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Density Functional study on the transesterification of triacetin assisted by cooperative weak interactions via a gold heterogeneous catalyst: Insights into biodiesel production mechanisms

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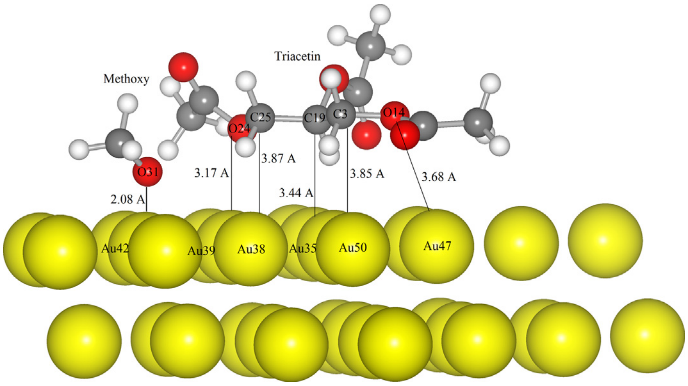
HIGHLIGHTS

- A DFT study reveals the feasibility to obtain biodiesel via a gold catalyst.
- Triacetin is used a model of triglycerides to reduce computational time.
- The triacetin transesterification is achieved by a van der Waals-driven attraction.
- Despite its nobility, Au is capable of catalyzing reactions that produce biofuels.

GRAPHICAL ABSTRACT



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ABSTRACT

A Density Functional study predicting a heterogeneous-catalyzed reaction to obtain biodiesel was performed. Triacetin simulated triglycerides in the presence of an Au(1 1 1) surface as the heterogeneous catalyst. Methoxy was implemented as alcohol solvent to understand the reaction trajectory along a three-step transesterification process. Reactants and products in the three-step process are adsorbed on the Au substrate through non-covalent interactions of the electrostatic-type, which are also mediated by a van der Waals attraction. Density of states indicated that the electronic structure nature of Au is preserved after the interaction with the organic moieties. This may be addressed to an enhanced stability of the Au(1 1 1) catalyst through the overall reaction. Charge transfer analysis revealed that the Au surface oxidation aids in the transesterification of triacetin and evidences that gold plays an important role in this catalytic process. Such results may provide fundamental insights into the design of heterogeneous catalysts for biodiesel production.

1. Introduction

Due to the high energy demand and continuous increase on fossil fuels consumption and its eventual depletion, it is necessary to

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increase renewable energy use. Biodiesel production can be a reliable solution since it may be obtained from a sustainable origin, such as vegetable oil, fat animal and microalgae. The conversion of vegetable oils as *Jatropha curcas* [1], soybean [2] or sunflower [3], and other sources as recycled fried oils into biodiesel, may be a sustainable alternative to produce biofuels. The profitability of biodiesel production relies on its use in a mixture with comercial diesel with an acceptable performance and no engine modifications. Biodiesel also gives an improved combustion due to the presence of oxygen and reduces toxicity to the environment. In addition, its biodegradability reduces the greenhouse effect due to a closed CO_2 cycle and triggers sustainable development of rural economies.

Vegetable oils and animal fats are formed by triglycerides that comprise esters of glycerol with three chains of aliphatic or olefinic free fatty acids with 12–24 carbon atoms. Transesterification is the most common technique to obtain biodiesel, where triglycerides react with a low molecular weight alcohol. This is usually performed with a homogeneous catalyst and the result is a mixture of fatty acid alkyl esters (biodiesel) and glycerol.

Despite the available techniques to produce biodiesel such as hydrolysis [4], pyrolisis [4], supercritical alcohol transesterification [5] or base-catalyzed transesterification [6], acid-catalyzed transesterification [7] and enzyme-catalyzed transesterification [8], homogeneous catalysis is the most popular methodology with the aid of alkaline catalysts such as KOH or NaOH and methanol or ethanol as the alcohol [9]. The use of homogeneous catalysts presents acceptable conversion rates, but the process is not as profitable as that obtained with conventional diesel, since the homogeneous catalyst is consumed. The use of high-quality feedstock (virgin or refined vegetable oil) is elementary since water and free fatty acids provoke side effects such as saponification or hydrolysis. As a consequence, the use of a heterogeneous catalyst would reduce the production cost, because a solid is recycled during the production mechanism [10] and esterification and transesterification may be yielded. On laboratory scale, a variety of basic solids including modified zeolites, hydrotalcites, alkaline metal supports have been proven in transesterification process with the aim of solving and simplifying biodiesel production [11,12,10].

