

Monoglyceride synthesis by glycerol transesterification on solid bases

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Introduction

Glycerol is the main byproduct of biodiesel production. Nowadays, glycerol surplus is becoming a matter of environmental and economic concern. Therefore, 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. Nowadays, 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.

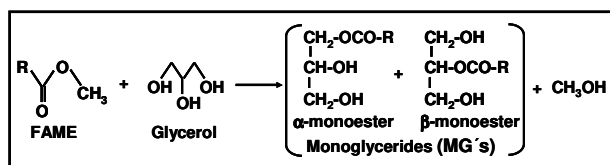


Figure 1: MG synthesis by transesterification of Gly with FAME.

temperature and Gly/FAME ratio on the MG yield was investigated as well as those of catalyst surface hydroxylation and basic properties.

Materials and Methods

High surface area MgO calcined at 623, 673, 773 and 873 K was prepared. The total base site density (n_b) was obtained from temperature-programmed desorption (TPD) of CO_2 . The chemical nature of surface basic sites was determined by Infrared Spectroscopy (IR) of CO_2 . Glycerolysis of FAME with Gly was carried out at 473-503 K in a glass semi-batch reactor with Gly/FAME = 1-6 (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.

Results and Discussion

All the basic catalysts contained weak (OH^-), medium-strength (M-O pairs, $\text{M}=\text{Mg}$, Li , Y) and strong base sites (O^{2-}) as determined by TPD and IR of CO_2 (Table 1). Preliminary catalytic results were obtained with MgO activated at 773 K (Figs. 2 and 3). 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, Figure 2. However, at more than 513 K polyglycerols started

In this paper, the solid base-catalyzed transesterification of Gly with oleic acid methyl ester was studied on several basic oxides. The effect of the reaction

Table 1. Physicochemical properties and catalytic results

Catalyst	S.A. (m^2g^{-1})	n_b^a (μmolg^{-1})	T_{calc} (K)	Catalytic results ^b			
				r_{FAME}^0 (mmol/hg)	Reaction time ^c (h)	Selectivity ^c (%)	
						MG	DG
Li/MgO	179	609	773	17.0	2	73.6	26.4
MgO	169	529	873	15.1	2.5	76.7	23.3
MgO	247	803	623	14.0	3	69.3	30.7
Y_2O_3	54	280	723	11.7	4	70.8	29.2

^a total base site density by TPD of CO_2 ; ^b at 493 K; ^c FAME conversion = 75 %

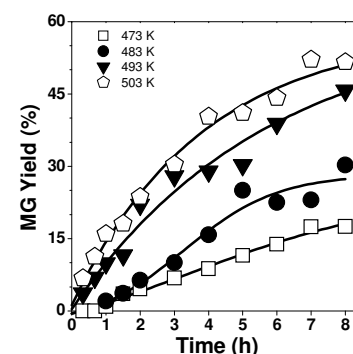


Figure 2: Effect of reaction temperature [MgO, $T_{\text{calc}}=773$ K, Gly/FAME=4.5]

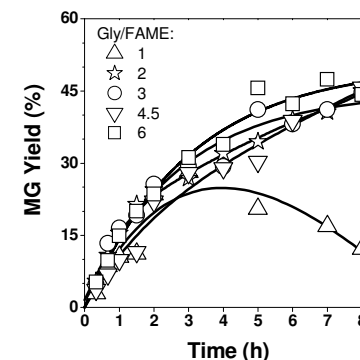


Figure 3: Effect of the Gly/FAME ratio [MgO, $T_{\text{calc}}=773$ K, $T=493$ K]

to form. A Gly/FAME molar ratio of 1 (stoichiometric ratio) shifted the reaction pathway to DG formation (consecutive reaction between FAME and MG) due to the fact that not enough Gly was present in the FAME phase. A Gly excess in the reactant mixture increased MG yield, Figure 3. Gly/FAME ratios in the range of 2-6 gave similar results probably suggesting a zero reaction order respect to Gly in the overall kinetics.

More dehydroxylated, i.e., less hydrophilic surfaces obtained at higher calcination temperatures (T_{calc}) were more active for MG formation (Table 1). This is attributed to the lower Gly affinity for dehydroxylated surfaces that facilitates the FAME surface activation. Stronger (Li/MgO) and weaker (Y_2O_3) solid bases than MgO were also tested showing that strong base sites are needed to promote this reaction (Table 1). This result is probably related to the fact that an O-H bond of Gly and the C-O bond of FAME need to be activated on the surface for the reaction to occur.

Significance

Glyceryl monooleate yields as high as 70 % were obtained using solid bases at mild conditions in less than 5 h. Thus, replacement of the environmentally unfriendly liquid bases used in the commercial process can be achieved with MgO and other similar solid bases. No TG was detected at any reaction condition in contrast to the homogeneous reaction.