

DFT: a dynamic study of the interaction of ethanol and methanol with platinum

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Abstract The interaction between alcohol molecules and platinum (Pt) was studied using molecular dynamics (MD; Born-Oppenheimer method). Alcohol molecules like ethanol and methanol present a similar molecular structure, with a methyl group (CH₃) at one end and a fragment of hydroxyl (OH) at the other. This fact generates two orientations that are considered in the interaction with Pt. The MD calculation results for these two orientations indicate a preferential orientation due to energy interactions. A plausible reaction mechanism that takes into account the interaction between Pt and alcohol is presented. The charge transference obtained from the Pt–alcohol interaction was also analyzed. The energy for the two orientations was calculated by indicating the preferential orientation. The methyl and hydroxyl groups are involved in heterolytic breakage of hydrogen bonds, joined to a carbon atom in the former and to an oxygen atom in the latter; however, the methyl group reaction seems to be the most important.

Keywords Ethanol · Density functional theory · Methanol · Molecular dynamics · Platinum

Introduction

Climate change has generated ecological problems that could be solved in part by changing our use of different kinds of fuel, e.g., by replacing commonly used hydrocarbon-based fuels with alcohol or hydrogen [1]. To this end, much effort has been focused on finding an alcohol substrate with potential for use in the generation of electricity [2]. Such a fuel might be obtained by fermentation of biomass, where alcohols, especially ethanol, are transformed through a steam reforming process [3]. Several alcohols, such as feedstock ethanol and methanol, are very attractive because of their relatively high hydrogen content, availability, ease of storage, and handling safety. In fact, as the products of biomass conversion are mainly hydrogen-rich gases, it would be more effective to use a fuel cell to convert hydrogen energy into electricity directly and efficiently with the use of a catalyst [4]. At the point of transformation, several important reactions are involved in the interaction between alcohols and the metal catalyst present on the anode or cathode.

The process of energy transformation has several different steps, one of which involves the fuel cells themselves. The fuel cell is characterized as the “feeder” supplying hydrogen or alcohol, wherein the handling of hydrogen is more complicated in comparison to alcohol. For this reason, many studies have focused their effort on developing fuel cells with membranes using alcohol as the main fuel. Ethanol and methanol have been proposed as a major energy source. Many fuel cells contain membranes populated with platinum (Pt) nano-particles that are

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impregnated over the anode and the cathode [5, 6]. Pt nanoparticle dispersion affects membrane performance, i.e., metal dispersion plays an important catalytic role. Pt dispersion at the anode and cathode can be evaluated by different spectroscopic methods in order to obtain evidence about performance and electro-catalytic properties [7, 8]. The metal nano-particles impregnated in the membrane exhibit important reactions with different fuels like hydrogen or alcohol. Metals such as Pt, Pd, Sn, and Ru supported in carbon matrixes are used to produce active electrocatalysts for the oxidation of methanol and ethanol [9, 10]. The different reactions in this oxidation process due to environment variables can be schematized, showing experimental and theoretical points of view by using interaction and activation energies [11, 12].

Catalysts facilitate reactions via the action of bond breaking in the reactant molecule, as is the case with ethanol or methanol on a Pt surface. For these cases it is important to note that the adsorption and activation energy involved in bond breaking of C–H and OR–H bonds is lowered by the influence of Pt particles. Methanol decomposition rates on Pt have been obtained by density functional theory (DFT) calculations in a procedure in which the reaction between methanol and Pt takes, for example, two primary decomposition pathways. The reaction begins with scission of both O–H and C–H bonds on the methanol molecule and, at this step, carbon is adsorbed. The C atom on Pt is fixed whereas the fragment containing O atoms remains free. The activation energy of ethanol in the gas phase is comparable to the activation energy of methanol [13–15].

