Platinum vs transition metal carbide surfaces as catalysts for olefin and alkyne conversion: binding and hydrogenation of ethylidyne

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Abstract. The development of heterogeneous catalysts with activity for the hydrogenation of unsaturated hydrocarbons is of economic importance. Ethylene (C2H4) and acetylene (C2H2) are probe molecules useful to understand the hydrogenation mechanisms, where the most studied surfaces are Pt(111) and Pd(111), however, they have a limited activity due to the formation and accumulation of ethylidyne (CCH) species. Therefore, alternative catalysts should be developed to limit and/or avoid the formation of ethylidyne on the surface. Transition metal carbides has been reported as alternative catalysts, with the additional advantage of lower prices. The thermodynamics of ethylidyne binding and its transformations on δ-MoC(001), TiC(001), and β-Mo2C(100) surfaces are studied by means of periodic DFT. The results indicate that ethylidyne could be transformed to ethyl and ethane on δ-MoC(001) and TiC(001) surfaces, which are relevant species to the Horiuti-Polanyi mechanism. Therefore, these surfaces could be an alternative to Pt(111) and Pd(111), since ethylidyne could be transformed to other species, avoiding or limiting their deactivation. Conversely, ethylidyne cannot be transformed to vinyl (CHCH2) or ethylene in a Horiuti-Polanyi-like mechanism; then, it is not thermodynamically feasible to use any of the studied surfaces in the selective hydrogenation of acetylene, since ethylidyne accumulation could poison the surfaces.

1. Introduction

The hydrogenation reactions of unsaturated hydrocarbons are of economic importance, since many chemical feedstocks and goods of high commercial value are produced in this way. These reactions are catalyzed by Pt-group metals; however, there are limitations in their use, since they are very expensive due to a low abundance of these elements in the Earth crust; additionally, they are not sulfur resistant [1], which is a disadvantage for their application to the current oil refining in the production of fuels. Therefore, alternative catalysts should be searched, particularly, transition metal carbides (TMCs) have been reported [2–4] as an alternative to the Pt-group metals, but very little is known about the details of the hydrogenation mechanism on the carbides.
In order to understand the catalytic potential of TMCs in the hydrogenation of unsaturated hydrocarbons, probe molecules should be considered. Ethylene (C₂H₄) hydrogenation is frequently used as a model reaction for olefin conversions, whereas acetylene (C₂H₂) hydrogenation is a model for alkyne transformations. Additionally, the latter reaction is also of industrial importance, since ethylene streams in oil refining can be cleaned by removing acetylene traces, i.e. by means of the selective hydrogenation of C₂H₂ into C₂H₄.

The hydrogenation of ethylene and acetylene has been widely documented [5–7], where the so-called Horiuti-Polanyi (H-P) mechanism is the most accepted one [6]. In C₂H₄ hydrogenation via the H-P mechanism, the intermediate and final species are ethyl (C₂H₅) and ethane (C₂H₆), respectively. For the case of C₂H₂ in its selective hydrogenation via H-P mechanism, the intermediate is the vinyl (CHCH₂) species. However, not only these species are present on the surface, but ethylidyne (CCH₃) is also present on the surface [6,8–10]. The role of ethylidyne is not completely clear yet; some authors [10,11] have pointing out that CCH₃ is formed on the surface, occupying sites, and limiting interactions of the hydrocarbon (C₂H₄) with the surface. However, other authors have proposed that CCH₃ does not deactivate the surface, but it serves as a hydrogen transfer agent [12,13]. Therefore, there is still an open discussion about the role of CCH₃.

In this work, the binding strength of ethylidyne on several surfaces is first considered; then, the thermodynamics associated with the transformation of ethylidyne (CCH₃) to other surface species is studied. These aspects are analyzed by computational calculations within the framework of periodic density functional theory. Based on previous reports on the catalytic activation and transformation of several molecules including ethylene and acetylene [14–16], δ-MoC(001), TiC(001), and β-Mo₂C(100) surfaces are selected to study the binding and hydrogenation of ethylidyne. Pt(111) and Pd(111) surfaces are taken as natural benchmarks.

