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Acetylene adsorption on δ -MoC(001), TiC(001) and ZrC(001) surfaces: A comprehensive periodic DFT study

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ABSTRACT

A comprehensive study of acetylene adsorption on δ -MoC(001), TiC(001) and ZrC(001) surfaces was carried out by means of calculations based on periodic density functional theory, using the Perdew-Burke-Ernzerhof exchange-correlation functional. It was found that the bonding of acetylene was significantly affected by the electronic and structural properties of the carbide surfaces. The adsorbate interacted with metal and/or carbon sites of the carbide. The interaction of acetylene with the TiC(001) and ZrC(001) surfaces was strong (binding energies higher than -3.5 eV), while moderate acetylene adsorption energies were observed on δ -MoC(001) (-1.78 eV to -0.70 eV). Adsorption energies, charge density difference plots and Mulliken charges suggested that the binding of the hydrocarbon to the surface had both ionic and covalent contributions. According to the C-C bond lengths obtained, the adsorbed molecule was modified from acetylene into ethylene-like on δ -MoC(001) surface (desired behavior for hydrogenation reactions) but into ethane-like on TiC(001) and ZrC(001). The obtained results suggest that δ -MoC(001) surface is expected to have the best performance in selective hydrogenation reactions to convert alkynes into alkenes. Another advantage of δ -MoC(001) is that, after C₂H₂ adsorption, surface carbon sites remain available, which are necessary for H₂ dissociation. However, these sites were occupied when C₂H₂ was adsorbed on TiC(001) and ZrC(001), limiting their application in hydrogenation of alkynes.

1. INTRODUCTION

Acetylene is the simplest hydrocarbon with two carbon atoms bonded together by a triple bond, an alkyne. It is widely used as a fuel and a chemical building block.¹ In the presence of metal catalysts, acetylene (C_2H_2) can react to give a wide range of industrially significant chemicals.¹ Thus, it is important to have a broad view of the bonding of acetylene with metals and different kinds of metal compounds.¹ Most of the catalysts used for the conversion of acetylene in several applications are those of the Pt-group metals like Pt, Pd, and Ru. However, due to the low abundance of the Pt-group metals in the Earth crust and its high commercial cost, there is a continuous search for alternatively cheaper materials than noble metals with similar catalytic activity. An interesting type of materials are transition metal carbides (TMCs). They are involved in the catalytic removal of acetylene from ethylene feed streams. The ethylene produced in the petrochemical industry, usually contains small amounts of acetylene, typically within the range of 0.5-2%.^{2,3} This small amount of acetylene causes deactivation of catalysts used for ethylene (C_2H_4) polymerization. The methodology for purifying ethylene streams relies on the selective hydrogenation of acetylene into ethylene.^{4,5} Pd-based catalysts are highly selective for the hydrogenation of C_2H_2 to C_2H_4 .⁴ Several studies have shown that the active phase in these catalysts consists of a layer of palladium carbide on top of the palladium metal.^{6,7} In this work, we perform a systematic study of the bonding of acetylene on different adsorption sites of δ -MoC(001), TiC(001) and ZrC(001) surfaces. The analysis of the acetylene adsorption behavior on these surfaces is necessary, because it is the first step in understanding the catalytic potential of TMCs in the selective hydrogenation of alkynes.

In the 1970s, Levy and Boudart reported that WC have a Pt-like behavior for the formation of water from hydrogen and oxygen at room temperature and the isomerization of 2,2-dimethylpropane to 2-methylbutane;⁸ while Kojima et al. reported on the catalytic activity of TiC, WC and TaC for ethylene hydrogenation,^{9,10} and Vértés et al. for aromatics hydrogenation.¹¹ Since then many works have appeared exploring the use of TMCs in catalysis, including several types of hydrogenation reactions.^{12–20} Well-defined surfaces such as TiC(001) and ZrC(001) exhibit a good performance for the dissociative chemisorption of H₂.²¹ Additionally, the δ -MoC(001) surface has been proposed as a potential catalyst for ethylene adsorption,¹² CO₂ hydrogenation²² and methane capture,²³ with it has the additional advantage of being resistant to oxidation.²⁴

To the best of our knowledge, this is the first systematic study of the bonding of acetylene on different adsorption sites of metal carbide surfaces. Moreover, from a fundamental point of view, it is interesting to compare the present results to those reported before for the bonding of alkenes and alkanes in TMCs.^{12,23} In selective hydrogenation reaction the desired product from acetylene hydrogenation is ethylene. Although the metal carbides considered in the present work are relatively simple from stoichiometric and structural points of view, i.e. they contain a 1:1 metal-to-carbon ratio and a rock salt-like crystal structure, they do exhibit important variations in electronic and structural properties¹² that can affect the bonding of acetylene, see Figure 1. Specifically, the differences in metal-carbon separation and positive charge on the metal centers (Mo < Ti < Zr)¹² can lead to significant divergence in the chemical properties of the considered surfaces.

