BNL-114355-2017-JA

**Acetylene and Ethylene Adsorption on a β -Mo₂C(100) Surface:
A Periodic DFT Study on the Role of C- and
Mo-terminations for Bonding and Hydrogenation Reactions**

C. Jimenez-Orzoco, J. A. Rodriguez

Submitted to Journal of Physical Chemistry C

September 2017

Chemistry Department

Brookhaven National Laboratory

**U.S. Department of Energy
USDOE Office of Science (SC),
Basic Energy Sciences (BES) (SC-22)**

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE- SC0012704 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Acetylene and Ethylene Adsorption on a β -Mo₂C(100) Surface: A Periodic DFT Study on the Role of C- and Mo-terminations for Bonding and Hydrogenation Reactions

Carlos Jimenez-Orozco,^a Elizabeth Florez,^b Andres Moreno,^a Ping Liu^c and José A. Rodriguez^{*c}

^a Química de Recursos Energéticos y Medio Ambiente, Instituto de Química, Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia UdeA; Calle 70 No. 52-21, Medellín, Colombia.

^b Departamento de Ciencias Básicas, Universidad de Medellín, Carrera 87 No 30-65, Medellín, Colombia

^c Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, USA.

ABSTRACT

Mo₂C catalysts are widely used in hydrogenation reactions, however, the role of the C- and Mo-terminations in these catalysts is not clear. Understanding the binding of adsorbates is key for explaining the activity of Mo₂C. The adsorption of acetylene and ethylene, probe molecules representing alkynes and olefins, respectively, was studied on a β -Mo₂C(100) surface with C- and Mo-terminations using calculations based on periodic density functional theory. Moreover, the role of the C/Mo molar ratio was investigated to compare the catalytic potential of cubic (δ -MoC) and orthorhombic (β -Mo₂C) surfaces. The geometry and electronic properties of the clean δ -MoC(001) and β -Mo₂C(100) surfaces have strong influence on the binding of unsaturated hydrocarbons. The adsorption of ethylene is weaker than that of acetylene on the surfaces of the cubic and orthorhombic systems; adsorption of the hydrocarbons was stronger on β -Mo₂C(100) than on δ -MoC(001). The C-termination in β -Mo₂C(100) actively participates in both acetylene and ethylene adsorption and is not merely a spectator. The results of this work suggest that the β -Mo₂C(100)-C surface could be the one responsible for the catalytic activity during the hydrogenation of unsaturated C $\equiv$ C and C=C bonds, while the Mo-terminated surface could be poisoned or transformed by the strong adsorption of C and CH_x fragments.

1. INTRODUCTION

Due to their outstanding properties, transition metals carbides have attracted the attention of the catalysis community.^{1,2} The elegant works of Boudart and co-workers have shown that metal carbide catalysts exhibit hydrogenation properties similar to those of expensive noble metals.^{3,4} Among the transition metal carbides, molybdenum carbide has been one of the most studied in the last years with several applications as a catalyst in reactions including the hydrogenation of olefins⁵⁻⁹ and aromatic hydrocarbons,¹⁰⁻¹² CO₂ transformation to methanol,^{13,14} Fischer-Tropsch synthesis,¹⁵ thiophene decomposition,¹⁶ methane reforming,¹⁷ ethane hydrogenolysis,¹⁸ and the water-gas shift-process.^{19,20} Although Mo₂C is active as a catalyst for the hydrogenation of C=C bonds,⁵⁻¹² no systematic study has appeared examining the bonding interactions of ethylene on well-defined surfaces of this carbide; additionally the catalytic potential of these catalysts for the hydrogenation of C≡C bonds have not been explored. Molybdenum carbides can adopt different structures depending on the carbon/metal ratio and they can exhibit terminations of C and Mo atoms, leading to different bonding modes on these terminations. *A priori*, it is not clear if the C or Mo centers are the active sites for the hydrogenation of C=C and C≡C bonds on Mo₂C catalysts, although many studies assume that the chemical transformations take place on Mo centers.^{5,21,22}

Among the crystal phases of molybdenum carbide,²³ three of them are the most used in catalysis, viz. cubic,^{13,22,24-29} hexagonal^{11,30-32} and orthorhombic.^{14,20,22,28,33} In general, molybdenum carbides can be represented as MoC_y, where the most investigated system is y = 0.5 (Mo₂C), i.e. a C/Mo molar ratio of 0.5. However, phases with y = 1 (MoC) have also been reported.^{22,25,28,29,34,35} Moreover, y also could be a non-integer number, leading to non-stoichiometric carbides.¹³ The chemistry of molybdenum carbides depends on their C/Mo ratio,

with a significant effect in the activity, stability, and selectivity in hydrogenation reactions.^{13,22,32} Xu et al¹³ and Posada-Perez et al²² have found that the C/Mo ratio is fundamental for CO₂ hydrogenation: The selectivity shifts towards hydrocarbons like CH₄ and C₂H₆ when using a hexagonal phase (C/Mo = 0.5), but moves towards CO and CH₃OH when employing the cubic phase (C/Mo = 1). The C/Mo ratio has also been reported as an important aspect in the dissociative chemisorption of H₂,³⁶ where the adsorption and dissociation behavior of the hydrogen molecule as well as its energy barriers are completely different on δ -MoC(001) and β -Mo₂C(001) surfaces. A δ -MoC(001) surface exposes 50% of Mo and 50% of C atoms distributed in a square array (Figure 1a, $a=2.19$ Å). In contrast, a β -Mo₂C(001) surface²² exposes terraces of pure (100%) Mo or pure C atoms (Figure 1b,c). Which terraces of Mo₂C can participate directly in the hydrogenation of unsaturated C=C and C $\equiv$ C bonds? There are several key aspects that are still not clear for hydrogenation reactions of unsaturated hydrocarbons like benzene,¹² naphthalene,¹⁰ toluene³² and cumene¹¹ on Mo₂C catalysts.

The main objective of this work is to study in detail the adsorption of ethylene and acetylene, two probe molecules for the hydrogenation of unsaturated hydrocarbons, on Mo- and C-terminated faces of β -Mo₂C(100) using periodic density functional theory. The goal is to identify patterns of reactivity among different adsorption sites. This work is organized as follows. First, the geometric and electronic parameters of clean β -Mo₂C(100) and δ -MoC(001) surfaces are presented as a point of reference before interactions with adsorbates. Then, individual adsorptions of acetylene and ethylene on the β -Mo₂C(100) surface are examined in detail on both C- and Mo-terminations. Finally, the role of C/Mo molar ratio in the adsorption of acetylene and ethylene is discussed, and the catalytic potential of β -Mo₂C(100) (Mo- and C-terminated) and δ -MoC(001) surfaces for hydrogenation reactions is considered.