This work is divided as follows: 1) the surface sites for ethylidyne adsorption are identified, together with geometry and electronic structure analysis; 2) thermodynamic factors that favor the formation of ethylidyne from ethylene and acetylene are studied; 3) Finally, the thermodynamics involved in the hydrogenation of ethylidyne to other species is analyzed, within the framework of total (C₂H₄ into C₂H₆) or selective hydrogenation (C₂H₂ into C₂H₄).

2. Methodology and computational details

2.1. Model

First, the bulk structures of platinum, palladium, TiC, δ-MoC, and β-Mo₂C were optimized, calculating cell parameters close to those found experimentally as reported in our previous works [14–16]. Then, the surfaces were created to generate the corresponding slab models: Pt(111), Pd(111), δ-MoC(001), TiC(001), and β-Mo₂C(100). It is worth to mention that the β-Mo₂C(100) surface has polar C or Mo terminations which are named as β-Mo₂C-C and β-Mo₂C-Mo, respectively; for details please refer to the reference [16]. For Pt(111) and Pd(111) a p(3x3) supercell was used, while for the other surfaces a p(2x2) was utilized. A slab of four layers was considered in all the cases, where the two topmost layers were relaxed while the inner layers were fixed to represent the bulk; a vacuum layer larger than 10 Å was considered in the slab models. The ethylidyne binding was analyzed on different surface sites for all the studied surfaces to cover a wide range of adsorption possibilities.

2.2. Computational details

The calculations were performed using the VASP code [17] within the framework of periodic density functional theory, using the PBE-GGA functional. The electronic density of the valence electrons were expanded in a plane-wave basis set whose associated kinetic energy do not exceeded 415 eV cutoff energy. The description of the effect caused by the core electrons in the valence region is described by the projected augmented wave (PAW) method of Blöch , implemented by Kress and Joubert [18]. A k-points grids were used for the numeral integration of the Brillouin zone, according to the Monkhorst-Pack scheme [19]. Particularly, a mesh of 5x5x5 was used to represent the bulk, while a mesh of 3x3x1 was utilized to represent Pt(111), Pd(111), δ-MoC(001), and TiC(001) surfaces. For the case of
\( \beta \)-Mo\(_2\)C(100) surface, a 5x5x1 mesh was used. The convergence criteria in subsequent iterations are variations in interatomic forces lower than 0.01 eV/Å, and changes in total energy lower than \(10^{-5}\) eV. A counterdipole was located in the direction perpendicular to the surface to avoid dipole coupling between repeated slabs, which is important mainly for polar surfaces (\(\beta\)-Mo\(_2\)C-C and \(\beta\)-Mo\(_2\)C-Mo), however, it was used for all the studied surfaces. For platinum (both bulk and surface) spin polarized calculations were performed.

For the binding of ethylidyne, the adsorption energy \(E_{\text{ads}}\) was calculated as shown in equation 1.

\[
E_{\text{ads}} = E_{\text{slab} + \text{ethylidyne}} - E_{\text{slab}} - E_{\text{ethylidyne}}
\]  

In equation (1), \(E_{\text{slab} + \text{ethylidyne}}\) is the energy of the adsorbed ethylidyne on a clean surface, \(E_{\text{slab}}\) is the energy of the clean surface, while \(E_{\text{ethylidyne}}\) is the energy of the isolated ethylidyne in an asymmetric box of 13x14x15 Å and optimized at the \(\Gamma\) point.

The reaction energy \(E_{\text{reaction}}\) for every step considered in the reaction pathways are calculated according to the general scheme represented in equation (2).

\[
E_{\text{reaction}} = E_{\text{product}_1} + E_{\text{product}_2} - E_{\text{reactant}_1} - E_{\text{reactant}_2}
\]

The electron density after ethylidyne binding is analysed by means of Charge Density Difference (CDD, named as \(\Delta \rho\)) schemes, calculated as shown in equation (3).

\[
\Delta \rho = \rho_{E-5} - \rho_5 - \rho_E
\]

In Equation 3, \(\rho_{E-5}\) is the electron density of ethylidyne on the surface, \(\rho_5\) is that of the surface in the adsorption geometry but without considering the adsorbate, and \(\rho_E\) is that of the ethylidyne in the adsorption geometry but without the presence of the surface.