This work is organized as follows. First, acetylene adsorption on Pd(111) is discussed as a benchmark. Second, the most stable adsorption modes for acetylene binding on δ -MoC(001),

TiC(001) and ZrC(001) surfaces are presented and explained taken into consideration the different properties of the carbide surfaces. Third, a contrast of acetylene bonding in carbides, metals and organometallic complexes is incorporated. Fourth, a comparison between methane, ethylene and acetylene bonding is included. And finally, the catalytic capability of TMC(001) surfaces to selectively transform acetylene into ethylene is discussed.

2. METHODOLOGY AND COMPUTATIONAL DETAILS

Calculations were performed using the Cambridge Serial Total Energy Package (CASTEP), version 5.5,²⁵ employing the Periodic Density Functional Theory. Exchange – correlation effects have been accounted by means of the Generalized Gradient Approximation (GGA) using PBE (Purdew – Burke – Ernzerhof) functional²⁶. The ionic cores were described using Vanderbilt-type ultra-soft pseudopotentials.²⁷ The valence electrons of C, Mo, Ti and Zr atoms were expanded in a plane-wave basis set whose associated kinetic energy do not exceed 350 eV cut-off energy.¹²

The numerical integration in the Brillouin zone was carried out through the Monkhorst – Pack scheme.²⁸ The convergence of the electronic relaxation was established when the total energy in subsequent iterations varied by less than 2×10^{-5} eV and the interatomic forces were lower than 0.05 eV/Å.

Bulk systems were optimized using a 5x5x5 k-points mesh, obtaining the respective cell parameters, which had errors < 3% with respect to the experimental values.¹² Then, from the optimized bulk structures, the (001) surface was created for every carbide according to the slab surface model, including a vacuum of more than 10 Å to avoid interactions between the

interlayered slabs. A (2x2) supercell was used, containing a slab of four layers with the two outermost relaxed^{12,21,24,29–31}.

The k-points mesh for the carbide surfaces was 3x3x1, established as enough for describing TMC(001) surfaces using CASTEP.¹² The isolated acetylene molecule was placed in a large unit cell with a broken symmetry of dimensions 13x14x15 Å and optimized using 350 eV and 5x5x5 as cut-off energy and k-points mesh, respectively. The optimized bond lengths were C-C = 1.21 Å and C-H = 1.07 Å, which are close to those reported for experimental measurements.³²

As a reference, acetylene was adsorbed over a Pd(111) surface. A (3x3) supercell was used, as well as 350 eV cut-off energy and (3x3x1) k-points mesh. The slab contains four layers with the two outermost relaxed and the inner layers were kept fixed to represent the bulk,³³ with a calculated lattice constant of 3.92 Å, close to the experimental value (3.88 Å). A vacuum of more than 10 Å was included between the interlayered slabs.

The adsorption energy (E_{ads}) on the carbides was calculated using the expression:

$$E_{ads} = E(carbide_{(001)}ad) - (Ecarbide_{(001)} + E_{hydrocarbon}) \quad (1)$$

In equation (1), $E(carbide_{(001)}ad)$ is the energy for the slab carbide with the adsorbed hydrocarbon, $Ecarbide_{(001)}$ is the energy of the optimized clean surface slab model and $E_{hydrocarbon}$ is the energy of the acetylene molecule. Equation (1) was also used in the case of adsorption on palladium, changing carbide(001) by Pd(111).

