Ethylene Adsorption on Platinum (111) Catalyst - A DFT-based Investigation

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Abstract: The ethylene decomposition catalyst plays an important role for the preservation of fruits and vegetables during long transportation and storage. Hence, ethylene decomposition to smaller molecules on different catalyst has been studied. However, the mechanism on how ethylene is broken down to its smaller byproducts (e.g. vinyl and ethylidyne) in relation with the intrinsic properties of the catalyst is not clear. Identifying the fundamental principles of ethylene interaction with the catalyst can guide researches on designing efficient and cheap catalysts for its decomposition. In this study, we have investigated the decomposition of ethylene to vinyl and ethylidyne on platinum surface, in particular, Pt (111), with the aid of the density functional theory (DFT)-based ab initio simulations. Different adsorption sites were considered: the top, bridge, fcc hollow and hcp hollow sites. On Pt (111), the length of carbon-to-carbon bond of ethylene on bridge site is elongated as compared with that of ethylene on top site. In addition, the binding energy on bridge site is larger than that on top site, however, the difference is very small. It implies that ethylene can also decompose to vinyl, and eventually to ethylidyne, on the top site. This supports previous experimental data wherein ethylene was detected to adsorbed on the top site at some temperature range and environmental set-up with oxygen. From the calculated adsorption energies, it was found that vinyl and ethylidyne are also stable on Pt (111) suggesting a thermodynamically easy decomposition. This is due to the effective hybridization of Pt's d-orbitals with that of ethylene's p-orbitals. From these results, we can say that platinum (111) is a potential catalyst for ethylene decomposition which can be used for the preservation of fruits and vegetables.

Key Words: catalysis; ethylene decomposition; vinyl; ethylidyne; platinum

1. INTRODUCTION

Current processes used to preserve fruits and vegetables for a long period of time is expensive and can damage the texture, consistency and other qualities of these commodities. Thus, researchers are looking for other ways to preserve their physiological qualities in a practical way. Ethylene was found to be the natural plant hormone responsible for the

ripening and eventually spoilage of these commodities. If the amount of ethylene inside the preserving environment of these commodities can be lessen to a negligible amount, then the ripening process and decay can be slowed down (Zhang et al., 2017). One effective and practical way to eliminate ethylene is by decomposing it to smaller molecules through catalysis. There are theoretical and experimental studies on the decomposition of ethylene (Shukri et al., 2016, 2014; Jiang et al., 2013; Basaran et al., 2011; Ge and King, 1999; Martin, et al., 1996). However, the mechanism on how ethylene is broken down to its smaller byproducts (e.g. vinyl and ethylidyne) in relation to the intrinsic properties of the catalyst is not clear. We have chosen as our starting metal platinum (111), since it is known to be a noble catalyst (Groß, 1999). Thus, we investigated the adsorption of ethylene, vinyl and ethylidyne on Pt (111) with the aid of the density functional theory (DFT) based ab initio calculations. The computational details, structural deformation and density of states of ethylene on Pt (111) are given in detail in the next sections.

2. COMPUTATIONAL DETAILS

The density functional theory (DFT) based calculations in this study were performed using Vienna Ab-initio simulation package (VASP) (Kresse et al., 1996) under the Perdew-Burke-Ernzerhof (PBE) (Perdew et al., 1996) with Grimme's DFT-D van der Waals correction (Grimme et al., 2010). The pseudo-potentials obtained from projected augmented wave (PAW) method (Kresse et al., 1999) were used to describe ionic cores.

We considered the (111) surface as the initial system since it is the most stable surface termination of Pt. It has a 3x3 unit cell with 5 atomic layers. A vacuum layer that is not less than 13Å was used to minimize the interaction of adjacent unit cells along the z-axis. At least -0.03eV/Å force precision and 10^{-5} eV energy precision were employed. To acquire these, we used a 5 x 5 x 1 *k-point* mesh and energy cut-off of at least 500 eV.

3. RESULTS AND DISCUSSION

3.1 Adsorption Energies of Ethylene on Pt (111) Surface

The adsorption energy (E_{ads}) of ethylene on platinum (111) surface is equivalent to the difference between the energies of the system (ethylene and surface) before and after adsorption. The greater the difference is, the larger the adsorption energy. This is calculated using the formula:

$$E_{ads} = E_{C_2H_4/surface} - E_{C_2H_4} - E_{surface} \text{ (Eq. 1)}$$

where: $E_{C_2H_4/surface}$ is the total calculated energy of the surface with adsorbed ethylene, $E_{C_2H_4}$ is the energy of isolated ethylene in the vacuum and $E_{surface}$ is the energy of clean (111) platinum surface.

The study considered four different sites of adsorption (top, bridge, fcc hollow, hcp hollow) with two different orientations (horizontal and vertical). Fig. 1 shows the two orientations for the top and bridge sites. The ethylene on the hollow sites is not stable. Either it has very low adsorption energy, or it moves to the neighboring bridge site. The system is most stable when ethylene is placed at the bridge site with the carbon atoms oriented horizontally on top of Pt atoms (-1.737eV). This implies that ethylene prefers more symmetric sites wherein all its C-H bonds lie on similar surfaces.

3.2 Structural Properties of Ethylene adsorbed on Pt (111)

The structural properties of ethylene the bond lengths, bond angles and (C-H)-(C-C) dihedral angles as adsorbed on Pt (111) are listed in Table 1.

