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Research article

Sulfonated porous carbon catalysts for biodiesel production: Clear effect of the carbon particle size on the catalyst synthesis and properties

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ABSTRACT

Sulfonated porous carbons (PCs-SO_3H) are prepared by the sol-gel reaction of resorcinol and formaldehyde. The porosity is maintained during drying using a cationic polyelectrolyte as pore stabilizer. It was found that varying the Resorcinol/Na_2CO_3 molar rate, different resins are produced which, after pyrolysis, give carbonaceous materials with different textural properties. It seems that a Resorcinol/Na_2CO_3 molar ratio of 200:1 was the optimal condition to produce a well-developed porous structure. Both resins and carbon materials are sulfonated by treatment with sulphuric acid. The relation between the carbon particles size, the sulfonation efficiency and its performance as a catalyst is studied. The higher amount of sulfonic groups, and thermal stability, as well as better catalytic performance, was obtained when smaller porous carbon particles were chosen by sieving. PCs-SO_3H exhibited high efficiency for the esterification reaction and high performance for biodiesel production. The catalysts can be recycled several times with a minimal loss of activity. Thermal analysis evidenced stability up to ca. 200 °C, allowing the use of this catalyst at high temperature. The simple synthesis and low cost of the PCs-SO_3Hs make them promising catalysts for the synthesis of biodiesel.

1. Introduction

Fuels derived from natural fats (e.g. vegetable oils) have become attractive owing to the fact that they are made of renewable resources [1]. However, the cost efficiency of its production is still a challenge. Therefore, the design of new and eco-friendly techniques needs to be investigated to make this process more competitive in the actual market. Enzymatic, heterogeneous or homogeneous catalysis are the actual technologies for biodiesel production [2–4]. Different lipases systems have been used in enzymatic catalysis for this purpose with high yields [5–7]. Despite the high production levels, enzymes constitute a major drawback for commercialization due to their high cost and low recyclability. In this sense, homogeneous catalyst (NaOH or KOH) can reduce substantially the production costs [8–10]. The reaction can be performed at low temperature and ambient pressure with high conversion rates, avoiding undesirable intermediate steps. Leung et al. demonstrate those homogeneous alkaline catalysts have as major drawbacks that they are highly hygroscopic and they adsorb water during its storage, diminishing the catalytic performance [11,12]. Furthermore, the alkaline catalyst produces soap in contact with water and free fatty acids, making the separation of biodiesel (esters) and glycerol a very difficult task. Alternatively, heterogeneous acid catalysts have been proposed as a proper alternative for biodiesel production. In this sense, the catalysis carry out using homogeneous acids compounds (e.g. H_2SO_4) is effective but it is hard to eliminate the acid from the reaction product. In that context, the heterogeneous catalysts are advantageous because they can be easily separated from the reaction product by filtration. However, a proper quantity of the active sites and accessibility to these sites is a stepping stone towards an optimum performance of the catalyst [13,14]. Several researchers have been studied different materials that can be used as acidic heterogeneous catalysts [2]. For example Twaiq et al. demonstrate that the zeolites are effective as catalysts in the palm oil cracking process [15]. Palm oil conversion of 80–100 wt.% and yield of gasoline fraction of 38–47 wt.% were obtained from the composite catalysts. Wenlei Xie et al., synthesized several heterogeneous acid catalysts based on SnO_2/SiO, WO_3/SnO and WO_3 supported on $AlPO_4$. In all the cases the catalysts were effective to transesterificate soybean oil giving fatty acids ethyl esters with an oil conversion between 70% to 82% [16–18]. Other materials which present capability for biodiesel catalyst are sulfated zirconium, Amberlite resins [19], and Nafion [20]. Common problems associated with solid acid catalysts are the low concentration of active sites, the hydrophilic nature of the catalyst surface, and the leaching of the active groups. The high cost of several catalysts production is also an obstacle to be produced in large-scale. In order to avoid the problems mentioned, has been reported various types of heterogeneous

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acid catalysts from sulfonated carbon [21,22]. In this type of catalysts, higher catalytic activity due to the presence of mesopores interconnected with micropores was observed. Lee demonstrates the ability of the carbonaceous materials to catalyze biodiesel reaction [23]. However, no detailed studies of the influence of the pore sizes, and the catalyst size have been made so far. Our group have previously synthesized porous carbons [24–28]; by pyrolysis of synthetic resins. The resins were made by sol-gel polycondensation of resorcinol and formaldehyde in the presence of a pore stabilizer, like a cationic polyelectrolyte (polydiallyl, dimethylammonium chloride) (PD). It has been demonstrated that the pore stabilizer allows maintaining the porosity during drying of the wet resin [29] avoiding complex drying method such as the use of supercritical fluids [30]. The use of PD as pore stabilizing agent makes the synthesis process cheaper and more environmentally friendly. Take into account the importance of the porosity and the porous size distribution; we study for the first time the influence of the Resorcinol/Na_2CO_3 ratio during the resin synthesis.

Finally, these types of porous carbons were sulfonated by reaction with concentrated sulfuric acid, in order to use it as an acid heterogeneous catalyst for biodiesel production. This work describes an in-depth study of the influence of the carbon size not only during biodiesel synthesis but also during sulfonation. To fulfill this aim, a previous sieving step was performed in order to study the influence of the particle size in the efficiency of the sulfonation procedure and then, its catalytic behavior. Based on the results it is demonstrated that the size of the catalyst particles is a very important parameter to take into account not only at the moment of produce biodiesel but also when this material is sulfonated. Moreover to test the efficiency of the produced catalyst, all the samples were used for two important reactions in biofuels production, i) the esterification of acetic and oleic acid with ethanol and ii) the transesterification of commercial sunflower oil with ethanol.

