



# Diffusion of hydrogen, carbon and oxygen in the presence of hydrogen coadsorbed onto iron surfaces

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## ARTICLE INFO

### Article history:

Received 5 May 2021

Revised 26 November 2021

Accepted 9 January 2022

Available online 15 January 2022

### Keywords:

GGA-PBE

Binding energy

Hollow site

Bridge site

Diffusion coefficient

## ABSTRACT

Density-functional theory calculations based on the GGA-PBE (generalized gradient approximation Perdew–Burke–Ernzerhof) exchange correlation functional were used to investigate the effect of hydrogen on the diffusion of adsorbed carbon, oxygen and hydrogen on the surface of Fe(100). The diffusion energy barrier was calculated for both clean surfaces and those with hydrogen, and it was found that hydrogen produced binding energies for carbon and oxygen. These bonds stabilized the binding of hydrogen with the Fe(100) surface. For all of the surface species studied here, the energy barrier was increased when hydrogen was coadsorbed, from 1.29 eV to 1.46 eV for C, from 0.33 eV to 0.53 eV for O and from 0.11 eV to 0.15 eV for H. An approximation of the diffusion coefficient was obtained from energy barrier calculations and a pre-exponential factor of diffusion was calculated. Carbon exhibited low diffusion at the surface under experimental temperatures, while oxygen diffusion was activated above 450 K and hydrogen was diffused in all the temperature ranges investigated.

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## 1. Introduction

Understanding the behavior of atoms on the surface of a metal is a key aspect of surface science. The adsorption and diffusion of atoms on metal surfaces is also one of the central aspects that must be taken into account when developing applications of surface science and engineering [1–3]. The adsorption and diffusion of carbon atoms at the surface of a catalytic material are fundamental processes in several applications as: the chemical vapor deposition of carbon nanomaterials and chemical reactions in heterogeneous catalysis [4–6]. In the same way, the understanding of oxygen adsorption on metal surfaces is the initial step for many processes such as oxidation, heterogeneous catalysis and corrosion [1]. Hydrogen can be used as the only element adhering to metal surfaces in order to form surface hydrides, in fuel cells used as energy storage devices, and in heterogeneous catalysis in combination with oxygen and carbon for the formation of hydrocarbons [2,7–9]. From

an experimental point of view, the diffusion of individual species and the effects of coadsorbates on the mobility of specific adsorbed atoms are processes that are very difficult to control; in addition, surface defects, varying experimental conditions and the capabilities of the instruments used mean that an analysis of the diffusion of atoms is complex. These issues can be partially overcome using computational methods, since some local interactions of the atoms are not possible to be observed in experimental processes, and certain approximations can be adopted to give a better understanding of the phenomenology. For instance, Jiang and Carter [5,10] used a projector augmented wave (PAW) method in conjunction with the GGA-PBE approach to study the diffusion of carbon atoms on clean Fe(110) and Fe(100) surfaces, and reported values of 1.18 and 1.47 eV, respectively. They also predicted that the limiting step for the incorporation of C into bulk Fe was the initial diffusion toward the subsurface. In this case, there were no differences between the segregation on different surfaces. Lastly, the formation of graphite may be more favorable in C-covered Fe(110) than in C-covered Fe(100). In the same vein, the adsorption of precovered hydrogen was studied to understand its effect on the CO dissociation process by Chun-Fang et al. [11], who used a DFT calculation with an Fe(111) surface. These authors found that for a clean Fe(111) surface, the energy barrier to the dissociation of CO was 1.53 eV,