The stoichiometric reaction requires 1 mol of triglyceride and 3 mol of methanol to form 3 mol of mono-alkyl ester and 1 crude glycerol [13,14]. (see Fig. 1). The homogeneous catalyst provides a faster reaction than the heterogeneous catalyst. However, in a homogeneous catalyst process, it is required more water to transfer catalysts from the organic phase to an aqueous phase. Therefore, the separation is more expensive for the final product.

It has recently been studied the effectiveness of solid acid catalysts such as Amberlyst® 15, Nafion® NR50, support phosphorus acid, sulfated zirconia, zeolites Hβ, and ETS-10 (H) [15,16]. Furthermore, solid base catalysts such as MgO and ETS-10 (Na, K) [13] can catalyze the transesterification reaction. However, the only activation energy known at experimental level corresponds to the first phase triglyceride-diglyceride reaction, ($\sim$12 kcal/mol) using Nafion® SAC-13 [17], as heterogeneous catalyst.

On the other hand, it has been found that when molecular gold is considered on a size smaller than 10 nm, it is able to catalyze reactions such as CO oxidation and organic compounds [18], to form C–C bonding [19], to hydrogenize and to dehydrogenize with high selectivity [20]. Haruta et al. [21] showed exceptional catalytic activity of Au nanoparticles in CO oxidation with low temperature. Mallat and Baiker [22] used noble metals as a heterogeneous catalysts to yield selectivity oxidation in OH alcohol groups to carbonyl, using molecular oxygen as oxidant. Theoretical studies showed that the addition of impurities on a Au(111) surface, allowed Au to adsorb a H atom ($Pd_{surf}Au(111)$ [23] is an example). Bimetallic nanoparticles such as Au@Ag, have also shown important technology applications in heterogeneous catalysts to biodiesel production [24]. Gold as a catalyst is directly related with particle size and possible explanations of the phenomena include the exceptional low coordination of superficial atoms [25], change of oxidation state and electronic structure of metal with the particles size [26], sensitivity to adsorption and dissociation of O_2 in different arrangements on the Au surfaces [27] and charge transfer between Au and metallic oxide supports.

The theoretical studies regarding the description of the homogenous and heterogeneous transesterification are scarce. For instance, Tapanes et al. [28] performed a theoretical and experimental study on biodiesel production from Jatropha curcas oil at the AM1 level. A tetrahedral intermediate was found and it was assigned to the difference between kinetics of methanolysis and ethanolysis and the alkoxide formation step. Hori et al. [29] showed a mechanism of the gas-phase acid-catalysed hydrolysis of methyl acetate in gas phase and in solution, using implicit and explicit molecules. It was also found that the reaction proceeds when an explicit solvent molecule is present, since solvent molecules increase the nucleophilicity of the attacking water molecule that corresponds to a weaker nucleophile than the hydroxide ion and allows cleavage of the -OCH group of acetic acid that is included in the reaction. Fox et al. [30] reported that methanol did not bond to carbonyl carbon to create an intermediate structure due to the absence of explicit solvent molecules. Using Density Functional Theory (DFT) at the B3LYP level [31], a systematic study on the kinetic aspects of methanolysis and hydrolysis of triacetin was performed. An acid-catalyzed methanolysis reaction was considered, where it was found that the central carbon-atom of glycerol was reactive in agreement with NMR data. It was proposed that triacetin required to react with ester carbonyl in order to allow transesterification. Other DFT/B3LYP studies were also performed on the alkaline-catalyzed transesterification of pentylic acid triglyceride [32] and monoglycerides of butyric and pentylic acids [33]. The calculated activation energies are in reasonable agreement with those found experimentally. On the other hand, a theoretical study of heterogeneous-catalyzed reactions of triglyceride-related moieties has only been performed in the pioneer work of Muñiz et al. [34], where the interaction of Sulfated Zirconia (SZ) slab as a heterogeneous catalyst with triacetin (as a model of triglyceride), was studied at the B3LYP level. In that work, explicit methanol solvent molecules were used and Gibbs free energies revealed the spontaneity of the three-step reaction mechanism for the transesterification of triacetin. An electronic charge transfer among the catalyst and the organic moieties was also evidenced in the reaction. Further, in that work [34], the QST3 scheme was used to calculate the activation energies through the reaction, which is in close agreement with those found experimentally.

The Au-catalyzed heterogeneous reaction has not been experimentally performed and a previous fundamental understanding is crucial to elucidate new methodologies on clean fuels production. The aim of this work is to predict the stability of the Au (111) surface as a heterogeneous catalyst and to give insights into the mechanisms behind the Au-catalyzed transesterification of triacetin, as a model of a triglyceride. This may open new routes to improve Biodiesel production.

2. Computational details

2.1. DFT calculations

All DFT periodic calculations were performed using FHI-aims computational code (Fritz Haber Institute ab initio molecular simulations) [35]. We employed PBE + vdW [36,37] functional to