Monoglycerides, the glycerol monoesters of fatty acids present surfactant and emulsifying properties. Therefore, they can be used in food, detergent, plasticizer, cosmetic and pharmaceutical formulations. The synthesis of monoglycerides (MG) by glycerolysis of methyl oleate, a fatty acid methyl ester (FAME) with glycerol (Gly), was studied on MgO in a four-phase reactor at 493K with a Gly/FAME = 4.5 (molar) and a catalyst/FAME = 30 g/mol. The chemical nature of the base site responsible for the catalytic activity was investigated, both experimentally and by density functional theory (DFT).

Control of the distribution of surface base sites on MgO catalysts was performed by treating MgO at different calcination temperatures. Identification of the chemical nature, and density and strength quantification of the catalyst base sites were carried out by TPD and FTIR of CO₂. Based on the FTIR and TPD results, MgO base sites were classified in strong, medium and weak sites; they were identified according to the carbonate species formed upon CO₂ adsorption as low coordination O²⁻ (O₃c or O₄c) located in corner or edge sites, O₅c in Mg-O pairs located on terrace sites and OH groups, respectively. Results of Fig. 1 revealed that the total base site density and the base strength distribution changed by increasing the MgO calcination temperature. In particular, these results show the decreased contribution of the strong base sites whereas the density of medium and weak sites changed slightly. Thus, by increasing the severity of the thermal treatment, elimination of surface defects such as corners or edges took place with the concomitant loss of strongly
basic oxygen anions.

The initial MG formation rate \( \dot{r}_{\text{MG}}^{0} \) decreased with the calcination temperature following a trend similar to that observed for the strong base site density in Fig. 1. Thus, the correlation of Fig. 2 suggests that strong base sites present in corners or edges of the non-uniform surface of MgO catalysts participate in the rate-determining step of MG formation. The expected role of these strong base sites is the H abstraction from the O-H groups of Gly as depicted in Fig. 3.

The molecular modeling of Gly and FAME adsorptions was carried out using terrace \((O_{5c})\), edge \((O_{4c})\), and corner \((O_{3c})\) sites for representing the MgO surface base sites, with the purpose of elucidating: i) how hydrophilic Gly and hydrophobic FAME molecules accommodate on the MgO surface; ii) what site configuration promotes the first reaction step (O-H bond breaking, Fig. 3); iii) whether or not the FAME molecule is adsorbed on the surface in the presence of the competing Gly molecule. Main results indicated that Gly was much more strongly adsorbed than FAME. Dissociative chemisorption of Gly took place on low coordination \(O^{2-}\) sites such as those on edges (strong base sites), as shown in Fig. 4, in agreement with the catalytic results of Fig. 2. Only one O-H bond of Gly dissociated at a time in agreement with the catalytic results showing that MG are the only primary reaction products. Thus, the proton abstraction from Gly OH groups, would take place on unsaturated oxygen anions and the resulting glyceroxides would react with FAME molecules weakly adsorbed on Lewis acid sites supplied by surface \(Mg^{2+}\).