In the present work, the interaction between alcohol (ethanol, methanol) and Pt was studied. Interaction among all fragments and Pt was achieved, taking into account two orientations of the alcohol molecules, the first considering an interaction with the methyl group (CH₃), and the second the interaction with the hydroxyl (OH) fragment. The interaction energy was calculated at different distances of separation between both molecules, by indicating how the molecules move until they collide with the Pt atom, considering both orientations. The electronic changes in the case of the interaction between the hydroxyl fragment and the Pt particle were analyzed to propose a possible mechanism for this interaction. The charge transference for each atom in the system was also studied. These changes in energy were used as a criterion to establish the structural modification in ethanol and methanol for those two interactions. It was found that there is a preferential direction in alcohol interactions with Pt.

Methods

The electronic structure of ethanol and methanol is commonly studied by first principles methods that include

electronic correlation and spin-orbital corrections. DFT [16], included in the NWChem software [17], was used in this case. A pure DFT method, containing Becke's gradient correction for exchange [18] and Perdew-Wang's correction for correlation [19], and B88-LYP methods were used for geometry optimization. In the case of the B88-LYP functional, the non-local correlation was provided by the LYP expression [20], and the correction was carried out by means of the VWN functional. The TZVP basis set was used in all calculations for light atoms. This computational level has shown good results for geometric optimization of molecules that contain hydrocarbons with methyl groups [21]. In the case of Pt, the LAN2DZ pseudo potential was used. These optimized geometries were used as the targets in the molecular dynamics (MD) study as a first guess, considering that they are the minimum energy items that can be strained following the different pathways of reaction. The last approach used in the optimization tasks was a quasi-Newton algorithm with line searches and approximate energy Hessian updates, as implemented in the NWChem package.

The MD simulation technique is important because it reveals the dynamic nature of nuclear particles, thus helping to gain a deeper understanding of the mechanism reaction of the alcohol–Pt atom system. These reactions are simulated by the Born-Oppenheimer semiclassical dynamics (BOSD) method. The electronic wave function was obtained by taking into account the fact that electrons are immersed in a field of instantaneously fixed nuclei, whereas the nuclear particle is immersed in an average electronic field. The heavy masses and very short spatial extension of the nuclear particles compared to those of electrons, allow the problem to be simplified by considering the nuclei as classical particles. In order for this to happen, each nucleus follows a Newtonian trajectory due to quantum forces derived from

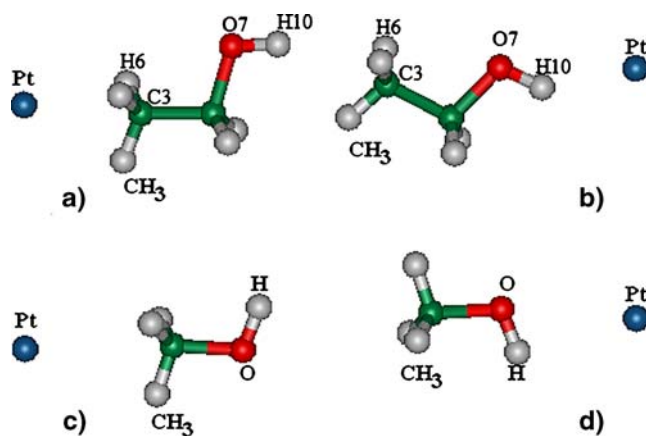
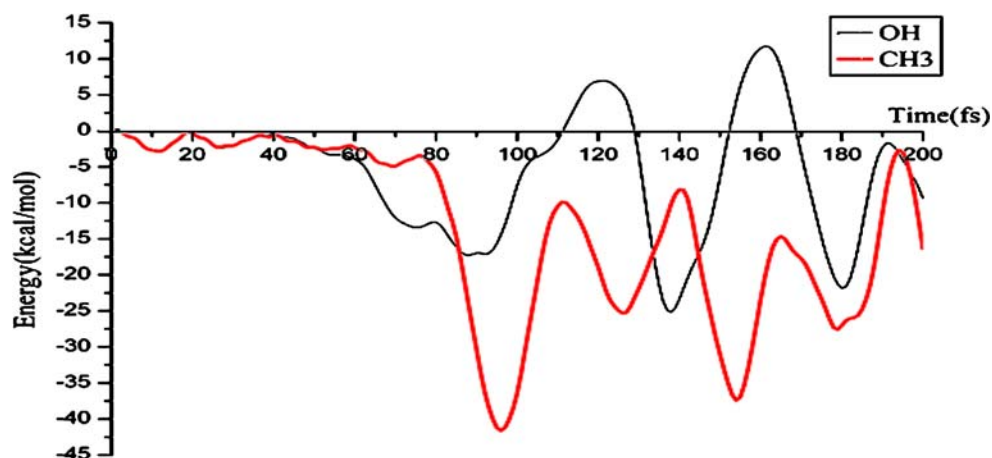


