Catalytic etherification of glycerol to produce biofuels over novel spherical silica supported Hyflon® catalysts

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HIGHLIGHTS

► Catalytic etherification of glycerol (GLY) with isobutylene (IB) was investigated.
► Ethers of glycerol as oxygenates additives for diesel fuel were prepared.
► Hyflon® based catalysts supported on spherical silica (SSHC) have been developed.
► Catalysts prepared on spherical silica work much better than A-15.
► Catalysts were found to be stable and easily reusable.

GRAPHICAL ABSTRACT
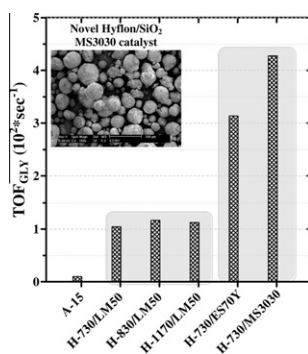
ABSTRACT

Etherification of glycerol (GLY) with isobutylene (IB) to produce biofuels was investigated in liquid phase using spherical silica supported Hyflon® catalysts (SSHC). As reference catalyst, Amberlyst® 15 (A-15) acid ion-exchange resin was used. Experiments were carried out in batch mode at a reaction temperature ranging from 323 to 343 K. SSHC were found to be very effective systems in etherification of glycerol with IB, providing cumulative di- and tri-ethers yields higher than that obtained by using A-15 catalyst. Furthermore, such catalysts were stable and easily reusable; no leaching of active phase was observed. The formation of poly-substituted ethers, suitable additives for conventional fuels, was favored by operating at an isobutylene/glycerol molar ratio >3 and low reaction time (<6 h); however, the concentration of mono-ether reached values lower than 3 wt.% only when SSHC catalyst was used. Turnover frequency of glycerol (TOF$_{GLY}$) highlighted that SSHC systems were much more active than A-15 catalyst: the accessibility and nature of active sites and the surface properties of catalysts were indicated as the main factors affecting the catalytic behavior. A lower acid site density of SSHC than that of A-15 catalyst was decisive in preventing the occurrence of oligomerization reaction which leads to the formation of di-isobutylene (DIB), precursors of gummy products.

1. Introduction

Transesterification processes to produce clean fuels by using vegetable oils and methanol as raw materials produce, along with fatty acid methyl esters (FAME), about 10 wt.% of glycerol as byproduct. Therefore, in order to maximize the economy of the process, new catalytic systems for glycerol conversion into added-value products need to be found (Pathak et al., 2010; Zheng et al, 2008; Behr et al., 2008). Among the transformation routes proposed, the production of biofuels from glycerol by etherification has received particular attention (Alcàntara et al., 2000; Bonura et al., 2007; Frusteri et al., 2009; Gaudin et al., 2011; Janaun and Elles, 2010; Klepáčová et al., 2003, 2005, 2006; Knifton and

Edwards, 1999; Melero et al., 2008; Ruppert et al., 2008; Yang et al., 2000; Posada et al., 2012; Yuan et al., 2010). Etherification takes place as the result of three consecutive steps with the formation of a mixture of two *mono-tert*-butylglycerol ethers (1-MBGE and 2-MBGE), two *di-tert*-butylglycerol ethers (1,3-DBGE and 1,2-DBGE) and one *tri-tert*-butylglycerol ether (TBGE). Side reactions which reduce ether yields can result in the formation of C_8 and C_{12} hydrocarbons from the acid-catalyzed dimerisation of isobutylene or the production of *tert*-butyl alcohol (TBA) from the hydration of IB if water is present in the reaction system (Lee et al., 2010). *Poly*-substituted ethers (*di*- and *tri*-ethers) are preferred as fuel additives due to their good miscibility with conventional diesel fuels. These oxygenated compounds, when blended with diesel or biodiesel fuels, improve engine performance (Melero et al., 2012) leading to a reduction in particulate matter, hydrocarbons, carbon monoxide and unregulated aldehydes emission (Kesling et al., 1994). Specifically, higher *poly*-ethers of glycerol possess suitable combustion properties, which improve the low temperature properties of diesel fuel (pour point and cold filter plugging point) and reduce the viscosity of biodiesel fuel. Ethers can also be considered as "octane-boosters" due to their branched alkyl substituents and thus they are alternatives to commercial methyl and ethyl *tert*-butyl ether, MTBE and ETBE, normally used (Noureddini et al. 2000; Kesling et al., 1994).

In an attempt to overcome problems associated to the use of strong acids in a homogeneous system, the first etherification experiments were carried out using commercial strong ion-exchange resins, like Amberlyst® 15, as solid catalysts (Klepáčová et al., 2003). Isobutylene is the main *O*-alkylation agent employed in such a reaction which takes place with a satisfying rate, but obtaining the desired *poly*-substituted ethers strongly depends on the reaction conditions. Besides, if reactants different from IB, such as TBA, are used, Amberlyst® is affected by swelling due to the formation of water, which affects catalytic activity and selectivity (Klepáčová et al., 2003, 2005; Melero et al., 2008). As the presence of water in the reaction medium can compete with acid active sites, thus deactivating the catalyst, the reaction equilibrium is affected preventing the formation of *poly*-substituted ethers. Since *mono*-ether is neither soluble in diesel nor in biodiesel, it must be removed from ether mixtures by distillation and this step influences the economics of the process. This limitation could be overcome by using a multifunctional reactor able to carry out "reactive distillation" to remove water produced as a distillate and thus attaining higher conversion (Kiatkittipong et al., 2011).