3. Results and discussion

3.1. Ethylidyne binding strength on platinum, palladium and transition metal carbide surfaces

A systematic analysis was carried out to identify the surface sites where ethylidyne is preferentially adsorbed. The results for the most stable structure on every studied surface are shown in Table 1 and Figure 1. The obtained results in this work for binding on Pt(111) and Pd(111) are in agreement with previous reports [20–23]. It is worth to mention that the binding energy extent is very strong as compared to the binding of C\(_2\)H\(_4\) (-0.53 eV to -1.93)[14,16] and C\(_2\)H\(_2\) (-1.78 eV to -4.23 eV)[15,16], but this is expected because the unsaturated carbon in CCH\(_3\) group is missing three ligands or bonds.

The bound ethylidyne on Pt(111) and Pd(111) surface occupies the same surface sites, i.e. it is located atop a surface hollow (Figure 1a). A similar behavior was observed for the adsorption on \(\delta\)-MoC(001) and TiC(001), where CCH\(_3\) is located a top surface hollows formed by 2 surface carbon and 2 metal atoms. Tests studies were carried out to analyze the thermodynamic favorability to form ethylidyne atop Mo, or C, or hollow surface sites, with respective \(\Delta G\) results of +0.98 eV, -0.62 eV, and -0.78 eV. Therefore, there is a preference to form ethylidyne atop a hollow surface, which also leads to the most stable adsorbed structure. For the case of TiC(001) all the analyzed structures converged to the same, i.e. a top hollow surface site as on the \(\delta\)-MoC(001) surface.

The molecular plane of ethylidyne is perpendicular to the surface plane for the systems mentioned above. However, the binding on \(\beta\)-Mo\(_2\)C-C and \(\beta\)-Mo\(_2\)C-Mo leads to different geometries, as the molecular plane of CCH\(_3\) is not perpendicular to the surface plane, with angles around 140º on \(\beta\)-Mo\(_2\)C-C and \(\approx\)85º on \(\beta\)-Mo\(_2\)C-Mo.
Table 1. Ethylidyne adsorption energy (E_{ads}) on metal and transition metal carbide surfaces

| Surface       | Pt(111)     | Pd(111)     | δ-MoC(001) | TiC(001) | β-Mo2-C-C | β-Mo2-C-Mo |
|---------------|-------------|-------------|------------|----------|-----------|------------|
| E_{ads} (eV)  | -5.86 [20–22] | -5.89 [22,23] | -6.06      | -5.64    | -6.01     | -6.28      |

![Figure 1](image1.png)

**Figure 1.** Geometry for the most stable structures in ethylidyne adsorption on several surfaces. Left: top view, right: side view. Dark gray, magenta, brown, and light gray, represents Pt, Mo, C, and H atoms, respectively. The symbol (≡) means adsorbate equivalent geometry on two surfaces.

In order to get a deeper understanding regarding the binding of ethylidyne on surfaces, a Charge Density Difference (CDD) analysis was carried out for CCH$_3$ adsorbed on Pt(111) and compared to its binding on δ-MoC(001), as a representative case of transition metal carbides. The CDD plots are different for both systems as shown in Figure 2. On Pt(111), the ethylidyne C-C bond length loses electronic density (Figure 2a), which indicates that this structure is more stable as compared to that observed in Figure 2b, where there is a charge increase in between the C-C bond of adsorbed ethylidyne on δ-MoC(001), hence the antibonding molecular orbitals of the adsorbate could be occupied, then favoring the C-C bond scission; however, on Pt(111) there are not earned electrons to occupy the antibonding orbitals of ethylidyne and then its scission is restricted. Additionally, there is an increase in electron density in between the surface and ethylidyne (Figure 2b), which is an indicative that the ethylidyne could eventually be moved and/or transformed, which is an opposite behavior as observed on Pt(111) since there is a decrease in the electron density in the region adsorbate-surface, leading to a stronger binding.

The CDD plot in Figure 2b also suggests that there is a charge redistribution between the adsorbate and the carbon surface atoms, a behavior not observed on Pt(111). This charge redistribution could play a key role in the transformation of ethylidyne to other species as discussed in section 3.3, i.e. CCH$_3$ could be transformed easier on δ-MoC(001) than on Pt(111), as the strength of the ethylidyne C-C is higher on Pt(111) and weaker on δ-MoC(001).

