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

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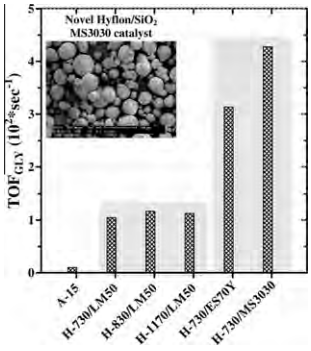
## HIGHLIGHTS

- 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

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## 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

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