Molecular Catalysis 440 (2017) 43–49

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

MCAT

DFT-based calculations of the adsorptions of acetic acid, triacetin, methanol and the alkoxide formation on the surfaces of zinc acetate

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ARTICLE INFO

Article history:
Received 30 September 2016
Received in revised form 14 March 2017
Accepted 8 July 2017

Keywords:
Zinc acetate
Biodiesel
Transesterification
Esterification
Adsorption

ABSTRACT

DFT calculations with periodic boundary conditions were performed in order to study the esterification/transesterification mechanisms involved in the biodiesel production. The simulation of the adsorptions of acetic acid, methanol and triacetin was carried out on zinc acetate as the catalyst. The adsorption energies of these processes could be obtained and PDOS of the zinc sites and the carboxylate group carbons of the acetic acid and the triacetin were explored for the evaluation of their acidity. The adsorption energies and the reaction barrier of the alkoxide formation showed that the triglyceride adsorption is very likely to occur first in transesterification processes. The barriers also denote that an alkoxide formation from the methanol is not favored and, consequently, a nucleophilic attack from the methanol molecule occurs.

1. Introduction

The search for new energy sources represents a great development for all technology areas, since fossil fuels are not renewable. Furthermore, the increase of environmental pollution and the magnification of the greenhouse effect are nowadays serious problems. One way to circumvent these issues is the production of green fuels based on renewable resources such as biodiesel. Biodiesel can be used in a mixture of fossil diesel, provides a better combustion and is biodegradable [12,39].

The production of biodiesel consists mainly of the transesterification of vegetable oils or animals fats (triglycerides) with alcohols such as methanol, thus forming a fatty acid methyl ester (FAME). The esterification of a free fatty acid (FFA) with an alcohol can also be done for the formation of FAME. Both reactions can also be performed simultaneously by choosing the correct catalyst [40]. When using the traditional alkaline catalysts in homogeneous media, biodiesel production requires a somewhat pure feedstock, which increases its production costs [29]. The presence of fatty acid during alkaline transesterification produces soaps, which can emulsify the mixture, difficulting the separation of the products. The water molecules present in the raw materials can also poison some catalysts especially in transesterification reactions. The presence of undesirable compounds (especially FFA and water) is also strictly controlled in the formulated biodiesel. Some authors suggest that the research of intelligent catalysts, which catalyze the reaction and remove the water formed as byproduct, may circumvent this problem [41,19].

Several works investigated the mechanisms of these reactions [40,43,7,8]. Tapanes et al. investigated the homogeneous catalysis of the transesterification by means of semi-empirical calculations [36]. Muñiz et al. studied this process catalyzed by sulfated zirconia by means of density functional theory (DFT) calculations [31]. These results suggested that the mechanism comprises the nucleophilic attack of the triglyceride by the alcohol molecule. It was already reported that this mechanism may also occur by the methanol adsorption on the Lewis basic sites of the catalyst. Thereafter, an intermediate based on an oxygen anion is formed and submitted to a subsequent nucleophilic attack to the triglyceride [40].

Hou et al. showed that acetates formed by Pb^{2+}, Cd^{2+} and Zn^{2+} are active for esterification/transesterification reactions and, in the case of zinc, it presents the highest conversion rate for FFA [18]. Furthermore, layered zinc carboxylates can be easily obtained *in situ* by using $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$ during the catalytic process [5,25]. Due to the increasing interest in esterification/transesterification reactions catalyzed by layered zinc carboxylates [25,9,10], our work aims to clarify some aspects of the mechanisms behind these processes.

For this purpose, we chose to simulate via DFT calculations and periodic boundary conditions the adsorptions of acetic acid,

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http://dx.doi.org/10.1016/j.mcat.2017.07.004
2468-8231/

methanol and triacetin on the surfaces of zinc acetate. Zinc acetate may occur as layered material formed by the interconnection of zinc tetrahedral and part of the carboxylate bridges will be broken if the reaction is performed above the material melting point, exposing Zn acid Lewis sites [1,32]. Consequently, the structure of zinc acetate is a very adequate simple model to investigate these mechanisms of the heterogeneous catalysis with the family of layered zinc carboxylates. Triacetin was picked for this study because it was already demonstrated that high-molecular-weight triglycerides can be modelled by this smaller molecule [26,24]. The alkoxide formation from the methanol adsorption was also studied in order to evaluate the kinetics behind this process.

2. Methodology

The slab models used for these calculations were constructed by the supercell $1 \times 2 \times 1$ of the PBE-optimized bulk system of the dehydrated zinc acetate [37]. The simulated cell parameters presented a good agreement with the experimental values (a = 14.6 Å, b = 4.8 Å, c = 9.2 Å, $\alpha = 90.00^\circ$, $\beta = 98.79^\circ$ and $\gamma = 90.00^\circ$ with the relative errors less than 3.3%) [14]. This specific supercell was adopted for this investigation because its facets lead to the same amount of atoms and, consequently, the same number of zinc sites. This choice of the supercell ensures that the studied facets have the same number of relaxed atoms. ets lead to the same amount of atoms and, consequently, the same number of zinc sites. This choice of the supercell ensures that the studied facets have the same number of relaxed atoms.

