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Influence of acidic properties of different solid acid catalysts for glycerol acetylation

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ABSTRACT

The glycerol esterification with acetic acid is studied in this work using propylsulfonic functionalized mesoporous silica (Pr-SO_3H-SBA-15), and compared with H-ZSM-5 and H-Beta zeolites. The reaction was carried out in a batch reactor using a 6:1 molar ratio of acetic acid to glycerol. The initial TOF for the glycerol conversion was significantly higher in the propylsulfonic mesoporous silica, as compared to the two zeolites. These two catalysts have acid sites densities ($\mu mol\ m^{-2}$) that are less than half than that displayed by the SBA-based catalyst. It was possible to obtain 96% conversion in 2.5 h, with 87% selectivity to the products of interest diacetylglycerol (DAG) + triacetylglycerol (TAG), being the ratio DAG/TAG = 1.7. The catalyst deactivates partly due to sulfonic groups loss and to coke deposition during the reaction, as observed when it was used in a second reaction cycle without any treatment in between cycles. The catalyst lost activity, but maintained the selectivity, associated to a non-selective site poisoning.

1. Introduction

Glycerol is a polyol obtained as a by-product during the synthesis of biodiesel by transesterification of triglycerides with methanol or ethanol. The increase in the biodiesel production in recent years has led to an accumulation of glycerol in the global market. Because of this, the price of glycerol has dropped dramatically, and numerous researches to find new applications and processes to obtain products of higher value added have been proposed.

Acetylation of glycerol by esterification with acetic acid has been studied as an interesting alternative, to obtain monoacetin (monoacetylglycerol MAG), diacetin (DAG) and triacetin (TAG) as products [1–7]. DAG and TAG are the more valuable compounds due to their wide applications as fuel additives and solvents [8–11]. Adding a small amount of TAG into biodiesel improves its viscosity and low-temperature properties. The decrease in the cloud point (CP) and pour point (PP) of biodiesel is due to the low freezing point of triacetin, while the higher viscosity of triacetin prevents a decrease of the cold filter plugging point (CFPP) [12].

One of the challenges in this reaction system is the separation of compounds, because they have similar boiling points [1,3,13,14]. Another drawback is the low selectivity towards the more important product (TAG), due to the formation of water and acetol by-products which negatively affects the thermodynamic equilibrium [15]. One way to improve the selectivity to TAG is using acetic anhydride as acetylating agent [17], or making two acetylation steps, first with acetic acid and then with acetic anhydride [15,16]. However, the disadvantage of this procedure is the price of the acetylating agent. Another alternative to effectively shift the chemical equilibrium is to use toluene to continuously remove the reaction water [18].

The glycerol acetylation reaction proceeds by an acid-catalyzed mechanism. Homogeneous catalysts can be employed. The disadvantages are the corrosion caused in the reactors, the production of toxic compounds, and the loss of catalysts due to the difficulty of their separation. For these reasons, different solid catalysts like commercial resins Amberlyst-15 and zeolites have been studied in order to substitute the liquids [1,19,20]. Kim et al. [21] reported studies with different catalysts, such as propyl sulfonic acid functionalized SBA-15 (Pr-SO_3H-SBA-15), sulfonic acid functionalized SBA-15 (SO_3H-SBA-15), and microcrystalline cellulose catalysts. Magnetic solid acid catalysts were also evaluated in this reaction [22]. Results obtained with the H-BETA zeolite ($SiO_2/Al_2O_3 = 25$) was reported by Sandesh et al. [23], while an H-ZSM-5 (Si/Al = 28) was previously used in this reaction [1].

SBA-15 materials containing sulfonic groups on its surface were tested in different esterification reactions, such as the esterification of free fatty acids with methanol [24–27]. The activity of these

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materials for these reactions suggests the presence of strong acid sites. Moreover, it was found that the structure and the acid sites nature of Pr-SO_3H-SBA-15 catalyst were responsible for the catalytic performance in the direct esterification of acrylic acid with cyclohexene [28]. These catalysts were also employed in the acetylation of glycerol [21,29,30]. It is important to highlight that the Pr-SO_3H-SBA-15 catalysts used in these three publications, have lower acid sites density than the catalyst used in the present study, as discussed below.

Comparative studies of several catalysts under identical reaction conditions are necessary in order to investigate the effect of surface acidity (amount and strength of acid sites) and the porous structure. In this work two microporous zeolites, H-ZSM-5 (Si/Al = 15) and H-Beta (Si/Al = 13), with a similar density but different strength of acid sites are studied. Furthermore, a mesoporous silica SBA-15 with propyl-sulfonic functional groups (Pr-SO_3H-SBA-15) is also evaluated. The activity and selectivity results are correlated with the acidic and textural properties, which were determined using several characterization techniques.

2. Experimental

2.1. Catalysts synthesis

The propyl-mercapto mesoporous silica (Pr-SH-SBA-15) material was synthesized by co-condensation of Tetraethylorthosilicate (TEOS, 98%, Aldrich) and Mercaptopropyltrimethoxysilane (MPTMS, 95%, Aldrich), in the presence of a copolymer poly(ethyleneglycol)-block-poly(propyleneglycol)-block-poly (ethyleneglycol) (PE-PP-PE Pluronic P123, Aldrich) as the structure-directing agent, and in HCl (Baker) acid medium, employing the sol-gel technique. The molar composition of each mixture for 4 g of copolymer was 0.0369TEOS:0.0041MPTMS:0.24HCl:6.67H_2O. The resultant solution was stirred for 20 h at 40 °C, after which the mixture was aged at 80 °C for 70 h under static conditions. Then, the solid product was recovered by filtration and dried in air at room-temperature overnight. To remove the template from the as-synthesized material, it was washed with ethanol under reflux for 24 h, using 100 ml of ethanol per gram of material. After thiol functionalization, the oxidation was made according to the method described by Bossaert et al. [31] by soaking the resulting solid in an aqueous dissolution of hydrogen peroxide (H_2O_2 30 vol%, Panreac). After the oxidation step, the solution was filtered and the solid was washed with ethanol. The wet solid was suspended (1 wt%) in 1 M H_2SO_4 solution for 2 h. The powder was then washed with water and ethanol and dried for 2 h at 120 °C. This catalyst was labeled Pr-SO_3H-SBA-15.