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while for a hydrogen-precovered surface, the energy barrier had a value of 1.17 eV. Previous reports by Amaya-Roncancio et al. [12,13] showed that coadsorbed hydrogen atoms increased the binding energy of C and O species after dissociation of CO. The formation energy of CH changed from 0.86 eV on a clean surface to 0.70 eV on a hydrogen-precovered surface. Finally, the formation energy of CH<sub>2</sub> changed from 1.67 to 1.22 eV for a hydrogen-precovered surface. Mavrikakis et al. [14] studied the adsorption and diffusion of several species of oxygen on Fe(110) using PW91. They concluded that the binding energy of oxygen atoms was lower than for carbon, with values of −6.90 and −7.60 eV, respectively. Furthermore, the diffusion barrier was estimated as 0.40 eV for oxygen on clean Fe(110), while for carbon this was 1.22 eV. The adsorption of hydrogen onto metal surfaces is of particular interest due to its wide range of applications in several fields of surface science. Previous reports of hydrogen adsorption on transition metals (Au, Cu, Ag and Pt) were calculated using GGA-PBE and ultrasoft pseudopotentials, and the energy barriers to diffusion on clean surfaces were reported as 0.40, 0.17, 0.09 and 0.21 eV, respectively [2]. Lilja and Skúlason [15] calculated the binding energies of hydrogen on different surfaces with BCC(110), FCC(111) and HCP(0001) crystalline structures and orientation, for 23 transition metals. They reported values of between −0.5 and −1.0 eV. The activation energies for the diffusion processes were between 0.04 and 0.28 eV. In all cases, when the adsorbed atom diffuses from one adsorption site to a neighboring site of the same type, there is an activation energy that remains equal in both the initial and final states. The effects of coadsorbates on the diffusion process have not been explored in previous studies.

In the present work, we carry out comprehensive calculations based on the frame of DFT. We calculate the adsorption energies and diffusion barriers of hydrogen, oxygen and carbon on clean and hydrogen pre-covered Fe(100) surfaces. We also estimate the diffusion coefficients for carbon, oxygen and hydrogen, and evaluate their behavior experimentally over a wide range of temperatures.

## 2. Computational methods

DFT calculations were carried out using the Quantum Espresso package [16]. The electron-ion interaction was described by ultrasoft pseudopotentials with a scalar relativistic correction, generated using the Rappe-Rabe-Kaxiras-Joannopoulos method (RRKJUS) [17]. The GGA was used for the PBE exchange/correlation density functional [18], with a cutoff energy of 60 Ry. Calculations were performed with a convergence threshold of  $1 \times 10^{-6}$  for self-consistency. The integration of the Brillouin zone was approximated using the Monkhorst-Pack scheme [19], with  $12 \times 12 \times 12$  k-point sampling in the bulk calculations and  $4 \times 4 \times 1$  k-point sampling in the slab calculations. The thickness of the space between the slabs was set to 10 Å, and a  $p(2 \times 2)$  supercell with six metal layers was used. The selected size was sufficient to allow us to describe the adsorption energy with an accuracy of 0.01 eV. The first three layers were fixed at the bulk position and the other three were allowed to relax, to describe the (100) surface on which H is adsorbed. The adsorption energy of hydrogen converged for a  $p(2 \times 2)$  model, and the results showed good agreement with calculated values of the adsorption energy on Fe(100) reported in our previous studies [12,13] and by Sorescu [20]. Geometric relaxation was done using a quasi-Newton BFGS algorithm, until the forces on each atom were less than  $10^{-5}$  eV/Å and the difference in energy between consecutive steps was less than  $10^{-5}$  eV. A study of the minimum energy paths was undertaken using the nudged elastic band (NEB) method [21], and the local minima were found using the conjugate gradient (CG) technique. All molecular and density plots were created using the XCrySDen package [22].

**Table 1**

Binding energies and atom-surface distances for adsorbed atoms on a Fe(100) surface and an H-coadsorbed Fe(100) surface.

Adatom	Distance (Å)	$\Delta d$ (Å)	Eads(eV)	$\Delta E$ (eV)
C	0.37	–	−9.95	–
O	0.52	–	−6.73	–
H	0.36	–	−2.24	–
C + H	0.39	0.02	−8.21	0.74
O + H	0.56	0.04	−6.57	0.16
H + H	0.35	0.01	−2.31	−0.07