Fig. 1a–d Initial position of ethanol and methanol molecules interacting with a platinum (Pt) atom taking a selective orientation. **a** Ethanol oriented by methyl group, **b** ethanol oriented by hydroxyl, **c** methanol oriented by methyl group, **d** methanol oriented by hydroxyl

Fig. 2 Ethanol-platinum (Pt) interaction energy values plotted for preferential orientations of ethanol [methyl group (CH₃) and hydroxyl (OH)] as considered in each step of the simulation



the electron potential plus the electrostatic force exerted by the other nuclear particles. This computational level has shown good results in MD calculations [22, 23]. In all calculations of dynamics characterized by a displacement-associated energy with a multiplicity of 1 and a charge of 0 used as a starting state, this feature implies a rearrangement of the electronic configuration of Pt, which has a basis configuration of 5d96s1; however, for our purposes, Pt is considered to adopt a basic configuration like that of nickel, i.e., 5d86s2. Therefore we have a free *d* orbital that can interact with organic fragments.

Results and discussion

The interaction between two molecules changes the electronic properties of the different species involved. Charge transference and structural modification as a function of total energy values also change. All these factors are associated with different reaction schemes. For the present problem, two different orientations (CH₃ and OH) were studied by MD simulation in order to depict the

different phases of the reaction. First, the ethanol molecule and Pt atom were placed at a certain distance with a large separation enough to guarantee that there is no initial interaction. Thus, the ethanol molecule receives an impetus in the direction of the Pt atom for collision. The Pt atom was therefore placed at an initial position separated by 3.5 Å from the CH₃ or OH fragments, and the distance decreased until collision occurred. The interaction between the ethanol molecule and Pt in either the methyl group (CH₃) or oxygen (OH) orientations is shown in Fig. 1.

In the first case, the MD calculation simulates the interaction between the Pt atom and the methyl (CH₃) group of ethanol. It was observed that two important events occur at the same time: first, a hydrogen ion is detached from the methyl group due to the effect of the Pt. Next, a charge carbon atom is added to the Pt atom. In the case of the interaction between Pt and the hydroxyl (OH) group of ethanol, a different behavior is found since a repulsive effect arises between ethanol and the Pt atom. In this repulsive effect there is a peculiar phenomenon, i.e., a momentary addition of oxygen to Pt; however, the hydrogen particle turns the Pt atom around and returns to

