



Research Paper

Microwave-assisted etherification of glycerol with *tert*-butyl alcohol over amorphous organosilica-aluminum phosphates



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ABSTRACT

The synthesis of organosilica-aluminum phosphates by a simple and cheap sol-gel method was carried out with varying amounts of two different silica precursors, 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (C) and (3-mercaptopropyl)trimethoxysilane (MPTMS); and several Al/P molar ratios. The solids were calcined in air, at different temperatures. The etherification of glycerol with *tert*-butyl alcohol was carried out in the liquid-phase under microwave irradiation and also by conventional heating. The incorporation of organosilica in the final solids took place in a 50–60%, as verified by TGA, ICP-MS, XPS and ^1H - ^{29}Si CP MAS NMR. The highest yield to h-GTBE (21%) was obtained at autogenous pressure, 85 °C and 15 min of reaction time under microwave, on the solid prepared with 10 mmol of C; Al/P = 1.5 and calcined at 250 °C. This material, with a balanced percentage of mesopores and macropores, also exhibited the highest number of acid sites determined by acid-base titration, as well as by results from TGA and by elemental analysis. The acidity and the hydrophilic character of the solids have been found to be key parameters for the catalytic activity, whereas porosity seems to be advantageous for the reusability of the solids, avoiding deactivation.

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1. Introduction

Over the last two decades, biodiesel has emerged as a competitive alternative to the fossil fuel due to intrinsic advantages such as low toxicity, biodegradability, renewability and biocompatibility. However, the formation of biodiesel generates glycerol as by-product (10 wt.% of the total biodiesel product). The growing trend in the biodiesel production has led to a large surplus of this glycerol and as a consequence a drop in its market value [1]. As the conventional application of glycerol could not cope with the excess production, several processes which employ glycerol to obtain added-value products are being investigated, including hydrogenolysis, dehydration, acetalisation, esterification, etherification and so on [2–5]. Among these different processes, etherification of glycerol to obtain glycerol *tert*-butyl ethers is an interesting alternative. In fact, di-*tert*-butyl glycerol ethers (DTBGs)

and tri-*tert*-butyl glycerol ether (TTBG), the so-called high ethers (h-GTBE), can be employed as excellent diesel and biodiesel additives due to their compatible physicochemical properties such as viscosity, flash point, cetane number, etc., providing a decrease in the emission of particulate matter, carbon oxide and carbonyl compounds in exhaust gases [6]. Furthermore, the low solubility of the mono-*tert*-butyl glycerol ethers (MTBGs) makes their use as fuel additives impossible. Therefore, the reaction must be shifted towards the formation of poly-substituted glycerol ethers.

Generally, the etherification of glycerol (G) is accomplished using isobutylene (IB) or *tert*-butyl alcohol (TBA) as reactants in the presence of acid catalysts. In particular, etherification of G with IB leads to higher yield values to h-GTBE than those obtained with TBA [7,8]. In fact, several papers have been published describing the production of poly-substituted ethers from G over different solid acid catalysts in the presence of IB [9–13]. However, the use of *tert*-butyl alcohol, a byproduct of polypropylene production, benefits mass transfer, suppresses isobutylene oligomerization and avoids using organic solvents in reaction mixtures.

Usually, the best catalytic results in the etherification of G with TBA have been obtained over acid resin catalysts, mainly over Amberlyst 15 (A-15) [7,14,15]. However, this A-15 usually presents

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a lack of thermal stability and suffers from swelling and shrinking in organic media. Furthermore, the sulfonic groups are the only part of the structure with hydrophilic character. For this reason, the water generated during the reaction would be adsorbed on these sulfonic groups, leading to a faster deactivation [16]. Thus, the synthesis of new catalytic systems remains challenging.

Frusteri et al. separately supported tungstophosphoric heteropolyacid (HPW-17) and a Nafion ionomer (N-17) on amorphous silica [16] attaining the best value of glycerol conversion (54%) on a phosphotungstic acid exchanged with cesium and supported on silica. Recently, cesium exchanged tungstophosphoric acid supported on tin oxide and different nanostructured MFI-type zeolites, have also been reported as good catalysts for this reaction [17,18]. González et al. [19] modified the surface and acid characteristics of three commercial Na-zeolites (mordenite, beta and ZSM-5) by different techniques. The best results were obtained on fluorinated beta zeolite ($Y_{h-GTBE} = 26\%$). They explained the differences in activity by the number of Bronsted acid sites and their strength, together with the accessibility of the reactants to these acid sites. In addition, sulfonated black carbons have exhibited a good catalytic performance in this reaction [20–22]. In fact, Gonçalves et al. [23] performed the reaction over different non-porous sulfonated black carbon catalysts obtained from biodiesel wastes, attaining a yield of 20% to h-GTBE with 80% of glycerol conversion at 120 °C and 8 h of reaction time. The “apparent” surface areas of those materials were lower than 10 m²/g. Thus, the population of sulfonic groups on the carbon surface seems to be essential for the etherification reaction.

Furthermore, we have recently reported this reaction on different sulfonic acid functionalized hybrid silicas obtained by oxidative cleavage of tetrasulfide bridges [24], concluding that a high density of acid sites, together with the non-porous structure, would explain the highest catalytic performance obtained (Y_{h-GTBE} around 28%) at 75 °C and 24 h of reaction time over the S₅₀TS₅₀O solid, synthesized by co-condensation of bis{3-(triethoxysilyl)propyl}tetrasulfide (BTEPTS) and tetraethyl orthosilicate (TEOS) with a molar ratio of 50-50 and subsequent oxidation of the tetrasulfide bridges with hydrogen peroxide. In addition, the hydrophilic character of the solids also played an important role in the deactivation of the catalysts.

