Catalysis Today 212 (2013) 31–37

Contents lists available at SciVerse ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Oxidative modifications of rice hull-based carbons for dibenzothiophene adsorptive removal

G.X. Yu[a,*], M. Jin[a], J. Sun[b], X.L. Zhou[b], L.F. Chen[c], J.A. Wang[c,**]

[a] School of Chemistry and Environmental Engineering, Jianghan University, Wuhan, Hubei 430056, PR China
[b] School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, PR China
[c] ESIQIE, Instituto Politécnico Nacional, Av. Politécnico S/N, Col. Zacatenco, 07738 México, D.F., Mexico

ARTICLE INFO

Article history:
Received 14 February 2012
Received in revised form
12 September 2012
Accepted 18 September 2012
Available online 15 November 2012

Keywords:
Rice hull
KOH-activation
Adsorptive desulfurization
Oxidative modification
Carbon surface chemistry

ABSTRACT

Four oxidative modifications using concentrated nitric acid, concentrated sulfuric acid, peracetic acid, and hot air, were employed to treat the rice hull (RH) activated by KOH at 750 °C, which produced four RH-based carbon materials with different surface chemical properties. The textural structures, surface chemical properties and surface topography were respectively characterized by N_2 adsorption, Boehm titration, Fourier transmission infrared (FT-IR) and scanning electron microscopy (SEM) techniques. Oxidative modifications resulted in changes of both the textural structures and the surface chemistry properties. Experimental results showed that the DBT adsorption behavior of RH-based carbon adsorbents fitted well the Langmuir isotherm equation. The DBT adsorption capacity was strongly influenced by the oxygen containing acid groups on the samples, and an excellent correlation between DBT adsorption capacity and the amount of the strong acid groups was observed, indicating that the amount of the strong acidic groups on RH-based carbons play the most important role in DBT adsorption. It was postulated that the formation of donor–acceptor complexes between the adsorbent and the adsorbate was largely responsible for the significant improvement of the DBT adsorption after oxidative modifications.

1. Introduction

Nowadays, it is commonly recognized that it is difficult to use the conventional hydrodesulfurization (HDS) technology for deeply reducing the sulfur concentration from the liquid hydrocarbon fuels, especially diesel fuel, to a level less than 30 ppm, to meet the environmental protection requirements [1]. In addition, due to steric hindrance toward active sites, the conventional HDS catalysts are less effective in the treatment of dibenzothiophene and its derivatives (DBTs) [2]. As a result, various deep desulfurization methods, such as ionic liquid extraction [3], oxidation [4–8], and adsorption [7–32], have been developed as an alternative or complementary desulfurization technology to produce ultra-low-sulfur diesel (ULSD).

The adsorptive desulfurization seems promising because it has a capability to reduce fuel to practically zero sulfur level. Various adsorbents have been reported, such as zeolites [9], activated alumina [10,11], and carbon-based adsorbents [12–32]. Among these adsorbents, carbon-based adsorbents have attracted much attention because of their proper textural properties like large surface area and satisfactory porous structure, and the abilities for surface chemical properties modification, and thus exhibiting high selectivity in the removal of dibenzothiophenes (DBTs) [13–19]. In addition, these carbon-based adsorbents can be prepared using a wide range of sources with relatively low cost.

Because the hydrophobic surface of aromatic components in liquid fuels can decrease aromatic organosulfurs adsorption on the surfaces of carbon adsorbents, some modifications used to improve the adsorption performance become necessary [13–19]. Some researchers [13–19,22–32] reported that introducing acidic groups to the surface of carbon can significantly enhance the adsorption performance of the aromatic organosulfurs and/or DBTs, which are probably related to acid–base interactions of slightly basic thiophenes with oxygen-containing acidic groups incorporated to the carbon matrix [5,15,16,31]. Moreover, the textural structures of adsorbents usually influence the adsorptive separation of DBTs from diesel fuel. It was reported, for example, that the mesopores would speed up the adsorption rate of DBT on activated carbon via increased kinetics of adsorption [20,22–28]. Some results also demonstrated that ultra-micropore volume is critical to achieve a high capacity of DBTs owing to strong dispersive interactions in pores similar in size to the adsorbate molecule [21–24,28].

Rice hull (RH) is a major by-product of the rice milling industry and one of the most commonly lignocellulosic materials with

---

* Corresponding author. Tel.: +86 027 84226806; fax: +86 027 84237379.
** Corresponding author. Tel.: +52 55 57296000x55261; fax: +52 55 55862728.
E-mail addresses: guoxianyu828@yahoo.com.cn (G.X. Yu), jwang@ipn.mx (J.A. Wang).

0920-5861/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cattod.2012.09.020

high ash content. The worldwide annual RH output is about 80 million tons [33]. In many countries, RH is usually used as a low-rank energy resource and even burnt off in the field or discarded, resulting in unfavorable effect on the environment. In this work, RH was used as starting material to prepare carbon-based adsorbents for adsorptive removal of DBT from DBT-containing n-octane solution. RH-based (RH750) and other four modified RH-based carbon adsorbents after oxidation treatment were prepared. They were respectively characterized by N_2 adsorption–desorption isotherms, Boehm titration, FT-IR, and SEM. The adsorption performances were investigated in order to obtain the fundamental understanding of the roles of textural structures and the surface functional groups of the samples in the adsorptive desulfurization, which are crucial in the design of a novel carbon-based adsorbent for deep desulfurization.

2. Experimental

2.1. Preparation of RH750 adsorbent

The starting carbon material (RH) used in this study was provided by Yu Men Rice Mill, China. The RH material as received was first washed with distilled and de-ionized water, and then dried in an oven at 110 °C for 12 h. Afterwards, the dried RH was grounded in a pulverizator and the mixtures were sieved. Only the fractions with particle diameter smaller than 0.25 mm were collected and used for the preparation of adsorbents.