2. METHODOLOGY AND COMPUTATIONAL DETAILS

In this work, to name molybdenum carbide crystal phases, we followed the nomenclature defined by the Joint Committee on Powder Diffraction Standards (JCPDS) data files. In this notation, the hexagonal and orthorhombic phases are denoted as α -Mo₂C and β -Mo₂C, respectively.³⁴ The other notation uses the early definition given by Christensen,³⁷ where the orthorhombic crystal phase was denoted as α -Mo₂C. Additionally, the notation for cubic molybdenum carbide is δ -MoC.^{23,25,29}

Periodic density functional theory calculations were carried out using the CASTEP package, version 5.5.³⁸ Exchange – correlation effects were accounted by means of the Generalized Gradient Approximation (GGA) using PBE (Purdew – Burke – Ernzerhof) functional³⁹ as implemented in CASTEP. Ultra-soft Vanderbilt-type pseudopotentials were used to describe the ionic cores.⁴⁰ The valence electrons were expanded in a plane-wave basis set within 350 eV cut-off energy as done in previous studies.^{20,24}

A grid of special **k**-points was used for the numerical integration in the Brillouin zone, which were automatically selected by means of the Monkhorst – Pack scheme.⁴¹ The electronic relaxation was considered converged when 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 structures were optimized using 5x5x5 **k**-points mesh, obtaining the respective cell parameters. Then, following the previous study by Wang et al.,⁴² the surface β -Mo₂C(100) was created from the optimized bulk structure by means of the slab surface model, including a vacuum of more than 10 Å between the interlayered slabs arising from periodic symmetry along the direction perpendicular to the surfaces: See Figure S1, Supporting Information. In our work, we use the geometry and notation shown in Figures S1b-d.

The supercell considered was p(2x2), the slab contains four layers with the two outermost relaxed and the inner layers were kept fixed to represent the bulk.^{25–27,34–36,43} In test calculations, we found very similar results for slabs with four and five layers. It is worth to mention that for β -Mo₂C(100), the surface could have C- or Mo- termination,^{22,34,42} which are denoted hereinafter as β -Mo₂C-C and β -Mo₂C-Mo, respectively (see Figure S1c and 1d in the Supporting Information). These surfaces have some polarity but the inclusion of a dipole correction in the calculations had a negligible effect in test studies (see Supporting Information). The grid of special **k**-points used for the numerical integration in the Brillouin zone were automatically selected by means of the Monkhorst – Pack scheme,⁴¹ particularly the 3x3x1 **k**-points mesh.

The isolated acetylene and ethylene molecules were placed in a large unit cell with a broken symmetry of dimensions 13x14x15 Å and optimized using 350 eV cut-off energy and performing a Γ -point optimization. The optimized bond lengths were close to the reported experimental values.^{44,45}

The adsorption energy (E_{ads}) was calculated:

$$E_{ads} = E(\beta\text{-Mo}_2\text{C}(100)ad) - (E(\beta\text{-Mo}_2\text{C}(100)) + E_{hydrocarbon}) \quad (1)$$

In equation (1), $E(\beta\text{-Mo}_2\text{C}(100)ad)$ is the energy for the carbide slab with the adsorbed hydrocarbon, $E(\beta\text{-Mo}_2\text{C}(100))$ is the energy of the optimized pristine surface slab and $E_{hydrocarbon}$ is the energy of the isolated ethylene or acetylene molecule. According to Eq. (1), a less negative value means a stronger adsorption. For ethylene adsorption on a δ -MoC(001) surface, the inclusion of van der Waals (vdW) corrections to the electronic energy has been reported to be useful for better describing the binding on that surface.²⁵ Therefore, in this work

the inclusion of vdW corrections was also considered for adsorptions on β -Mo₂C-C and β -Mo₂C-Mo, according to the dispersion corrections developed by Grimme⁴⁶ as implemented in CASTEP 5.5. Test studies were performed for Zero-point-energy corrections to the binding energies^{47–49} and showed very minor effects on the values of the calculated adsorption energies or on their reported trends (see Supporting Information). For the most stable adsorption structures we performed also calculations with the VASP code⁵⁰ obtaining very similar results to those found with CASTEP (see Supporting Information).

3. RESULTS AND DISCUSSION

3.1. Properties of a clean β -Mo₂C(100) surface

The calculated results for a bulk β -Mo₂C system are very close to those reported experimentally.^{37,51} The fractional coordinates of the C and Mo atoms in the unit cell and the cell parameters of the optimized bulk structure, which are summarized in Table 1, are very similar to experimental values reported by Parthé and Sadagopan,⁵¹ and Christesen.³⁷ The calculated cell parameters are also in agreement with previous calculations.⁵² The errors in the calculations are negligible with respect to experimental data for the corresponding cell parameters (below to 0.7%). Our previous works revealed that the adsorption of ethylene and acetylene on δ -MoC(001) strongly depends on the structural and electronic parameters of the surface.^{25,29} Therefore, it is important to understand these properties for the pristine β -Mo₂C(100) surface, in both C- and Mo-terminations (see Figure S1c and 1d in the Supporting Information). The geometry parameters of the first layer of the slab (the outermost one) for β -Mo₂C-C and β -Mo₂C-Mo surfaces are shown in Table 2 and in Figure 1b,c. The β -Mo₂C(100) surface has polar terminations of Mo and C, i.e. in every layer there are *only* C *or* Mo atoms (see Figure S1b,

Supporting Information). For the β -Mo₂C(100) surface, one can find several distances between Mo-Mo and C-C atoms (see Table 2 and Figure 1b,c). In general, there are five values for Mo-Mo lengths in β -Mo₂C-Mo, while three C-C lengths in the β -Mo₂C-C surface. Moreover, in both polar surfaces, the C-C lengths are larger than Mo-Mo, which suggest that some adsorbates, like unsaturated hydrocarbons, could interact more easily with a β -Mo₂C-Mo surface. However, the geometric parameters alone cannot explain the chemistry of clean surfaces.

Electronic factors strongly influence the binding of adsorbates. Therefore, the Mulliken charges are shown in Figure 2 and Table 2. The β -Mo₂C-C surface has C atoms exposed with a negative charge, which could favor orbital overlap between C_{adsorbate} – C_{surface} atoms forming covalent bonds. On the other hand, the Mo atoms in a β -Mo₂C-Mo surface have a positive charge, which would render this surface very active for the adsorption of unsaturated hydrocarbons such as C₂H₂ and C₂H₄. These adsorbates could interact well with the exposed Mo atoms in the β -Mo₂C-Mo surface via electrostatic interaction. In the next section, we will analyze the adsorption modes of C₂H₂ and C₂H₄ on β -Mo₂C-C and β -Mo₂C-Mo clean surfaces.

