

Adsorption of atmospheric gases on cementite {010} surfacesDavid Muñoz Ramo^{1, a)} and Stephen J. Jenkins^{1, b)}*Department of Chemistry, University of Cambridge, Cambridge,
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We study the adsorption of a series of small molecules on the nonstoichiometric {010} surface of cementite (θ -Fe₃C) by means of first-principles calculations. We find that CO, N₂, H₂O and CH₄ prefer to adsorb over iron atoms in an atop configuration. O₂, CO₂ and the OH radical prefer a configuration bridging two iron atoms and CH₂O adsorbs in a configuration bridging a surface iron atom and a surface carbon atom. Adsorption energies are small for H₂, CO₂ and CH₄, indicating a physisorption process, while those for CO, CH₂O and especially for O₂ and the OH radical are large, indicating a strong chemisorption process. H₂O and N₂ display adsorption energies between these two extremes, indicating moderate chemisorption. The dissociation of H₂, CH₂O, the OH radical and O₂ are favoured on this surface. Comparison with adsorption on Fe{100} surfaces indicates that most of these gases have similar adsorption energies on both surfaces, with the exception of CO and the OH radical. **In addition, we find similarities between the reactivities of cementite and Mo₂C surfaces, due to the similar covalent character of both carbides.**

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INTRODUCTION

Iron carbides are involved in many key chemical reactions of industrial interest. One of the most interesting is the Fischer-Tropsch process, through which hydrocarbons are synthesized from syngas (H_2 and CO) obtained from sources like coal, biomass or natural gas. Iron catalysts are routinely used for this reaction, and are prepared through reduction of iron oxide particles with syngas. This reduction ultimately leads to metallic iron and iron carbides in varying proportions, which are the active phases for the Fischer-Tropsch process. Different carbides with varying Fe/C stoichiometries have been observed during the reaction¹. The role of each carbide in this reaction is still not well known. Carbides have also been observed to play some role in the formation of carbonaceous deposits on the surface of iron at high temperatures, generally with adverse consequences. The deposits formed on the surface may stop the Fischer-Tropsch process by blocking active sites², or induce metal corrosion by dusting, a process in which iron disintegrates into small metal particles³. Iron carbides have been postulated to enhance this process by means of the creation of carbide scales over the metal surface, which then promote graphite growth and subsequent breaking of the metal particle^{4,5}. Other applications of iron carbides involve carbide nanoparticle engineering for oxygen reduction reactions⁶ or electrochemical sensors⁷, among others. Understanding of the detailed microscopic mechanisms for the processes taking place on the surface of these systems is still incomplete and further work is needed. In this sense, it is useful to analyze the adsorption of simple gases like CO , CO_2 , H_2O or H_2 on typical iron carbides in order to shed further light upon the different steps of the reactions involved.

The reactivity of iron carbides can also be rationalized in the framework of the general chemistry of transition metal carbide surfaces. Many studies have explored the reactivity of these carbides in the search for substitutes to well-known noble metal catalysts, finding similar catalytic behaviour and advantages like better tolerance to sulfur poisoning and coke formation, for a lower economic cost^{8,9}. In general, these studies observe that the addition of carbon to the metal lattice modulates the reactivity of the metal on the surface and renders it suitable for many catalytic processes of technological interest¹⁰⁻¹⁵.

Motivated by our interest in the reactions of typical small gases on iron carbide, we study in this work the geometry, energetics and related properties of several gas adsorbates on

surface of a well known iron carbide, θ -Fe₃C (cementite), by means of first-principles simulations using Density Functional Theory (DFT). This material is a representative iron carbide phase, obtained through carburization of iron above 700 K^{16,17}. The unit cell of this carbide is orthorhombic, with twelve iron atoms and four carbon atoms¹⁸. Each iron atom is connected to three carbon atoms, and each carbon atom is surrounded by eight iron atoms. Cementite is a ferromagnetic metal, with a magnetic moment of 1.72-1.78 μ_B on each iron atom¹⁹. Previous DFT calculations have studied surface stability on this material, finding that {001} is the most stable stoichiometric surface^{20,21}. Recently, calculations on nonstoichiometric cementite surfaces have found that an iron-deficient {010} surface is more stable under a wide range of conditions²². With regards to the adsorption of gases on cementite surfaces, previous studies have focused on the case of the CO molecule. Michalsky et al.²³ found that CO adsorbs over the {001} surface in a hollow site defined by four iron atoms, with an adsorption energy of about 1.7 eV at low coverage. Zhao et al.²² find similar values for the adsorption on the nonstoichiometric {010} surface, although in this case the CO molecule sits on top of an iron atom. Adsorption of water and OH on the {001} surface have also been calculated by Michalsky et al., finding adsorption energies of about 0.4 eV and 0.7 eV, respectively²³.

In this work, we investigate the adsorption of CO, H₂O and OH, along with other common gases, on cementite, at low and high coverage. We also consider reactions in which these gases dissociate on the surface. Finally, we compare our results with the case of adsorption on pure iron **and on other transition metal carbides**.

II. COMPUTATIONAL METHOD

The DFT calculations in this work have been performed using a plane wave basis set and periodic boundary conditions, as implemented in the CASTEP code²⁴. The PBE exchange-correlation functional has been chosen, as it provides a good match between experimental and DFT lattice constants²¹⁻²³. The Tkatchenko-Scheffler semiempirical correction has been applied to account for van der Waals interactions²⁵. Vanderbilt ultrasoft pseudopotentials have been used for these calculations, with a plane wave cutoff of 360 eV. The pseudopotential for iron includes nonlinear core corrections. With this setup, a bulk 48-atom cell has been used to obtain the energy and relaxed geometry of the structure. For this calcu-

lution, a Monkhorst-Pack scheme has been used to sample the Brillouin zone; a $5 \times 4 \times 6$ k -point mesh size was deemed appropriate to properly describe bulk cementite. Tolerances for energy convergence and forces were set at $5 \cdot 10^{-7}$ eV and 0.01 eV/Å, respectively. This optimized geometry has been used to create slabs with thicknesses of at least 8.5 Å in the z direction to ensure the convergence of the surface energy; the k -point mesh in this direction has been reduced to 1 in each case. A vacuum gap of 15 Å has been included to prevent interactions between the slab images in the periodic approach. In the case of stoichiometric slabs, the number of atoms has been kept at 48. Nonstoichiometric slabs have been designed by progressively removing atomic layers from the stoichiometric models. In the geometry optimization step, the positions of 24 atoms in the central region of each slab have been fixed. For the gas adsorption studies, the most stable slab has been used with two different supercell sizes, (1×1) and (2×2) and k -point meshes of $5 \times 4 \times 1$ and $2 \times 2 \times 1$, respectively. **Testing of possible dipole effects on adsorption energies and geometries was performed by running calculations with a molecule adsorbed symmetrically on each surface of the slab. This test was done on surfaces with N_2 , CO_2 and O_2 . The resulting adsorption energies and geometries showed no significant difference with those obtained from calculations performed with only one molecule adsorbed on one side of the slab. Therefore, we omitted dipole moment corrections in all other calculations.** Bader atomic charges have been calculated using the Topology code developed in our group^{26,27}.

