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Acid-catalyzed etherification of bio-glycerol and isobutylene over sulfonic mesostructured silicas

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ABSTRACT

Sulfonic-acid-functionalized mesostructured silicas have demonstrated an excellent catalytic behavior in the etherification of glycerol with isobutylene to yield *tert*-butylated derivates. Di-*tert*-butylglycerols (DTBG) and tri-*tert*-butylglycerol (TTBG) have shown to be valuable fuel additives leading to decreases in the emission of particulate matter, hydrocarbons, carbon monoxide and unregulated aldehydes. Likewise, said ethers can also act as cold flow improvers for use in biodiesel, reducing also its viscosity. The activities and selectivities achieved over sulfonic acid-functionalized mesostructured silicas are comparable or even superior to those displayed by widely used macroporous commercial acid resins. Under optimized reaction conditions, these mesostructured catalysts yield a complete glycerol conversion with a combined selectivity towards DTBG and TTBG up to ca. 90%. Furthermore, no formation of undesirable isobutylene oligomers is observed. The acid strength of the sulfonic acid sites has also been found to be an important factor affecting the catalytic performance of these materials.

1. Introduction

Mono-alkyl esters of fatty acids (biodiesel) obtained from transesterified vegetable oils or animal fats are an attractive and environmentally friendly alternative to petrodiesel fuel. Biodiesel is biodegradable, renewable and non-toxic, and exhibits improved lubricity, higher flash point, reduction of most exhaust emissions, close heat combustion and viscosity, and similar or even superior cetane number in comparison to diesel [1]. Glycerol is the main by-product of the transesterification process, whose production is equivalent to approximately 10 wt.% of the total produced biodiesel.

Production of biodiesel in the European Union has grown exponentially in the last years. According to the *European Biodiesel Board*, the production in EU was 5 millions of metric tons (MTm) in 2006 with a fast and sharp annual increase of ca. 28% from year 2000. Moreover, the Directive 2003/30/EC of the European Union has stated that by the end of the year 2010 member states should ensure a biofuels proportion of 5.75%, calculated on the basis of energy content, for all the petrol fuels used for transport purposes [2]. That implies an increase in the biodiesel manufacturing up to 10 MTm for the year 2010, which means ca. 1 MTm per year of glycerol. With this expected increased production of biodiesel, a glut of glycerol will be created which will reduce the glycerol market prices. In this context, an important research is currently starting in order to find new applications for this expected low-cost feedstock [3,4]. These strategies include selective oxidation, hydrogenolysis to obtain propylene glycol, dehydration to yield acrolein, fermentation towards 1,3-propanediol, synthesis of epichlorohydrin, or even reforming towards syngas [3]. Apart of these alternatives, the transformation of glycerol into fuel oxygenates by means of etherification [5–9] and esterification reactions [10,11] is being explored. This approach is a promising and economically viable alternative since not only makes a good use of the glycerine by-product but also increases the yield to biofuel in the overall biodiesel production process.

Special interest is focused on the preparation of alkyl ethers of glycerol by etherifaction with isobutylene [6–9]. Isobutylene reacts with glycerol in presence of acid catalysts to yield a mixture of mono-, di-, and tri-*tert*-butyl glycerol ethers (MTBG, DTBG, and TTBG, respectively). Higher ethers (DTBG and TTBG) are excellent additives with a large potential for diesel and biodiesel formulation. These oxygenated compounds, when incorporated into standard diesel fuel, have lead to a decreasing in particles, hydrocarbons, carbon monoxide and unregulated aldehydes emissions [12].

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Likewise, these ethers can act as cold flow improvers for use in biodiesel, reducing also its viscosity [7]. This issue is of significant importance due to the growing demand of new additives specifically for biodiesel that are biodegradable, non-toxic and renewable. In addition, these derivates can also be used as octane boosters for gasoline, as an alternative to commercial trialkylethers (MTBE and ETBE) [13].

This reaction has been usually performed over sulfonic resins [14–16] and homogenous acid catalysts (mainly *p*-toluenesulfonic) [16]. Usually, low surface areas and lack of thermal stability are the major drawbacks of sulfonic resins. On the other hand, the use of conventional homogenous acid catalysts must be avoided to comply with the increasingly strict environmental regulations. The incorporation of organosulfonic groups over mesostructured silicas have generated effective solid acid catalysts with enhanced catalytic properties as compared with conventional homogeneous and heterogeneous acid catalysts [17]. Moreover, these type of silica materials functionalized with organosulfonic acid groups have been used previously for the conversion of biorenewable molecules [18–21], showing better catalytic performances than the commercial sulfonated resins. These highly surface materials, with large interconnected mesopores and high accessibility of strong Brönsted acid sites might be suitable candidates for this etherification reaction.