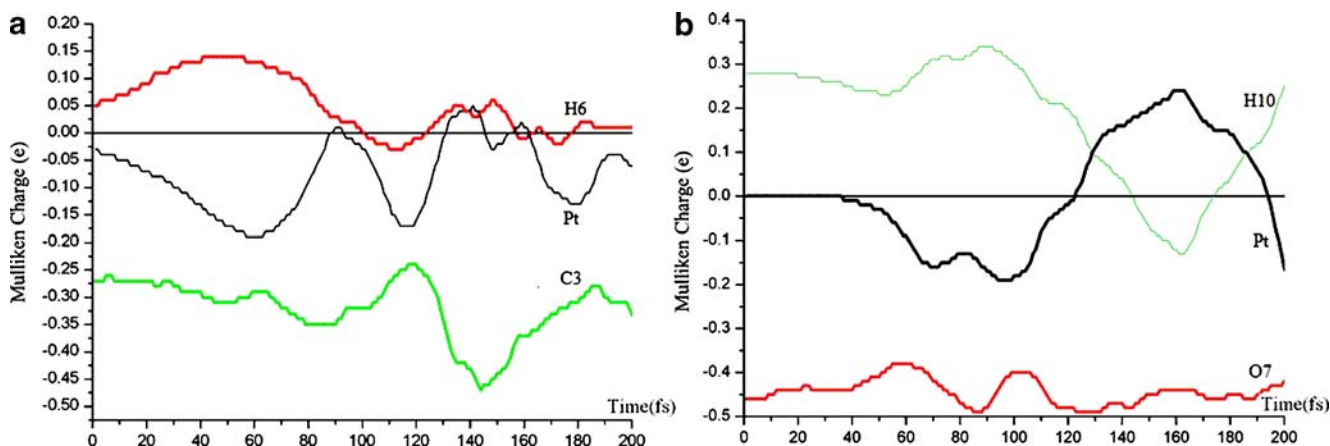
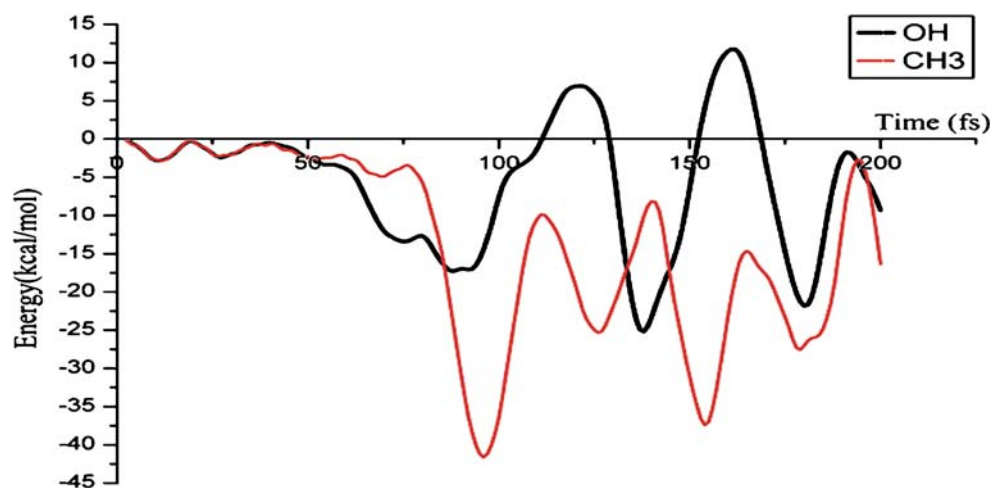


Fig. 3 Values of partial charge for atoms Pt, H, C and O in each step of the simulation when ethanol interacts with Pt in two cases: **a** methyl group, **b** hydroxyl

Fig. 4 Interaction energy values at each step of the simulation considering a preferential orientation when methanol collides with Pt in two cases (OH and CH₃)



the oxygen atom with a new bond. All these phenomena can be observed in the changes of the interaction energy as well as in the simulation.

The energy value changes of the interaction between the CH₃ group and OH fragment of ethanol with the Pt atom were determined. These energy values are used to schematise the structural modification as breaking bonds, atom additions and deformation of angles. In the first 100 fs, the values for the adsorption energy are obtained, revealing the attractive effect. Two plots (OH fragment and CH₃ group) that corresponded to this change in interaction energy were analyzed (Fig. 2). In the case of the energy interaction associated with the interaction of CH₃ with Pt, a minimum value of -41 kcal/mol is observed; this result is associated with a double effect (detachment of a hydrogen ion due to the effect of the Pt and addition of carbon on the same Pt atom), whereas that in the interaction with OH presents a minimum value of -17 kcal/mol, which corresponds to oxygen addition on the Pt atom and ejection of hydrogen. The energy value changes from negative to positive; this change is associated to the repulsive effect mentioned above.

The partial charge for each atom involved in the interaction has a relationship with the energy contribution. Considering the energy modifications, a Mulliken population analysis of the charge was carried out in order to explain the charge transference. The values of partial charge are plotted considering the representative atoms that contribute to the reaction. The plot shows the charge transference among the consecutive atoms: Pt, C3, H6, H10 and O7 (Fig. 3). There are two important items to consider: first, the orientation of the methyl group with respect to the Pt atom and H6, where there is a charge transference at the moment of hydrogen entrapment and carbon adsorption; second, the charge transference between Pt and H10 atoms in the hydroxyl orientation as a consequence of the adsorption of the oxygen atom on Pt with the momentary detachment of H10. This adsorption occurs before the occurrence of the repulsive effect.

