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

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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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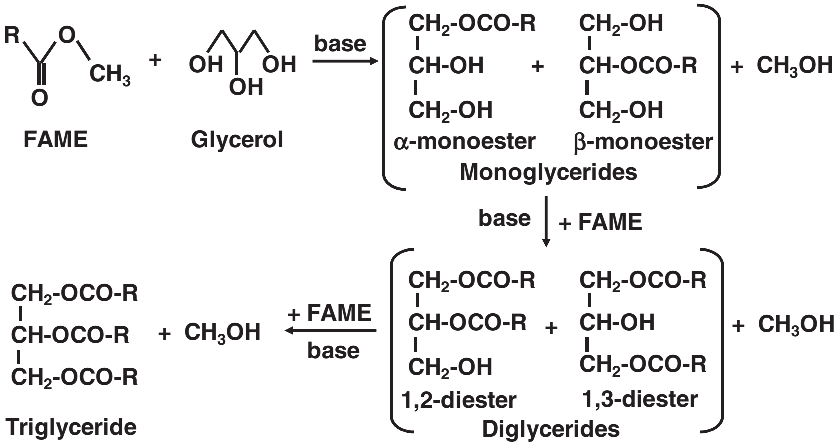

Scheme 1. Monoglyceride (MG) synthesis by glycerolysis of FAME and consecutive reactions to diglycerides (DGs) and triglycerides (TGs).

the advantages of using Lewis base catalysts such as single or mixed oxides to enhance the activity or Brønsted base catalysts to improve the selectivity of methyl oleate glycerolysis. Furthermore, Bancquart et al. [6] attempted for the first time to correlate the activity of methyl stearate glycerolysis with the total basicity of different single oxides. Thus, investigations with the aim to identify the chemical nature of the base sites and to determine the base strength requirements for glycerolysis reactions are still lacking as well as studies on the kinetic role played by the base sites. Thus, in this paper we continue our studies of the glycerolysis of an unsaturated FAME, methyl oleate (C18:1), focusing on the MgO active sites. It is well known that in addition to the weak Lewis acid sites supplied by the Mg^{2+} cations, MgO presents surface base sites provided by different oxygen species, from OH^- sites to coordinatively unsaturated O^{2-}, which present a wide range of basic properties [10–12]. It has been shown that MgO promotes different reactions and that depending on the reaction base strength requirements, the species participating in the kinetics can be a weak, medium or strong base site [10,13,14].

Therefore, our goal here is to ascertain the MgO base site responsible for the catalytic activity and to get insight into the base site strength requirements for the reaction. We discuss also the role of the catalyst active sites (Mg^{2+} cations and oxygen species) in the surface activation of both reactants in the reaction mechanism.

The identification of the chemical nature and basic properties of the catalyst active site was achieved by varying both, the total basicity of MgO and the contribution of the different base surface species, and then testing the resulting materials with the purpose to correlate the activity with the density of the particular base site that promotes the glycerolysis of methyl oleate.

Furthermore, the role played by the MgO surface sites in the reaction kinetics was investigated by complementing the catalytic studies with several characterization techniques and density functional theory (DFT) calculations of the FAME and Gly adsorptions on model MgO surface sites. The reactants are complex molecules; in the case of FAME, the molecule combines a long hydrophobic tail with a hydrophilic head, whereas in what concerns to Gly, this polyol contains three hydroxyl groups that can participate in the reaction. Although in a previous work [15] the theoretical calculations of the Gly interaction with alkaline earth metal oxides have been discussed, to the best of our knowledge, the molecular modeling of the distinct interaction of Gly and FAME with the MgO surface, with the aim of elucidating both the nature of the active site and the surface activation of C═O, O–H and other bonds participating in the glycerolysis reaction, has never been reported.

2. Materials and methods

2.1. Catalyst preparation

Magnesium oxide samples were prepared by hydration with distilled water of low-surface area commercial MgO (Carlo Erba 99%; 27 m^2/g) [16]. 250 ml of distilled water was slowly added to 25 g of commercial MgO and stirred at room temperature. The temperature was then raised to 353 K and stirring was maintained for 4 h. Excess of water was removed by drying the sample in an oven at 358 K overnight. The resulting $Mg(OH)_2$ was decomposed in a N_2 flow to obtain high-surface area MgO which was then stabilized for 18 h in N_2 either at 673, 773 or 873. Samples were finally ground and sieved, and the particles with average particle size of 177–250 μm were used for the catalytic experiments.

2.2. Catalyst characterization

BET surface areas were determined by N_2 physisorption at 77 K in a NOVA-1000 Quantachrom sorptometer. The structural properties of MgO catalysts were determined by X-ray diffraction (XRD) using a Shimadzu XD-D1 diffractometer equipped with Cu-Kα radiation source ($\lambda = 0.1542$ nm). Analysis was carried out using a continuous scan mode at 2°/min over a 2θ range of 20–80°. The Scherrer's equation was used to calculate the mean crystallite size of the samples.

Catalyst basic properties were measured by temperature-programmed desorption (TPD) and infrared spectroscopy (FTIR) of CO_2. For the TPD experiments, samples were pretreated in situ in a N_2 flow at 723–773 K to remove water and carbonates formed during storage, cooled down to room temperature, and then exposed to a flowing mixture of 3% of CO_2 in N_2 until surface saturation was achieved (5 min). Weakly adsorbed CO_2 was removed by flushing with N_2. Finally, the temperature was increased to 773 K at a ramp rate of 10 K/min. Desorbed CO_2 was converted in CH_4 on a methanation catalyst (Ni/Kieselghur), and then analyzed using a flame ionization detector (FID). Total base site numbers (N_b, μmol/g) were measured as the evolved CO_2 obtained by integration of TPD curves.

The chemical nature of adsorbed surface CO_2 species was determined by FTIR after CO_2 adsorption at room temperature and sequential evacuation at increasing temperatures. The sample was pressed in a wafer and degassed in vacuum at 723–773 K for 1 h and then cooled down to room temperature. The spectrum of the pretreated catalyst was then taken. After admission of 5 kPa of CO_2 and evacuation at 298, 373, 473 and 573 K, the CO_2 adsorption spectra were recorded at room temperature. Spectra of the adsorbed