The adsorption energy, E_{ads} , has been calculated as

$$E_{ads} = E(\text{slab} + \text{adsorbate}) - E(\text{slab}) - E_{ref}(\text{adsorbate}) \quad (1)$$

where $E(\text{slab} + \text{adsorbate})$ is the energy of the slab with the molecule adsorbed, $E(\text{slab})$ is the energy of the clean slab, and $E_{ref}(\text{adsorbate})$ is the energy of the free molecule. Calculation of the reference energies for each molecule in the gas phase have been performed in a periodic boundary box with sides 10 Å long to ensure that there was no interaction between images. Energies of the dissociated species have also been calculated with Equation 1. **Transition states and reaction barriers have been calculated for the dissociation process of some of the adsorbed molecules. They have been obtained by means of a combination of linear and quadratic synchronous transit methods as implemented in CASTEP.**

RESULTS

We show here our results regarding relative stability of the different surfaces considered and our analysis of adsorbed molecules over the most stable surface. We also provide results regarding dissociation of adsorbed species.

A. Bulk and surface models

Our study starts with the evaluation of the performance of the Tkatchenko-Scheffler van der Waals correction on the properties of the bulk and surfaces. For the bulk, we obtain lattice parameters of 4.895, 6.642 and 4.356 Å. They are slightly smaller compared with regular PBE values (4.997, 6.702 and 4.444 Å) and experimental ones (5.087, 6.748 and 4.521 Å)¹⁸. However, the differences are less than 2%, so we consider that PBE with the van der Waals correction describes reasonably well this structure. We proceed now to the determination of the most stable surfaces for cementite. Surface energies, γ , for all the terminations considered are shown in Table I for the PBE functional, with and without van der Waals correction. Our plain PBE results compare well with the values obtained by other groups^{20,21}. Inclusion of van der Waals corrections leads to a **significant** increase in the surface energies of all terminations considered, **as observed in calculations performed for surfaces of other systems like NaCl or MgO²⁸**. **However, the energy differences between different slabs are comparable to the plain PBE values, and** the relative order of stability of stoichiometric surfaces is similar to that found in other calculations, with the exception of the {001} and {111} terminations: the van der Waals-corrected calculation places the {111} surface energy slightly below that of the {001} surface, while plain GGA results find the opposite order. **Nonetheless**, in agreement with Zhao et al.²², we also find that the {010} surface becomes more stable at a wide range of chemical potentials if one considers a nonstoichiometric slab created by removing two atom layers from the top and bottom of the slab. We label this slab {010}_n. This additional stabilization is driven by the large relaxation inwards of the surface carbon atoms, whose concentration is higher at the surface of the {010}_n slab than at the surface of the stoichiometric slabs considered. Therefore, we are using the {010}_n surface as the base model for our adsorption calculations.

TABLE I. Surface free energies γ (in J/m²) for each of the slabs considered in this study. Values with and without vdW correction are shown. All values are calculated at the lowest C chemical potential

Surface	γ (PBE)	γ (PBE+vdW)
{001}	2.45	4.43
{111}	2.52	4.30
{110}	2.60	4.48
{101}	2.67	4.61
{010}	2.75	4.78
{011}	2.83	4.83
{100}	2.94	4.87
{010} _n	2.08	3.94

Figure 1 shows the {010}_n surface models used in this study. We have investigated adsorption with two supercell models, (1 × 1) and (2 × 2). **We have defined coverage in relation to the number of surface Fe atoms on this slab; each one defines 0.25 ML. So, the (1 × 1) and (2 × 2) models correspond to coverages of 1 ML and 1/4 ML respectively.** In this surface, iron atoms are arranged in alternating rows that form "peaks" and "valleys" separated by carbon atoms. We have considered seven different adsorption sites as indicated in the figure: at the top of iron atoms (A and G in the figure), top of carbon atom (B), iron-iron bridging (E), iron-carbon bridging (F), 3 iron triangle center (D) and 2 iron - 1 carbon triangle center (G). Note that iron positions A and G are not equivalent, as the A position is at a "peak" row and the G position is at a "valley" row.

B. Adsorption of gases

We study the adsorption of different gases at each site identified on the surface of cementite, with different orientations. These molecules are CO, CO₂, N₂, H₂O, O₂, CH₂O (formaldehyde), CH₄, H₂ and the OH radical. **Adsorbate configurations have been obtained by placing each molecule on each of the adsorption sites described in Figure 1 at a distance of about 1.5 Å from the surface. We have considered**

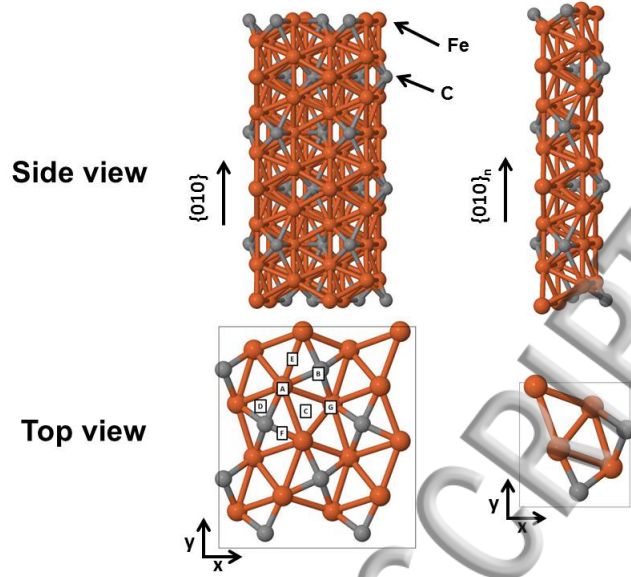


FIG. 1. Fe_3C $\{010\}$ surface models used for the ab initio calculations. Pictures on the right and left sides correspond to the (1×1) and (2×2) models, respectively. In the top view, only the first layer of the slab is shown. Possible adsorption sites are indicated at the (2×2) model (top view) with letters from A to F.

starting configurations in which the molecule lies flat over the surface, and configurations with the molecular axis perpendicular to the surface. For the flat configurations, the molecules were in orientations either parallel or perpendicular to the surface rows. For the perpendicular configurations, we considered both ends of the molecule as starting points. For the dissociated molecules, we considered nearest and next-nearest neighbour positions. In order to keep the discussion compact, we report only the most stable surface-adsorbate configuration for each species. Other configurations with higher energies are reported in the Supplementary Information.