In the next section, the thermodynamics associated with the formation of ethylidyne from ethylene and/or acetylene is studied, where the structures shown in Figure 1 and Table 1 are used.
Figure 2. CDD plot for binding of ethylidyne on Pt(111) and δ-MoC(001) surfaces, side view. Blue and yellow represents the regions where the charge (0.03 e/Å³) was lost and earned, respectively, after ethylidyne adsorption. The labels of colors for atoms are the same as in Figure 1.

3.2. Ethylene and acetylene as source of ethylidyne: Thermodynamics on Pt(111), Pd(111), δ-MoC(001), TiC(001), and β-Mo₂C(100) surfaces

The formation of ethylidyne has been reported on Pt(111) and Pd(111) surfaces, as a consequence of the decomposition of ethylene and acetylene on these surfaces. The formation of ethylidyne is thermodynamically favorable as shown in Figure 3a, where the starting point is an adsorbed ethylene on well-defined surface sites, as reported previously [14–16]. The thermodynamic feasibility for the formation of ethylidyne from adsorbed ethylene is also observed on δ-MoC(001), TiC(001), β-Mo₂C-C, and β-Mo₂C-Mo surfaces, however, the extent of the Gibbs free energy is higher on β-Mo₂C-C (ΔG= -1.83 eV), which indicates that ethylidyne could be preferentially formed on this surface. If adsorbed acetylene is the source of ethylidyne (Figure 3b), there is a thermodynamic favorability to form (CCH₃) only on Pd(111) and δ-MoC(001), with a preference for the latter surface. Notice that the formation of CCH₃ on β-Mo₂C-C is not favorable (ΔG= +0.13 eV), an opposite behavior as compared to its formation when adsorbed ethylene is the source (ΔG= -1.83 eV). It is worth to mention that the surface sites for locating hydrogen atoms are known [5,24,25], then they are located according to the previous results in order to have a mass balance; the same applies for the results of section 3.3.

Figure 3. Thermodynamic feasibility (ΔG in eV units) for the formation of ethylidyne from a) ethylene, b) acetylene. Label of colors: red, black, violet, blue, green, and brown, represents reaction on Pd(111), Pt(111), δ-MoC(001), TiC(001), β-Mo₂C-C, and β-Mo₂C-Mo, respectively. Adsorption mode of ethylene on Pt(111) is specified [14].
3.3. Hydrogenation of ethylidyne on platinum, palladium, and transition metal carbide surfaces

In this section, the thermodynamic favorability to transform ethylidyne into other hydrogenated species is analyzed. The hydrogenation of ethylene and acetylene is usually explained by means of the Horiuti-Polanyi (H-P) mechanism. In the case of \( \text{C}_2\text{H}_4 \), the intermediate in the H-P mechanism is the ethyl specie (\( \text{C}_2\text{H}_5 \)), while the final product is ethane (\( \text{C}_2\text{H}_6 \)). Therefore, the feasibility to transform ethylidyne into \( \text{C}_2\text{H}_4 \), \( \text{C}_2\text{H}_5 \), or \( \text{C}_2\text{H}_6 \) is explored.

The selective acetylene hydrogenation via the H-P mechanism involves the vinyl specie (\( \text{CHCH}_2 \)) as intermediate, and ethylene (\( \text{C}_2\text{H}_4 \)) as product. Therefore, the hydroconversion of ethylidyne into these species was studied.

3.3.1. Hydrogenation towards ethylene, ethyl, and ethane. For all the considered surfaces, there is not a thermodynamic driving force to form ethylene from ethylidyne, which is a clear evidence that once ethylidyne is formed, there is no way to recover the ethylene. However, on \( \delta\text{-MoC}(001) \) and TiC(001) surfaces, \( \text{CCH}_3 \) could be hydrogenated into ethyl and ethane, key species in the hydrogenation of ethylene via the H-P mechanism. For the other surfaces, the \( \Delta G \) values indicate that ethylidyne remains adsorbed on them (Figure 4). These results are in agreement with the CDD plots in Figure 1, as \( \text{CH}_3 \) on Pt(111) is very stable, but on \( \delta\text{-MoC}(001) \) it has a weaker interaction, which favors \( \text{CCH}_3 \) transformation to ethyl and ethane. Therefore, \( \delta\text{-MoC}(001) \) and TiC(001) surfaces could be interesting systems to be further studied both experimentally and theoretically.

