

CATALYTIC WET AIR OXIDATION OF PHENOL BY SURFACE-MODIFIED ACTIVATED CARBONS

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Introduction

Activated carbons are primarily used as effective and inexpensive adsorbents for various liquid or gas phase applications. In addition to this more conventional application, they can also be used as catalyst supports or even direct catalysts. This is due to their high porosity and specific chemical characteristics such as oxidation/reduction and electron transfer capabilities. Furthermore, comparing to many conventional catalysts, they are inexpensive alternatives and have a high level of chemical inertness and thermal stability.

Some activated carbons have been utilized for catalysing gas-phase reactions in industry, for example in the production of phosgene and oxidation of SO₂, NO, and H₂S in air pollution control [Radovic and Rodriguez-Reinoso, 1997]. Researchers also reported effectiveness of carbon materials for catalysing other gas-phase reactions such as dehydrogenation of alkylbenzenes [Pereira et al., 1999]. However, the use of activated carbon catalysts are less explored in liquid-phase reactions.

The pioneering work of our research group [Fortuny et al., 1998] as well as other reports [as summarized by Stuber et al., 2005] indicate that activated carbons can be promising catalysts for the Catalytic Wet Air Oxidation (CWAO) of phenolic compounds in waste water treatment. The ideal activated carbon catalyst should have a maximum phenol conversion and an appropriate selectivity for minimizing the production of toxic intermediates. In order to develop effective activated carbon catalysts for economically feasible processes, it is necessary to understand the impact of physico-chemical properties of activated carbons on their catalytic activities. This important issue is less explored and deserves further investigation that is the main goal of this paper.

Surface chemistry of activated carbon plays a crucial role on its catalytic activity in the CWAO reaction. As known in the carbon literature, depending on the origin and mode of preparation, various surface functionalities such as oxygen-, nitrogen-, and phosphorous-containing groups, plus inorganic elements/species (e.g., calcium and iron oxides/hydroxides) can be found on the carbon surface. Depending on the characteristics of these surface organic or inorganic groups, plus the intensity of the π electrons of aromatic sheets, activated carbons might have different levels of reactivity for different reactions.

In addition to the importance of surface chemistry, textural porosity of activated carbon is also an important factor that cannot be ignored. For the access of reactants to the reactive sites the first issue is the accessibility. In other words, only the reactive sites on the surface that is accessible to reactive molecules are useful for reactions. This depends on the size and geometry of reactant molecules and pore size distribution of the activated carbon. The extent of the blockage of carbon pores by reaction products (for example as a result of polymerisation) and therefore deactivation of the catalyst, can also be related to the carbon porosity.

To understand the impact of the surface chemistry and textural porosity of activated carbon on its catalytic performance for the CWAO of phenolic compounds, a systematic study has been performing in our laboratories. This is to particularly understand the importance of surface area and pore size distribution, mineral content (especially iron), and various surface functionalities on the phenol adsorption and conversion.

Experimental

Materials. Virgin activated carbons used in this study were: (1) HD, HD4000, a mesoporous coal-based activated carbon obtained from Norit Inc. (USA); and (2) ME, a microporous coal-based activated carbon, purchased from Merck (Spain). Obtained carbons were crushed and the 25–50 mesh sizes were separated, then repeatedly washed with deionised water to remove all the fines, and finally oven-dried overnight at 105°C. Activated carbons were treated, using a combination of the following surface modification protocols:

Demineralization. Extensive washing with 1N HCl followed by washing with deionised water. The objective of this treatment was to significantly reduce the inorganic content (including iron) of activated carbons.

Steam treatment. Carbon samples were heat treated under steam at 800°C for 5 h (until reaching an approximate burn-off of 45%) for opening the pores and increasing the mesoporosity. This treatment was performed with the help of Dr. Karanfil's research group at the Environmental Engineering and Science Department of Clemson University (South Carolina, USA).

Hydrogen treatment. Hydrogen treatment at 900°C for 3 h was performed to remove surface functionalities under a reactive and reductive atmosphere and also stabilize the carbon surface against the re-oxidation as a result of air exposure.

A list of modified activated carbons is shown in Table 1.

Table 1. Description of modified activated carbons.

Activated Carbon	Description
HD	Virgin HD4000
HDD	Demineralized HD
HDDH	Hydrogen-treated HDD
HD DS	Steam-treated HDD
HDDSH	Hydrogen-treated HD DS
ME	Virgin Merck
MED	Demineralized ME
MEH	Hydrogen-treated ME
MEDH	Hydrogen-treated MED

Adsorption isotherms. Phenol adsorption isotherms were obtained at 20°C ($\pm 2^\circ\text{C}$) in oxic conditions. Solutions with phenol concentrations ranging between 0.5 and 6.0 g/l were used to evaluate the adsorption capacity at high concentrations. In each case, 0.5 g of AC was allowed to equilibrate with 100 ml of phenol solution at different concentrations. They were stirred for 2 h, and left 0.5 h to let the AC to settle. The equilibrium time was determined based on the preliminary kinetics studies of selected samples. The final concentration of the samples was measured by HPLC (high pressure liquid chromatography).