The other case examined here is that of a methanol molecule interacting with a Pt atom. In this interaction, the same conditions for the simulation as for ethanol were considered. The values of energy for OH and CH₃ showed

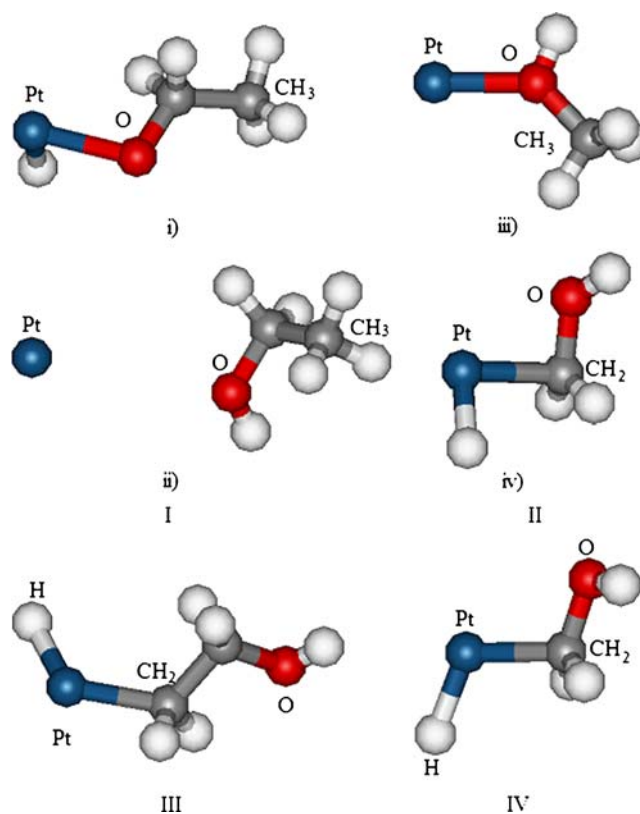


Fig. 5 Intermediate and final arrangements of the interactions of ethanol and methanol with Pt obtained by Born-Oppenheimer molecular dynamics (BOMD) calculations. Transfer of the hydrogen and carbon atoms are depicted. New bonds between both carbon and hydrogen and the Pt atom form as shown: *I* Hydroxyl orientation of ethanol (*i* intermediate interaction, *ii* repulsive effect in the final interaction), *II* methyl group orientation of ethanol, *III* hydroxyl orientation of methanol (*iii* intermediate interaction again, *iv* rotational effect in the final interaction), *IV* methyl group orientation of methanol

a different behavior due to the interatomic and electronic modifications at each step of the simulation. The interaction energy of OH shows several minimums in the first 100 fs. The first corresponds to the addition of oxygen to the Pt atom and has a value of -12 kcal/mol. Second, rotation of the methanol molecule avoiding interaction of the OH fragment with Pt and favouring the addition of carbon (CH_3) and detachment of a hydrogen atom from this fragment. This procedure shows a transition from a maximum to a minimum localized at a value of -36 kcal/mol. The energy corresponding to the addition of the carbon atom and hydrogen ion of the CH_3 group in this last orientation in the case of methanol shows a minimum value of -31 kcal/mol. Plots and schematics of these procedures are shown in Figs. 4; and 5, respectively.

Conclusions

This paper reports some interesting findings with respect to atomic bond modification in the elucidation of possible initial reaction mechanisms in the interaction between ethanol or methanol and a Pt atom. The main feature of the interaction is that double effects occur in CH_3 by achieving the required energy to select a preferential orientation. The results indicate that the CH_3 fragment is the preferred end in both molecules for the initial dehydrogenation in the presence of Pt. Another important conclusion is that Pt reduces the interaction energy required to trap the hydrogen particle.

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