

Experimental and theoretical study of the glyceride isomer selectivity for glycerolysis of methyl oleate on MgO

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Introduction

The synthesis of monoglycerides (MG) and diglycerides (DG) by glycerolysis of fatty acid methyl esters (FAME), **Figure 1**, is an attractive option to transform bio-glycerol (Gly) into valuable chemicals. In this work, the liquid-phase MgO-promoted glycerolysis of methyl oleate (FAME with C18:1) to give glycerides was studied both, experimentally and by Density Functional Theory (DFT) with the purpose to elucidate selectivity issues.

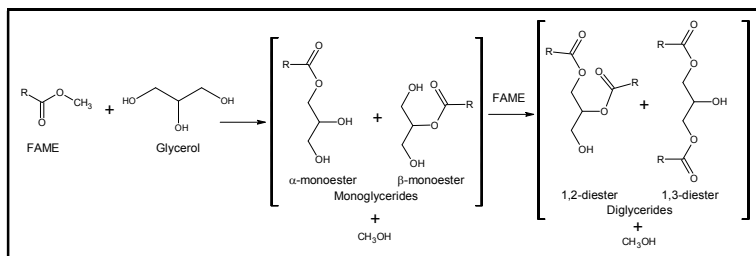


Figure 1. Reaction scheme for glycerolysis of FAME.

Materials and Methods

The glycerolysis of FAME was carried out at 483-503 K and Gly/FAME = 2-6 (molar ratio) in a batch reactor [1]. Reaction products were α - and β -glyceryl monooleates (MG), 1,2- and 1,3-glyceryl dioleates (diglycerides, DG). Molecular modeling of Gly and FAME adsorptions as well as of the glycerolysis reaction was carried out using the Vienna Ab-initio Simulation Package (VASP) for periodic calculations and a model of stepped MgO surface.

Results and Discussion

Catalytic results showed that strongly basic low coordination O^{2-} surface sites of MgO participate in kinetically relevant steps of the glycerolysis reaction. Changes in the selectivity toward the different mono and diglyceride isomers were investigated by varying the reaction temperature and the Gly/FAME ratio. Selectivity to α -MG is enhanced by increasing the reaction temperature, **Figure 2**. The effect of the Gly/FAME ratio on the selectivity to glycerides and on isomer distribution was almost negligible. The main product was always α -

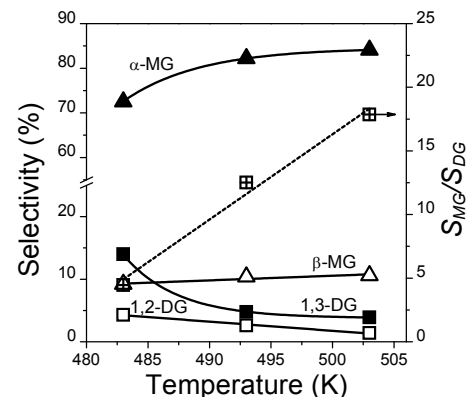


Figure 2. Effect of the reaction temperature on glyceride selectivity and on S_{MG}/S_{DG} selectivity ratio at FAME conversion of 35 % [Gly/FAME=4.5].

energetically favored dissociation of the O-H bond at position 2 of Gly that leads to β -glyceroxide. They predict that, in agreement with the catalytic results, α -MG is favored over β -MG and that the β -glyceroxide species participates in the pathways conducting to both, α - and β -MG isomers. Thus, synthesis of α -MG, **Figure 3**, occurs by C–O coupling of β -glyceroxide with FAME at one of the two primary OH groups of the β -glyceroxide species. Two transition states (TS) and a tetrahedral intermediate (TI) are involved in either α -MG or β -MG isomer formation; but the pathway toward β -MG is limited by formation of the TI due to large steric effects whereas the TI leading to α -MG is relatively easy to form.

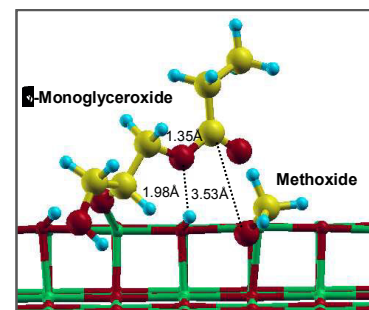


Figure 3. Optimized structures of α -monoglyceroxide and methoxide species. Red:O; Green:Mg; Cyan:H; Yellow:C.

Significance

Molecular modeling explains why α -MG forms preferentially despite that dissociation of O-H bond at position 2 of Gly is energetically favored. Mechanisms for α -MG and β -MG formation are postulated; a β -glyceroxide species participates in the pathways toward both isomers.

References

1. C.A. Ferretti, S. Fuente, R. Ferullo, N. Castellani, C.R. Apesteguía, J.I. Di Cosimo, *Appl. Catal. A: General* 413–414, 322 (2012).