CWAO experiments. These experiments were carried out in a fixed bed reactor, operating in trickle flow regime to reduce polymerisation reactions, which are prevalent in slurry systems as previously demonstrated. This system is later referred to as TBR system. The experimental set-up consisted of a 6 l stirred glass tank for the liquid feed solution, which was connected to a high precision metering pump (Eldex, Recipro HP Series model AA-100-S-2 CE) that could deliver up to 500 ml/h at a maximum pressure of 350 bar. This pump fed a trickle bed reactor which was a titanium tube (20 cm in length and 1.1 cm ID) filled with the activated carbon. A thermocouple was inserted axially into the reactor to measure the temperature inside the bed. The active carbon was retained by a stainless steel mesh at the bottom of the reactor. The reactor was placed in a temperature controlled air convection oven ($\pm 1^\circ\text{C}$). The air used as oxidant in the reaction was supplied from a high pressure tank equipped with a pressure regulator. The gas and liquid streams were mixed and preheated before entering the reactor. There were two vessels to separate the outlet effluent, and a 2 ml tube for taking samples. A rotameter placed at the end of the line allowed measuring the air flow rate at the exit of the reactor. All the experiments were conducted for about 60 h. The air flow rate was held constant at 2.4 ml/s. The liquid space velocity was set to 8.2 h⁻¹ which is equivalent to a space time of 0.12 h, according to the weight of the catalytic bed (~7 g). Phenol feed concentration was always 5 g/l. The experimental conditions were fixed at a temperature of 140°C and 2 bar of oxygen partial pressure, giving a total working pressure of 13.1 bar. Outlet liquid samples were periodically withdrawn and stored at ~4°C until they were analyzed by HPLC. Also pH was measured for all samples.

Characterization of activated carbons. Selected physico-chemical characteristics of activated carbons were determined according to the following methods:

Surface area analysis. Surface area and porosity of activated carbons were estimated from nitrogen isotherm at 77 K using a Micromeritics 2020 ASAP instrument. Surface area was determined from BET equation, total pore volume from the near saturation uptake (at the relative pressure of 0.98), micropore volume from the Dubinin-Radushkevich equation, and volumes of meso plus macropores from subtracting the micropore volume from the total volume.

pH of point of zero charge (pH_{pzc}). Mass titration method was used to determine the point of zero charge of each sample. 5 wt % carbon slurries in deionised water were prepared, then shaken for 24 h and the final pH of the slurry was measured and taken as the pH_{pzc} .

Mineral content. Samples were digested in concentrated nitric acid by a microwave digestion equipment. Diluted solutions were analyzed by Inductively Coupled Plasma (ICP) atomic emission spectroscopy.

Results and Discussion

Characteristics of activated carbons. Selected physicochemical characteristics of virgin and modified activated carbons are shown in Table 2. These results will be briefly discussed below.

Table 2. Physical characteristics of activated carbons.

Sample	pHpzc	SA _{BET} (m ² /g)	V _{mic} D-R (cm ³ /g)	V _{tot} (cm ³ /g)	V _{mes+mac} (cm ³ /g)
HD	5.2	681	0.279	0.774	0.495
HDD	4.0	816	0.337	0.852	0.515
HDDH	9.4	732	0.301	0.789	0.488
HDDS	7.6	1046	0.429	1.020	0.591
HDDSH	10.3	1018	0.403	0.997	0.594
ME	7.4	1261	0.473	0.610	0.137
MED	6.9	1272	0.484	0.592	0.108
MEH	10.7	1213	0.451	0.646	0.195
MEDH	10.3	1275	0.490	0.685	0.195

Surface area and porosity data indicate that HD is a mesoporous activated carbon, while ME is a predominantly microporous carbon (Table 2). The objective of steam treatment was to enhance porosity while the objective of hydrogen treatment was to remove surface functionalities, particularly oxygen-containing acidic groups, and stabilize the carbon surface for resistance to re-oxidation upon the exposure to the atmospheric air or during the adsorption/wet oxidation experiments. Data shows that steam treatment had a more significant impact on surface area and porosity of carbons, comparing to hydrogen treatment and demineralization.

