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Green acid catalyst obtained from industrial wastes for glycerol etherification

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ABSTRACT

In this work several carbonaceous wastes (glycerin (G), waste coffee grounds (WC) and polyethylene terephthalate (PET)) were successfully used as precursors to obtain carbon-based catalysts to transform crude glycerol (from biodiesel production) into value added compounds through glycerol etherification. The X-ray diffraction data showed that the produced carbons are amorphous materials. MEV/EDS analyses showed much dispersed surface groups with an increased amount of sulfur (3.5 to 8.2%). Very promising results were obtained for glycerol etherification, reaching about 80% conversion and a high selectivity for the MTBG species (3-tert-butoxy-1,2-propanediol). The catalysts obtained from PET and WC wastes lead to the highest glycerol conversion and selectivity for MTBG, probably due to the higher acidity. These successful results suggest that these catalysts can be applied for glycerol waste conversion in order to obtain value added compounds.

1. Introduction

The development of new materials with high performance and reuse ability has motivated the researches to produce value added catalysts to be used in several catalytic processes [1–3]. Carbonaceous materials are interesting solids to be used in heterogeneous catalysis because of their extraordinary textural characteristics such as tunable and uniform pore sizes and high surface area [4]. Nevertheless, the carbon production generally faces the problem of the lack of raw material to be carbonized and transformed. Thus, the transformation of renewable waste materials into carbonaceous materials that can be applied in different industrial processes, especially those involving adsorption and catalysis, is of great technological importance.

Approximately 8 million tons of coffee are produced globally each year, leading to a large amount of residue generation, such as the waste coffee grounds [5]. The waste coffee grounds offers a viable feedstock for carbon production, since this solid presents high carbon content, typically higher than 50% [6]. Another important carbonaceous waste which is generated in a large extent during the biodiesel production is the glycerin, corresponding to about 10 wt.% of the total biodiesel production [7]. In addition, the increasing world use of PET polymer leads to a considerable increase in the residue generation. The PET is one of the polymers most found in the solid urban residues [8].

Therefore, the use of waste carbonaceous solids such as waste coffee grounds, glycerin and PET can be considered as an interesting alternative to overcome the problem of the lack of raw material to the carbon production. Furthermore, even carbon-based materials with a low surface area may be suitably modified, for example, by the generation of acid groups on the surface to be used in reactions where these groups are demanded.

An important route in which modified carbons could be employed would be the conversion of residual glycerin from biodiesel production into new compounds with higher added value. The reactions concerning glycerol valorization are of great industrial interest. According to Souza et al. in 2014, many possibilities for the use of residual glycerin have been investigated, especially employing catalytic processes [9]. Catalytic conversion reactions of glycerol, which is a highly reactive molecule, favor obtaining chemical products with high added value. Such products can be obtained by reactions such as selective oxidation and hydrogenolysis, dehydration, steam reforming, thermal reduction in synthesis gas, oligomerization/polymerization, selective transesterification, epichlorohydrin synthesis, and etherification [7,10–13]. The etherification process can be industrially important since it converts the glycerol into a compound of lower viscosity and higher volatility. The obtained products can be potentially used as a fuel additive or even as solvent [14]. Some studies reported in the literature indicate that high acidity and proper pore structure of the catalysts favor the reaction [15–18].

The glycerol etherification can be performed with several alcohol sources, e.g. tert-butyl alcohol. The reaction products can be used as oxygenated additives for fuels, such as diesel and biodiesel, leading to an environmentally and economically attractive production cycle [19,20].

Taking into account these premises, in this work we propose to transform several industrial wastes, such as glycerin (G), waste coffee

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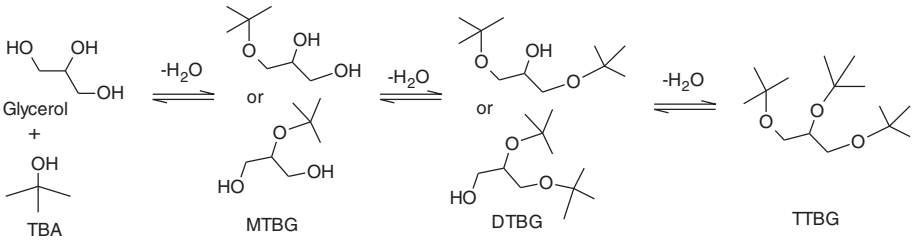

Fig. 1. Etherification reaction of glycerol with tert-butyl alcohol.

grounds (WC) and polyethylene terephthalate (PET), into a value-added material: an acid carbon to be used as catalyst in the glycerol etherification reaction.

