Modeling of transesterification process on triacetin through acid and base heterogeneous catalysts for Biodiesel production: A DFT Study

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The increase on the cost of petroleum-derived fuels has raised the search of renewable fuels, particularly biodiesel. Biodiesel is made of fatty acid alkyl esters, derived from vegetable oils. Its production is obtained through transesterification, consisting of conversion of those oils, composed mainly of triglycerides into biofuel. The conversion is achieved, after several transesterification reactions take place, involving the reaction of an alkoxy group with methanol or ethanol. This reaction is usually catalyzed by a homogenous catalyst. Nevertheless, the use of a heterogeneous catalyst is more preferable due to economic and environmental concerns, but has not been commonly implemented . The use of a solid acid or base heterogeneous catalysts is of high relevance since they are capable to catalyze both transesterification and esterifications reactions at the same time[1,2,3]. This is crucial where lower-quality feedstocks like deep-frying oils are used. In this direction, theoretical understanding of transesterification in terms of quantum electronic structure has not been explored so far. In this study we used DFT at the B3LYP level[4] to calculate reaction routes, taking triacetin as a triacylglycerol model[5].Besides, we fully optimized model clusters of the acid heterogeneous catalysts6 Nafion® (**1**)and Zirconium sulfate $Zr(SO_4)_2$ (**2**) and the base heterogeneous catalyst MgO (**3**). Such complexes were optimized with triacetin to study transesterification with the TZVP basis set and pseudopotentials for the metal atoms and the standard 6-31G++(2d2f,p) basis set, for the non-metal atoms. HOMO-LUMO interactions, Potential energy surfaces mapping and Fukui indexes of nucleophilic and electrophilic attack were analyzed to determine active sites around catalysts 1-3 model systems.

Several geometric arrangements were characterized to compute the free energy reaction profile of one-step heterogeneous-catalyzed mechanism in methanol, using a polarized continuous model.Ground state structures were found and Absorption energies were calculated among the cluster models and triacetin. Internal Reaction Coordinate calculations were performed for the lowest energy structures Triacetin-heterogenous catalyst and reaction paths with its corresponding potential barrier were found, indicating the structural changes that the catalyst undergo in the absorption process. Consequently, we theoretically proposed the most stable reaction routes to be achieved during the heterogeneous catalyzed-based transesterification process using acid and base heterogenous catalysts.The calculated free energies for the reaction profiles will aid to adopt the optimal conditions to experimentally perform transesterification reactions in the biodiesel production. All calculations were performed with computational code Gaussian09[6].

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