Kinetic study of the mono and diglyceride synthesis by 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 interesting option to transform glycerol (Gly) into value-added chemicals. In this work, the glycerolysis of methyl oleate (FAME with C18:1) was studied on MgO. A kinetic model was postulated based on previous experimental evidence and theoretical calculations by Density Functional Theory (DFT).
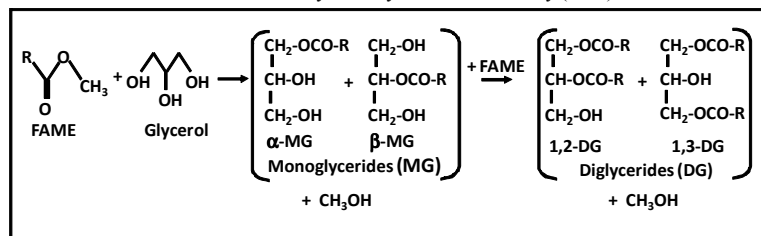

Figure 1: Reaction scheme for glycerolysis of FAME

Materials and Methods

The glycerolysis of FAME was carried out at 483-503 K and Gly/FAME = 2, 3, 4.5 and 6 (molar ratio) in a batch reactor. The reaction products: α- and β-glyceryl monooleates (MG), 1,2- and 1,3-glyceryl dioleates (diglycerides, DG) were analyzed by gas chromatography after silylation. Glyceryl trioleate (triglyceride, TG) was never observed under these conditions. DFT molecular orbital calculations were performed using the hybrid B3LYP functional. Calculations were carried out using the Gaussian-03 program package on model MgO surface sites representing Mg and O apical corners, an edge and a terrace.

Results and Discussion

Figure 2 shows an example of the catalytic results obtained on MgO. Similar experiments were carried out at different temperatures and Gly/FAME ratios. A reaction mechanism was postulated in which the first step, Figure 3, is Gly dissociative adsorption on a Mg_s-O_s pair forming a glyceroxide anion. Simultaneously, FAME interaction with a Mg_s through the oxygen of the C=O function might take place, with concomitant polarization of the C=O bond. The Gly O-H bond breaking is a necessary step of the glycerolysis reaction mechanism and polarization of the FAME carbonyl bond would favor the attack of the glyceroxide anion on the carbonyl carbon, Figure 3. DFT calculations showed that activation and dissociation of the O-H bond of Gly more likely occur on strong low coordination O^{2-}
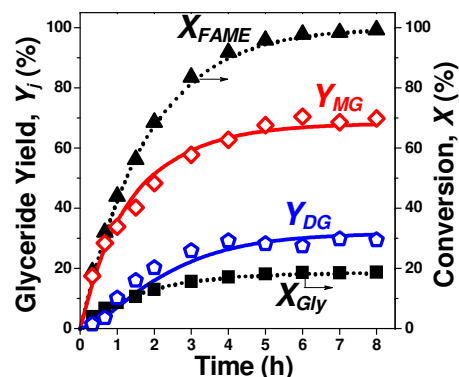

Figure 2: FAME and Gly conversions and glyceride yields on MgO [Gly/FAME = 4.5; T = 493 K]
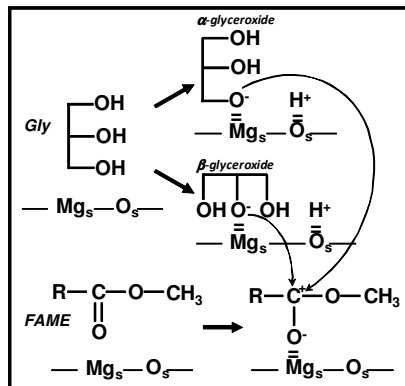

Figure 3: Gly and FAME adsorption on MgO

(corner and edges) in agreement with catalytic results showing that the rate-limiting step (r.l.s) is promoted by strong base sites [1]. Furthermore, calculations predicted that only one O-H bond dissociates at a time, indicating that only MG are primary products of the reaction and that DG form consecutively, as postulated in Figure 1 and indicated by the zero initial slope of the DG data points in Figure 2. DFT calculations also

Figure 4: LHHW surface reaction mechanism

indicated that Gly (-1.85eV) is more strongly adsorbed than FAME (-0.67eV) and that polarization of the FAME C=O bond, as depicted in Figure 3, is almost negligible, suggesting a weak FAME-surface interaction. Thus, for kinetic modeling purposes, the FAME adsorption was disregarded. With all this information, a single site LHHW reaction mechanism for complex reactions was postulated, Figure 4. In that mechanism, the r.l.s are the surface reactions for MG and DG formation (steps 2 and 4). A good correlation was obtained between the kinetic model results (lines) and the experimental results (data points) of Figure 2. This kinetic model also suitably interprets experimental results at other reaction conditions.

Significance

A LHHW kinetic model for FAME glycerolysis was postulated. Model assumptions were based on DFT calculations of Gly and FAME adsorption on MgO and catalytic results.

References

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