2. Material and methods

2.1. Preparation of the carbons

The black carbons (BC) were prepared by using several carbonaceous wastes as precursors: glycerin (G), waste coffee ground (WC) and polyethylene terephthalate (PET). The BC materials were prepared by the partial carbonization of the wastes, adapting the procedure described in previous works of our research group [21,22]. The waste coffee grounds used to produce the black carbon were obtained from dried solid residue produced after preparation of the coffee beverage and the PET powder waste was generated during the grinding of the PET bottles for recycling in the PET industry. The carbons prepared from the residues were obtained by controlled pyrolysis under N_2 flow (100 cm^3 min^{-1}), heated at 673 K in a tubular furnace at a rate of 10 K min^{-1} and kept in this temperature for 4 h. The BCs were named as CWC (carbon prepared from waste coffee grounds) and CPET (carbon prepared from PET). The prepared BCs were chemically treated with fuming sulfuric acid, containing about 20% of SO_3. The treatment was performed using 50 mL of sulfuric acid and 5 g of the BC under reflux at 353 K for 2 h.

The black carbon prepared from glycerin biodiesel waste (S-CG) was prepared by hydrothermal synthesis using a mixture of glycerin (from Oxiteno—Brazil) and sulfuric acid (96% v/v, Carlo Erba) at a mass ratio of 1:3, under a temperature of423 K for 2 h.

After carbonization and acid treatment, all the black carbons were repeatedly washed with water until the removal of soluble acid and oven-dried at 393 K for 24 h. The BCs were named as S-CWC (carbon prepared from waste coffee grounds), S-CPET (carbon prepared from PET) and S-CG (carbon prepared from glycerin).

2.2. Black carbon characterization

Textural properties of the different BCs were determined by nitrogen adsorption measurements at 77 K in an Autosorb-1MP equipment (Quantachrome Instruments).

The surface chemistry was studied by Fourier transform infrared spectroscopy (FTIR) analysis using a Varian 3100 FT-IR spectrometer. The analyses were performed mixing the dried BCs with potassium bromide (KBr) in a weight ratio of 1:100 and ground into fine powder. The spectra were then acquired by accumulating 100 scans at 4 cm^{-1} resolution in the 400–4000 cm^{-1} range. For the acid density quantification, 0.5 g of BCs was added into 25 mL of NaOH 0.1 mol L^{-1} (Nuclear). Afterwards, these solutions containing the BCs were stirred for 72 h, at room temperature, and filtered prior to titration. Then, 10 mL of filtered solutions was titrated with HCl (Vetec) 0.1 mol L^{-1} in an automatic titrator (Metrohm 905 Titrando). The experiments were performed in triplicate.

The acidity properties were analyzed by Temperature Programmed Desorption method (TPD) using NH_3 as probe molecule. The analyses were performed on a Quantachrome ChemBet 3000 equipment containing a TCD detector, using a current of 150 mA and an attenuation of 32. After that, a 0.2 g sample of the catalyst was treated at 100 °C with continuous flowing helium at 80 cm^3 min^{-1} for 60 min, and the temperature for NH_3 adsorption was 50 °C. The TPD–NH_3 profiles were obtained at 10 °C min^{-1} up to 700 °C.

The amount of sulfur on the BC surface was determined by Energy DispersiveX-ray Spectrometry (EDS). The analyses were performed on a JEOL JSM-6701F field emission scanning electron microscope operating at 10.0 kV and 10.0 mA.

2.3. Catalytic activity of black carbons

2.3.1. Glycerol etherification

Catalytic activity in the etherification of glycerol (99.5% — Sigma-Aldrich) with tert-butyl alcohol (TBA, 99.7% — Sigma-Aldrich) was

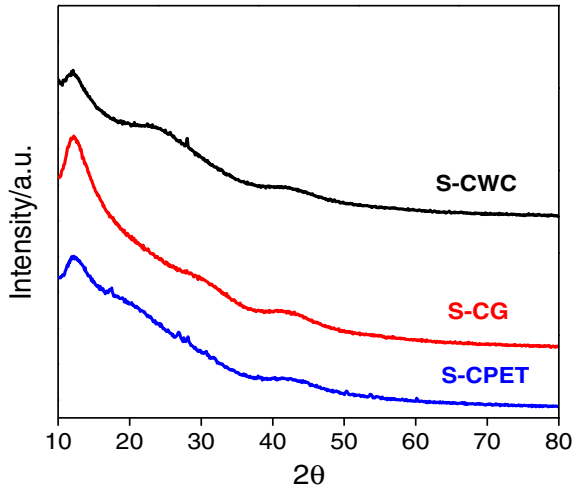

Fig. 2. XRD patterns of the carbons S-CWC, S-CG and S-CPET.

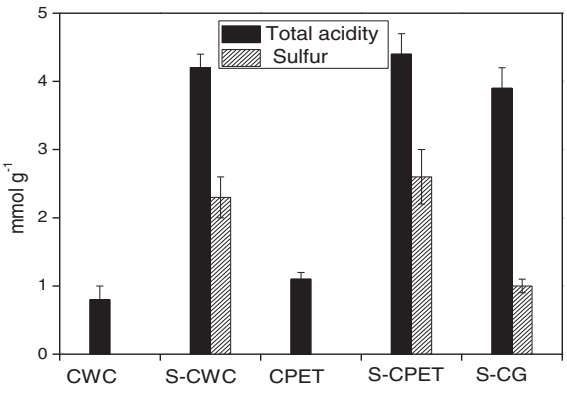

Fig. 3. Carbon acidity and sulfur content obtained by EDS analysis.