The objective of acid treatment was to remove minerals (particularly iron) that might have some impact on the catalytic activities of carbon. Iron content of both virgin HD and ME carbons was about 0.3 wt%. Demineralization decreased the iron content for both carbons to half of the initial value. Iron content of MEH was also close to that of the ME.

pHpzc values show that HD has a slight acidic to neutral surface while ME has a neutral surface. For both carbons demineralization had a small impact on the surface acidity. High temperature steam treatment increased the surface basicity of HHD carbon. In all cases hydrogen treatment produced a highly basic surface. High temperature hydrogen treatment dissociates majority of the surface oxygen groups and significantly decreases surface polarity.

Adsorption isotherms. Phenol adsorption isotherms of different activated carbons are shown in Figure 1. It should be noted that although the experiments were performed under oxidic conditions but due to the short equilibrium time (~2 h) of experiments the phenol polymerization was not significant, as confirmed in earlier studies.

Overall, the phenol removal of ME carbons was higher than that of HD carbons, primarily due to higher micropore volume. It is believed that for adsorption of small size organic compounds a higher micropore volume will enhance the uptake, because of the overlapping potential effects of adsorption in carbon micropores with sizes close to the adsorbate size [e.g., Karanfil and Dastgheib, 2004].

In literature it is suggested that adsorption of small-size organic compounds is reduced by an increase in the surface polarity of activated carbon. Surface polar and hydrophilic sites (including oxygen groups and metal species), particularly those located at the entrances to the carbon micropores, act as centers for formation of water clusters that hinder the access of the synthetic organic adsorbates to the adsorption sites [e.g., Karanfil and Dastgheib, 2004]. Therefore, a reduction in the surface hydrophilicity expected to increase the adsorption of phenol. This might be the reason for increase in the phenol adsorption by HD and ME as a result of demineralization. As previously mentioned, the mineral contents of MED and HDD were almost half of ME and HD, respectively.

Data indicate that hydrogen treatment, except for HDDS (steam-treated carbon), did not significantly increase the phenol uptakes. A comparison of HDDS and HDDSH characteristics indicates that surface area and pore volume data of both carbons are almost identical and their difference is only in their surface chemistry. This suggests that considerable reduction in the surface polarity (mainly from removal of acidic oxygen functionalities) was occurred only for the HDDS carbon. Further characterizations are needed to fully understand the observed results.

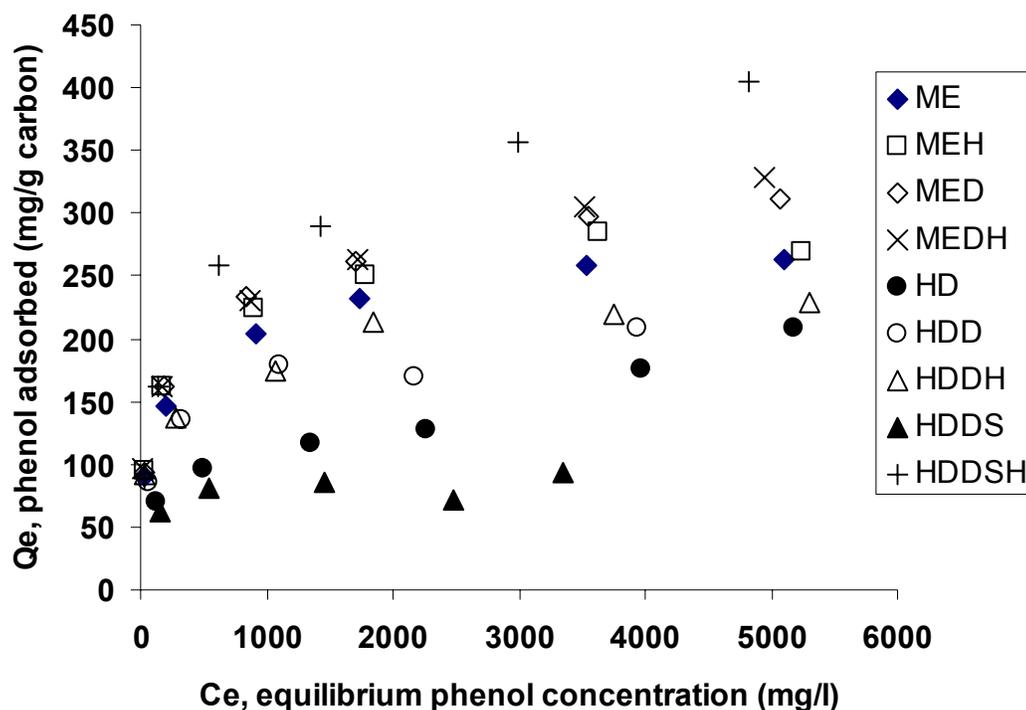


Figure 1. Adsorption isotherms of phenol by activated carbons at 20°C.

Catalytic performance of carbons in the TBR system. The results of CWAO of phenol in TBR system is shown in Figure 2. Phenol disappearance during the first ~10 h is primarily from the adsorption, while later phenol removal after ~20 h (that reaches a steady level) can be attributed to mostly catalytic oxidation.