Within the scope of this work, the etherification of glycerol with isobutylene has been studied over different sulfonic acid-modified mesostructured silicas. A multivariate analysis has been used to assess the conditions (isobutylene/glycerol molar ratio and temperature) that yield the best catalytic results in terms of glycerol conversion and selectivity towards the di- and tri-derivates, while minimizing the formation of the mono-derivate compound (MTBG) and the extension of the isobutylene dimerization. MTBG has relatively high water solubility and thus is not suitable as diesel-blending agent, whereas isobutylene oligomers could lead to the formation of undesirable deposits in the motor during the combustion. Finally, the catalytic performance of these sulfonic acid-modified mesostructured silicas has been benchmarked with other commercial acid catalysts.

2. Experimental

2.1. Catalysts preparation

Propylsulfonic-acid-functionalized mesostructured silica (Pr-SBA-15) was synthesized following a previously reported procedure [22]. Molar composition of the synthesis mixture for 4 g of templating block-copolymer (Pluronic 123, $EO_{20}PO_{70}EO_{20}$, BASF) was: 0.0369 tetraethylorthosilicate (TEOS, Aldrich); 0.0041 mercapto-propyltrimethoxysilane (MPTMS, Aldrich); 0.0369 H_2O_2; 0.24 HCl; ≈6.67 H_2O.

Arenesulfonic-acid-functionalized mesostructured silica (Ar-SBA-15) was synthesised as described elsewhere [23]. For this catalyst, the molar composition of the synthesis mixture for 4 g of copolymer was as follows: 0.0369 TEOS: 0.0041 chlorosulfonylphenylethyltrimethoxy-silane (CSPTMS, Gelest): 0.24 HCl: ≈6.67 H_2O. In both cases, the amounts of sulfur precursors (MPTMS and CSPTMS) have been selected to provide 10% of total silicon moles. These two sulfonic acid-modified mesostructured silicas provide different acid strengths, as introduced by the different molecular environments of the sulfonic acid sites (Pr-SBA-15 < Ar-SBA-15).

Commercial acid catalysts: Nafion®-SiO_2 composite (SAC-13) with resin content in the range of 10–20 wt.% was supplied by Sigma–Aldrich. Acidic macroporous resins Amberlyst 15 and Amberlyst 36 (Rohm and Haas), and Purolite CT-275 (Purolite) were also tested in the present work.

2.2. Catalysts characterization

Textural properties of sulfonic acid-modified mesostructured silicas have been evaluated by means of nitrogen adsorption and desorption isotherm at 77 K using a Micromeritics TRISTAR 3000 system. Data were analyzed using the BJH model and pore volume was taken at $P/P_o = 0.975$ single point. Structural characterization was completed by X-ray powder diffraction (XRD) patterns, which were acquired on a PHILIPS X'PERT diffractometer using Cu Kα radiation. Data were recorded from 0.6° to 5° (2θ) using a 0.02° step resolution. Acid capacity was measured through the determination of cation-exchange capacities using aqueous sodium chloride (2 M) solutions as cationic-exchange agent. Released protons were then potentiometrically titrated [22,23]. Sulfur contents were assessed by means of Elemental Analysis (HCNS) in a Vario EL III apparatus, in combination with the information obtained from thermogravimetric analyses (SDT 2960 Simultaneous DSC-TGA, from TA Instruments).

Table 1 summarizes the most relevant physicochemical properties for the two sulfonic acid-modified mesostructured silicas. Data from XRD and N_2 adsorption isotherms evidence high mesoscopic ordering and high surface areas along with narrow pore size distributions around 8–9 nm (size enough to avoid the steric constraints imposed by pore size when relatively bulky substrates such as glycerol derivatives are considered). For both samples, prepared by co-condensation of the different silanes, high incorporation yields for the sulfonic-acid moieties (over 90%) are observed. Likewise, for Pr-SBA-15, complete oxidation of the precursor thiol groups into sulfonic moieties can be deduced from actual sulfur content and acid capacity by titration.

Table 1
Physicochemical, textural and acidity-related properties for sulfonic-acid-modified mesostructured silicas

Sample	Textural properties					Acid properties		
	d_{100}[a] (Å)	Pore size[b] (Å)	BET area (m^2/g)	Pore volume[c] (cm^3/g)	Wall thick.[d] (Å)	Acid capacity[e] (meq/g)		Organic incorp.[f] (%)
						Sulfur	H^+	
Pr-SBA-15	111	82	666	1.19	32	1.17	1.21	91
Ar-SBA-15	103	80	720	1.03	26	1.20	1.24	99

[a] $d(1\,0\,0)$ spacing, measured from small-angle X-ray diffraction.
[b] Mean pore size (D_p) from adsorption branch applying the BJH model.
[c] The pore volume (V_p) was taken at $P/P_o = 0.975$ single point.
[d] Average pore wall thickness calculated by a_o-pore size ($a_o = 2d(100)/\sqrt{3}$).
[e] Acid capacities defined as milliequivalents of acid centers per gram of catalyst, obtained either directly by titration (meq H^+/g) or indirectly from sulfur content by elemental analysis (meq S/g).
[f] Organic incorporation estimated from actual sulfur content and maximum theoretical content.