



Catalytic etherification of glycerol by *tert*-butyl alcohol to produce oxygenated additives for diesel fuel

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ABSTRACT

The heterogeneous catalytic etherification of glycerol with *tert*-butyl alcohol was investigated in presence of lab-made silica supported acid catalysts. As reference, two commercial acid ion-exchange resins were also used. Experiments were carried out in batch mode at T_R ranging from 303 to 363 K. An increase in reaction temperature favors the formation of *di*-substituted ethers. The etherification reaction proceeds according to a consecutive path and the surface reaction between adsorbed glycerol and protonated *tert*-butanol (tertiary carbocation) can be considered as the rate determining step. Steric hindrance phenomena and water hinder the formation of *tri*-substituted ether (TBGE). As expected, water removal was necessary to allow the higher ethers formation. The specific activity (turnover frequency, TOF) of A-15 catalyst is significantly higher than that of the other studied acid systems, due to the wide pore diameter that allows an easier accessibility of the reagent molecules.

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1. Introduction

Recently, exhaust gases emitted by internal combustion engines were considered primarily responsible for environmental pollution and human diseases [1–5].

Biodiesel is currently used as a valuable fuel for diesel engines. In spite of a slight power loss, exhausts contain less particulate matter. Biodiesel is a mixture of methyl esters of fatty acids (FAMES) obtained by the transesterification reaction of vegetable oils with methanol in presence of a basic catalyst [1,2]. Such a catalytic process converts raw triglycerides into FAMES, but produces glycerol as side product.

If biodiesel is produced on a large scale, adequate technologies capable of converting glycerol into added value chemicals are necessary [3,4]. In particular, great attention has been already devoted to the conversion of glycerol into oxygenated additives for liquid fuels [3,5–7]. In this context, an industrially relevant route for the conversion of glycerol into oxygenated chemicals involves the etherification to *tert*-butyl ethers [5,7–10].

It is well known that the addition of oxygenated additives to diesel fuels could represent a promising way enhancing the combustion efficiency in internal combustion engines with a significant reduction of pollutant emissions. Among several oxygenated additives proposed to blend with diesel, the ethers of

glycerol could hold a prominent role [7–10]. In particular, *tert*-butyl ethers of glycerol with a high content of *di*-ethers are considered promising as oxygenated additives for diesel fuels (diesel, biodiesel and their mixtures). However, mono-*tert*-butyl ethers of glycerol (MBGEs) have a low solubility in diesel fuel; therefore, in order to avoid an additional separation step, the etherification of glycerol should address the formation of *di*- and *tri*-ethers [5,7–9,11].

The etherification of glycerol can be carried out using heterogeneous acid catalysts like strong acid ion-exchange resins [12–18]; however, the utilization of large-pore zeolites has also been widely investigated [19–22]. Usually, low surface areas and lack of thermal stability are the major drawbacks of sulfonic resins. 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 [23]. Moreover, these type of silica materials functionalized with organosulfonic acid groups have been used previously for the conversion of biorenewable molecules [24–27], showing better catalytic performances than that of the commercial sulfonated resins. Currently, these highly surface materials characterized by interconnected mesopores and high accessibility of acid sites represent the best systems for the etherification reactions [28].

The synthesis of *tert*-butyl ethers (GTBEs) from isobutene and glycerol on ion-exchange resins has been already investigated extensively [8–10]. Isobutene (IB) is produced by catalytic cracking and steam cracking fractions of petroleum refining and by isobutane dehydrogenation [5,7]. What appears more attractive

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is to produce GTBEs by the glycerol etherification reaction in a solid–liquid catalytic process, by using *tert*-butyl alcohol (TBA). In fact, the use of TBA, as both reactant and solvent, instead of gaseous isobutylene, allows to overcome the technological problems arising from the need to use solvents able to dissolve glycerol (*i.e.*, dioxane, dimethyl sulfoxide) and typical drawbacks of a complex three-phase system (mass transfer phenomena) [9,29].

This study focused on the etherification of glycerol with *tert*-butyl alcohol over different solid acid systems. Attention was given primarily to investigate the main limiting factors for large scale process development.

2. Experimental

2.1. Catalysts and chemicals

Two solid acid supported catalysts were prepared by the incipient wetness method using a silica carrier (S.A._{BET}, 250 m² g⁻¹) and two solutions containing 17 wt.% of Nafion[®] ionomer (N-17) and 17 wt.% of tungstophosphoric heteropoly acid (HPW-17), respectively. An aliquot of the HPW-17 sample was mixed with a solution containing cesium to exchange a fraction of H⁺ protons with Cs⁺ (Cs-HPW). In addition, two commercial acid ion-exchange resins, Nafion[®] on amorphous silica (SAC-13) and Amberlyst[®] 15 dry (A-15), were used as reference catalysts.

Glycerol anhydrous (purity ≥99.5%) and *tert*-butyl alcohol (purity ≥99.7%), supplied by Fluka (Buchs, Switzerland), were used as reactants. Standard compounds for GC analysis were supplied on-demand by Aldrich.