3. RESULTS AND DISCUSSION

3.1. Acetylene adsorption structures on Pd(111), δ -MoC(001), TiC(001), and ZrC(001) surfaces

Pd-based catalysts are highly selective for the conversion of C_2H_2 into different chemicals.⁴ Thus, the Pd(111) surface was taken as a reference for the adsorption of acetylene. The molecule was adsorbed in three coordination modes: π -M, di- σ -MM, and μ -hh (see Figure 2). The notation used in this work for π - and di- σ -bonds is consistent with the nomenclature reported in the literature regarding acetylene bonding.^{34,35} On the Pd surface, acetylene was strongly chemisorbed and the magnitude of the adsorption energy depended on the adsorption mode: i.e. π -M (-0.90 eV), di- σ -MM (-1.69 eV) and μ -hh (-2.20 eV). Binding to the metal induced a significant increase in the C-C bond length. Moreover, the C-C bond elongation obtained is similar to free ethylene (1.33 Å) in π -M and di- σ -MM coordination modes, and between free ethylene and ethane (1.39 Å) in μ -hh mode. The C_2H_2 adsorption energies and geometry parameters obtained in this work are in agreement with the values reported for acetylene bonding on Pd(111) in previous theoretical studies.^{2,33,36} The most stable structure on Pd(111) involved bonding on a hollow surface site (see Figure 2c). This geometry cannot be reproduced in the TMC(001) surfaces, see Figure 1, and is different from that obtained for C_2H_2 on silicon surfaces where the molecule adsorbs forming four σ -bonds with silicon surface atoms.

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In order to analyze the acetylene adsorption capability of the TMC(001) surfaces, several adsorption modes were evaluated as shown in Figure 3. In summary, the blue lines indicate that both acetylene C-C and C-H bond axes (molecular axis) were parallel to the surface plane; this

applies for 1, 2, 3, 4, 5 and 8 coordination modes. On the other hand, blue squares in Figure 3 (coordination modes 6, 7, and 9) indicate that the acetylene C-C bond axis was perpendicular to the surface plane, i.e. one C-H bond axis directed towards the surface and the other C-H bond axis directed towards the vacuum.

On the TMC(001) surfaces, the acetylene molecule can interact with C centers not present in clean Pd(111) or other metal surfaces, Figure 3. A full set of the results obtained for acetylene adsorption on the TMC(001) surfaces is presented in Table 1, while the most relevant adsorption modes on the carbide surfaces and on Pd(111) are summarized in Table 2. The geometry of the most stable structures are shown in Figure 4 and their Charge Density Difference (CDD) is plotted in Figure 5. In general, the C₂H₂ molecule is activated on all the evaluated surfaces but to a different extent. Additionally, acetylene adsorption energies on the δ -MoC(001) surface are much lower than those obtained on TiC(001) and ZrC(001). Taken into account only stable structures where the C-C bond length is modified (see Table 1), the acetylene adsorption strength follows the trend:

$$\delta\text{-MoC(001)} (-1.78 \text{ to } -0.70 \text{ eV}) \ll \text{ZrC(001)} (-3.69 \text{ to } -0.19 \text{ eV}) < \text{TiC(001)} (-3.75 \text{ to } -0.76 \text{ eV})$$

As we will see below, this trend in reactivity can be explained taking into account differences in structural and electronic properties of the carbide substrates. With respect to Pd(111), the carbide surfaces offer the possibility of binding carbon and/or metal centers. In the following section, we will examine the binding on these different types of adsorption sites.

3.1.1. Acetylene bonding on carbon centers of transition metal carbides

The bonding of hydrocarbons on carbon centers of the TMCs is closely related to properties of the clean surfaces. The Mulliken charge for surface metal atoms follow the trend: $\delta\text{-MoC}(001) < \text{TiC}(001) < \text{ZrC}(001)$, see Figure 1. According to this trend and the results shown in Table 1, the greater the positive charge in surface metal atoms (more negative charge in $\text{C}_{\text{surface}}$ atoms), the greater the interaction of C_2H_2 in a di- σ -CC mode. This is due to the higher electron density at the $\text{C}_{\text{surface}}$ atoms on $\text{TiC}(001)$ and $\text{ZrC}(001)$, and it is related to the stability of the structures obtained for acetylene adsorption on these surfaces (see Table 1), where C_2H_2 is chemisorbed strongly on $\text{TiC}(001)$ and $\text{ZrC}(001)$ but weakly on $\delta\text{-MoC}(001)$.

Another parameter to consider in the adsorption of acetylene is the structure or geometry of the carbide surfaces. According to the geometry parameters for the pristine TMC(001) surfaces, the distance between $\text{C}_{\text{surface}}$ atoms was similar in $\delta\text{-MoC}(001)$ and $\text{TiC}(001)$ (3.06-3.08 Å) but higher in $\text{ZrC}(001)$ (3.32 Å).¹² Therefore, the geometry parameters does not explain the effect of adsorption via di- σ -CC mode as it happens for $\text{Pd}(111)$ via di- σ -MM mode (distance $\text{Pd-Pd} = 2.77$ Å, lower to the M-M distance in the carbides¹²). Therefore, the electronic factors would be the ones responsible for the strong adsorption of C_2H_2 on $\text{TiC}(001)$ and $\text{ZrC}(001)$ surfaces.