3.2.Acetylene and ethylene adsorption on a β -Mo₂C(100) surface

In order to analyze the acetylene and ethylene adsorption on a β -Mo₂C(100) surface, several adsorption modes were evaluated, sketched in Figure 3 and summarized in Table 3. On the C-terminated face of β -Mo₂C(100), an open surface, an adsorbate can interact with C atoms in the first layer and Mo atoms in the second layer. Thus, there can be hybrid (C,Mo) adsorption sites. In the case of Mo-terminated face of β -Mo₂C(100), the atoms in the top layer form a dense

array but interactions with C atoms in the second layer are still possible (Mo,C hybrid sites). The nomenclature used is illustrated with a few examples:

- In modes 1 and 2 in Table 3, the C_2H_2 and C_2H_4 molecules are adsorbed with their molecular plane parallel to the surface and they interact only with C or Mo atoms in π -C (or Mo) and di- σ -CC (or MoMo) configurations.
- C-top, Mo-h1 denotes the hybrid bonding mode. From a top view, one $C_{hydrocarbon}$ atom is located atop on a $C_{surface}$ atom (C-top) and the other $C_{hydrocarbon}$ atom is situated atop to the Mo closest to the surface (hollow Mo1, Mo atom located in the second layer).
- C-h, Mo-h2, another hybrid mode, means that from a top view, one $C_{hydrocarbon}$ is located atop on a $C_{sub-surface}$ hollow ($C_{sub-surface}$ in hollow C1, located in the third layer) and the other $C_{hydrocarbon}$ is located on top a Mo furthestmost from the surface (hollow Mo2, located in the fourth layer).

3.2.1 Acetylene binding to the β - $Mo_2C(100)$ surface

For the β - Mo_2C -Mo surface, as shown in Figure 3 and Table 3, we examined a series of adsorption structures where the molecule was bond only to Mo or to hybrid Mo,C sites. For the π -M and di- σ -MoMo, the optimized structure shifts into the hybrid Mo,C mode Mo-h, C-h2, which belongs to the most stable structure (adsorption energy of -4.23 eV). Hence, at the end there is a preference for hybrid Mo,C adsorption structures (see Table 4). In all the cases listed, the geometry parameters of the adsorbed acetylene molecule changed, with an elongation of C-C bond from 1.21 Å to ~ 1.45 Å (length close to free ethane), and the corresponding modification of the sp into a sp^2 -like hybridization. The top part of Figure 4 (a-c) shows the three most stable structures found for acetylene on the β - Mo_2C -Mo surface. For the most stable structure (Figure

4a), the $C\equiv C$ bond axis is located perpendicular to the Mo-Mo distance labeled as “*c*” in Figure 1c, located with one $C_{\text{hydrocarbon}}$ atom on top a Mo-hollow (Mo-h) and one $C_{\text{hydrocarbon}}$ atom on top a C-hollow C2 (C-h2) from a top view. Therefore, the nomenclature for the most stable structure is Mo-h, C-h2, to indicate the location of every $C_{\text{acetylene}}$ atom on the hybrid Mo,C sites the surface. For the second most stable structure the adsorption geometry is also Mo-h, C-h2 (Figure 4b). However, there is a difference from the Mo-h, C-h2 from a top view, where the sub-surface Mo atoms (located in the third layer of the slab) have different surroundings as shown in Figures 5a,b. The binding energy values of acetylene on $\beta\text{-Mo}_2\text{C-Mo}$ denote extremely strong chemisorptions (-3.61 to -4.23 eV), where there is also a charge transfer from $\beta\text{-Mo}_2\text{C-Mo}$ surface to acetylene molecule producing an increase in Mulliken charge $\sim -1.1e$ (Top of Figure 4). Therefore, an ionic contribution to the bonding is favored as shown in the CDD schemes (Figures 6a,b), where a slight covalent contribution is also observed (red zones in between surface-adsorbate).

Acetylene adsorption on both $\beta\text{-Mo}_2\text{C-C}$ and $\beta\text{-Mo}_2\text{C-Mo}$ surfaces let to three stable structures in every case (see Table 4, Figure 4). It is worth to mention that on a $\beta\text{-Mo}_2\text{C-C}$ surface, the magnitude of the adsorption energy (-1.87 to -0.81 eV) was substantially lower than on a $\beta\text{-Mo}_2\text{C-Mo}$ surface (-4.23 to -3.61 eV). The bonding interactions with a C-terminated surface are in a range which implies that this surface configuration must be considered as the active phase for the hydrogenation of $C\equiv C$ bonds. The binding of acetylene on the Mo-terminated surface is so strong that it probably leads to the destruction of the molecule with C atoms remaining on top of the surface. A modification of the $C\equiv C$ bond length and a change in the hybridization was also observed for the adsorption of C_2H_2 on the $\beta\text{-Mo}_2\text{C-C}$ surface, but it was different from that obtained on $\beta\text{-Mo}_2\text{C-Mo}$. For the $\beta\text{-Mo}_2\text{C-C}$ surface, the most stable

structures involve adsorption on hybrid C,Mo sites (see Figures 4d,e). Therefore, an interaction atop C_{surface} atom (π -C mode) led to one stable structure (-0.81 eV), but its stability was lower when compared to the interactions involving sub-surface Mo atoms in a hybrid C,Mo site (-1.87 and -1.21 eV). Nevertheless, the adsorption at hybrid sites of β -Mo₂C-C can be a good precursor for hydrogenation. The covalent contribution to the bonding of C₂H₂ on β -Mo₂C-C is higher compared to the β -Mo₂C-Mo surface according to the CDD analysis, with a covalent contribution involving C_{surface} atoms (see red zones in between acetylene and surface in Figures 6a,b). Additionally, there is also an ionic contribution to the bonding for the adsorption at hybrid sites (Figure 4d,e), while the contribution for that at atop C_{surface} atom is null, due to the absence of a Mulliken charge in the adsorbed C₂H₂ molecule, i.e. the ionic contribution to the bonding is only significant for adsorption on hybrid C,Mo sites.

The preferred adsorption sites for $C_{\text{acetylene}}$ atoms are located over atop Mo *and* C hollows, i.e. hybrid Mo,C or C,Mo (Table 4 and Figure 4). Indeed, according to the geometric parameters (Table 2) and the C $\equiv$ C bond length (gas molecule), it is not possible for the acetylene to bind in a $C_{\text{surface}}-C_{\text{surface}}$ bridge mode. Therefore, one $C_{\text{acetylene}}$ atom interacts with a site possessing less negative charge to compensate the earned electron density coming from the $C_{\text{acetylene}}-C_{\text{surface}}$ interaction, i.e. $C_{\text{acetylene}}$ interacts with sub-surface Mo atoms at a Mo-hollow site. As a result, the final geometry of the most stable structure on β -Mo₂C-C surface is C-h, Mo-h2. According to the observed geometry and the discussion given above, it is inferred that every $C_{\text{acetylene}}$ atom has a threefold bonding to the surface atoms at distances $< 2 \text{ \AA}$, involving hybrid C,Mo and Mo,C sites.

The difference in the binding of acetylene on β -Mo₂C-C and β -Mo₂C-Mo surfaces relies on charge migration once the hydrocarbon is adsorbed on the surface. The Mulliken charges for

the clean surface atoms are shown in Figure 2 and Table 2. Once C_2H_2 is approaching to the surface, there is migration of electrons from the surface to the acetylene π^* -antibonding orbitals until achieving a structure with minimal energy. As a consequence, there is a net negative Mulliken charge. For the $\beta\text{-Mo}_2\text{C-Mo}$ surface, the Mulliken charge on the C_2H_2 adsorbed is in average close to $-1.08e$ (Figure 4a-c). In the case of $\beta\text{-Mo}_2\text{C-C}$, the binding of acetylene involves covalent and ionic contributions (see Figures 6a,b) and there are bonding modes with a negligible net charge transfer (Figure 4f).