Table II displays the adsorption energies obtained in this study and Figure 2 shows the most stable geometry of each adsorbed molecule. Table III shows the changes in bond length on each adsorbed molecule. Table IV shows the Bader charges calculated for the different molecules and the surface atoms participating in the adsorption. All the molecules studied have a stable adsorbed configuration over the surface of cementite. We find that CO , N_2 , H_2O and CH_4 prefer to adsorb over iron atoms in an atop configuration (site A in Figure 1). H_2 also adsorbs over an iron atom in an atop configuration. On the other hand, O_2 ,

TABLE II. Adsorption energies for the undissociated (E_{ads}) and dissociated (E_{diss}) molecules considered in this study, and dissociation barriers (E_{TS}) for the low coverage case. All energies are given in eV

Molecule	1/4 ML			1 ML	
	E_{ads}	E_{diss}	E_{TS}	E_{ads}	E_{diss}
CO	-1.98	-1.12	-	-2.03	-0.11
CO ₂	-0.61	-1.10	0.75	-0.72	-0.42
N ₂	-1.11	0.38	-	-1.14	0.19
H ₂ O	-0.87	-1.11	3.10	-0.82	-0.61
O ₂	-2.14	-4.55	1.69/0.21	-2.11	-4.47
CH ₂ O	-1.64	-1.66	1.79	-1.63	-1.47
CH ₄	-0.33	-0.23	-	-0.36	0.02
OH	-3.18	-3.45	3.84	-3.54	-3.14
H ₂	-0.50	-0.97	0.43	-	-0.57
H adatom	-0.68	-	-	-0.36	-
O adatom	-2.60	-	-	-2.24	-

CO₂ and the OH radical prefer a configuration bridging two iron atoms (site E in Figure 1). Finally, CH₂O prefers to adsorb in a configuration where its oxygen atom sits on site E and its carbon atom adsorbs over a surface carbon atom (site B in Figure 1).

As Table II shows, the adsorption energy of CH₄ is very small, around 0.3 eV, which points to a very weak physisorption process. As a result, the geometry of this molecule suffers little distortion and its bond lengths are very similar to those found in the gas phase (see Table III). CO₂ and H₂ also have small adsorption energies indicative of a physisorption process, but show some significant elongation of their bonds (and bending in the case of CO₂) and charge transfer from the surface to the molecule (see Table IV). H₂O and N₂ have slightly larger adsorption energies, consistent with a moderate chemisorption process, although their geometries remain unaltered by the adsorption process; there are, however, significant changes at the surface. The iron atom over which N₂ adsorbs is slightly pulled away from the surface and about 0.35 electrons are transferred to the molecule. In the case of H₂O, the molecule does not accumulate any extra charge, but the nearest iron atom loses

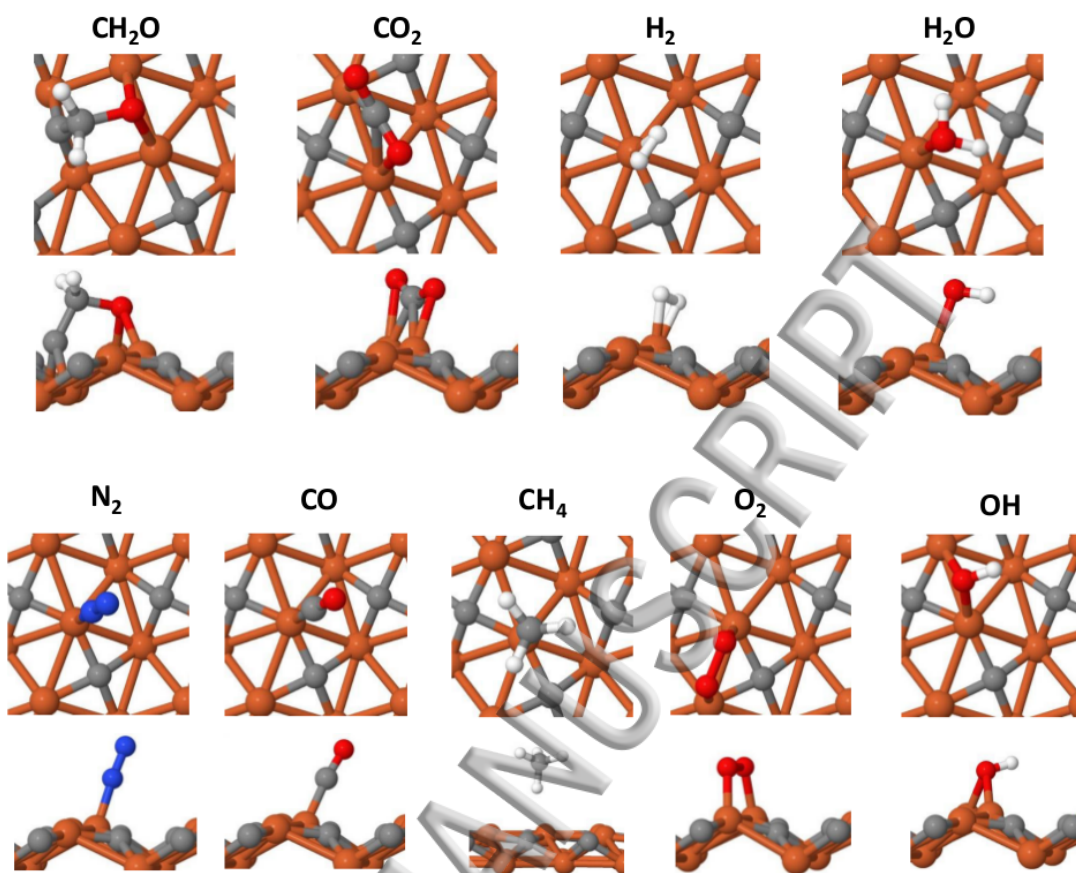


FIG. 2. Most stable configurations of the adsorbed molecules analyzed in this study. For each molecule, top and side views are displayed. For clarity, only the first layer of the slab is shown.

about 0.2 electrons to the surface carbon atoms.