Overall, ME carbons showed a higher phenol conversion comparing to HD carbons that might suggest the importance of microporosity and a high micropore volume for the phenol conversion.

Results indicate that for both microporous and mesoporous carbons (i.e., ME and HD) the most significant changes are observed after the demineralization treatment (Figure 2). Reducing the iron content of ME and HD by 50% of the original amount, decreased the steady state phenol conversion considerably, that is indicative of catalytic effect of iron for phenol oxidation as suggested in the literature [Quintanilla et al., 2006]. Further high temperature heat treatment of MED and HDD under hydrogen did not improve the performance of the activated carbons. Figure 2 also shows that hydrogen treatment of HDD and ME did not increase the phenol disappearance rate.

Similarly, steam treatment of HDD did not considerably change the phenol conversion despite an increase in the micropore volume. However, a considerable enhancement in the conversion was observed after hydrogen treatment of HDDS. This suggests that a combination of steam treatment (to increase the microporosity) followed by high temperature hydrogen treatment (to reduce the surface acidity and stabilize the surface to resist to re-oxidation) might be an effective method to increase the catalytic activity of activated carbon for phenol oxidation.

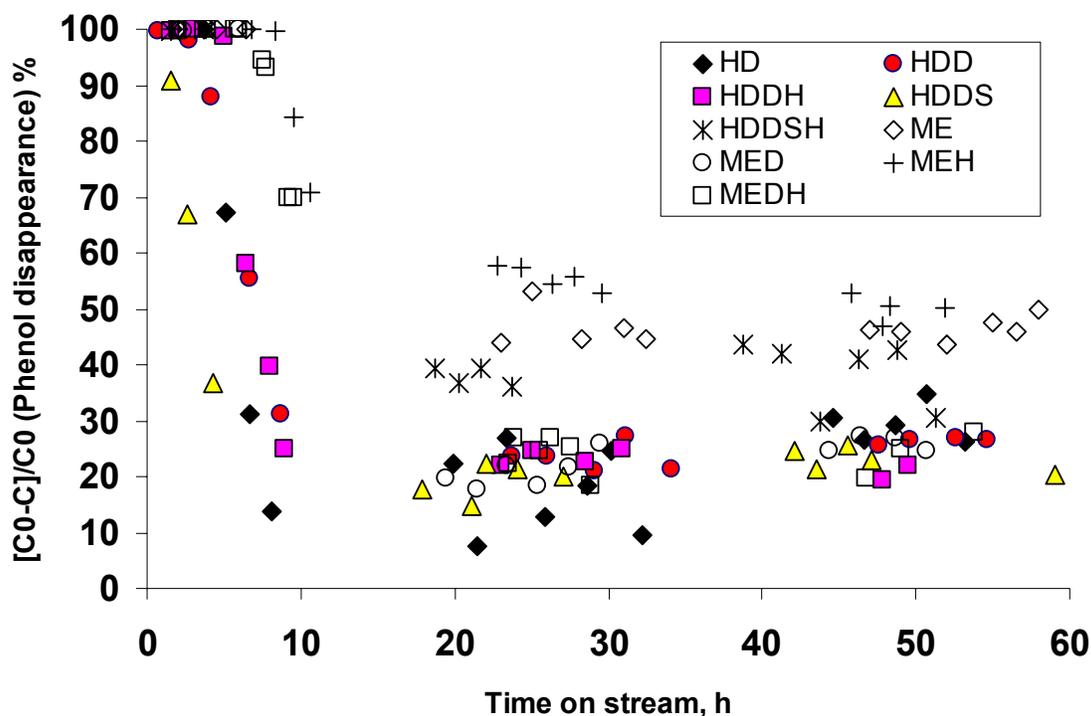


Figure 2. Phenol removal/conversion by different activated carbons in the TBR system at 140°C, 2 bar of oxygen partial pressure and 0.12 h of spatial time.

Conclusions

In this study two microporous and mesoporous activated carbons were subjected to a combination of demineralization, hydrogen treatment, and steam treatment. Batch adsorption isotherms and continuous wet

air oxidation experiments for phenol solutions were conducted. Results of this study indicate that phenol adsorption can be increased by demineralization and in some cases by high temperature hydrogen treatment. Increase of micropore volume and decrease of surface polarity can enhance the phenol adsorption.

On the other hand, it appears that the most significant parameter that controls the phenol conversion in oxidation reactions is the iron content. Data also suggests that a combination of steam treatment (to increase the microporosity) followed by high temperature hydrogen treatment (to reduce the surface acidity and stabilize the surface to resist to re-oxidation) might be an effective method to increase the catalytic activity of activated carbon for phenol oxidation.

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