According to the C-C bond lengths obtained, the C_2H_2 adsorption on the $\beta\text{-Mo}_2\text{C-C}$ surface can be useful in ethylene formation, i.e. in a selective hydrogenation reaction, since the binding energies are in the range -1.87 to -0.81 eV, and the $C\equiv C$ bond length elongation was towards $C=C$ ($1.30\text{-}1.39$ Å). On the contrary, the adsorption on a $\beta\text{-Mo}_2\text{C-Mo}$ surface is not advantageous since it probably will destroy the surface due to the strong adsorption energies in the range -4.23 to -3.61 eV. The $C\equiv C$ bond was elongated towards a single C-C bond (1.45 Å), which is a disadvantage in a selective hydrogenation reaction to produce C_2H_4 .

3.2.2 Ethylene adsorption on the $\beta\text{-Mo}_2\text{C}(100)$ surface

The results for ethylene adsorption are presented in Table 5 and the most stable structures for adsorption on the $\beta\text{-Mo}_2\text{C-C}$ and $\beta\text{-Mo}_2\text{C-Mo}$ surfaces are shown in Figure 7. There are clear differences with respect to acetylene adsorption. This is due to the nature of the adsorbate, including both geometric and electronic factors. According to the molecular geometry, the $C=C$ bond length in free ethylene (1.33 Å) is longer than that of acetylene (1.21 Å); therefore, when approaching to the surface, C_2H_4 has a greater chance to form bridges on surface atoms. Regarding electronic factors and the molecular orbital diagrams for ethylene and acetylene, C_2H_4

requires a lower number of electrons to occupy its π^* -antibonding orbitals (two electrons) as compared to C_2H_2 (four electrons in two orbitals energy degenerated). The two most stable structures for ethylene adsorption on $\beta\text{-Mo}_2\text{C-Mo}$ involve an atop and a hollow site, C-h2 geometry (Table 5, Figure 5c,d). They do not have the same binding energies (-1.93 vs -1.68 eV) as a consequence of different surrounding from a top view, as sketched in Figures 5c,d. On $\beta\text{-the Mo}_2\text{C-C}$ termination, the most stable configuration for adsorbed ethylene has the molecule bonded to a surface C atom and to the Mo atoms of a hollow site (Table 5, Figure 7d). In a pure $\pi\text{-C}$ bonding configuration (Figure 7e) the bonding interactions are not very strong but they are no negligible.

According to the Mulliken charges (Figure 7) and the CDD plots (Figures 6c,d), the binding of ethylene on the $\beta\text{-Mo}_2\text{C-Mo}$ surface has both covalent and ionic contributions. In both surface terminations, i.e. $\beta\text{-Mo}_2\text{C-Mo}$ and $\beta\text{-Mo}_2\text{C-C}$, ethylene is modified towards ethane, as indicated by the stretched C-C bond length from 1.33 Å to ~ 1.5 Å (close to free ethane), while the hybridization is changed from sp^2 to sp^3 -like. The ethylene adsorption energy strength follows the trend:

$$\beta\text{-Mo}_2\text{C-C} (-0.94 \text{ to } -0.52 \text{ eV}) < \beta\text{-Mo}_2\text{C-Mo} (\text{from } -1.93 \text{ to } -0.98 \text{ eV})$$

A similar behavior regarding charge transfer in the binding on $\beta\text{-Mo}_2\text{C-C}$ and $\beta\text{-Mo}_2\text{C-Mo}$ surfaces was observed for the adsorption of ethylene.

There is a covalent contribution to the bonding in the adsorption of ethylene, mainly on $\beta\text{-Mo}_2\text{C-C}$ surfaces, as shown in the CDD plot (see Figure 6c). This behavior can be explained by the orbital overlap between $C_{\text{ethylene}} - C_{\text{surface}}$ on the $\beta\text{-Mo}_2\text{C-C}$ surface, which is due to the

presence of “charged” carbon atoms on the surface (q_1 in Figure 2a). For the β -Mo₂C-Mo system, the Mo atoms exposed on the surface are close to each other, as shown in the geometric parameters (Figure 1c and Table 2); therefore, the electron transfer from the surface to C₂H₄ is higher and, accordingly, the ionic contribution to the bonding is higher in β -Mo₂C-Mo as compared to the β -Mo₂C-C system for C₂H₄ adsorption (-1.01e vs -0.27e in Figure 4).

There is an electron transfer from sub-surface Mo layer in the β -Mo₂C-C surface towards the adsorbate through the top C layer (see Figure 8). For C₂H₂ adsorption, there is not a variation in the charge of top C layer ($\Delta Q=0e$). However, for C₂H₄ adsorption there is a $\Delta Q=0.13e$. This is due to a change in the geometry of top C layer once ethylene is adsorbed, inducing the shift upward of a C_{surface} atom ~ -0.4 Å (see Figure 7d) relative to the clean surface. It favors a covalent contribution to the bonding of ethylene, as shown in the CDD plot (Figure 6d); additionally, the C_{ethylene}-C_{surface} bond length was 1.47 Å, a typical length of a single C-C bond in saturated hydrocarbons. The upward shift of surface atoms was observed only for adsorptions on the β -Mo₂C-C termination, but not for β -Mo₂C-Mo. This was seen for the two most stable structures for C₂H₄ adsorption (Figure 7d,e) and for the third most stable C₂H₂ adsorbed structure (Figure 4f), with an upward shift of 0.40, 0.46, and 0.55 Å, respectively.

According to the discussion given above, from the relative values in adsorption energies, it is established that the β -Mo₂C-C surface should have the better performance during the hydrogenation of both C₂H₂ and C₂H₄. If one varies the C/Mo ratio from 2 to 1 changing the orthorhombic β -Mo₂C for the cubic δ -MoC system, what could the effect be on the binding of acetylene and ethylene to the carbide substrate? In the next section we analyze the importance of the C/Mo molar ratio in the interactions with ethylene and acetylene.

3.3. The role of the molar ratio C/Mo on C₂H₂ and C₂H₄ adsorption: δ -MoC(001) vs β -Mo₂C(100)

The interaction of acetylene and ethylene on δ -MoC(001)^{25,29} and β -Mo₂C(100) surfaces has different characteristics, including significant variations in the adsorption energies and the elongation of C $\equiv$ C and C=C bond lengths as shown in Figure 9. For comparison purposes, results with Pt and Pd are also included for the most stable structure in every case.^{25,29} The β -Mo₂C(100)-Mo surface exhibits the largest reactivity and induces the largest structural perturbations in the adsorbates. Overall, it can be observed that acetylene adsorption is stronger than that of ethylene in all the evaluated metal and metal carbide surfaces. Additionally, the C $\equiv$ C bond length is elongated after adsorption on all the surfaces, while for all the surfaces, the C=C bond length is not significantly modified, particularly when ethylene is adsorbed on a δ -MoC(001) surface.

