



Sulfonated niobia and pillared clay as catalysts in etherification reaction of glycerol



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ABSTRACT

Sulfonated niobia (HY-340 CBMM) and pillared clay (Fluka) were tested in the catalytic conversion of glycerol by etherification reactions. The solids were treated with concentrated fuming sulfuric acid (AS100 and NS100), and a 30% aqueous solution of this acid (AS30 and NS30). Both the presence of sulfur and the increase in the acidity of the solids demonstrate the suitability of the sulfonation process, especially in samples treated with concentrated fuming sulfuric acid. The best catalyst for the reaction of etherification with *tert*-butyl alcohol was AS100, with a glycerol conversion of 95% after 5 h at 393 K and yield of 60.3, 33.2 and 5.4%, respectively for mono-*tert*-butyl-glycerol (MTBG), di-*tert*-butyl-glycerol (DTBG) and tri-*tert*-butyl-glycerol (TTBG).

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1. Introduction

Several processes have been used for the chemical transformation of glycerol, a valuable by-product of biodiesel production [1]. Among these processes, the conversion of glycerol into oxygenated fuels through etherification reactions has recently been explored [2–5]. This approach represents a promising and economic alternative, since it makes use of a by-product of biodiesel production allowing increased yield of a biodiesel manufacturing process. Ethers, in particular, may be used as additives to diesel, since they have the ability to promote cleaner burning in internal combustion engines. Mixtures of *tert*-butyl ethers of glycerol with a high content of diethers, and particularly triethers, are known as potential additives for biodiesel [6,7]. These ethers can act reducing emissions of particulate matter, hydrocarbons, carbon monoxide, and aldehydes, and reduce the viscosity of the biodiesel, favoring their use. This topic is of great importance because of the growing demand for new additives, specifically for biodiesel, which are biodegradable, non-toxic and renewable.

Glycerol etherification with *tert*-butyl alcohol (TBA) is an acid catalyzed reaction, resulting in a mixture of mono-*tert*-butyl-glycerol (MTBG), di-*tert*-butyl-glycerol (DTBG) and tri-*tert*-butyl-glycerol (TTBG). Some unwanted by-products can also be formed

as a result of polymerization reactions. MTBG is the main product obtained in glycerol etherification, as a result of the electrophilic attack of the *tert*-butyl cation (a tertiary carbocation) preferably on the primary carbon of glycerol due to steric hindrance and electrostatic effects exerted by –OH glycerol groups. However, DTBG and TTBG are preferred as potential oxygenate additives to diesel fuels because of their ease of blending and non-polar properties.

Most studies uses isobutylene (IB) as the etherification agent [8–10]. However, it should be noted that the use of TBA, in substitution of IB, avoids both the need of solvents and the mass transfer limitation phenomena related to the complex three-phase system [11]. Moreover, TBA is a by-product of the large-scale propylene oxide production and it also can be produced from biosources, like starch or lignocellulosic biomass [12,13]. A highly acidic solid acid catalyst is required to initiate the reaction between two alcohols [14]. Different types of acidic heterogeneous solid catalysts such as sulfuric acid, sulfonated styrene-divinyl-benzene copolymers and *p*-toluene-sulfonic acid, have been studied in glycerol conversion and their high activity is caused by the Brønsted acid sites of the sulfonic group. The reaction between glycerol and TBA at 1:4 molar ratio can produce mono, di and tri butyl glycerol ethers. Reactions are typically promoted between 343 and 373 K, with TBA:glycerol molar ratio of 4:1. Gu et al. [14] reported that glycerol and TBA at 1:1 molar ratio does not undergo self-etherification. Glycerol conversion reaches values close to 100% after 5–8 h of reaction, with selectivities to DTBG + TTBG as high as 80% [11,15]. The highest yield for glycerol ethers (DBGE + TBGE) was obtained with an amount of catalyst equivalent to 7.5 wt% with respect to the mass

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of glycerol [11]. In general, the most suitable catalysts are commercial resins such as Amberlyst®, but the major limitation on the use of these resins is their thermal stability (393 K for Amberlyst®-15, reaching up to 463 K for Amberlyst®-70). Furthermore, both activity and selectivity losses were observed during consecutive tests [8,16].

Another possibility of active catalysts in these reactions is represented by niobia and pillared clays. Niobium-containing catalysts have attracted great interest in heterogeneous catalysis as a catalyst and support for a variety of important reactions. Niobia has a high acidity, which, curiously, is maintained in aqueous environments and this particular property is favorable to the dehydration reaction in aqueous phase [17–20]. Various attempts have been made to develop catalysts from pillared smectite clays. Due to their small particle size (<2 μm) and high intercalation capacity, some clay minerals present high surface area, useful in adsorption and catalysis processes [21]. Moreover, many specimens show catalytic properties, especially after having been submitted to small modifications in their composition or structure. Thermal stability, associated with the ease of access of reagent molecules into the interlayer catalytic sites, make the use of pillared clays as catalysts increasingly attractive [22]. Compared with most oxides commonly used as supports, it is possible to regard pillars as responsible for some form selectivity in the reactions, since a two-dimensional network of interconnected micropores is created which can adsorb mono ethers which undergo further etherification [23]. The active sites of the catalyst adsorb both fresh glycerol and the product (MTBG), undergo further etherification and produce DTBG and TTBG. So the extent of bulk ethers adsorption depends upon the porosity of the catalyst.

