

Monoglyceride synthesis by glycerolysis of methyl oleate on MgO: catalytic and theoretical investigation of the active site

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Introduction

During biodiesel synthesis by oil or fat transesterification, glycerol (Gly) is obtained as the main co-product, representing 10 % of the biodiesel production. Nowadays, glycerol surplus is becoming a matter of environmental concern and conversion

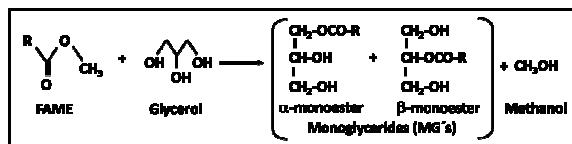


Figure 1: MG synthesis by glycerolysis of FAME

of Gly into high value-added chemicals or fuels is needed. Monoglyceride (MG) synthesis by glycerolysis of fatty acid methyl esters (FAME), Figure 1, is an interesting option to transform this biomass-derived compound into fine chemicals. In this work, the glycerolysis of oleic acid (C18:1) methyl ester was studied using MgO. The chemical nature of the base site for promoting the MG synthesis was investigated using several characterization techniques and Density Functional Theory (DFT) calculations.

Materials and Methods

High surface area MgO stabilized at $T_{\text{calc}} = 623, 673, 773$ and 873 K was prepared. The number and chemical nature of the base sites were measured by TPD and FTIR of CO_2 . Glycerolysis of FAME was carried out at 493 K and $\text{Gly}/\text{FAME} = 4.5$ (molar ratio) in a batch reactor. The reaction products: α - and β -glyceryl monooleates (MG's), 1,2- and 1,3-glyceryl dioleates (diglycerides, DG's) and glyceryl trioleate (triglyceride, TG) were analyzed by gas chromatography after silylation. DFT molecular orbital calculations were performed using the hybrid B3LYP functional. All the calculations were carried out using the Gaussian-03 program package. The terrace site at MgO (100) surface was represented by the $\text{Mg}_{25}\text{O}_{25}$ (Mg-ECP)₂₅ cluster and the topological defects by $\text{Mg}_{22}\text{O}_{22}$ (Mg-ECP)₁₉ (edge sites) and $\text{Mg}_{22}\text{O}_{22}(\text{Mg-ECP})_{12}$ (corner sites) clusters. The atoms of MgO have been described by the 6-31G basis set, and those of glycerol and FAME molecules have been treated with the 6-31G** basis.

Results and Discussion

In order to get insight into the chemical nature of the basic sites responsible for glycerolysis activity, a set of MgO catalyst treated at different T_{calc} was prepared and characterized. By FTIR of CO_2 , Figure 2, all the MgO catalysts showed different CO_2 adsorption species on surface sites having the following base strength order: unidentate

carbonate species (U.C.) formed on strongly basic O_{3c}^{-2} or O_{4c}^{-2} anions located in corners or

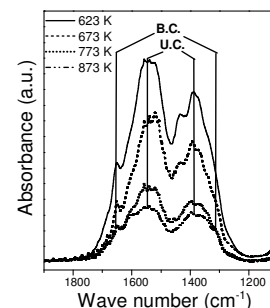


Figure 2: FTIR spectra of CO_2 on MgO stabilized at different T_{calc}

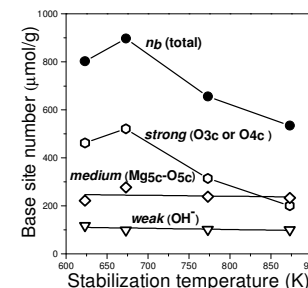


Figure 3: Base site number by TPD of CO_2 vs. T_{calc}

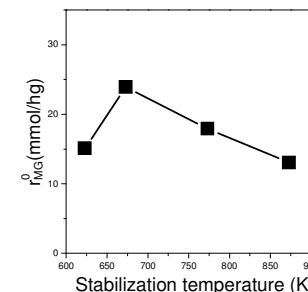


Figure 4: Initial MG formation rate on MgO vs. T_{calc}

edges > bidentate carbonate species (B.C.) formed on medium-strength $\text{Mg}_{5c}^{2+}\text{-O}_{5c}^{2-}$ pairs located on terraces > bicarbonate species on weak OH^- groups. The higher band intensity of U.C. species suggests that the MgO surface contains mainly strong base sites in a number that decreases upon increasing T_{calc} . Based on the identification of the surface oxygen species by FTIR, the contribution of these species was determined by deconvolution of the CO_2 TPD curves. The effect of T_{calc} on the total number of base sites (n_b) and on the contribution of each surface species is presented in Figure 3, showing that the strong base sites are affected by the increase of T_{calc} whereas the other surface species remain unchanged.

Glyceryl monooleate (MG) yields as high as 70% can be obtained at 493 K on MgO treated at different T_{calc} with 30% DG and no TG formation. The initial catalytic activity of MgO for the glycerolysis reaction was affected by T_{calc} (Figure 4) in a similar way to the base sites (Figure 3) indicating that the reaction mainly takes place on strong base sites, such as the coordinatively unsaturated oxygen anions present in corners or edges (O_{3c}^{-2} or O_{4c}^{-2}).

Preliminary DFT calculations reveal that Gly chemisorbs non-dissociatively on terrace sites whereas dissociative chemisorption of the O-H bond occurs on strong base sites (edges and corners) in agreement with the results of Fig. 3 and 4. The O-H bond breaking is a necessary step of the glycerolysis reaction mechanism. Gly chemisorption through the primary OH groups is favored over that of the secondary OH, in line with the catalytic results showing that the major MG isomer is α -MG ($\approx 62\%$ selectivity). Besides, calculations suggest that Gly adsorbs more strongly than FAME on MgO. Results suggest that the reaction i) is preferentially promoted by low-coordination oxygen anions where Gly primary OH groups dissociate; ii) probably follows an Eley-Rideal mechanism with negligible FAME adsorption.

Significance

Catalytic and theoretical calculations indicate that strong low-coordination surface oxygen anions are the active sites that contribute the most to the glycerolysis reaction toward monoglyceride formation on MgO.