The binding of unsaturated ethylene on C_{surface} sites of δ -MoC(001) surface produces a slight upward shift of the C_{surface} atoms.²⁵ For adsorption of acetylene and ethylene on β -Mo₂C-C surface, there is also an upward shift of C_{surface} atoms in the range 0.40 to 0.46 Å for C₂H₄ and 0.55 Å for C₂H₂. In the case of δ -MoC(001) surface,²⁵ the C₂H₄ binding involves an upward shift of 0.69 Å. Therefore, the surface modification upon ethylene adsorption is lower in β -Mo₂C-C compared to a δ -MoC(001) surface.

For acetylene binding, the adsorption energy follows the trend:

$$\delta\text{-MoC(001)} (-1.78 \text{ eV})^{29} < \beta\text{-Mo}_2\text{C-C} (-1.87) << \beta\text{-Mo}_2\text{C-Mo} (-4.23 \text{ eV})$$

The adsorption energies of acetylene over δ -MoC(001) and β -Mo₂C-C surfaces are very close (i.e., energy difference < 0.1 eV), and the elongations of C $\equiv$ C are also similar (see Figure 9). This result indicates that the acetylene binding behavior is similar on a non-polar carbide surface (δ -MoC(001)) compared to that on a polar carbide substrate with a C-termination (β -Mo₂C-C). In spite of being equivalent in terms of binding energy and C $\equiv$ C bond elongation, the surface sites in both cases are completely different. The acetylene adsorbed on δ -MoC(001) is parallel to a surface Mo-C bridge locating C_{acetylene} atoms atop surface atoms. On the contrary, the acetylene adsorption on β -Mo₂C-C is on hollows, with C_{acetylene} atoms located on surface C and Mo hollow sites (see Figure 4d-f). The extent of the C $\equiv$ C bond length elongation is also different, i.e., towards ethane-like on β -Mo₂C-Mo, but towards ethylene-like on β -Mo₂C-C and δ -MoC(001) surfaces.

For the case of ethylene binding, the adsorption energy follows the trend:

$$\delta\text{-MoC(001)} (-0.53 \text{ eV}) < \beta\text{-Mo}_2\text{C-C} (-0.94) < \beta\text{-Mo}_2\text{C-Mo} (-1.93 \text{ eV})$$

This trend indicates that a molar ratio C/Mo = 0.5 (β -Mo₂C) favors a stronger adsorption of ethylene, even though the polarity of the surface (C- or Mo-termination). As mentioned above, the strongest adsorption is observed on the β -Mo₂C-Mo surface (see Figure 9). In fact, this surface can be poisoned, limiting its catalytic capability for the hydrogenation of acetylene and ethylene if the hydrocarbon is adsorbed first than hydrogen. This can serve as the basis for further studies considering the combined effect of hydrogen and hydrocarbon.

The C=C bond on β -Mo₂C-C and β -Mo₂C-Mo is elongated towards that of ethane, i.e., an obtained C-C length close to free C₂H₆ with an hybridization in a sp³-like geometry. However, the C=C is not modified on δ -MoC(001),²⁵ which is a desired behavior in selective hydrogenation of acetylene. The binding of ethylene and therefore the preference to hydrogenation on δ -MoC(001) surface is enhanced when considering vdW correction.²⁵ The inclusion of vdW corrections for ethylene adsorption on β -Mo₂C-C and β -Mo₂C-Mo surfaces are shown in Table 5. It was seen that the vdW only affects the energy, but not the geometry. For the β -Mo₂C-Mo surface, vdW are not necessary since ethylene is chemisorbed. For the binding of C₂H₄ on β -Mo₂C-C surface, the inclusion of vdW contributes to the electronic energy in the range 58 to 96%, suggesting that vdW forces help to describe better the binding of ethylene on the β -Mo₂C-C surface. In the case of C₂H₂ adsorption, the vdW contribution for β -Mo₂C-C and β -Mo₂C-Mo surfaces (see Table S1 in the Supporting Information) is not necessary, since the acetylene binding on both surfaces is strong.

Overall, the decrease of the C/Mo ratio from 1 to 0.5 ratio favors increased binding of acetylene and ethylene, but this may not be good when considering reactions of hydrogenation or, in general, chemical manipulation of the adsorbates. For Mo₂C catalysts, on the basis of its moderate reactivity, the β -Mo₂C-C termination is proposed to be responsible of the catalytic activity shown in the hydrogenation of unsaturated hydrocarbons, actively participating in the binding of adsorbates, and it is not merely a spectator as commonly considered in many articles.

4. CONCLUSIONS

In this work, a series of adsorption modes for acetylene and ethylene were studied on the β -Mo₂C(100) surface, considering C- and Mo-terminations. Additionally, the role of the C/Mo

molar ratio over the adsorption of hydrocarbons was addressed by comparing adsorbate interactions on the cubic (δ -MoC) and orthorhombic (β -Mo₂C) crystal phases. The studies were carried out by means of calculations based on periodic density functional theory, using the Perdew-Burke-Ernzerhof exchange-correlation functional, and accounting for the vdW correction to the electronic energy.

The geometric and electronic properties of the clean β -Mo₂C-C and β -Mo₂C-Mo surfaces strongly influenced the binding of the adsorbates. The molecules were adsorbed on hybrid C₂Mo and Mo₂C sites formed between surface and sub-surface layers. Overall, the preference for C₂H₂ adsorption was on hollows, but for C₂H₄ the preference involved atop surface atoms.

Strong adsorption energies (-4.23 and -1.93 eV) and a large elongation of the C $\equiv$ C and C=C bond lengths, let us to suggest that β -Mo₂C-Mo is not appropriate as a catalyst in the hydrogenation of acetylene and ethylene. The results of this work show that the β -Mo₂C-C and δ -MoC(001) surfaces have a high catalytic potential for hydrogenation of unsaturated hydrocarbons like olefins and alkynes, which opens the ways to address more complex molecular systems such as benzene,¹² naphthalene,¹⁰ toluene,³² and cumene.¹¹

5. CORRESPONDING AUTHOR

Dr. Jose A. Rodriguez, E-mail: rodriguez@bnl.gov

6. SUPPORTING INFORMATION

Surface structures, acetylene adsorption energies, reproducibility of results, dipole effect, slab thickness effect and Zero Point Energy corrections.

7. ACKNOWLEDGMENTS

Part of this research was carried out at Brookhaven National Laboratory in the Chemistry Department and in the Center for Functional Nanomaterials, which is a U.S. DOE Office of Science User Facility, under Contract No. DE-SC0012704. A.M and C.J-O acknowledge to the Universidad de Antioquia for the financial support through “Programa Sostenibilidad”. C.J-O Acknowledges his PhD scholarship provided by the Colombian National Science Foundation (COLCIENCIAS).