The Pauling electronegativity difference between carbon and metals are: $\text{C-Mo} = 0.39$, $\text{C-Ti} = 1.01$ and $\text{C-Zr} = 1.22$. Thus, the charge of the $\text{C}_{\text{surface}}$ atoms in the clean surface increases following the trend: $\delta\text{-MoC}(001)$ (-0.66e) < $\text{TiC}(001)$ (-0.75e) < $\text{ZrC}(001)$ (-0.82e). Once acetylene approaches to the surfaces of $\text{TiC}(001)$ and $\text{ZrC}(001)$ (see Figure 6), a $\text{C}_{\text{surface}}\text{-C}_{\text{acetylene}}$ bond is formed, with a length close to that of a single C-C bond in free ethane (~ 1.5 Å). Therefore, there is an important covalent contribution to the bonding (red zones in between

surface and acetylene in Figure 6, CDD plot). Moreover, the C_2H_2 charge (Q_{ace} in Figure 6) indicates that there is also an ionic contribution to the bonding, yielding a charge polarization as shown in the blue zones of Figure 6 (charge isosurfaces).

On the contrary, on a δ -MoC(001) surface there is not bonding of acetylene via a di- σ -CC mode. A charge re-distribution within C_2H_2 molecule was observed after adsorption (see isosurface, Figure 4a), which was not shared with the $C_{surface}$ atoms and rather moved to about 3 Å away from the surface.

3.1.2. Acetylene adsorption on metal centers of transition metal carbides

For analyzing the binding of unsaturated hydrocarbons to metal centers, we should refer to the models developed for the bonding of olefins and alkynes in organometallic compounds.⁴⁰ Olefin binding on metal surfaces is usually described by means of the Dewar-Chatt-Duncanson (D-C-D) model.⁴⁰ According to this model, based on the molecular orbital theory, an alkene donates electron density into an empty metal d-orbital from a π -symmetry bonding orbital between the carbon atoms. At the same time, the metal donates electrons back from a filled d-orbital into an empty π^* -antibonding orbital of the alkene. Both of these effects tend to reduce the carbon-carbon bond order, as the bonding also induces a rehybridization in the carbon atoms from sp^2 towards sp^3 .⁴⁰ Using this binding scheme, it is possible to describe the C-C bond elongation of C_2H_4 on Pd(111) surface (calculations performed under the same methodology for C_2H_2), due to the occupancy of LUMO orbitals and then the decrease in the bond order, which leads to an elongation of the ethylene C-C bond length (from 1.33 Å to 1.40-1.45 Å, $E_{ads} = -0.91$

to -1.10 eV). A similar scheme of the D-C-D model can be used for explaining alkynes binding on metal surfaces.

In the bonding of C_2H_2 to metal sites, the σ -donation is from the acetylene π_{xy} -orbital to a metal hybrid dp^2 ($d_{xy}+p_x+p_y$) orbital and from the acetylene π_z -orbital to a d^2 ($d_{xz}+d_{yz}$); while the π -back donation is from the $d_{x^2-y^2}$ metal orbital to a π_{xy}^* -antibonding acetylene orbital and from the d^2 ($d_{xz}+d_{yz}$) again to a π_{xy}^* -antibonding acetylene orbital.⁴⁰ In the carbides, not only metal centers but the carbon centers have influence in hydrocarbons bonding, involving a complex scheme according to molecular orbital theory.

The C_2H_2 adsorption on metals centers leads to a stable structure on the δ -MoC(001) surface, in contrast such adsorption motif is not stable on TiC(001) and ZrC(001) (see Table 1). This is related to the structural and electronic properties of clean surfaces seen in Figure 1. The positive charge on Mo atoms is lower compared to Ti and Zr. Therefore, the π -back donation from surface hybrid Mo orbitals is favored, where the donation is restricted due to the higher positive charge of Ti and Zr atoms (see Q_M in Figure 1). In addition, the $C_{surface}$ atoms in δ -MoC(001) are less negatively charged than those on TiC(001) and ZrC(001). As a consequence, the electron migration towards the adsorbate and further occupation of acetylene π^* -antibonding orbitals are favored for acetylene adsorption on δ -MoC(001), while the molecule is not activated on metal centers of TiC(001) and ZrC(001). Finally, the “extra” π -orbital of acetylene (not seen in ethylene) favors the orbital overlap with surface hybrid Mo orbitals, easily occupying C_2H_2 π^* -antibonding orbital, decreasing the bond order and as a consequence, elongating the C-C bond length from 1.21 Å to 1.30 Å (close to free ethylene). In summary, the D-C-D model describes acetylene adsorption on the δ -MoC(001) surface, and only on this monocarbide surface there are stable structures when considering anchoring to metal centers.