KOH activation is usually applied in the preparation of carbon materials with high surface area from different precursors such as pitch, coal, needle coke, and biomass. In this work, the dried RH sample was mixed with 45 wt.% of KOH solution at a weight ratio of 1:3, and the slurry mixture was dried at 100 °C for 24 h. Then, the dried slurry was placed into a muffle furnace and heated at 750 °C for 1 h at a temperature increasing rate of 2.5 °C/min without any inert gas protection. Finally the KOH activated RH sample was cooled to room temperature in air. The sample was washed with deionized water until the pH value of filtrates was 7. Afterwards it was dried at 110 °C for 12 h. The dry sample was grounded and the particles with diameter smaller than 100 meshes were collected and stored for use. The obtained sample was labeled as RH750.

2.2. Oxidative modifications of RH-based carbon adsorbents

Oxidation with nitric acid: 40 g of RH750 and 200 ml of a concentrated nitric acid (68 wt.%) were mixed in a 500 ml glass conical flask with an electric stirrer. The mixture was kept at 40 °C for 24 h, and then filtered to remove the solution. The nitric acid treated RH750 was further washed with the distilled water until the filtrate became neutral. The filter cake was dried at 110 °C in a vacuum oven for 36 h, and then, was stored in a glass bottle with a cover before use. Nitric acid-oxidized RH750 was labeled as RH750-HN.

Oxidation with concentrated sulfuric acid: 40 g of RH750 and 200 ml of a concentrated sulfuric acid (98 wt.%) were mixed in a 500 ml glass conical flask with an electric stirrer. The mixture was kept at 40 °C for 24 h, and then, filtered to remove the solution. RH750 was filtered, thoroughly washed with deionized water, dried at 120 °C, and stored in a sealed container. Concentrated sulfuric acid-oxidized RH750 was labeled as RH750-HS.

Oxidation with peracetic acid: 40 g of RH750 and 200 ml of peracetic acid (38 wt.%) were mixed in a 500 ml glass conical flask with a electric stirrer. The mixture was kept at 40 °C for 24 h, and then filtered. The filtered solids were thoroughly washed with deionized water, dried at 120 °C, and stored in a sealed container. Peracetic acid-oxidized RH750 was labeled as RH750-HC.

Air oxidation treatment: 40 g of RH750 was placed in a crucible within a muffle furnace. The sample was treated in air for 3 h at 350 °C. The air treated RH750 was labeled as RH750-HT.

2.3. Characterization of RH-based carbon adsorbents

BET surface areas of the samples were measured by N_2 physisorption at 77.3 K (ASAP 2010, Micromeritics). Before the experiment, the samples were heated at 120 °C and then outgassed at this temperature under a vacuum of 10^{-5} Torr for 5 h. The micropore volume (V_{Micro}) was measured by BJH method and the total pore volume (V_{Total}) was calculated from the volume of adsorbed nitrogen.

Fourier transform infrared spectra (FT-IR) were recorded between 4000 and 400 cm^{-1} (Bruker IES-88 FT-IR analyzer) to characterize the surface feature of the samples. The FT-IR spectra were recorded using KBr wafers containing 0.5 wt.% of the sample. These wafers were dried overnight at 120 °C before the spectra were recorded. The spectra were obtained by scans of 64 with a resolution of 4 cm^{-1}.

The morphology of the samples was detected on a scanning electron microscope (JSM-6360LV). The images were generated in the back scattered electron signal mode, which yielded better quality pictures. In some cases, where a higher resolution was required, the settings were changed to the secondary electron mode.

2.4. Boehm titration

For carbon materials, surface acid properties are often characterized by Boehm titration [34]. Each of the adsorbent samples (0.1 g) was separately put into three 100 ml cone-shaped flasks with corks. Then 25 ml of 0.1 mol/l sodium hydrogen carbonate, sodium hydroxide were respectively added to each flask by using drip tubes. The flasks were laid in a shaker at 25 °C and shaken for 1 h, and then were aged for 48 h. The solids were filtered and washed using a proper amount of de-ionized water and 50 ml of 0.1 mol/l hydrochloride solution to remove off excessive free bases. The filtrate with sodium hydrogen carbonate must be heated for 0.5 h to remove off carbon dioxide. 0.1 mol/l of sodium hydroxide solution was used to reversely titrate the excessive acid until the solution looks pale red with phenolphthalein as an indicator.

The amount of total acidic groups on the adsorbent surface was expressed as the consumed amount of sodium hydroxide. The strong acidic groups were expressed as the consumed amount of sodium hydrogen carbonate, whilst the amount of the moderate strong acidic groups and the weak acidic groups were expressed as the difference of consumed sodium hydroxide and sodium hydrogen carbonate.

2.5. Surface pH of RH-based carbon adsorbents

0.1 g sample of dry adsorbent powder was added to 20 ml of distilled water without CO_2 and the suspension was kept in a plastic bottle and shaken periodically for two days until the pH value was stable. The final pH of the slurry was indicated as the surface pH of the solid.

2.6. DBT adsorption performance on the RH-based adsorbents

To examine the DBT adsorption equilibrium of the above samples, both 25 g of the model oil with an initial sulfur concentration of 300 ppm and 0.03–0.1 g of adsorbent was simultaneously added to a flat bottom flask. The mixture was firstly stirred at 25 °C for 12 h, and then was filtrated. The amount of DBT captured over the adsorbent during a period of 12 h was expressed as sulfur adsorption amount. Sulfur compound was analyzed by GC920-FPD gas