8. REFERENCES

- (1) Hwu, H. H.; Chen, J. G. Surface Chemistry of Transition Metal Carbides. *Chem. Rev.* 2005, *105* (1), 185–212.
- (2) Oyama, S. T. *The Chemistry of Transition Metal Carbide and Nitrides*, 1st ed.; Blackie academic & professional, 1996.
- (3) Choi, J.-S.; Bugli, G.; Djéga-Mariadassou, G. Influence of the Degree of Carburization on the Density of Sites and Hydrogenating Activity of Molybdenum Carbides. *J. Catal.* 2000, *193* (2), 238–247.
- (4) Lee, J. S.; Volpe, L.; Ribeiro, F. H.; Boudart, M. Molybdenum Carbide Catalysts II. Topotactic Synthesis of Unsupported Powders. *J. Catal.* 1988, *112* (1), 44–53.
- (5) Frühberger, B.; Chen, J. G. Reaction of Ethylene with Clean and Carbide-Modified Mo(110): Converting Surface Reactivities of Molybdenum to Pt-Group Metals. *J. Am. Chem. Soc.* 1996, *118* (46), 11599–11609.
- (6) Shi, Y.; Yang, Y.; Li, Y.-W.; Jiao, H. Activation Mechanisms of H₂, O₂, H₂O, CO₂, CO, CH₄ and C₂H_x on Metallic Mo₂C(001) as Well as Mo/C Terminated Mo₂C(101) from Density Functional Theory Computations. *Appl. Catal. A Gen.* 2016, *524*, 223–236.
- (7) Espinoza-Monjardín; Cruz-Reyes, J.; Del Valle-Granados, M.; Flores-Aquino, E.; Avalos-Borja, M.; Fuentes-Moyado, S. Synthesis, Characterization and Catalytic Activity in the Hydrogenation of Cyclohexene with Molybdenum Carbide. *Catal. Letters* 2008, *120* (1–2), 137–142.
- (8) Hou, R.; Chang, K.; Chen, J. G.; Wang, T. Replacing Precious Metals with Carbide Catalysts for Hydrogenation Reactions. *Top. Catal.* 2015, *58* (4–6), 240–246.
- (9) Zhang, J.; Weicheng, W.; Shiyang, L. In Situ IR Spectroscopic Study on the Hydrogenation of 1,3-Butadiene on Fresh Mo₂C/ γ -Al₂O₃ Catalyst. *China Pet. Process. Petrochemical Technol.* 2014, *16* (4), 32–37.

- (10) Ardakani, S. J.; Liu, X.; Smith, K. J. Hydrogenation and Ring Opening of Naphthalene on Bulk and Supported Mo₂C Catalysts. *Appl. Catal. A Gen.* 2007, *324*, 9–19.
- (11) Dhandapani, B.; St. Clair, T.; Oyama, S. T. Simultaneous Hydrodesulfurization, Hydrodeoxygenation, and Hydrogenation with Molybdenum Carbide. *Appl. Catal. A Gen.* 1998, *168* (2), 219–228.
- (12) Rocha, A. S.; Rocha, A. B.; da Silva, V. T. Benzene Adsorption on Mo₂C: A Theoretical and Experimental Study. *Appl. Catal. A Gen.* 2010, *379* (1–2), 54–60.
- (13) Xu, W.; Ramirez, P. J.; Stacchiola, D.; Rodriguez, J. A. Synthesis of α -MoC_{1-X} and β -MoC_y Catalysts for CO₂ Hydrogenation by Thermal Carburization of Mo-Oxide in Hydrocarbon and Hydrogen Mixtures. *Catal. Letters* 2014, *144* (8), 1418–1424.
- (14) Posada-Pérez, S.; Viñes, F.; Rodriguez, J. A.; Illas, F. Fundamentals of Methanol Synthesis on Metal Carbide Based Catalysts: Activation of CO₂ and H₂. *Top. Catal.* 2015, *58* (2–3), 159–173.
- (15) Schaidle, J. A.; Thompson, L. T. Fischer–Tropsch Synthesis over Early Transition Metal Carbides and Nitrides: CO Activation and Chain Growth. *J. Catal.* 2015, *329*, 325–334.
- (16) Rodriguez, J. A.; Dvorak, J.; Jirsak, T. Chemistry of Thiophene on Mo(110), MoC_x and MoS_x Surfaces: Photoemission Studies. *Surf. Sci.* 2000, *457* (1–2), L413–L420.
- (17) Oshikawa, K.; Nagai, M.; Omi, S. Characterization of Molybdenum Carbides for Methane Reforming by TPR, XRD, and XPS. *J. Phys. Chem. B* 2001, *105* (38), 9124–9131.
- (18) Qi, K.-Z.; Wang, G.-C.; Zheng, W.-J. Structure-Sensitivity of Ethane Hydrogenolysis over Molybdenum Carbides: A Density Functional Theory Study. *Appl. Surf. Sci.* 2013, *276*, 369–376.
- (19) Wyvratt, B. M.; Gaudet, J. R.; Thompson, L. T. Effects of Passivation on Synthesis, Structure and Composition of Molybdenum Carbide Supported Platinum Water-Gas Shift Catalysts. *J. Catal.* 2015, *330*, 280–287.
- (20) Liu, P.; Rodriguez, J. A. Water-Gas-Shift Reaction on Molybdenum Carbide Surfaces: Essential Role of the Oxycarbide. *J. Phys. Chem. B* 2006, *110*, 19418–19425.
- (21) Gao, F.; Wang, Y.; Tysoe, W. T. Ethylene Hydrogenation on Mo(CO)₆ Derived Model Catalysts in Ultrahigh Vacuum: From Oxycarbide to Carbide to MoAl Alloy. *J. Mol. Catal. A Chem.* 2006, *249* (1–2), 111–122.
- (22) Posada-Pérez, S.; Viñes, F.; Ramirez, P. J.; Vidal, A. B.; Rodriguez, J. A.; Illas, F. The Bending Machine: CO₂ Activation and Hydrogenation on δ -MoC(001) and β -Mo₂C(001) Surfaces. *Phys. Chem. Chem. Phys.* 2014, *16* (28), 14912.
- (23) Hugosson, H. W.; Eriksson, O.; Nordström, L.; Jansson, U.; Fast, L.; Delin, A.; Wills, J. M.; Johansson, B. Theory of Phase Stabilities and Bonding Mechanisms in Stoichiometric and Substoichiometric Molybdenum Carbide. *J. Appl. Phys.* 1999, *86* (7), 3758–3767.
- (24) Shi, X. R.; Wang, S. G.; Wang, H.; Deng, C.-M.; Qin, Z.; Wang, J. Structure and stability of β -Mo₂C bulk and surfaces: A density functional theory study. *Surf. Sci.* **2009**, *603* (6), 852–859.
- (25) Jimenez-Orozco, C.; Florez, E.; Moreno, A.; Liu, P.; Rodriguez, J. A. Systematic Theoretical Study of Ethylene Adsorption on δ -MoC(001), TiC(001), and ZrC(001) Surfaces. *J. Phys. Chem. C* 2016, *120* (25), 13531–13540.
- (26) Viñes, F.; Sousa, C.; Illas, F. A Systematic Density Functional Study of Molecular Oxygen Adsorption and Dissociation on the (001) Surface of Group IV - VI Transition Metal Carbides. *J. Phys. Chem. C* 2007, *111* (1), 16982–16989.
- (27) Florez, E.; Gomez, T.; Rodriguez, J. A.; Illas, F. On the Dissociation of Molecular