Table 1. Structural Parameters of Ethylene in Vacuum and on the Top and Bridge Sites of Pt (111)

Parameters	Site		
	Vacuum	Top	Bridge
C-H Bond (Å)	1.090	1.094	1.097
C-C Bond (Å)	1.330	1.416	1.448
(CH)-(CC) θ (°)	0.000	13.970	18.772

These parameters are increased upon adsorption on both sites of the surface compared to their values when ethylene is in a vacuum. However, ethylene's parameters are greater when placed on the bridge site than when it is on the top site. Apparently, ethylene experiences more structural strain when adsorbed on the bridge site than on the top site. This can be related to the orientation of ethylene upon adsorption on these sites. From Fig. 1(a-b), ethylene's C-C bond is elongated as it lies on top of the same surface atom. However, on the bridge site (Fig. 1(c-d)), its C-C bond is further stretched as each of its C atom lies on different Pt atoms. Thus, ethylene on the bridge site experiences more apparent stress than that on the top site.
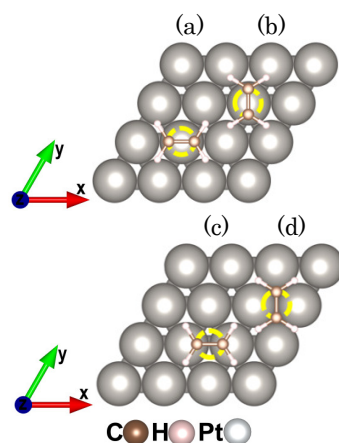
Fig. 1. On the surface of Pt (111), ethylene prefers to adsorb on (a) top$_{bridge-to-bridge}$, (b) top$_{hollow-to-hollow}$, (c) bridge$_{top-to-top}$ or (d) brdige$_{hollow-to-hollow}$.

3.3 Density of States of Ethylene adsorbed on Pt (111)

In order to understand further the interaction of ethylene with Pt (111) surface, we investigated the density of states of ethylene as it approaches the surface. We initially positioned ethylene at a far distance of 3.05Å to its stable distance of 2.15Å, with a decreasing increment of 0.30Å. The electron transfer to ethylene at 3.05 Å is 0.06e$^-$, which increases to 0.10e$^-$ at 2.75Å. However, upon reaching the distance of 2.45Å down to 2.15Å, the electron transfer decreases to 0.08e$^-$ then finally, 0.04e$^-$. Despite the increase in C-

C bond lengths and dihedral angles of C-H bond from C-C bond, the measured electron transfer from surface to ethylene is just 0.04e$^-$. This could be due to the back donation of electrons.

Fig. 2 displays the density of states of the p-orbital of ethylene and d-orbital of the Pt (111) catalysts, before (broken lines) and after (solid lines) ethylene's adsorption. Ethylene's HOMO (green spike around -3eV to 0eV) and LUMO (green spike around 3eV to 6eV) broaden as they hybridize with the d-orbitals of the metal catalyst (solid blue). But their interaction does not only involve the orbitals oriented perpendicular to the surface. Furthermore, the σ bonds of ethylene (green dotted lines around -6eV to -2eV) also broadens and shifted further (orange solid lines). Unlike the ethylene's HOMO and LUMO, which are π bonds attributed to its out-of-the-plane p_z-orbital, ethylene's σ bonds are contributed by its p_x (p_y)-orbitals which interact with the $d_{xz}(d_{yz})$-orbital of the metals.
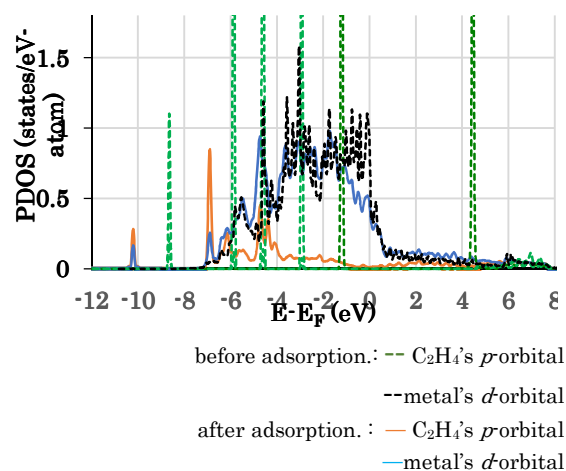

Fig. 2. Partial density of states of ethylene on Pt (111).

3.4 Adsorption of Vinyl and Ethylidyne on on Pt (111)

Vinyl and ethylidyne were also found to be stable on Pt (111) surface with adsorption energies of -1.584eV and -2.071eV, respectively. The adsorption energy of vinyl is smaller than ethylene (-1.737eV)

inferring an exothermic process for the dehydrogenation of ethylene to vinyl on Pt(111). Also, there is an endothermic process for the dehydrogenation of vinyl to ethylidyne on Pt(111) as indicated by the larger adsorption energy for ethylidyne than that of vinyl. These results denote that the decomposition of vinyl to ethylidyne would be thermodynamically easier than ethylene to vinyl.

4. CONCLUSIONS

We have investigated the adsorption of ethylene, vinyl and ethylidyne on Pt (111) with the aid of the density functional theory (DFT). We found that these molecules are stable on Pt (111) with adsorption energies suggesting a thermodynamically easy decomposition. This can be attributed to Pt's *d*-orbitals that effectively hybridized with the *p*-orbitals of ethylene. These results can be use as benchmark for other materials to create guidelines in designing the most efficient and practical catalyst for ethylene decomposition.

5. ACKNOWLEDGMENTS

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