In contrast with the previously described cases, CO, O₂, OH and CH₂O establish stronger bonds with the surface and thus their geometry is more distorted and their adsorption energies are remarkably larger, between 1.6 eV and 3.2 eV, indicative of a strong chemisorption process. O₂ adsorption leads to a significant elongation of the diatomic bond (see Table III) and a large charge transfer between the slab and the molecule leading to an increase of -0.4 units in the charge of each oxygen atom, according to the Bader charge analysis. The iron atoms directly attached to the adsorbed molecule increase their charge, going from +0.56 to +0.83 units. The OH radical maintains the length of the OH bond, but its oxygen atom gains about 0.5 electrons from the surface iron atom to which it is bonded. In adsorbed CH₂O, the C-O bond is elongated by about 0.1 Å and 0.69 electrons are transferred from the surface to the molecule, mainly coming from the iron and carbon atoms over which the molecule is adsorbed. Finally, in the case of CO, the C-O bond length is elongated by

only 0.03 Å in the adsorbed configuration. The molecule does not sit directly over one iron atom, but is displaced horizontally about 0.6 Å from this position and tilted by 68.3° from the surface plane. About 0.3 electrons are transferred from the slab to the molecule. This charge is evenly transferred from all iron atoms at the top layer of the slab. We calculated the CO phonon stretching and obtained a value of 2072 cm⁻¹; this value along with the small change observed in the C-O bond length indicates that this molecule is not strongly activated when adsorbed over Fe₃C {010}_n. Comparison with the PBE non-van der Waals calculation of Zhao et al.²² shows that the van der Waals correction leads to a slightly larger adsorption energy by 0.3 eV.

In general, we do not find any significant change in geometry or adsorption energy with coverage for the molecules studied except in the CO and CO₂ cases. In CO, increased coverage leads to reduction of the tilting of the molecule by about 20°. In CO₂, the geometry of the adsorbate does not suffer any major change, but increased molecule-molecule interactions lead to slightly larger adsorption energies.

C. Dissociated species

We also considered the adsorption of dissociated species at the cementite surface. Here, we present our results for the most stable configurations. The different energies for the dissociated adsorbates are shown in Table II. We focus first on the low coverage results. The stability of the adsorbed fragments with respect to the intact molecule heavily depends on the molecule considered. For N₂, dissociation is unfavourable with energies much higher than those of the intact molecule. Dissociation is also prevented in the case of CO, although the difference in energy between the adsorbed molecule and the adatoms is smaller. The dissociation of the CH₄ molecule is also slightly unfavoured. All other molecules have stable dissociated configurations. CO₂ and H₂O dissociation energies are slightly lower than those of the intact molecules. A significantly larger dissociation energy is found for H₂, CH₂O and the OH radical. Finally, O₂ has a very stable dissociated configuration with a difference of about 2.3 eV with respect to the adsorbed molecule. At high coverage, all dissociated species are less stable than at low coverage and dissociation of the adsorbed molecule is not favoured. **We have also calculated the adsorption energy for the isolated O and H adatoms. When compared to the adsorption energy of dissociated H₂ and O₂**

TABLE III. Relevant bond lengths and angles of the adsorbed molecules considered in this study at 1/4 ML coverage. $d(A-B)$ is the bond length between atoms A and B in the molecule. $d(A-S)$ is the distance of the molecule from the surface, measured from its closest point. $d(A-B)$ values in brackets correspond to the molecule in the gas phase. In CO_2 , O_2 and CH_4 , $d(A-B)$ refers to the bond length between the central atom and the other atoms. In the case of CH_2O , the values for the C-O and C-H bonds are shown separately.

Molecule	$d(A-B)$ (Å)	$d(A-S)$ (Å)
CO	1.18 (1.15)	1.76
CO_2	1.25 (1.18)	1.94
N_2	1.18 (1.16)	1.78
H_2O	0.98 (0.98)	2.17
O_2	1.41 (1.24)	1.86
CH_2O	C-O bond 1.35 (1.22)	2.01
	C-H bond 1.10 (1.12)	
CH_4	1.11 (1.10)	2.08
OH	0.98 (0.99)	1.98
H_2	0.88 (0.75)	1.62

TABLE IV. Bader charges of the atoms in the adsorbed molecules and of the surface atoms directly interacting with the adsorbed molecule at 1/4 ML coverage (in units of electrons)

Molecule	molecule charge (gas)	molecule charge (ads)	Fe_{top} charge
CO	1.11(C), -1.10(O)	0.80(C), -1.11(O)	0.60
CO_2	2.08(C), -1.04(O)	1.52(C), -1.12(O)	0.82(Fe1), 0.72(Fe2)
N_2	0.00	-0.35(N1), 0.00(N2)	0.68
H_2O	0.95(H), -1.91(O)	0.96(H), -1.93(O)	0.76
O_2	0.00	-0.41	0.83
CH_2O	0.89(C), 0.10(H), -1.04(O)	0.37(C), 0.006(H), -1.06(O)	0.7(Fe), -0.65(C)
CH_4	-0.22(C), 0.10(H)	-0.22(C), 0.01(H)	0.63
OH	-0.94(O), 0.94(H)	-1.47(O), 0.94(H)	0.90
H_2	0.00	-0.05	0.56

at low coverage, we obtain a significant stabilization of the adatoms as a result of decreased adsorbate to adsorbate interactions. This decrease in energy is of about -0.20 eV per atom for H and -0.33 eV per atom for O.

The geometries of the dissociated species are shown in Figure 3. We observe similar arrangements of the fragments for each case. Oxygen adatoms tend to adsorb in a pyramidal geometry on site D, with each adatom having two Fe-O bonds and one C-O bond and protruding from the surface. Hydrogen adatoms attach to the surface carbon atoms (site B). Carbon adatoms sit in a similar arrangement to oxygen adatoms on site D, with two Fe-C bonds and a C-C bond in a pyramidal setting that protrudes from the surface. In contrast, nitrogen adatoms are adsorbed on site E in a bridging configuration between two iron atoms. OH fragments behave like the case of the OH radical previously described. Finally, the CH_x fragments' adsorption geometry depends on the number of H atoms that they have; CH_2 sits on site D in a pyramidal arrangement similar to that of the oxygen and carbon adatoms, while CH_3 prefers site E in a bridging configuration similar to that of the nitrogen adatom.

