

## Catalytic and DFT study of the MgO active site participating in glycerolysis reactions toward monoglycerides

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Monoglycerides, the glycerol monoesters of fatty acids present surfactant and emulsifying properties. Therefore, they can be used in food, detergent, plasticizer,

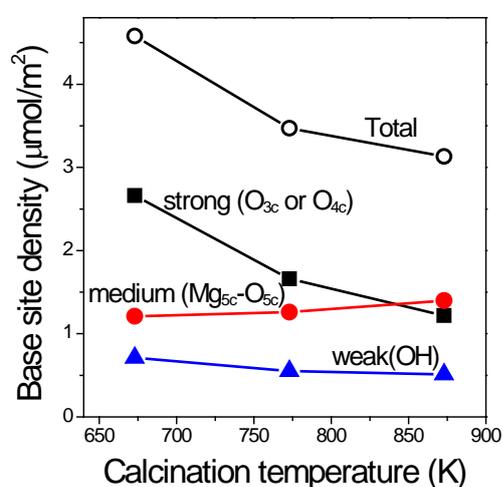


Fig. 1: Effect of calcination temperature on MgO base site distribution by TPD of CO<sub>2</sub>

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 CO<sub>2</sub>. 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 CO<sub>2</sub> adsorption as low coordination O<sup>2-</sup> (O<sub>3c</sub> or O<sub>4c</sub>) located in corner or edge sites, O<sub>5c</sub> 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

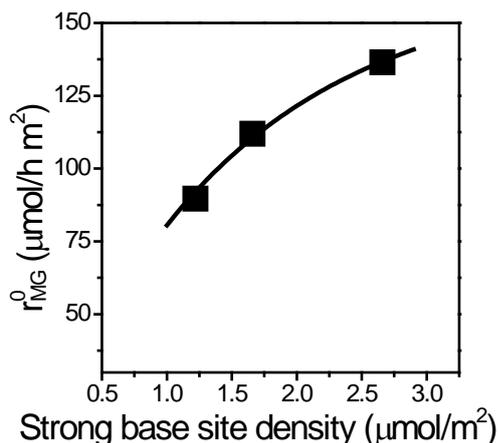


Fig. 2: Initial MG formation rate as a function of MgO strong base site density

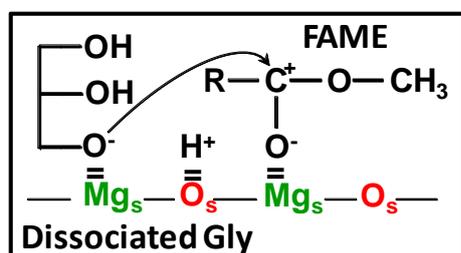


Fig. 3: Gly dissociative adsorption with formation of surface proton and glyceroxide species and FAME surface activation

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,

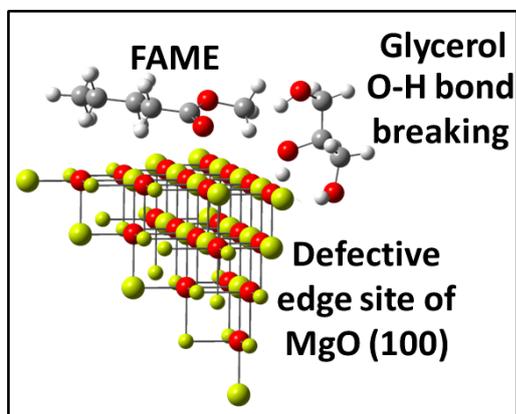


Fig. 4: FAME and Gly adsorption on a MgO defective  $Mg_{22}O_{22}(Mg-ECP)_{19}$  edge site, [green: Mg; red: O]

basic oxygen anions.

The initial MG formation rate ( $r_{MG}^0$ ) decreased with the calcination temperature following a trend similar to that observed for the strong base site density in Fig. 1. Thus, the observation of Fig. 2 suggests that strong base sites present in corners or edges of the non-porous surface of MgO catalysts participate in the rate-determining step of MG formation. The expected role of these strong base sites in 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

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  $Mg^{2+}$ .