## 3. Results

### 3.1. Adsorption of C, O and H on Fe(100) surfaces

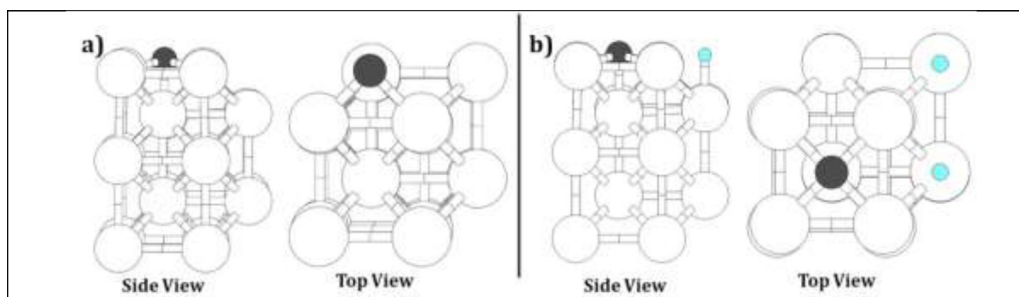
The binding energy  $E_{bind}$  of an adatom was calculated for an Fe(100) surface and an H coadsorbed Fe(100) surface using the expression:

$$E_{bind} = E_{total} - E_{slab} - E_{atom}, \quad (1)$$

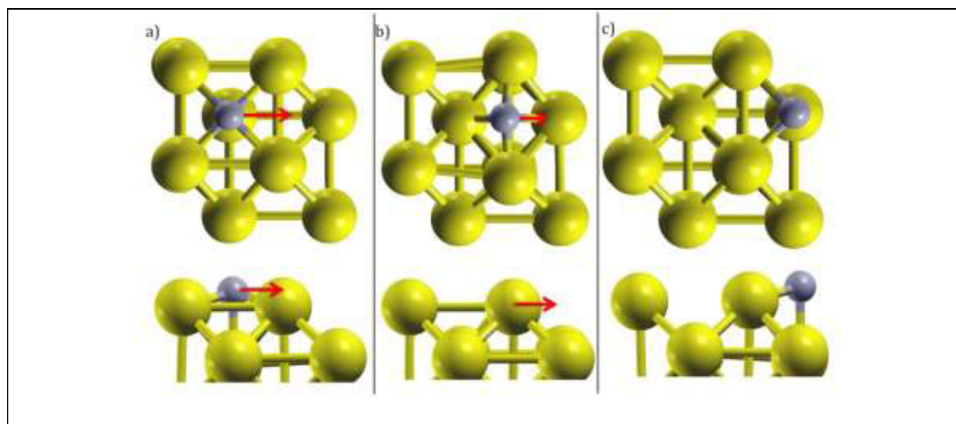
where  $E_{total}$  is the total energy of the C/Fe(100) or C + 2H/Fe(100),  $E_{slab}$  is the energy of the clean Fe(100) surface or the energy of 0.5 monolayers (ML) of H-preadsorbed Fe(100) surface, and  $E_{atom}$  is the energy of the isolated C, O or H.

All the species studied here were considered to be adsorbed onto a hollow site as initial and final states of diffusion, taking into account that previous studies have shown this sites as preferential adsorption site compared with Top and Bridge for the involved species [12]. In the same way, the 0.5 ML of coadsorbed H was assumed to be adsorbed onto neighboring hollow sites, as shown in Fig. 1. The distance of an adatom from the Fe surface (i.e., C-Fe, O-Fe and H-Fe) was calculated as the distance of the adsorbed atom from the plane formed by the four Fe atoms, which forms the hollow site in the surface layer. In the case of a bridge site, the distance was calculated from the transversal line linking the atoms at the site.

The calculated values of the binding energies for carbon, oxygen and hydrogen show that all species are strongly bonded to the surface. For a clean surface, the values obtained for C, O and H were −9.95, −6.73 and −2.24 eV, as shown in Table 1. Since these values are only comparative, it is important to note that for surfaces where there is hydrogen coadsorption, these values will be modified. When C is in the presence of 0.5 ML of coadsorbed H, the calculated value of the binding energy increases to −8.21 eV, indicating that in this case, a C atom is still strongly bonded to the surface; however, for a surface with the presence of hydrogen, there is a charge density from the Fe surface, weakening the C-Fe bond and decreasing it by about 0.74 eV (Table 1). In the same way, the C-Fe distance increased from 0.37 to 0.39 Å, as shown in Table 1. For oxygen, the calculated value of the binding energy was −6.73 eV for a clean Fe(100) surface, and in the presence of coadsorbed H, the value increased to −6.57 eV. The variation in the binding energy was 0.16 eV for oxygen, being lower than for the previous case, but showing the hydrogen effect in the binding energy. The O-Fe distance increased to 0.04 Å (Table 1). In contrast to C and O, the adsorption of hydrogen onto clean surfaces had a calculated binding energy of −2.24 eV, while for 0.5 ML of coadsorbed H, the calculated value was −2.31 eV, a decrease of −0.07 eV. In the case of C and O atoms, the energy difference shows that the presence of H decreases the energetic stability of Oxygen and Carbon. The mentioned decrease could occur only for the taken of charge density from the surface of other specie coadsorbed to C or O. As the unique change presented in the surface was the incorporation of Hydrogen on the surface, This indicates that hydrogen atoms on the surface takes a charge density from Fe, which stabilizes the