We have also calculated reaction barriers for those cases where the dissociated configuration is favoured, namely H_2 , CO_2 , O_2 and CH_2O (see Table II for the barrier energies, and the supplementary information for information about the geometry of the transition states). We find the lowest barrier for the H_2 and CO_2 cases, with values below 0.8 eV, which suggest that these species will easily dissociate on the $\{010\}_n$ surface. In the case of O_2 , we find a large barrier of 1.7 eV for the straightforward reaction towards the most stable dissociated state. However, a much smaller barrier of 0.2 eV is found for the dissociation to a less stable dissociated state where one of the adatoms sits on a bridging position between two Fe atoms, as shown in Figure 3. A large barrier is found for H_2O dissociation; it is expected that such a high barrier will effectively prevent dissociation of this molecule on the surface.

Our results for CO and H_2 can be compared with the existing literature. In the case of H_2 , we see similar trends to those discussed for the adsorption over $\{001\}$, $\{010\}$ and $\{100\}$ stoichiometric surfaces²⁹: a dissociated state easy to access thanks to a low reaction barrier, where hydrogen adatoms tend to attach to surface carbon atoms. The main difference is that on those surfaces, the smaller amount of surface carbon leads to the adsorption of only one hydrogen adatom over carbon; the other one adsorbs over an iron atom. On $\{010\}_n$, the

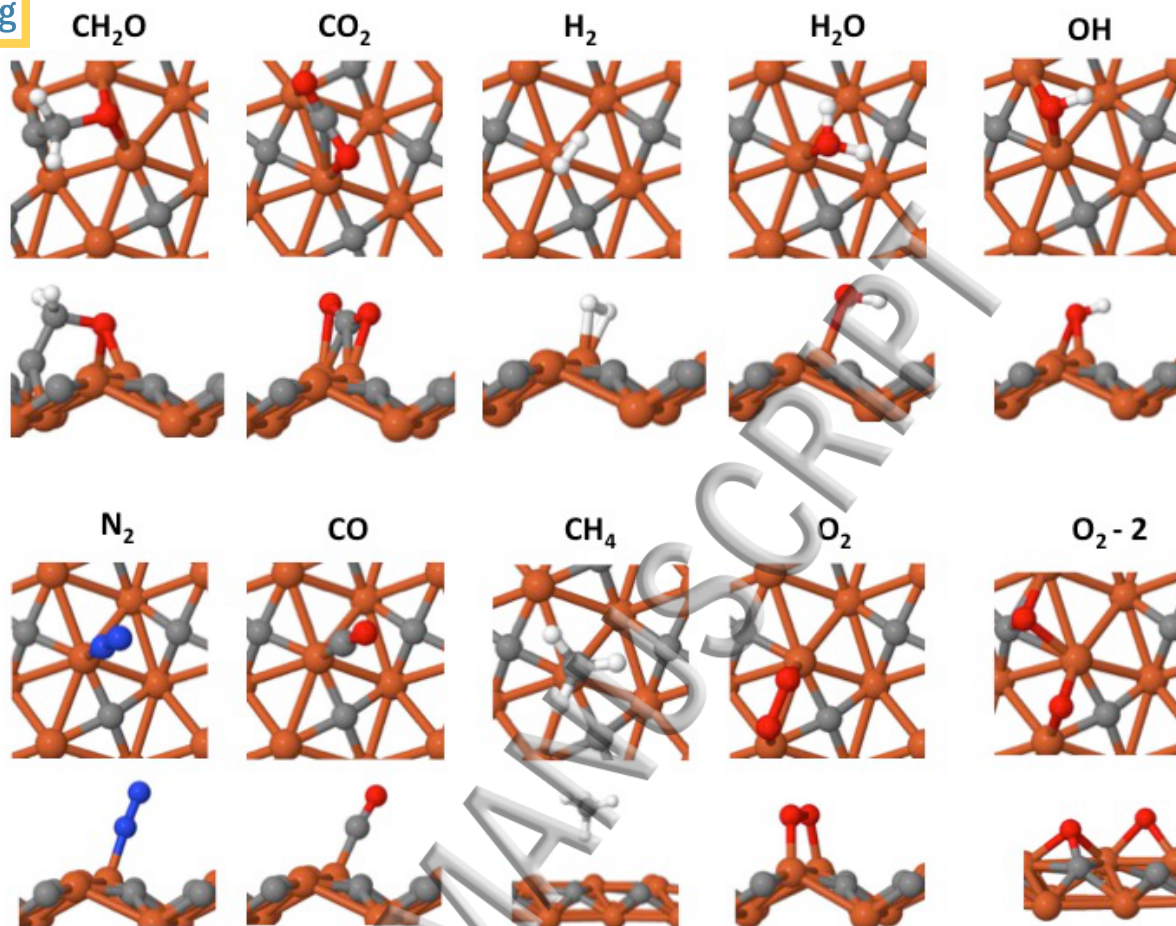


FIG. 3. Geometry configurations of the most stable dissociated molecules adsorbed over nonstoichiometric cementite {010}. Also, the second most stable minimum for dissociated O_2 is shown with label O_2-2 . For each molecule, top and side views are displayed. For clarity, only the first layer of the slab is shown.

larger amount of surface carbon permits to have the adsorption of two hydrogen adatoms over nearby surface carbon atoms. The adsorption energy for the dissociated state is, however, slightly smaller in our calculation.

IV. DISCUSSION

We compare adsorption on cementite with results obtained by other DFT studies on $Fe\{100\}$ and other common transition metal carbides.

TABLE V. Adsorption energies on Fe{100} and on cementite {010}_n at low coverage, in eV

Molecule	E_{ads} Fe{100}	E_{ads} Fe ₃ C {010} _n
CO	-2.14 ³⁰	-1.98
CO ₂	-0.25 ³¹	-0.61
N ₂	-0.98 ³²	-1.11
H ₂ O	-0.38 ³³ , -0.41 ³⁴	-0.82
O ₂	-	-2.14
CH ₂ O	-1.47 ³⁵	-1.64
CH ₄	-0.05 ³⁶	-0.33
OH	-4.14 ³³	-3.18
H ₂	-0.08 ³⁷	-0.50

A. iron {100}

Table V summarizes the differences between adsorption energies in Fe{100} and cementite {010}_n.