Since no experimental data regarding the existing surfaces of zinc acetate is available in the literature, as far as we know, we chose to study only low-index surfaces, such as (001) and (010). These surfaces are more likely to present less dangling bonds than the other ones. After the cell optimization of zinc acetate and the subsequent construction of the supercell, the surfaces were later formed by the insertion of a vacuum layer of 17 Å along the directions (001) and (010), thus forming two-layer-thick slabs. Throughout the discussion of the results, the analysis of the electronic structure (PDOS, Bader charge and charge density difference plots) will show that this thickness was appropriate to conduct our simulations. The lattice vectors and the second layer of the slab were fixed during all optimizations, while the surface atoms were allowed to relax.

All ab initio calculations were performed using the codes available in the Quantum Espresso package [13], which implements the Density Functional Theory [17,20] under periodic boundary conditions [27] with plane wave functions as a basis set [4]. The geometry optimizations of the adsorptions and the surfaces were performed with the generalized gradient approximation (GGA/PBE) [33]. The van der Waals-aware functional vdW-DF was also tested in order to observe the role of these interactions in these simulations [11].

The ion cores were described by Vanderbilt ultrasoft pseudopotential [38], and the Kohn-Sham one-electron states were expanded in a planewave basis set with a cutoff energy of 50 Ry (500 Ry for the density). The calculations were performed with Monkhorst-Pack [30] meshes of $1 \times 3 \times 1$ and $1 \times 1 \times 3$ for the surfaces (001) and (010), respectively, and the equilibrium atomic positions of the adsorptions were found by minimizing the total energy gradient. The Marzari-Vanderbilt smearing technique was used [28] with a broadening of 0.01 Ry in order to smooth the Fermi distribution for the surfaces. For each set of cell parameters, the relative ion positions were relaxed until all of the force components were lower than 0.026 eV/Å. All of the molecular graphics were generated by the XCRYSDEN graphical package [22,21].

The stability of these surfaces was determined by the direct comparison of their converged total energies and also by the comparison of the surface energies. The surface energy was estimated by the following equation [42]:

$$E_{surface} = \frac{E_{slab} - E_{bulk}}{A_{slab}} \tag{1}$$

where E_{slab}, E_{bulk} and A_{slab} are, respectively, the total energy of the respective slab, the total energy of the bulk and the surface area of the respective slab.

In order to study the stability of these surfaces with respect to the temperature, the Gibbs free energy ($G = H - TS$) of the slabs were computed for the PBE-optimized structure. The calculation method of the Gibbs free energy is reported elsewhere [6]. The phonon calculations were carried out to determine the vibrational contribution of both surfaces. The phonon calculations were based on the harmonic approximation using the Density Functional Perturbation Theory (DFPT) [2,3] at the Γ-point, and the convergence threshold was set to 10^{-14}. In order to reduce the computational costs, these calculations were performed for 48 degrees of freedom regarding the zinc atoms and the oxygen atoms surrounding them.

The energetic study of the adsorption of the studied molecules was performed by considering the interaction of 1 molecule on the surface. The adsorption energies (ΔE_{ads}) of acetic acid, triacetin and methanol were estimated by the following equation.

$$\Delta E_{ads} = E_{surface/molecule} - E_{molecule} - E_{surface} \tag{2}$$

where $E_{surface/molecule}$, $E_{molecule}$ and $E_{surface}$ are, respectively, the total energy of the adsorption of the respective molecule on the surface, the total energy of the molecule and the total energy of the pure surface. The total energy of the molecule was calculated by having the studied species in a cubic cell of 20 Å. In order to ensure that the interactions between the periodic images of the adsorbates are decoupled, we tested these adsorptions on a supercell $2 \times 4 \times 1$ and used the same equation for the computation of the adsorption energies. Due to the size and the amount of atoms of this expanded supercell, these simulations were performed with a cutoff energy of 25 Ry (250 Ry for the density) and at the Γ-point. The total energies of the isolated molecules, in this case, were also calculated in the same supercell.

Charge density difference plots were also made in order to analyze the stabilization of the molecules on the surface. These plots were carried out by the following equation.

$$\Delta\rho(r) = \rho(r)_{surface/molecule} - \rho(r)_{molecule} - \rho(r)_{surface} \tag{3}$$

where $\rho(\mathrm{r})_{surface/molecule}$, $\rho(\mathrm{r})_{molecule}$ and $\rho(\mathrm{r})_{surface}$ are, respectively, the charge density of the whole system, the charge density of the molecule and the charge density of the pure surface.

The minimum energy path (MEP) was constructed in order to obtain the transition state, the reaction barrier and the main structural modifications involved in the process of the alkoxide formation from methanol. The calculation of the MEP connecting different minimum geometries is based on the climbing image nudged elastic band (CI-NEB) method which accurately describes the MEP between the initial and the final states of a reaction, and evaluates the transition state and the energy barrier [15,16]. A total of 7 configurations were used to compute the MEP and each geometry was optimized to establish the MEP on the potential surface of the system until energy variations were less than 0.1 eV/Å.

3. Results and discussion

3.1. Comparison between the surfaces (001) and (010)

The direct comparison between the total energies of the surfaces indicates that the surface (001) is more stable, i.e., the surface (010) is more reactive. The energy difference between the surfaces