Even though C_2H_2 adsorption on metal centers of δ -MoC(001) is stable with binding energies in the range -0.70 to -0.83 eV (π -M geometry in Table 1), the most stable structure (-1.78 eV) involves not only a Mo center but a carbon center, i.e. adsorption in a bridge Mo-C (di- σ -CM geometry in Table 1). The D-C-D model was proposed for olefins and alkynes bonding in a π -M-kind adsorption mode, in a triangle M-C-C site.⁴⁰ However, the binding in metal carbides involves different geometries due to the new C_{surface} not seen on metal surfaces. Therefore, for the most stable structure on δ -MoC(001), the D-C-D model alone does not explain acetylene bonding. Additionally, a covalent $C_{\text{acetylene}}-C_{\text{surface}}$ bond should be considered (red zones in between C_2H_2 and δ -MoC(001) in Figure 5a).

3.2.Comparing the bonding of acetylene on carbides, metals and organometallic complexes

Acetylene adsorption or binding has been reported for several systems. In this part, we compare our results for adsorption on metal carbides to the bonding of acetylene reported: 1) On silicon surfaces,³⁷⁻³⁹ which have a technological importance in the field of microelectronics; 2) In bimetallics systems like W-Fe,⁴¹ which have been reported as potential catalysts for selective hydrogenation of acetylene; And 3) In organometallic compounds,^{1,42,43} due to its widespread use in organic and inorganic chemistry.

Adopting the most stable structure (Table 2), the binding energies for C_2H_2 on the δ -MoC(001) surface are within the range of the theoretical values reported for adsorption on silicon surfaces ($\sim$ -1.2 to -2.9 eV)³⁹ and the bond dissociation energy values reported for some

organometallic compounds (~ -0.5 eV to -2.23 eV),^{42,43} but lower than seen on bimetallic Fe-W surfaces (-1.71 to -2.86 eV).⁴¹ In the case of TiC(001) and ZrC(001), the corresponding binding energies are above the values reported for all three systems.

For the most stable structures in this work, acetylene C-C bond length was modified upon adsorption. This behavior has been observed in some organometallic systems (high-valent compounds) which in turn depends on the nature of the metal, its oxidation state and the ligands attached to it.^{42,43} On the contrary, C₂H₂ adsorption on silicon surfaces produces a large increase of the C-C bond length to ~ 1.6 Å,³⁷ which is larger than expected for free ethylene (1.33 Å) and ethane (1.53 Å), suggesting that in silicon surfaces there is not a direct relation between adsorption energies and the extent of the C-C bond elongation. Acetylene adsorption on W-Fe bimetallic surfaces induces a C-C bond elongation in the range 1.36 – 1.42 Å, where the authors proposed a good catalytic performance in the selective hydrogenation reaction of C₂H₂, together with a mechanistic study on W@Fe(111) surface.⁴¹ According to the C-C bond lengths obtained on TMC(001) surfaces, it is proposed that acetylene could be transformed into ethane-like upon adsorption on TiC(001) and ZrC(001) surfaces (i.e., C-C bond between 1.45–1.47 Å), and into ethylene-like structure upon adsorption over δ -MoC(001) surface (i.e., C-C bond between 1.30–1.37 Å).

3.3 Comparing the bonding of methane, ethylene and acetylene on transition metal carbides

From a fundamental point of view, it is interesting to evaluate the capability of TMC(001) surfaces to transform alkanes, alkenes and alkynes. Therefore, in this section, the bonding of the simplest hydrocarbon of every family (methane, ethylene, and acetylene) is analyzed and discussed.