Coupled with the fact that studies mainly focus on catalyst development for etherification of glycerol with isobutylene, sulfonic commercial resins with low thermal stability have been reported as the most active catalysts for glycerol etherification. In this work we investigated the possibility of promoting the acidity of two inorganic solids, niobia and pillared clay, by a simple procedure of sulfonic acid-functionalization. Besides not using expensive reagents for sulfonation, the solids exhibit high thermal stability, enabling their use in more drastic reaction conditions. The activity and selectivity of these catalysts in the etherification of glycerol was also evaluated. Sulfonated materials have been characterized by Fourier Transform Infrared spectroscopy (FTIR), nitrogen adsorption, Temperature-Programmed Desorption (TPD), X-ray Diffraction (XRD) and Energy Dispersive X-ray Spectrometry (EDS). The solids have been tested as catalyst for etherification of glycerol. The effect of the temperature, the TBA:glycerol molar ratio as well as the reusability of the catalysts have also been evaluated and compared to the commercial resins Amberlyst®-15 and Amberlyst®-70.

2. Materials and methods

2.1. Catalysts preparation

Samples of aluminum pillared clay (Fluka) and niobia (HY-340 CBMM) were sulfonated by treatment with fuming sulfuric acid (20% free SO₃) or a 30% aqueous sulfuric acid solution. Treatments were carried out using 100 mL of sulfuric acid and 10 g of each solid kept under stirring at ambient temperature for 10 h. All samples were filtered and repeatedly washed with warm water until neutrality and then dried in an oven at 393 K for 24 h. Solids were identified as (i) parent pillared clay: A, (ii) pillared clay treated with fuming sulfuric acid: AS100, (iii) pillared clay treated with 30% aqueous sulfuric acid solution: AS30, (iv) parent niobia: N, (v)

niobia treated with fuming sulfuric acid: NS100 and (vi) niobia treated with 30% aqueous sulfuric acid solution: NS30.

2.2. Characterization

Textural properties of the solids were obtained by nitrogen adsorption measurements at 77 K in an Autosorb-1MP device (Quantachrome Instruments). The “apparent” surface area was estimated according to the BET equation, based on the adsorption data in the partial pressure range (P/P_0) from 0.05 to 0.25. Prior to the measurements, the samples were outgassed at 423 K and 1.3×10^{-3} Pa for 4 h, to remove moisture.

Chemical functional groups present in the samples surface, especially sulfonic acid groups in the treated samples, were determined by infrared spectroscopy using a Varian 3100 FT-IR Spectrometer. The analyses were performed mixing dried samples with potassium bromide (KBr) in a 1:30 weight ratio and ground into fine powder. This mixture was dried at 373 K for 24 h and thin pellets were made in manual equipment. The spectra were then acquired at this temperature by accumulating 100 scans at 4 cm^{-1} resolution in the range of $400\text{--}4000 \text{ cm}^{-1}$.

NH₃ temperature programmed desorption was used to determine the acid properties of the catalytic materials. The experiments were conducted on a Quantachrome ChemBet 3000 device. The catalysts (100 mg) were pretreated at 423 K for 30 min and then cooled to 373 K under a He flow. The pretreated samples were saturated with 5% NH₃/He for 1 h at 373 K, with subsequent flushing with helium at 373 K for 2 h to remove the physisorbed ammonia. TPD analysis was carried out from 373 K to 1073 K at a heating rate of 10 K min^{-1} .

X-ray diffraction patterns were obtained using a Philips X'Pert PW3373 diffractometer, with Cu K α radiation and an excitation power of 2 kW (40 kV and 50 mA).

The amount of sulfur on the carbon surface was determined by EDS. 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 tests

Glycerol (99.5%—Sigma-Aldrich) etherification with *tert*-butyl alcohol (TBA, 99.7%—Sigma-Aldrich) was carried out in a 300 mL stainless steel batch reactor with a mechanical stirrer and under autogenous pressure. The system was previously purged 2–3 times with N₂ in order to remove the air and the experiments were performed under inert atmosphere, typically at 393 K, with 5 wt% of catalyst and TBA:glycerol molar ratio varying from 4:1 to 8:1. The reaction time was measured from the moment the system achieved operating temperature (20 min after closing the reactor). Samples were analyzed by gas chromatography (GC/FID, Agilent 7890A, DB-Wax 30 m \times 0.25 mm \times 0.25 μm) using acetonitrile as internal standard. The identification of the reaction products was done by a gas chromatograph coupled to a mass spectrometer (GC-MS, Shimadzu QP-2010Plus, SGE BP-20-strong Wax 30 m \times 0.25 mm \times 0.25 μm) and confirmed according to the method described by Jamróz et al. [24]. Replicates of the reactions yielded data presenting coefficients of variation under 5%. The coefficient of variation for GC/FID replicate quantification was below 3%. The mass balance of the reactions analyzed presented values above 95%.

Glycerol conversion (%), product yield (%) and product selectivity (%) were calculated using the following equations:

$$\text{Glycerol conversion (\%)} = \frac{\text{moles of glycerol reacted}}{\text{moles of glycerol taken}} \times 100\% \quad (1)$$

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