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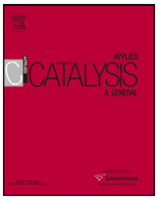

Monoglyceride synthesis by glycerolysis of methyl oleate on MgO: Catalytic and DFT study of the active site

C.A. Ferretti[a], S. Fuente[b], R. Ferullo[b], N. Castellani[b], C.R. Apesteguía[a], J.I. Di Cosimo[a,*]

[a] Catalysis Science and Engineering Research Group (GICIC)-INCAPE (UNL-CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina
[b] Group of Materials and Catalytic Systems (GMSC)-Department of Physics (UNS-CONICET), Av. Alem 1253, 8000 Bahía Blanca, Argentina

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ABSTRACT

The synthesis of monoglycerides by glycerolysis of methyl oleate, a fatty acid methyl ester (FAME), was efficiently promoted on strongly basic MgO. The chemical nature of the base sites responsible for the catalytic activity was investigated, both experimentally and by density functional theory (DFT). MgO catalysts stabilized at different temperatures were used to control the distribution of surface base sites. The nature, density and strength of the catalyst base sites were characterized by TPD and FTIR of CO_2. Catalytic results suggested that the synthesis of monoglycerides was promoted mainly on strongly basic low coordination O^{2-} surface sites.

The molecular modeling of glycerol (Gly) and FAME adsorptions was carried out using terrace, edge and corner sites for representing the MgO surface. Results indicated that Gly was more strongly adsorbed than FAME. Dissociative chemisorption of Gly with O–H bond breaking was favored on low coordination O^{2-} surface sites such as those on edges, in agreement with the experimental results. Thus, the proton abstraction from the OH groups of Gly, a necessary step in the reaction mechanism, would take place on unsaturated oxygen anions and the resulting glyceroxides would react with weakly adsorbed FAME molecules.

1. Introduction

The participation in the fuel market of biomass-derived fuels such as biodiesel or bioethanol is growing worldwide. Most of the biodiesel is produced by oil or fat transesterification and glycerol (Gly) is simultaneously obtained as the main co-product in an amount that represents 10% of the biodiesel production. This increasing Gly surplus has generated the need for new applications intended to convert glycerol into value-added chemicals. In this framework, monoglyceride (MG) synthesis by Gly transesterification results in an attractive option to transform this biomass-derived compound into fine chemicals.

Monoglycerides, the glycerol monoesters of fatty acids present surfactant and emulsifying properties that help hydrophilic and lipophilic substances mix together. Therefore, they can be used in food, detergent, plasticizer, cosmetic and pharmaceutical formulations [1,2].

In previous works [3,4] we discussed the different routes for MG synthesis by esterification of fatty acids (FAs) or by transesterification (glycerolysis) of triglycerides (TGs) or fatty acid methyl esters (FAMEs). We concluded that the reaction route from FAME yields MG with a definite acyl group composition (FAMEs are easier to separate by fractional distillation than FAs) whereas in TG glycerolysis the products contain the acyl group distribution of the oil or fat [5]. Furthermore, we discussed the benefits of using a heterogeneously catalyzed process for MG synthesis from Gly and FAME in contrast to the homogeneous or enzymatic processes. We reported the reaction conditions needed to implement this reaction in a four-phase reactor under kinetic control and also to reach maximum MG yield. Thus, the effect of experimental variables such as stirring rate, catalyst particle size, reaction temperature, Gly/FAME ratio, and catalyst load was studied using methyl oleate as a model FAME molecule [4]. We also concluded that glycerolysis of FAME (Scheme 1) is efficiently promoted by base catalysts such as MgO [3], in agreement with previous work [6]. Moreover, we investigated the effect of adding basic promoters such as Li to MgO and found that on Li-containing MgO catalysts the initial monoglyceride formation rate increased linearly with the sample Li content following the enhanced overall catalyst base strength [7].

Several papers study the heterogeneously catalyzed kinetics of transesterification reactions for biodiesel synthesis or other applications at low temperatures [8,9], but there are almost no reports devoted to elucidate the active site in glycerolysis reactions that proceed at higher temperatures and involve multiphase reactors. In this regard, the pioneering work by Corma et al. [1] discussed

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[*] Corresponding author. Tel.: +54 342 4555279; fax: +54 342 4531068.
E-mail address: dicosimo@fiq.unl.edu.ar (J.I. Di Cosimo).

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