CO: CO adsorbs on Fe{100} with a geometry that depends on coverage. At low coverage, CO attaches to a hollow site surrounded by four iron atoms in a flat configuration, while at high coverage it attaches vertically to a top-layer iron atom in a similar way to what our calculations find for the cementite case. E_{ads} is -2.14 eV³⁰, which is slightly larger than in cementite. The dissociated species is more stable on Fe{100} by a difference of 0.3 eV. In cementite, the dissociated configuration is higher in energy than the unbroken molecule on the surface.

H₂O: H₂O adsorption on Fe{100} takes place on top of an iron atom, with E_{ads} between -0.38 eV and -0.41 eV (see^{33,34} and references therein). This value is about half of that found in our cementite calculations. The molecule lies flat over the surface, in a similar way to what we obtain in cementite. Its dissociation into H and OH has been calculated, with a E_{diss} of 0.88 eV and a barrier of 0.4 eV. The dissociated state on cementite is more stable by about 0.2 eV.

CO₂: this molecule adsorbs with a geometry similar to that obtained in our calculations for cementite, with the molecule aligned along two nearest neighbour iron atoms³¹. The adsorption energy is about 0.3 eV smaller than in the cementite case.

N₂: the geometry of adsorbed N₂ on Fe{100} is different from what we obtain for cementite. The molecule adsorbs flat on the hollow site formed by four iron atoms on the surface³², instead of adopting a vertical configuration over one iron atom. The adsorption energy is slightly smaller than in cementite.

O₂: in contrast with the case of cementite, the molecule adsorbs dissociatively on Fe{100} without creating any stable molecular adsorbate. The dissociated configuration with the two oxygen adatoms on the Fe{100} surface is very stable; an adsorption energy of about 8 eV is reported³⁷, which is much larger than the adsorption energy obtained in our cementite calculations.

CH₂O: formaldehyde adsorbs flat in a hollow site on Fe{100}³⁵, while it adsorbs in a bridging position between iron and carbon atoms in cementite. Adsorption is slightly more favourable in the cementite case.

CH₄: this molecule weakly physisorbs both on Fe{100}³⁶ and on cementite.

OH: the geometry of the adsorbed molecule on Fe{100} is very similar to that found in our cementite calculations; the oxygen atom is linked to two iron atoms in a bridging configuration³³. In this case, the adsorption energy is larger by about 1 eV with respect to cementite.

H₂: on Fe{100}, this molecule weakly adsorbs over one iron atom³⁷, with a similar geometry to that found in the cementite case at low coverage. The adsorption energy is much smaller than in the cementite case. The dissociation of the molecule is favoured; this state is about 0.8 eV more stable than the adsorbed molecule and the barrier for dissociation is about 0.1 eV. The hydrogen adatoms are adsorbed over the four-coordinated hollow site. In cementite, the dissociated state is about 0.5 eV more stable than the adsorbed molecule and the barrier for dissociation is also larger. The hydrogen adatoms sit on top of surface carbon atoms.

From this comparison we infer that adsorption of small gases on cementite {010}_n is more favorable than on Fe{100} for most cases. However, the Fe{100} calculations do not include van der Waals corrections. Our analysis of the CO adsorption with and without van der Waals correction in Section III B indicates that this correction increases the adsorption energy by about 0.3 eV. Assuming this value is a good approximation to the van der Waals correction of the other molecules, we may use it to estimate corrected iron adsorption energies. Taking this correction into account, we observe that adsorption energies on iron {100}

and cementite $\{010\}_n$ are similar for most molecules studied in this work, with the exception of CO and the OH radical, where adsorption on the iron surface is clearly favoured.

B. Other carbides

We compare our results with data present in the literature for DFT calculations of several representative transition metal carbides: TiC, ZrC and Mo_2C . We focus our comparison on stable surfaces with high C content, similar to the cementite $\{010\}_n$ surface studied in this work. Table VI summarizes the adsorption energies of several gases for these carbides in comparison with the cementite results. In general, we find that adsorption over the cementite surface is similar to the behaviour observed in the Mo_2C case¹⁵, and remarkably different from the reactivity found in carbides of early transition metals like TiC and ZrC ^{10–14}. In both cementite and Mo_2C $\{101\}$, CO and O_2 strongly chemisorb on the surface metal atoms with significant charge transfer from the surface to the molecule. H_2 and H_2O display a weaker adsorption with no charge transfer in both cases as well. We also find some differences between adsorption on cementite and on Mo_2C : a weaker adsorption in the case of CO_2 despite having similar adsorption geometry in both cases, and a larger dissociation barrier for the H_2O case. Nonetheless, there are more similarities than differences in the chemical behaviour of the Mo_2C and cementite surfaces, which we attribute to the properties of Fe and Mo: both have a significantly larger electronegativity than Ti or Zr and their carbides have a stronger covalent character. As a result, the metal atoms at the surface are able to better transfer charge and establish strong chemical bonds with adsorbates like O_2 or CO.

V. CONCLUSIONS

We have performed calculations on the adsorption of CO, CO_2 , H_2O , H_2 , CH_4 , CH_2O , N_2 and OH on a nonstoichiometric $\{010\}$ surface of Fe_3C . We find that adsorption is favorable in all cases considered, although with different adsorption energies. CH_4 displays the weakest adsorption, followed by H_2 , CO_2 , H_2O and N_2 . These molecules adsorb either in a bridging

TABLE VI. Adsorption energies of several molecules on the surface of the carbides TiC, ZrC, Mo₂C and on cementite {010}_n at low coverage, in eV

Molecule	TiC {001}	ZrC {001}	Mo ₂ C {101}	Fe ₃ C {010} _n
CO	-0.76 ¹¹	-	-1.92 ¹⁵	-1.98
CO ₂	-0.83 ¹⁴	-1.60 ¹⁴	-1.14 ¹⁵	-0.61
H ₂ O	-0.42 ¹¹	-0.49 ¹³	-0.84 ¹⁵	-0.82
O ₂	-0.45 ¹⁰	-0.87 ¹⁰	-2.25 ¹⁵	-2.14
H ₂	-0.48 ¹²	-0.66 ¹²	-0.53 ¹⁵	-0.50

position between two iron atoms (CO₂ case) or on top of a surface iron atom (other cases). O₂, CO, OH and CH₂O strongly adsorb over the surface; CO does it on top of one Fe atom, while the other molecules adopt bridging configurations. Dissociation is favoured in all cases except for CO and N₂. Carbon and oxygen adatoms adopt a pyramidal configuration where they are linked to two iron atoms and one carbon atom at the surface. The hydrogen adatom is attached on top of a carbon surface atom. Comparison with adsorption on Fe{100} surfaces indicates that most small atmospheric gases have similar adsorption energies on both surfaces, with the exception of CO and the OH radical. In these two particular cases, adsorption on cementite is less favourable than on the iron surface. **In addition, the reactivity of cementite surfaces to these gases behaves in a similar way to that of Mo₂C surfaces, due to the similar covalent character of both carbides compared with early transition metal carbides like TiC.**

VI. SUPPLEMENTARY MATERIAL

We include a document (supplemental1.pdf) with pictures describing the geometry and adsorption energies of other local minima and transition states of the adsorbed molecules studied in this work. Another file, structures.txt, includes structural data in pdb format for all the structures studied in this work.