Furthermore, a mesoporous silica SBA-15 without functional groups was synthesized employing the procedure described by Zhao et al. [32]. In the preparation, 4 g of Pluronic P123 block copolymer were dissolved in an aqueous solution of HCl (2 mol L^{-1}) and stirring at 35 °C. Then, TEOS was added drop by drop while stirring for 20 h. The mixture was then heated to 80 °C for 24 h. In this case, the molar composition used was 1TEOS:5HCl:0.018PEO:184H_2O. Finally, the solid material obtained was washed with water, dried at 120 °C and calcined for 6 h at 540 °C.

Commercial H-ZSM-5 (CBV-3020E, Si/Al = 15) and H-Beta (UOP, Si/Al = 13) zeolites were also used in this study.

2.2. Catalysts characterization

Nitrogen adsorption-desorption isotherms were recorded at the temperature of liquid nitrogen (−196 °C) in a Micrometrics ASAP 2020 instrument. Before adsorption, samples were evacuated by heating at 100 °C or at 250 °C for the Pr-SO_3H-SBA-15 and for zeolites respectively, in vacuum, with a pressure lower than 4×10^{-2} mbar during 12 h. The lower temperature of treatment for the mesoporous material was selected according to the thermal stability of the functional groups. The surface was calculated according to the Brunauer–Emmett–Teller (BET) equation, in the relative pressure range 0.01–0.10 [33]. The micropore volume and external area in zeolites was derived from the t-plot, according to Lippens and de Boer [34]. The pore size distribution in the mesoporous materials was obtained by the BJH method [35].

The XPS analyses were carried out employing a multi-technique system (SPECS) equipped with a dual Mg/Al X-ray source and a hemi-spherical PHOIBOS 150 analyzer operating in the fixed analyzer transmission (FAT) mode. The spectra were obtained with pass energy of 30 eV and the Mg anode was operated at 200 W, measuring the core level signals of O 1s, Si 2p, S 2p and C 1 s and with a multi-channel detector. The working pressure in the analyzing chamber was lower than $2\ 10^{-8}$ mbar. The samples were mounted on a sample rod, placed in the pre-treatment chamber of the spectrometer, submitted to evacuation for 10 min at 120 °C, and then evacuated at ultra high vacuum for 2 h. The software CasaXPS (Casa Software Ltd, UK) was used to process the spectra. For the estimation of the intensities the integral of each peak was calculated after subtracting a Shirley-type background and fitting the experimental curve to a combination of Lorentzian and Gaussian lines. The C1 peak (284.6 eV) was used as reference to the binding energy values. Sensitivity factors provided by the manufacturers were employed for the quantification of the elements.

FT-IR spectra of samples SBA-15 and Pr-SO_3H-SBA-15 were collected in an FT-IR Spectrometer Spectrum 1000, Perkin Elmer, employing KBr in the frequency range of 4000–400 cm^{-1}.

Scanning electron microscopy (SEM) was carried out on Philips 505 microscope. For preparation of samples, a small amount of sample was placed on carbon tape and sputter coated with gold.

The amount and strength of acid sites in the zeolites was evaluated by Pyridine Temperature- programmed desorption (TPD). Approximately 10 mg of catalysts, sandwiched by quartz wool, was loaded in a quartz tube. The catalysts were pretreated in-situ in N_2 flow (30 ml min^{-1}) at 350 °C for 1 h. After cooling down to room temperature, the sample was saturated with pyridine. Then, pure nitrogen was flowed and the temperature was increased up to 150 °C, maintaining this temperature until no physically adsorbed pyridine was detected. The TPD experiment was carried out heating at 12 °C min^{-1} in nitrogen flow from 150 °C to 750 °C. Pyridine coming out of the sample cell passed through a methanation reactor. To this reactor a H_2 stream was also fed, quantitatively converting Pyridine to CH_4, using a Ni catalyst. The CH_4 was continuously measured by a FID detector.

The change in acidity due to functionalization in the Pr-SO_3H-SBA-15 catalyst was determined by potentiometric titration, because the decomposition of the functional groups interferes with the determination by pyridine TPD. A known mass of the solid to be analyzed was suspended in acetonitrile. The suspension was titrated using a solution of *n*-butylamine in acetonitrile (0.1 mol L^{-1}) at 0.05 ml min^{-1}. The electrode potential variation was obtained on a digital pH meter (Metrohm 794 Basic Titrino apparatus with a double junction electrode).

The electrical potential of the catalysts dissolved in acetonitrile was determined for the three catalysts used in the present study. This value is indicative of the strength of the acid sites.

The thermal stability of the Pr-SO_3H-SBA-15 catalyst was studied by thermogravimetry (TGA), in a Netzsch STA 449F3 instrument. Approximately 5 mg of sample was loaded into an alumina crucible and heated at 10 °C min^{-1}, from 20 °C to 700 °C, with a N_2 flow rate of 50 ml min^{-1}. The differential thermal gravimetric profiles (DTG) were obtained from the TGA profiles.

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