On the other hand, we have also reported the excellent catalytic behavior of both pure and amorphous mesoporous aluminum phosphate (AlPO₄) and those modified by transition metals producing acrolein from pure glycerol in liquid phase [25] or aqueous solution of glycerol in gas phase [26]. The high water tolerance and the pore size exhibited by AlPO₄ are some advantageous properties for the etherification reaction, although the strength of its acid sites is not sufficient. In order to overcome this, we have synthesized aluminum phosphates in the presence of two different organosilicas, either containing a sulfonic group 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane or a sulfonic group precursor (3-mercaptopropyl)trimethoxysilane, by a sol-gel method similar to that employed in the synthesis of pure AlPO₄ [25]. The composition and the textural and physicochemical properties of the synthesized solids were also evaluated. Thus, the acidity of the solids was measured by acid-base titration and compared with the results obtained from thermogravimetric analysis (TGA) and from elemental analysis (sulfur content). The catalysts were tested in the etherification of glycerol with *tert*-butyl alcohol in the liquid phase by microwave irradiation and in some cases, with conventional heating for comparative purposes. The stability of the best catalysts was also tested by reusing them in subsequent reactions. Furthermore, a commercial Amberlyst-15 was also studied as a reference catalyst.

2. Experimental

2.1. Preparation of catalysts

The organosilica-aluminum phosphates were synthesized by a sol-gel method as follows: an aqueous solution of AlCl₃·6H₂O was kept under magnetic stirring (900 rpm) and mixed with H₃PO₄ (85 wt.%) in an ice-water bath. After 1 h, 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (C) or (3-mercaptopropyl)trimethoxysilane (MPTMS) was added dropwise. Then, aqueous ammonia was slowly added until a pH of 5 was reached. The final synthesis gel was then kept at room temperature for 24 h. The solid obtained was filtered off and washed with isopropyl alcohol and dried at 120 °C for 24 h. Finally, the solids were calcined. The catalysts obtained using C as organosilica will be denoted as C(x)AlPO(y)-T where x is the mmol of organosilica added to the initial mixture, ranging from 2.5 to 10; y is the Al/P molar ratio (1.5, 1 or 0.5) and T is the calcination temperature (250 or 310 °C). In the material prepared with the other organosilica precursor, 10 mmol of MPTMS was added to the initial mixture, the Al/P molar ratio was 1 and the calcination temperature was 210 °C. This solid will be denoted as MPTMS(10)AlPO(1). After calcination, this solid was treated with H₂O₂ in order to oxidized the thiol group (-SH) to sulfonic group (-SO₃H) in accordance with a previously reported procedure [27]. In this case, the oxidation post-treatment was carried out during 3 h at room temperature and also at 50 °C using conventional heating and microwave (*Milestone Flexiwave Microwave*) for comparison purposes. These materials will be denoted as MPTMS(10)AlPO(1)-(T) where T is the oxidation temperature. The solid oxidized at room temperature will be denoted as MPTMS(10)AlPO(1)-RT and those oxidized using microwave heating will be denoted with Mw at the end of the name. Finally, all the solids were powder screened to <0.149 mm, to avoid internal diffusion limitations in the reactions.

2.2. Characterization of the catalysts

XRD powder diffraction patterns were obtained using a Discover (Bruker) diffractometer equipped with Cu K α radiation. Finely ground samples were scanned at a speed of 2 °/min ($2\theta = 2-70^\circ$). Textural properties were determined from the N₂ adsorption-desorption isotherms at -196 °C, using a Micromeritics ASAP 2010 apparatus. Prior to measurements, all the samples were degassed at 120 °C for 12 h. The specific surface area of each solid, S_{BET}, was determined by using the BET method at relative pressures in the range p/p₀ = 0.05–0.3 assuming a cross-sectional area of 0.162 nm² for the nitrogen molecule. The values of pore volume and the pore size distributions were calculated by the Barret-Joyner-Halenda (BJH) method. The C, H, N and S content was determined by elemental analysis, according to the Dumas method, based on the complete combustion of the sample in an oxygen-enriched atmosphere and the subsequent analysis of the gases by gas chromatography with a TCD detector. A Eurovector Elemental Analyser EA3000 equipped with Callidus software (EuroVector SpA, Milan, Italy) was used. Regarding the aluminum, phosphorus and silicon content in the materials, an Inductive Coupled Plasma (ICP) in a Philips PU 70,000 sequential spectrometer equipped with an Echelle monochromators (0.0075 nm resolution) and coupled to Mass Spectrometry was used. XPS spectra were recorded with a SPECS Phoibos HAS 3500 150 MCD, being the residual pressure in the analysis chamber 5 × 10⁻⁹ Pa. Accurate binding energies were determined with respect to the position of the Si 2p peak at 103.4 eV. The peaks were decomposed using a least-squares fitting routine (Casa XPS software) with a Gaussian-Lorentzian (70:30) using Shirley baselines. Thermogravimetric analyses (TGA) were recorded on a Setaram Setsys 12 thermal analysis station by heating in air from 30 to

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