VI. ACKNOWLEDGEMENTS

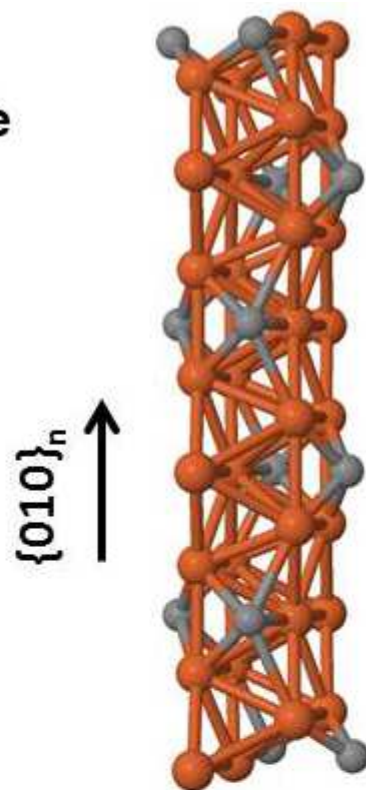
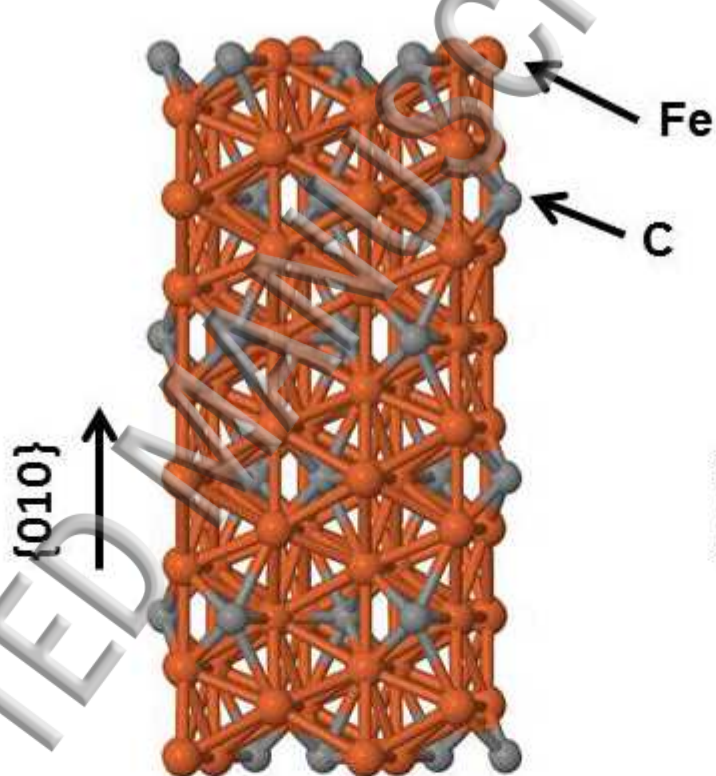
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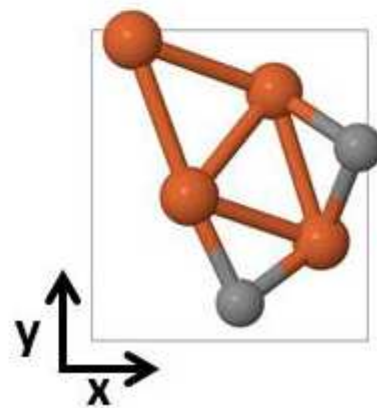
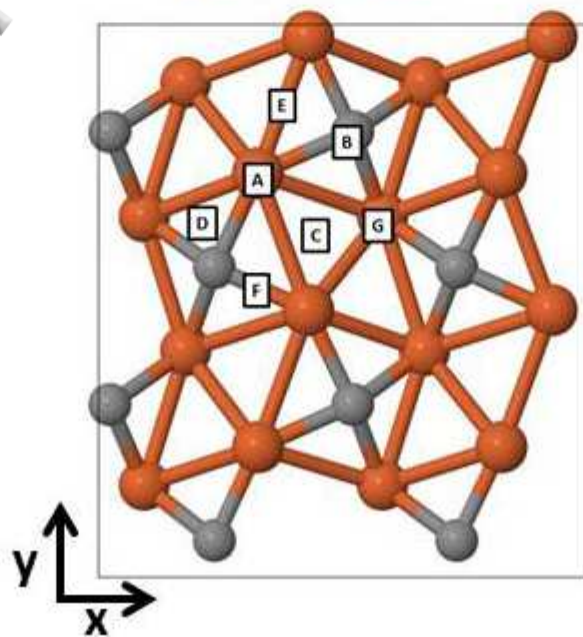
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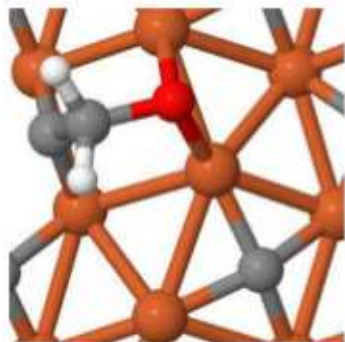
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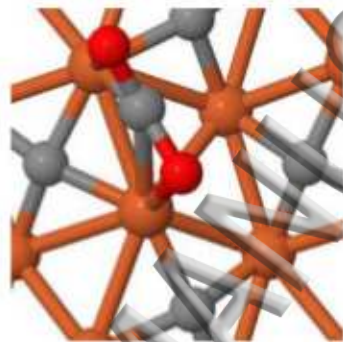
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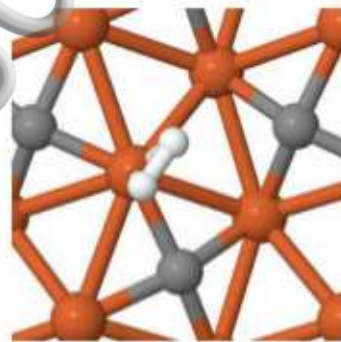
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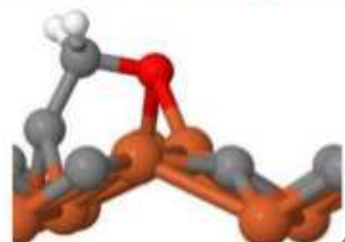
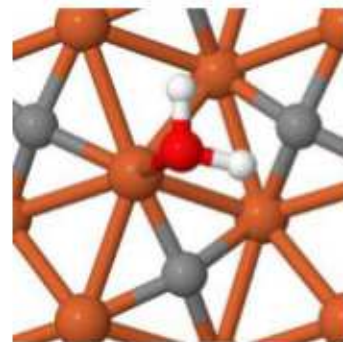
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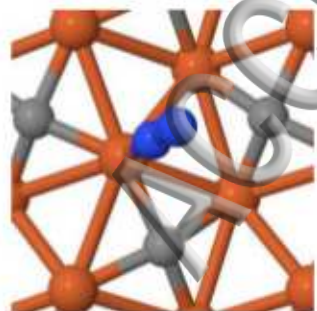
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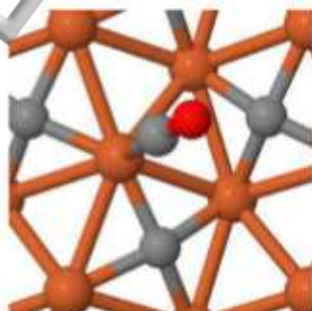
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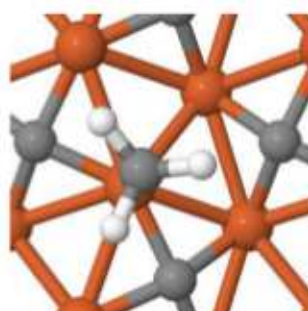
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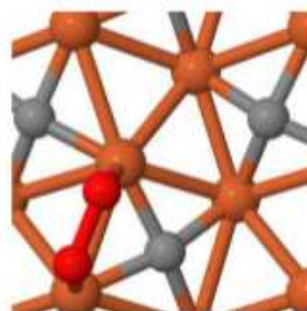
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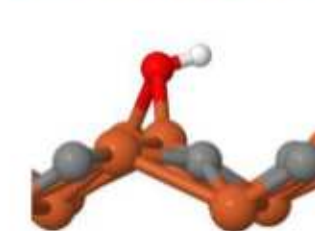
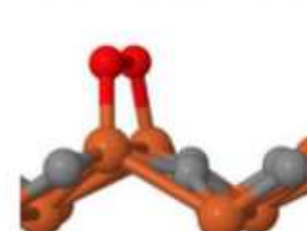
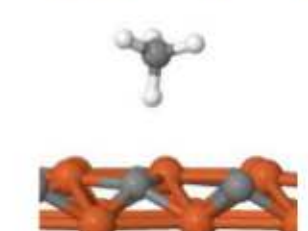
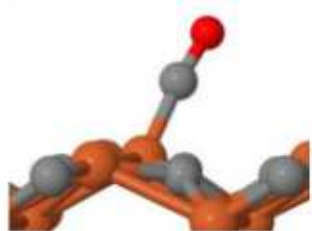
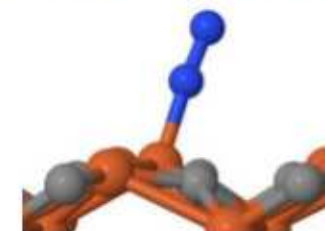
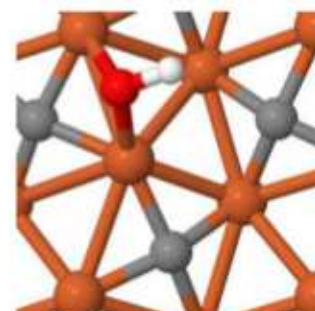
CH_4