3.3.1. Methane and acetylene binding on a δ -MoC(001) surface

The adsorption of methane has been previously studied only on the δ -MoC(001) surface using DFT calculations.²³ The theoretical results show that the molecule binds through its H atoms to Mo and C sites of the carbide surface. The magnitude of the adsorption energy on both types of sites is very similar, with values close to -0.5 eV without van der Waals correction, and -0.9 eV when the correction is included. In contrast, acetylene binds very well to a hybrid C, Mo site of δ -MoC(001) with a large adsorption energy of -1.8 eV without the need to add a van der Waals correction. The adsorption of methane on δ -MoC(001) produces a negligible distortion in the geometry of the molecule, while on the same carbide surface, acetylene undergoes a significant elongation of the C-C bond and a change in the configuration of the C-H bonds. The low-lying pi-orbitals around the unsaturated C-C bond in acetylene are probably responsible for these differences in chemical reactivity. This is reflected in the Charge Density Difference plots corresponding to the most stable structure for adsorption of CH₄ and C₂H₂ (including C₂H₄) on δ -MoC(001) surface (Figure 7). In general, the greater the charge transfer from the surface to the adsorbate, the stronger the adsorption. In other words, a greater ionic contribution to the bonding leads a higher adsorption energy.

3.3.2. Ethylene and acetylene adsorption on δ -MoC(001), TiC(001) and ZrC(001) surfaces

It is worth to mention that the adsorption energy values for ethylene binding on TMC(001) have been reported to be well described using van der Waals (vdW) correction to the electronic energy,¹² due to the weak interaction between C₂H₄ and TMC(001) surfaces (below $|-0.53|$ eV). The results obtained in this work for C₂H₂ adsorption on TMC(001) lead to higher binding energy values (above $|-0.70|$ eV) and a clear formation of chemical bonds. Therefore, we considered that the description of acetylene adsorption in transition metal carbides surfaces does not require significant vdW corrections to the energy.

3.3.2.1. C₂H₂ and C₂H₄ adsorption on metal centers of the carbides

On metal centers, the most stable structure for ethylene adsorption on δ -MoC(001) (adsorption energy, -0.53 eV) and ZrC(001) surfaces (-adsorption energy, -0.12 eV, respectively) is in a π -M mode, i.e. interaction of ethylene with one surface metal atom.¹² However, the molecule is not activated, i.e. the C-C bond length stays intact. In contrast, acetylene adsorption via π -M mode is not a stable structure and the C-C bond length is modified from 1.21 Å to 1.30 Å (close to free ethane). In general, the π -back donation from the surfaces to acetylene is favored due to the higher probability of occupying acetylene π^* -antibonding molecular orbitals, as compared to ethylene, decreasing in that way the C-C bond order for acetylene on the δ -MoC(001) surface (see Table 1), while the C-C bond order of ethylene remains unchanged.¹²

3.3.2.2. Adsorption of C₂H₂ and C₂H₄ on carbon centers of the carbides

Ethylene adsorption via di- σ -CC mode is only stable on TiC(001) surface.¹² The most stable found for acetylene adsorption on TiC(001) and ZrC(001) surfaces involve a di- σ -CC mode. The similarity in electronic properties of the TiC(001) and ZrC(001) clean surfaces (see Figure 1) suggest that ethylene and acetylene should be adsorbed on both TiC(001) and ZrC(001) via di- σ -CC mode. The weak bonding in this mode on ZrC(001) is related to the surface-adsorbate charge transfer capability of the carbide surface. The Mulliken charge of ethylene via di- σ -CC mode on TiC(001) and ZrC(001) surfaces was -0.66e and -0.36e, respectively; for acetylene it was -0.68e and -0.72e, respectively. The lower charge transfer from the ZrC(001) surface to C₂H₄ is related to the low migration of electron density into ethylene π^* -antibonding orbitals and as a consequence, there is not an elongation of C=C bond length and the structure is among the most stable ones.¹² On the contrary, for C₂H₂ adsorption, the extent of the Mulliken charge is similar for TiC(001) and ZrC(001) surfaces, therefore, the migration of electron density from the carbide surface to acetylene is equivalent in both cases and as a consequence, the acetylene C $\equiv$ C bond was elongated due to the occupancy of π^* -antibonding orbitals. In summary, the extent of charge migration from the surface to the adsorbates can explain the difference in the behavior of binding of acetylene and ethylene on TiC(001) and ZrC(001) surfaces.

3.4. TMC(001) surfaces as catalyst for selective hydrogenation of acetylene

According to the results shown in Figure 4 and Table 1, C₂H₂ adsorption on TiC(001) and ZrC(001) surfaces induces an elongation of C-C bond length from 1.21 Å into ~1.5 Å, similar to the C-C bond length in ethane, while on δ -MoC(001) surface the C-C bond is elongated from

1.21 Å to ~1.33 Å, similar to that in free ethylene. This suggests that δ -MoC(001) can allow a “controlled” transformation from C_2H_2 to C_2H_4 . This could be an advantage in terms of selective hydrogenation reactions, where the target is olefins.

