.40 and 0.95 mm was then collected for the use in this study.

2.1.2. Demineralization

To remove ash or inorganic elements contained in biomass, dilute acid leaching as developed in our previous study [18] was used. Demineralization conditions were: leaching temperature (25 °C); nitric acid concentration (0.5 M); leaching time (8 h); mass ratio of nitric acid solution to pine bark (20) and particle size (0.40–0.95 mm). After soaking with acid solution, samples were filtered and washed with de-ionized water until a constant pH was reached, followed by oven drying at 105 °C to a constant weight.

2.1.3. Impregnation

Incipient wet impregnation in aqueous solution (IMPA) was used in this study to prepare activated carbon supported iron catalyst with $Fe(NO_3)_3{\cdot}9H_2O$ as the catalyst precursor. The theoretical ratio of iron to activated carbon is 10% by weight. After impregnation, the slurry was stirred for 24 h, and then dried in air at 105 °C to a constant weight.

2.1.4. Microwave pyrolysis

The pyrolysis is carried out in a microwave reactor consisting of five major components: a microwave source, the transmission duct, a quartz reactor, a data log system, and a microwave leakage detection system, as shown in Fig. 1. The microwave generator has a frequency of 2450 MHz, with a peak power output of 1200 W. The cylindrical quartz reactor has a diameter of 43 mm and a height of 250 mm. For the safety concern, both ends of the reactor are sealed with o-ring and stainless steel sealers. The microwave leakage is monitored by a leak detection system. To accurately measure the reactor temperature, an infrared pyrometer was installed, and the measured temperature was used to control the reactor temperature via controlling the microwave power output via a PID controller. The unit also includes a water cooling system to capture the unadsorbed microwave. A nitrogen carrier gas is used to provide inert atmosphere and to prevent the pyrometer from fouled by the condensed bio-oil. A vapor condenser is used to cool the pyrolysis vapor and condense the tar, and a data logging system is used to record the reactor temperature and microwave power output.

Because dry biomass has a low microwave absorption rate, 2 g biochar of $\sim$2 mm in diameter was premixed with 8 g pine bark samples to improve the microwave absorption rate so as to achieve the desired target temperature in each experiment.

The premixed sample was loaded into the quartz reactor, and N_2 as a carrier gas was turned on at a flow rate of 100 mL/min for 30 min to drive out the air. During the experiment, the microwave power was initially set to 1000 W and the power varied according to the difference between the reactor temperature and the set temperature automatically by a Programmable Logic Controller (PLC). After the measured temperature reached the set point, the power decreased to a fixed value to maintain the reactor temperature to the set temperature point. After carbonization, the carrier gas was switched to CO_2 for activation. At the end of the experiment, the microwave generator was shut down and the carrier gas was switched back to N_2 until the reactor was cooled down to room temperature.

For the purpose of comparison, three other catalyst samples were prepared from the microwave reactor and four other catalyst samples were prepared from an electric furnace following different preparation procedures at 450 °C with 10% Fe loading. The details of the preparation methods were documented in Table 1.

The other samples were prepared following those procedures. For samples M3 and M4, activated carbon was first prepared following the same pyrolysis procedure in a microwave. The prepared activated carbon was then impregnated with $Fe(NO_3)_3$ using the IMPA method. After impregnation, the slurry was stirred for 24 h, and then dried in air at 105 °C to a constant weight before calcined in the microwave furnace. For samples E1 and E2, the demineralization and impregnation procedures were the same as M1 and M2, but the samples were carbonized and activated in an electric