In summary, the novelty of this work are; 1) the influence of the molar ratio between resorcinol and sodium carbonate on the porosity of the catalyst is investigated; 2) it has been demonstrated that the sulfonation procedure is more effective if the carbon size is controlled; 3) not only the esterification reaction but also de transesterification reaction (biodiesel production) is performed more efficiently by controlling the catalyst size; 4) The sulfonic group are strongly attached to the carbon being stable upon heating to 200 °C; 5) the sulfonation of small porous carbon microparticles seems a suitable method to produce cheap and environmentally friendly heterogeneous acid catalysts combining a high surface area and an excellent catalytic performance (Scheme 1), thus making this material a promising candidate for industrial scale production.

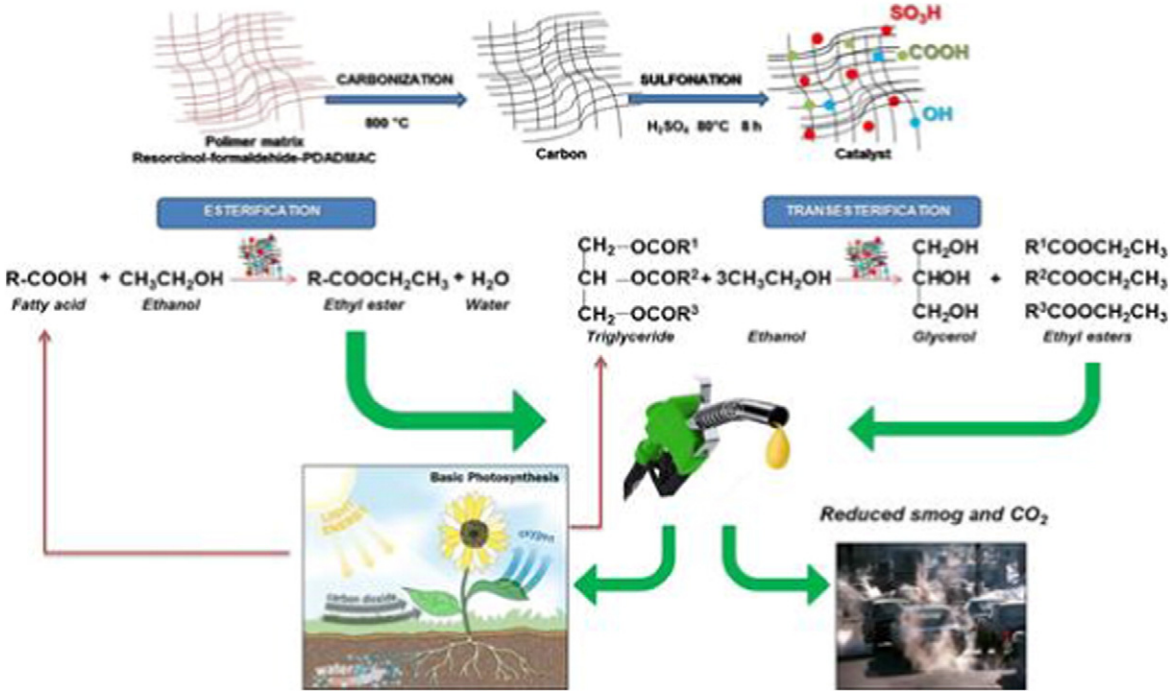
Moreover, it is demonstrated that the catalyst can be employed several cycles remaining its catalyst activity.

2. Experimental

2.1. Materials

Resorcinol (Fluka), Formaldehyde (Cicarelli), sodium carbonate (Cicarelli), and polydiallyl, dimethylammonium chloride (BDH) were employed to synthesize porous resins. For sulfonation procedure concentrated H_2SO_4 (Cicarelli, 98%) was used. In order to obtain the catalyst acid groups quantity $NaHCO_3$ (Sigma-Aldrich), Na_2CO_3 (Sigma-Aldrich), NaOH (Sigma-Aldrich, 99.998%), Na_2SO_4 (Sigma-Aldrich) and HCl (Sigma–Aldrich, 99.999%), were employed. All the chemicals were analytical quality reagents.

The esterification reactions were carried out using acetic (Fluka, analytical quality) or oleic (Riedel-de Haën, analytical quality) acid and bioethanol (98%, provided by BIO4 Bioetanol Río Cuarto S.A., Río Cuarto, Argentina). KOH (Sigma-Aldrich, analytical quality) was used to obtain the acetic acid conversion. The transesterification was performed using commercial sunflower oil (Natura). The chromatogram of the commercial oil (Natura) gave the following composition: Linoleic acid: 74%, Oleic acid: 14%, Palmitic acid: 8%, Stearic acid: 4%. For comparison with the carbon based catalysts prepared in this work, commercial solid acid catalysts were also tested: Nafion® 117 and Amberlite®-IR 120. Nafion® 117 (Dupont) is a fluorinated aliphatic polymer bearing sulfonic groups (—$CF_2CF_2SO_3H$). The material used in this work is in the form of cylindrical and spherical pellets, lengthwise striations. The mean size of the pellets is below 200 μm. A number of sulfonic groups is 1.10 ± 0.07 meq/g. Amberlite®-IR 120 is a cation exchange resin



Scheme 1. Biodiesel production cycle from renewable bio-oils via catalytic transesterification and esterification using heterogeneous acid catalyst based on porous carbon obtained from the sol-gel polycondensation of resorcinol and formaldehyde in the presence of a PD.