On the contrary, the strong chemisorption of acetylene on TiC(001) and ZrC(001) (above -3.5 eV) suggests that both surfaces could not be appropriate for their application in hydrogenation reactions to C_2H_4 . This is because the surface may be poisoned (or modified) by hydrocarbon deposition limiting hydrogenation reactions. In addition, acetylene occupies the active sites for the dissociative chemisorption of H_2 , as reported by Florez et al.;²¹ yet this aspects are beyond the scope of this work and further studies are required.

Among the studied surfaces, δ -MoC(001) is expected to have the best performance in hydrogenation reactions, particularly applied in purification of ethylene streams containing acetylene, due to its lower adsorption energy. It allows an elongation of the C-C bond to a length close to ethylene (~1.33 Å). Moreover, in addition to the most stable adsorption structure on δ -MoC(001), there are other five sites to adsorb the hydrocarbon, three of this modes elongate acetylene C-C bond (see Table 1). On the contrary, on TiC(001) and ZrC(001) there is not such a variety of surface sites and the strong adsorption limits other interactions between C_2H_2 and the surfaces. Accordingly, deactivating the catalyst and modifying the surfaces may be required to promote the catalytic cycle.

According to the results obtained in this work, if both ethylene and acetylene are present in a mixture, the preference would be towards acetylene transformation instead of C_2H_4 using metal carbides. Further experimental and theoretical studies are required for designing a selective TMC-based catalysts for hydrogenation of acetylene into ethylene and avoiding ethane formation.

4. CONCLUSIONS

A comprehensive study of acetylene adsorption on Pd(111), δ -MoC(001), TiC(001) and ZrC(001) surfaces was carried out by means of calculations based on periodic density functional theory, using the Perdew-Burke-Ernzerhof exchange-correlation functional. The presence of C sites and variations in the structural and electronic properties of the carbide surfaces led to a diversity of binding modes.

The extent of the acetylene adsorption on TMC(001), where the C-C bond length in the hydrocarbon was modified, follows the trend: TiC(001) (-3.75 to -0.76) > ZrC(001) (-3.69 to -0.19 eV) > δ -MoC(001) (-1.78 to -0.70 eV). Acetylene adsorption on TiC(001) and ZrC(001) is stronger than on Pd(111), but it is similar for the δ -MoC(001) and Pd(111) surfaces. According to the C-C bond elongation, the acetylene molecule could be transformed into a ethylene-like structure on δ -MoC(001) surface but into ethane-like on TiC(001) and ZrC(001) surfaces.

For acetylene, the most stable structures are di- σ -CC mode on TiC(001) and ZrC(001) surfaces and di- σ -CM on δ -MoC(001).

The obtained results suggest that δ -MoC(001) surface is expected to have the best performance in hydrogenation reactions, particularly applied in purification of ethylene streams containing acetylene. In terms of adsorption energy and C-C bond elongation, δ -MoC(001) surface showed a Pd-like behavior, not observed for TiC(001) and ZrC(001) surfaces. Another advantage of δ -MoC(001) as a catalyst for hydrogenation reactions is that there are C_{surface} sites available after C_2H_2 adsorption, which are necessary for hydrogen binding on the surface.

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Table 1. Acetylene adsorption energy (E_{ads}) on TMC(001), geometry obtained in every case (see nomenclature in Table 1 and Figure 1) and C-C bond length. ^a

δ -MoC(001)			TiC(001)			ZrC(001)		
E_{ads} (eV)	C-C (Å)	Geometry	E_{ads} (eV)	C-C (Å)	Geometry	E_{ads} (eV)	C-C (Å)	Geometry
-1.78	1.37	di- σ -CM	-3.75	1.45	di- σ -CC	-3.69	1.47	di- σ -CC
-0.83	1.30	π -M	-0.76	1.39	μ -CM	-0.19	1.38	σ -C
-0.79	1.40	di- σ -CM ^b	-0.10	1.22	π -M	-0.17	1.22	π -M
-0.70	1.30	π -M	-0.08	1.21	π -M	-0.01	1.22	μ -CM
-0.53	1.21	Top-h	-0.07	1.22	π -M	0.00	1.21	Top-h
-0.46	1.21	Top-M	-0.02	1.21	Top-C	0.03	1.21	Top-C
-0.42	1.21	di- σ -MM	0.04	1.21	di- σ -MM	0.05	1.32	π -C
-0.15	1.21	Top-C	0.05	1.21	Top-M	0.11	1.21	di- σ -MM
-0.07	1.21	di- σ -CC	0.07	1.21	Top-h	0.12	1.21	Top-M

^a C-C bond lengths: Free C_2H_2 = 1.21 Å, free C_2H_4 = 1.33 Å, free C_2H_6 = 1.53 Å.