- Hydrogen by Au Supported on Transition Metal Carbides: Choice of the Most Active Support. *Phys. Chem. Chem. Phys.* 2011, *13* (15), 6865–6871.
- (28) Posada-Pérez, S.; dos Santos Politi, J. R.; Viñes, F.; Illas, F. Methane Capture at Room Temperature: Adsorption on Cubic δ -MoC and Orthorhombic β -Mo₂C Molybdenum Carbide (001) Surfaces. *RSC Adv.* 2015, *5* (43), 33737–33746.
 - (29) Jimenez-Orozco, C.; Florez, E.; Moreno, A.; Liu, P.; Rodriguez, J. A. Acetylene Adsorption on δ -MoC(001), TiC(001) and ZrC(001) Surfaces: A Comprehensive Periodic DFT Study. *Phys. Chem. Chem. Phys.* 2017, *19* (2), 1571–1579.
 - (30) Wang, T.; Li, Y.-W.; Wang, J.; Beller, M.; Jiao, H. Dissociative Hydrogen Adsorption on the Hexagonal Mo₂C Phase at High Coverage. *J. Phys. Chem. C* 2014, *118* (15), 8079–8089.
 - (31) Luo, Q.; Wang, T.; Walther, G.; Beller, M.; Jiao, H. Molybdenum Carbide Catalysed Hydrogen Production from Formic Acid - A Density Functional Theory Study. *J. Power Sources* 2014, *246*, 548–555.
 - (32) Vitale, G.; Guzmán, H.; Frauwallner, M. L.; Scott, C. E.; Pereira-Almao, P. Synthesis of Nanocrystalline Molybdenum Carbide Materials and Their Characterization. *Catal. Today* 2015, *250*, 123–133.
 - (33) Schweitzer, N. M.; Schaidle, J. a; Ezekoye, O. K.; Pan, X.; Linic, S.; Thompson, L. T. High Activity Carbide Supported Catalysts for Water Gas Shift. *J. Am. Chem. Soc.* 2011, *133* (8), 2378–2381.
 - (34) Politi, J. R. D. S.; Viñes, F.; Rodriguez, J. A.; Illas, F. Atomic and Electronic Structure of Molybdenum Carbide Phases: Bulk and Low Miller-Index Surfaces. *Phys. Chem. Chem. Phys.* 2013, *15* (30), 12617.
 - (35) Viñes, F.; Sousa, C.; Liu, P.; Rodriguez, J. A.; Illas, F. A Systematic Density Functional Theory Study of the Electronic Structure of Bulk and (001) Surface of Transition-Metals Carbides. *J. Chem. Phys.* 2005, *122* (17), 174709.
 - (36) Posada-Pérez, S.; Viñes, F.; Valero, R.; Rodriguez, J. A.; Illas, F. Adsorption and Dissociation of Molecular Hydrogen on Orthorhombic β -Mo₂C and Cubic δ -MoC (001) Surfaces. *Surf. Sci.* 2017, *656* (August 2016), 24–32.
 - (37) Christensen, A. N. A Neutron Diffraction Investigation on a Crystal of Alpha-Mo₂C. *Acta Chem. Scand. A* 1977, *31*, 509–511.
 - (38) Segall, M. D.; Probert, M. J.; Pickard, C. J.; Hasnip, P. J.; Clark, S. J.; Refson, K.; Payne, M. C. First Principles Methods Using CASTEP. *Zeitschrift fuer Krist.* 2005, *220* (5–6), 567–570.
 - (39) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 1996, *77* (18), 3865–3868.
 - (40) Vanderbilt, D. Soft Self-Consistent Pseudopotentials in a Generalized Eigenvalue Formalism. *Phys. Rev. B Rapid Commun.* 1990, *41* (11), 7892–7895.
 - (41) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* 1976, *13* (12), 5188–5192.
 - (42) Wang, T.; Li, Y.; Wang, J.; Beller, M.; Jiao, H. High Coverage CO Adsorption and Dissociation on the Orthorhombic Mo₂C (100) Surface. *J. Phys. Chem. C* 2014, *118* (100), 3162–3171.
 - (43) Gomez, T.; Florez, E.; Rodriguez, J. A.; Illas, F. Reactivity of Transition Metals (Pd, Pt, Cu, Ag, Au) toward Molecular Hydrogen Dissociation: Extended Surfaces versus Particles Supported on TiC(001) or Small Is Not Always Better and Large Is Not Always Bad. *J.*

- Phys. Chem. C* 2011, *115* (1), 11666–11672.
- (44) Herzberg, G.; Stoicheff, B. P. Carbon-Carbon and Carbon-Hydrogen Distances in Simple Polyatomic Molecules. *Nature* 1955, *175*, 79–80.
 - (45) Gallaway, W. S.; Barker, E. F. The Infra-Red Absorption Spectra of Ethylene and Tetra-Deutero-Ethylene under High Resolution. *J. Chem. Phys.* 1942, *10* (2), 88–97.
 - (46) Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *J. Comput. Chem.* 2006, *27* (15), 1787–1799.
 - (47) Grev, R.S.; Janssen, C.L.; Schaefer, H.F. Concerning Zero-point Vibrational Energy Corrections to Electronic Energies, *J. Chem. Phys.* 1991, *95*, 5128-5132.
 - (48) Govender A.; Ferré D.C.; Niemantsverdriet, J.W. A Density Functional Theory Study on the Effect of Zero-point Energy Corrections on the Methanation Profile on Fe(100). *Chemphyschem*, 2012, *13* (6), 1591-1596.
 - (49) Schaidle, J. A.; Blackburn, J.; Farberow, C. A.; Nash, C.; Steirer, K. X.; Clark, J.; Robichaud, D. J.; Ruddy, D. A. Experimental and Computational Investigation of Acetic Acid Deoxygenation over Oxophilic Molybdenum Carbide: Surface Chemistry and Active Site Identity. *ACS Catal.* 2016, *6* (2), 1181–1197.
 - (50) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations using a Plane-Wave Basis Set, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, *54* (16), 11169-11186.
 - (51) Parthé, E.; Sadogopan, V. The Structure of Dimolybdenum Carbide by Neutron Diffraction Technique. *Acta Crystallogr.* 1963, *16* (3), 202–205.
 - (52) Liu, H.; Zhu, J.; Lai, Z.; Zhao, R.; He, D. A First-Principles Study on Structural and Electronic Properties of Mo₂C. *Scr. Mater.* 2009, *60* (11), 949–952.

Table 1. Cell parameters of β -Mo₂C and its fractional coordinates of Mo and C atoms.^a

	Cell parameters		
	a (Å)	b (Å)	c (Å)
Experimental ⁵¹	4.724	6.004	5.199
This work	4.737	6.043	5.218
Error (%)	0.28	0.65	0.37
	Fractional coordinates: C atom		
	x	y	z
Experimental ^{37,51}	0.000	0.374	0.250
This work	0.000	0.378	0.250
Error (%)	0.00	1.07	0.00
	Fractional coordinates: Mo atom		
	x	y	z
Experimental ^{37,51}	0.250	0.125	0.083
This work	0.246	0.122	0.079
Error (%)	1.60	2.40	4.82

^a The experimental values were taken from references 37 and/or 51.

