

MONOGLYCERIDE SYNTHESIS ON SOLID BASES

Cristián Ferretti, Roberto Olcese, Carlos Apesteguía and Isabel Di Cosimo*

Catalysis Science and Engineering Research Group (GICIC)- INCAPE (UNL-CONICET), Santiago del Estero 2654,(3000) Santa Fe, Argentina

*e-mail: dicosimo@fiq.unl.edu.ar

Glycerol is the main byproduct of biodiesel production. Nowadays, due to the large glycerol surplus, new ideas to convert glycerol in more valuable compounds are needed. Monoglyceride (MG) synthesis by glycerol (Gly) transesterification with fatty acid methyl esters (FAME), Figure 1, is an attractive option to transform this biomass-derived compound into fine chemicals. MG's are used as surfactants in food, cosmetics and pharmaceuticals. Currently, this process is promoted by corrosive, non-recyclable liquid mineral bases. Then, the use of a solid base catalyst would present several technological and environmental advantages.

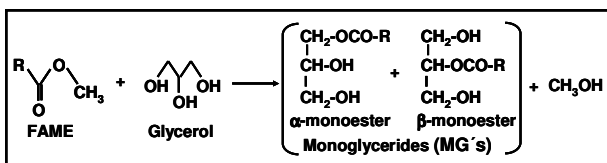


Figure 1: MG synthesis by transesterification of Gly with FAME.

In this paper, the solid base-catalyzed transesterification of Gly with methyl oleate was studied using MgO-based catalysts and Y_2O_3 .

The effect of varying the reaction conditions was investigated as well as that of catalyst surface basic properties. MgO catalysts calcined at 623, 673, 773 and 873 K and Li-promoted MgO were prepared as described previously [1]. The total base site density (n_b) was obtained from TPD of CO_2 . The chemical nature of surface basic sites was determined by FTIR of CO_2 . Glycerolysis of FAME with Gly was carried out at 473-503 K in a glass semi-batch reactor with a typically Gly/FAME = 4.5 (molar ratio). 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 [2].

The solids contained weak (OH^-), medium-strength (M-O pairs, M=Mg, Li, Y) and strong base sites (O^{2-}) as determined by TPD and IR of CO_2 .

Preliminary catalytic results were obtained with MgO activated at 773 K.

Four phases were present inside the reactor and therefore, conditions to rule out diffusional limitations had to be determined; operation at high stirring rates (700 RPM) and with small particle sizes (177-250 μm) was necessary to ensure kinetic control. MG yield was enhanced at increasing reaction temperatures in the range of 473-503 K but above 513 K polyglycerols started to form. A Gly/FAME = 1 (stoichiometric ratio) shifted the reaction pathway toward DG formation (consecutive reaction between FAME and MG) whereas a Gly excess in the reactant mixture increased MG yield and gave similar results for Gly/FAME ratios of 2-6, suggesting a zero reaction order respect to Gly in the overall kinetics.

The reaction seems to be promoted on surface basic sites as indicated by the similar trends of n_b and the initial MG formation rate as a function of the calcination temperature (T_{calc}), Figure 2. Stronger (Li/MgO) and weaker (Y_2O_3) solid bases than MgO were also tested (Figure 3) confirming that strong base sites promote this reaction. Glycerol monooleate yields as high as 70 % and 100% FAME conversions were obtained using solid bases at mild conditions in less than 5 h. No TG was detected at any reaction condition in contrast to the homogeneously-catalyzed reaction. Thus, replacement of the environmentally unfriendly liquid bases used in the commercial process can be achieved with MgO and other similar solid bases.

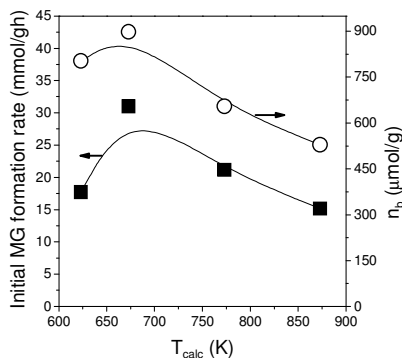


Figure 2: MgO activity and base site density vs. T_{calc}

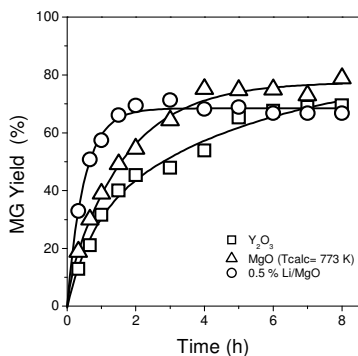


Figure 3: MG yield on solid bases [493 K, Gly/FAME = 4.5]

References

1. Díez, V.K., Apesteguía, C.R., and Di Cosimo, J.I. *J. Catal.* 240, 235 (2006)
2. Tallent, W.H. and Kleiman, R. *J. Lipid Research* 9, 146 (1968).