^b Hydrogen atoms non-eclipsed under a Newman projection.

Table 2. Ethylene and acetylene adsorption energies (eV) in several adsorption modes, for the most stable structures on δ -MoC, TiC, ZrC and Pd ^a surfaces. The hydrocarbon C-C bond length (Å) is shown in parenthesis. ^b

Hydrocarbon	δ -MoC(001)	TiC(001)	ZrC(001)	Pd(111)
di- σ -CC mode				
Ethylene ^c	0.04 (1.34)	-0.45 (1.64) ^d	0.22 (1.34)	--
Acetylene	-0.07 (1.21)	-3.75 (1.45) ^e	-3.69 (1.47) ^e	--
di- σ -CM mode				
Ethylene ^c	--	-0.05 (1.34)	-0.08 (1.34)	--
Acetylene	-1.78 (1.37) ^e	--	--	--
π -M mode				
Ethylene ^c	-0.53 (1.36) ^d	-0.10 (1.35)	-0.12 (1.34)	-0.91 (1.40)
Acetylene	-0.83 (1.30)	-0.10 (1.22)	-0.17 (1.22)	-0.90 (1.27)
di- σ -MM mode				
Ethylene ^c	0.12 (1.49)	0.00 (1.34)	0.19 (1.34)	-1.10 (1.45) ^d
Acetylene	-0.42 (1.21)	0.04 (1.21)	0.11 (1.21)	-1.69 (1.32)

^a μ -hh not considered.

^b Free acetylene: C-C=1.21 Å, free ethylene: C-C=1.33 Å, free ethane: C-C= 1.53 Å.

^c Some values taken from ref. ¹².

^d Most stable structures for ethylene adsorption.

^e Most stable structures for acetylene adsorption.

Figure 1. Charge isosurfaces($0.05 \text{ e}/\text{\AA}^3$) for pristine surfaces. Q_M : Mulliken charge for metal atoms. $Q_M=0.78e$, $0.75e$, and $0.56e$ for a), b), and c), respectively.

Figure 2. Acetylene adsorption modes on Pd(111) surface. Top: top view, bottom: side view. Numbers in each figure belongs to C-C bond length. C, brown; H, light beige; Pd, gray balls. Q_{ace} : acetylene Mulliken charge.

Figure 3. TMC(001) surface. a) Surface sites. Left: top view, right: side view b) Adsorption modes evaluated. Blue lines (C-C adsorbate axis parallel to surface) and squares (C-C axis perpendicular to the surface) represent C_2H_2 molecule. M (Mo, Ti, Zr), yellow; C, brown.

Figure 4. Geometry (adsorption modes) of the most stable structures for acetylene adsorption on TMC(001) surfaces. Top: top view, bottom: side view. C-C: adsorbed acetylene bond length.

Figure 5. Acetylene adsorption for most stable structures on TMC(001). Top: CDD (from -0.1 to $0.1 \text{ e}/\text{\AA}^3$), bottom: isosurfaces ($0.05 \text{ e}/\text{\AA}^3$). In isosurfaces, blue and yellow represent the zones where electron density was earned and lost, respectively. Q_{ace} : Acetylene Mulliken charge.

Figure 6. Acetylene adsorbed via di- σ -CC mode. Top: CDD (from -0.1 to $0.1 \text{ e}/\text{\AA}^3$); bottom: isosurfaces ($0.05 \text{ e}/\text{\AA}^3$). In isosurfaces, blue and yellow represent the zones where electron density was earned and lost, respectively. Q_{ace} : Acetylene Mulliken charge.

Figure 7. CDD (top, from -0.1 to 0.1 e/Å³) and charge iso-surface (bottom, 0.05 e/Å³) for most stable adsorbed C₂H₂, C₂H₄ and CH₄ structures on δ -MoC(001) surface. Q_i belongs to hydrocarbon Mulliken charge.

Graphical Abstract