O_2



OH



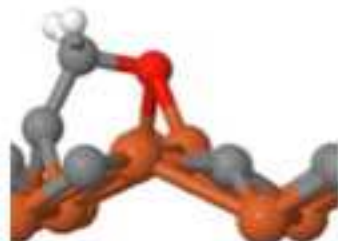
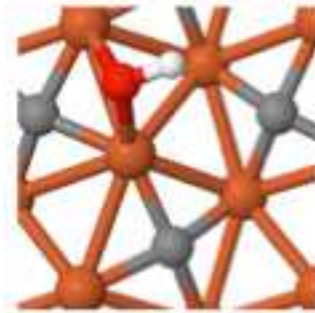
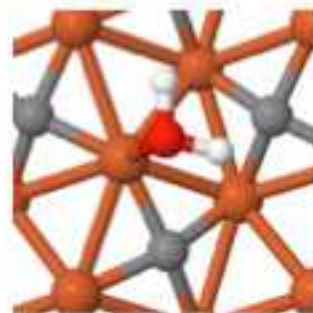
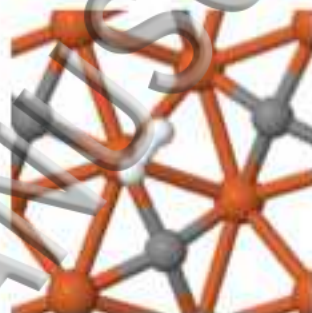
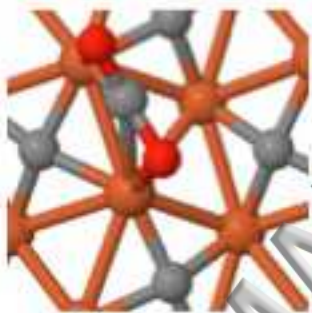
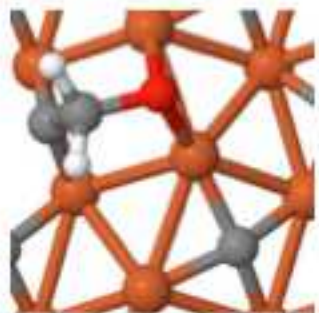
CH_2O

CO_2

H_2

H_2O

OH



N_2

CO

CH_4

O_2

$\text{O}_2 - 2$