![Figure 4](image_url)

**Figure 4.** Thermodynamics (\( \Delta G \) in eV) for ethylidyne hydrogenation into ethylene, ethyl, and ethane on several surfaces. The labels explaining the colors are the same as in Figure 3.

3.3.2. Hydrogenation towards acetylene, vinyl, and ethylene. The hydrogenation of ethylidyne to species involved in the H-P-like mechanism for \( \text{C}_2\text{H}_2 \) selective hydrogenation, i.e. vinyl and ethylene, is not possible on any of the considered surfaces (Figure 5). Among the different surfaces considered, the highest positive \( \Delta G \) value for reaction towards vinyl and acetylene is observed on the \( \delta\text{-MoC}(001) \) surface, which suggests that this surface should not be used in hydrogenation of acetylene, since the deposition of ethylidyne could have a direct impact on the catalytic activity of the surface, i.e. the surface could be poisoned. However, further studies are required to support this hypothesis.
Figure 5. Thermodynamics ($\Delta G$ in eV) for ethylidyne hydrogenation into acetylene, vinyl, and ethylene on several surfaces. The labels specifying the colors are the same as in Figure 3.

4. Conclusions
Ethylidyne species are usually formed on Pt(111) and Pd(111) surfaces as a consequence of the decomposition of ethylene and acetylene. In this work, the thermodynamics associated with the formation and hydrogenation of ethylidyne on transition metal carbide surfaces was studied. The results indicate that there is a thermodynamic feasibility to form ethylidyne on Pt(111), Pd(111), $\delta$-MoC(001), TiC(001), $\beta$-Mo$_2$C-C, and $\beta$-Mo$_2$C-Mo surfaces.

Surface sites were identified, where ethylidyne preferentially adsorbs. There are geometry equivalences in the binding on Pt(111) and Pd(111) (trifold hollow site), and on $\delta$-MoC(001) and TiC(001) (a hollow site formed by 2 surface C and 2 metal atoms). On these four surfaces, the ethylidyne molecular plane is perpendicular to the surface plane, while it lies at 85º and 140º, relative to the surface plane, on $\beta$-Mo$_2$C-Mo and $\beta$-Mo$_2$C-C surfaces, respectively.

The Charge Density Difference (CDD) analysis indicates a different behavior in terms of electronic structure for the adsorbed ethylidyne on Pt(111) and $\delta$-MoC(001). The CDD plots suggest that ethylidyne could be transformed to other species on $\delta$-MoC(001) but not on Pt(111), which is in agreement with the findings regarding hydrogenation reactions.

There is a thermodynamic feasibility to transform ethylidyne into ethyl and ethane, key species in the ethylene hydrogenation via the H-P mechanism, particularly on $\delta$-MoC(001) and TiC(001). On the contrary, there is no way to transform ethylidyne on any of the surfaces, into vinyl and ethylene, key species in the H-P mechanism, related to acetylene selective hydrogenation.

The results indicate that $\delta$-MoC(001) and TiC(001) could have a better performance compared to traditional Pt(111) and Pd(111) surfaces in hydrogenation reactions of olefins, since adsorbed ethylidyne is readily transformed on $\delta$-MoC(001) and TiC(001) surfaces, avoiding its accumulation on the surface, which could have a direct impact in the catalytic performance. This study open the doors to address more complex systems, both theoretically and experimentally, taking $\delta$-MoC(001) and TiC(001) as potential substitutes of Pt(111) and Pd(111) as catalysts in hydrogenation reactions of olefins. Finally, any of the studied surfaces are recommended for alkyne selective hydrogenation, since CCH$_3$ cannot be transformed to vinyl or ethylene species; these clean surfaces should be modified to modulate the transformations of hydrocarbons in the selective hydrogenation of alkynes.
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