Table 2. Geometric and electronic parameters for β -Mo₂C(100) surface

β -Mo ₂ C-C		β -Mo ₂ C-Mo	
Geometric parameters ^a			
Label	Distance (Å)	Label	Distance (Å)
a	3.08	a	3.24
b	6.04	b	2.82
c	5.12	c	3.16
--	--	d	2.93
--	--	e	2.84
Electronic parameters ^b			
Label	Charge (e)	Label	Charge (e)
q1	-0.58	q1	0.19
q2	0.55	q2	0.08
--	--	q3	-0.63

^a See Figure 1

^b See Figure 2.

Table 3. Acetylene and ethylene adsorption modes evaluated on β -Mo₂C(100) surface.

Label ^a	Adsorption mode	
	C ₂ H ₂ and C ₂ H ₄ ^b on β -Mo ₂ C-C	C ₂ H ₂ and C ₂ H ₄ ^b on β -Mo ₂ C-Mo
Mode1	π -C	π -M
Mode2	di- σ -CC	di- σ -MoMo
Mode3	C-top, Mo-h1	Mo-top, Mo-h
Mode4	C-top, Mo-h2	Mo-top, C-h1
Mode5	di- σ -MoMo	Mo-top, C-h2
Mode6	C-h, Mo-h1	Mo-h, C-h1
Mode7	C-h, Mo-h2	Mo-h, C-h2
Mode8	C-C axis perpendicular to surface plane ^c	

^a Numbers as shown in Figure 3.

^b Additional structures were considered with H atoms pointing towards the surface.

^c Not shown in Figure 3.

Table 4. Adsorption energy and geometry (C-C bond length and adsorption mode) of acetylene adsorption on β -Mo₂C(100) surface with Mo and C terminations. Only the most stable structures are shown.

E _{ads} (eV)	C-C (Å) ^a	Geometry
β -Mo ₂ C-Mo		
-4.23	1.45	Mo-h, C-h2 ^b
-4.01	1.44	Mo-h, C-h2 ^b
-3.61	1.44	Mo-h, C-h1
β -Mo ₂ C-C		
-1.87	1.39	C-h, Mo-h2
-1.21	1.36	C-h Mo-h1
-0.81	1.30	π -C

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

^b There are two different C Mo-h, C C-h2 sites (see Figures 5 a,b).

Table 5. Ethylene adsorption energies and geometries on β -Mo₂C(100) surface with (DFT+vdW) and without (DFT) van der Waals correction to the electronic energy. Only the most stable structures are shown.

DFT (eV)	DFT + vdW	% vdW	C-C (Å) ^a	Geometry
β -Mo ₂ C-Mo				
-1.93	-2.50	29.5	1.48	Mo-top, C-h2 ^b
-1.68	-2.23	32.7	1.46	Mo-top, C-h2 ^b
-1.49	-2.07	38.9	1.48	Mo-top, Mo-h
-1.44	-2.05	42.4	1.47	Mo-h, C
-1.15	-1.76	53.0	1.49	Mo-h, C-h2
-1.11	-1.66	49.5	1.47	Mo-top, C-h1
-0.98	-1.63	66.3	1.46	π -M
β -Mo ₂ C-C				
-0.94	-1.49	58.5	1.51	C C-top, C Mo-h1
-0.53	-1.04	96.2	1.48	π -C
-0.52	-1.29	--	1.44	C C-h, C Mo-h1

^a Free ethylene: C-C=1.33 Å, free ethane: C-C= 1.53 Å.

^b Surroundings of Mo-top atoms are different (see Figure 5 c,d).

TOC

Figure 1. Geometry parameters for a) δ -MoC(001), b) β -Mo₂C(100)-C termination, and c) β -Mo₂C(100)-Mo termination of clean surfaces. Top layer of slab. Mo, magenta; C, brown. For the β -Mo₂C(100) surface, distance values for the respective letters are shown in Table 2.

Figure 2. Electronic parameters for the clean polar $\beta\text{-Mo}_2\text{C}(100)$ surface in a) C-termination and b) Mo-termination. *Top*: Top view of iso-surface of $0.05 \text{ e}/\text{\AA}^3$ (red: charge earned, blue: charge lost). Mulliken charges for the respective q_i are shown in Table 1. C, red; Mo, blue. *Bottom*: CCD plot, side view, from -0.1 (red) to 0.1 (blue) $\text{e}/\text{\AA}^3$.

Figure 3. Surface sites (top view) of β - $\text{Mo}_2\text{C}(100)$ for evaluation of hydrocarbons adsorption. Mo: Magenta, C: brown. Yellow letters and blue lines represent the evaluated adsorption modes (see Table 1). *Top*: β - $\text{Mo}_2\text{C}-\text{C}$, *bottom*: β - $\text{Mo}_2\text{C}-\text{Mo}$.

Figure 4. Most stable structures for acetylene adsorption on $\beta\text{-Mo}_2\text{C-Mo}$ (a-c) and $\beta\text{-Mo}_2\text{C-C}$ (d-f). *Top*: Top view, *bottom*: side view. Q : acetylene Mulliken charge.

a) Acetylene: site 1 ($E_{\text{ads}} = -4.23$ eV)

b) Acetylene: site 2 ($E_{\text{ads}} = -4.01$ eV)

c) Ethylene: site 1 ($E_{\text{ads}} = -1.93$ eV)

d) Ethylene: site 2 ($E_{\text{ads}} = -1.68$ eV)

Figure 5. Difference in notations for adsorptions on $\beta\text{-Mo}_2\text{C-Mo}$ surface. Difference between two types of a), b) acetylene Mo-h, C-h2; c), d) Mo-top, C-h2 adsorption modes. Top view. Red lines represent the adsorbed hydrocarbon. The subsurface 3rd layer (in C_2H_2 adsorption) and 1st layer surface (in C_2H_4 adsorption) are colored to highlight the differences in its surroundings.

Figure 6. Charge Density Difference (CDD) slices from $-0.1\text{e}/\text{\AA}^3$ (blue) to $0.1\text{e}/\text{\AA}^3$ (red) for the structures shown in Figure 4. a) b) Acetylene; c) d) Ethylene.

Figure 7. Most stable structures for ethylene adsorption on $\beta\text{-Mo}_2\text{C-Mo}$ (a-c) and $\beta\text{-Mo}_2\text{C-C}$ (d-f). *Top*: Top view, *bottom*: side view. Q: ethylene Mulliken charge.

Figure 8. Mulliken charge migration (blue arrows) scheme for acetylene and ethylene adsorption on polar $\beta\text{-Mo}_2\text{C}(100)$ surface in a) C-termination, and b) Mo-termination. Surface (top) and sub-surface (bottom) layers are sketched. ΔQ : Mulliken charge variation after hydrocarbon binding for the atoms involved in the adsorption in every layer.

Figure 9. Acetylene and ethylene adsorption energies (E_{ads}) on several metal and metal carbides surfaces. Carbon-carbon bond lengths due to elongation of $\text{C}\equiv\text{C}$ (from 1.21 Å in gas phase) and $\text{C}=\text{C}$ (from 1.33 Å in gas phase) are included on top of blue and red bars (in Å), respectively.