2.2. Catalysts characterization

Surface area (SA_{BET}) and pore volume (PV) were determined by the nitrogen adsorption/desorption isotherms at 77 K using a Carlo Erba (Sorptomatic Instrument) gas adsorption device. Before analysis, all the samples were outgassed at 423 K under vacuum for 2 h. The isotherms were elaborated according to the BET method for surface area calculation, with the Horwarth–Kavazoe (HK) and Barrett–Joyner–Halenda (BJH) methods used for micropore and mesopore evaluation, respectively.

The active phase loading and thermal stability were evaluated by thermo-gravimetric (TG) analyses in the range 293–873 K using a Netzsch STA409C analyzer, running in air atmosphere with a heating rate of 10 K/min.

Acid sites were determined by potentiometric titrations with the zero point charge (ZPC) method. About 0.1 g of each sample was dispersed in an aqueous solution of NaNO₃ 0.5 M under stirring. Acidity, measured by an electrode Orion ROSS, was calculated on the basis of the pH at which particles suspended in solution had zero charge.

The list of catalysts used in this study is summarized in Table 1.

2.3. Catalytic testing

The etherification reaction between glycerol and *tert*-butyl alcohol was carried out in liquid phase in a 100 cm³ stainless steel

“jacketed-batch reactor” (Autoclave Engineers, Inc.) under a stirring frequency of 1200 min⁻¹, in order to limit the influence of external mass transfer phenomena. Experiments were performed under different reaction conditions: (i) under pressure; (ii) at reaction temperatures ranging from 303 to 363 K; (iii) by operating at different reaction times and (iv) at both different catalyst/glycerol and alcohol/glycerol ratios.

The experimental procedure was the following: a well defined amount of glycerol and dry catalyst were loaded into the reactor and heated up to a prefixed reaction temperature (in 10 min). Before the addition of *tert*-butanol, the reactor was fluxed with nitrogen to remove the air; then, *tert*-butanol was injected into the reactor by a syringe: this was taken as the starting point of the reaction. At the end of the experiments, the reactor was cooled down (at 298 K) by an ice-bath until the vapour pressure of the mixture turned down to the atmospheric one, thus allowing all the gas phase compounds to condense. After the opening of the autoclave, we collected a completely liquid mixture, without any solidification of TBA on the reactor walls. The liquid reaction mixture was analyzed *off-line* by a gas chromatograph, HP 6890N, provided with a capillary column HP Innowax (1, 30 m; *i.d.*, 0.53 mm; film thickness, 1.0 μm) under the following oven temperature program: from 40 to 220 °C (with a heating rate of 20 °C min⁻¹) and at 220 °C for 3 min. An automatic sampler Agilent 7683B Series was used (0.2 μl of samples were injected), each data set being obtained, with an accuracy of ±1%, from an average of three independent measurements using the external standard method (*n*-heptane, 8 wt.% in respect to the reaction mixture). The samples were not collected at different reaction times for avoiding to spill out a not representative sample of the reaction system due to the different density of the mixture compounds. Water content was calculated by considering the reaction stoichiometry and confirming the result by a quantitative TCD analysis. In each experiment, carbon balance was close to 98%.

3. Results and discussion

Physico-chemical properties of catalysts are summarized in Table 2.

Catalysts are characterized by different surface area ranging from 53 to 207 m² g⁻¹ and porosity comprised between 0.07 and 0.80 cm³ g⁻¹. In terms of SA and porosity, the data obtained with SAC-13 sample are similar to that provided by the supplier. Furthermore, all the catalytic systems show an average pore diameter (APD) increasing with the porosity, apart from A-15 that is characterized by a wide pore texture (300 Å), although it has the lowest SA (53 m² g⁻¹). The acid capacity of A-15 sample was significantly higher than the other investigated samples.

In order to collect quantitative data approaching the equilibrium composition and to obtain a reliable comparison of the catalytic functionality at a prefixed time (6 h), preliminary experiments using different solid acid catalysts were carried out at 0.1 MPa, 343 K, with a *tert*-butanol-to-glycerol molar ratio (*R*_{A/G}) equal to 4. The results shown in Fig. 1 demonstrate that a low catalyst/glycerol ratio equivalent to 1.2 wt.% (much lower than that so far reported in literature [7–10]) is adequate to guarantee high glycerol conversion. Indeed, after 6 h of reaction, low glycerol conversion levels were reached using SAC-13, N-17 and HPW-17 catalysts (8–15 mol.%), while by the Cs-HPW and A-15 samples, characterized by higher acid capacity (Table 2), the reaction takes place at higher rates, reaching at the end of the reaction a glycerol conversion of 54 and 82 mol.%, respectively.

Considering that catalysts are characterized by different acid capacity, the turnover frequency (TOF) of glycerol was reported as a function of the number of acidic sites (see Fig. 2). TOF values were determined from the initial reaction rate (glycerol conversion <5%)

Table 1
List of solid acid catalysts used in this study.

Code	Active phase	Carrier
HPW-17	Phosphotungstic acid	SiO ₂ (Cabosil LM50; S.A. _{BET} =250 m ² g ⁻¹)
Cs-HPW	Phosphotungstic acid exchanged with cesium	SiO ₂ (Cabosil LM50; S.A. _{BET} =250 m ² g ⁻¹)
N-17	Nafion [®] polymer	SiO ₂ (Cabosil LM50; S.A. _{BET} =250 m ² g ⁻¹)
SAC-13	Nafion [®] polymer	Amorphous silica
A-15	Amberlyst [®] -15 dry resin	–

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