As alternatives to Amberlyst®, several solid acid catalysts have been investigated. Yang et al. (2000) proposed the use of different cation-exchange resins, while Klepáčová et al. (2003, 2005, 2007) suggested the use of H-Y and H-Beta large-pore zeolites. Melero et al. (2008) proposed the use of sulfonic-acid functionalized mesostructured silica and reached interesting results in terms of glycerol conversion and *di*- and *tri* ethers formation, without observing isobutylene oligomerization. Janaun and Ellis (2010), in order to overcome the limit of reaction temperature imposed by the use of organic resins catalysts, suggested the use of non-porous materials, like sulphonated carbon. A different approach was proposed by Calatayud et al. (2009) who claimed the use of basic MeO-based materials, containing a proper balance between acid and basic Lewis sites to avoid the formation of glycerol oligomers. However, basic systems are active in glycerol etherification at a temperature much higher (>473 K) than that required by using acid systems (323–363 K) and, in drastic reaction conditions, catalysts could be affected by leaching. In addition, low surface area, lack of thermal stability (mainly in case of ion-exchange resins) or mass transfer resistance could limit catalyst activity and stability as well as oligomer formation. The presence of impurities in crude glycerol can reduce *poly*-ethers yield (Pagliaro and Rossi, 2008; Da Silva

and Mota, 2011). Consequently, to reduce the presence of undesired impurities, such as diisobutylene and *mono*-ethers, a "step-distillation method" should be employed (Melero et al. 2010) although this step negatively increases the costs of the process. The "ARCO" (Gupta et al., 1995) and the "Bhern and Obendorf" technologies (Behr and Obendorf, 2003) are the main processes proposed to obtain mixtures containing high amounts of *poly*-substituted ethers. However, in such homogeneous catalytic processes, uneconomic multi-step procedures must be performed to recover glycerol *tert*-butyl ethers (Di Serio et al., 2010).

Therefore, new catalytic technologies to obtain valuable *poly*-ethers of glycerol in one step, with heterogeneous systems, need to be developed. On this account, in the present study, a new acid solid catalyst was developed by combining the hydrophobic and acid properties of Hyflon®, used as active species, and the textural properties of spherical silica carriers. Hyflon® is a perfluorosulfonic ionomer (see Fig. 1 in Supplemental data), produced by Solvay Solexis, similar to the widely employed Nafion ionomer. In particular, this study was aimed at developing a novel class of acid catalysts active in the etherification reaction of glycerol with IB, not affected by leaching of active phase and easily separable from the reaction medium to obtain a clean reaction product.

2. Methods

2.1. Catalysts and chemicals

Different solid acid supported catalysts were prepared by the conventional incipient wetness method (Schwarz, 1995) using two spherical silica, *MS3030* and *ES70Y* (Surface Area, 300 and 295 $m^2 g^{-1}$, respectively) supplied by PQ Corporation (Liverpool, UK), and a *LM50 silica* (Fumed silica, Surface Area, 150 $m^2 g^{-1}$) supplied by Cab-O-Sil Division-Rheinfelden, as carriers.

Alcoholic solutions containing about 17 wt.% of Hyflon® Ion S4X perfluorosulfonic ionomers at different equivalent weights (EW, *730*, *850*, *1170*) were used as acid precursors. The EW corresponds to the concentration of sulfonic acid groups in each equivalent unity. As declared by the supplier, the acidity values were 1.23, 1.09 and 0.95 meqH$^+$g$_{ion}^{-1}$, respectively for *H730*, *H850*, *H1170* ionomers. After impregnation, catalysts were dried in air at 393 K for 12 h. At the end of reaction, catalysts were recovered, washed in distilled water and ethanol and dried at 353 K for 12 h to be reused for a new experiment. In addition, Amberlyst® 15 dry (*A-15*) was used as reference catalyst. Anhydrous glycerol (purity ⩾99.5%), supplied by Fluka (Buchs, Switzerland), and isobutylene 3.0, by GHC Gerling HOLZ% Co. Handels GmbH (Hamburg, Germany), were used as reactants.

2.2. Catalysts characterization

Surface area (SA$_{BET}$) and pore volume (PV) values were determined from the nitrogen adsorption/desorption isotherms at 77 K using a Carlo Erba (*Sorptomatic Instrument*) gas adsorption device. Before analysis, the samples were outgassed at 383 K under vacuum for 3 h. The isotherms were elaborated according to the BET (Brunauer, Emmett, Teller) method for surface area calculation (Brunauer et al., 1938).

Active phase loading and thermal stability of catalysts were evaluated by thermo-gravimetric and differential calorimetric (TG-DSC) analysis in the range of 293–1193 K using a *Netzsch Simultaneous Thermal Analysis Instrument* STA409C analyzer, running in air with a heating rate of 10 K min^{-1}.

Potentiometric titrations were performed to evaluate the acid capacity (meq g$_{cat}^{-1}$) of the catalytic systems. Prior to each measurement, about 200 mg of catalyst were placed under