**Fig. 1.** Adsorption of atomic species onto a hollow site of (a) a clean Fe(100) surface, and (b) an H-coadsorbed Fe(100) surface (white atoms represent Fe; gray atoms represent adsorbed species; cyan atoms represent coadsorbed H).



**Fig. 2.** Diffusion of a carbon atom onto a Fe(100) surface: (a) initial state at a hollow site, (b) diffusion through a bridge site, and (c) final state at an adjacent hollow site (C atoms are shown in gray, and Fe atoms in yellow).

adsorption state. The H-Fe distance changed from 0.36 to 0.35 Å (Table 1). e calculated values presented here are in agreement with those reported by Huo et al. [11], who found that the binding energy of a C atom on Fe(111) surfaces had a value of  $-7.80$  eV at an adsorption site labeled as quasi-plane. Similarly to oxygen atoms, these researchers reported a binding energy of  $-5.87$  eV on the quasi four-fold sites of the Fe(111) surfaces. Our results are consistent with the findings of Li et al. [23,24] studied the hydrogenation of carbon on Fe(110) surfaces, reporting a binding energy for H atoms on a clean Fe(110) surface of  $-1.50$  eV. The authors cited above reported the diffusion of carbon atoms to the surface in the presence of hydrogen and an increase in the C-Fe distance in the presence of H at the Fe surface. This effect causes some surface deformation.

### 3.2. Effect of carbon diffusion on coadsorbed hydrogen on Fe(100) surfaces

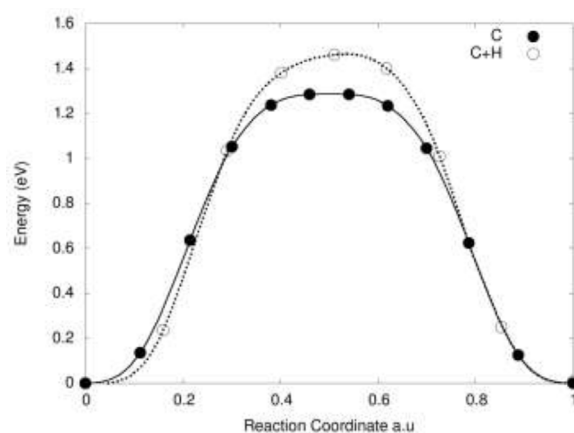
In the case of carbon atoms, diffusion on a clean Fe(100) surface occurs when carbon is transmitted through the bridge sites. The surface diffusion of carbon is a special case, since the atom does not pass through the bridge sites; instead, it replaces the Fe-Fe bonds generated between the atoms at the bridge sites, as shown in Fig. 2. In this diffusion pathway, the initial and final states are made up of carbon atoms adsorbed onto hollow sites, as can be seen from Fig. 2.

For the diffusion of C onto a clean Fe(100) surface, the highest energy value found along the diffusion pathway, when a C atom is located between the Fe atoms forming the bridge site, was 1.29 eV with respect to the initial hollow state (Table 2 and Fig. 3). As described above, a bridge site is structurally modified during the diffusion of a C atom, since the C atom is bonded to the two Fe atoms of the bridge site, thus increasing the Fe-Fe distance. In the same

**Table 2**

Diffusion barriers and distances of C atoms from the plane generated by the four atoms at hollow sites and for the two Fe atoms at the bridge sites of Fe(100).

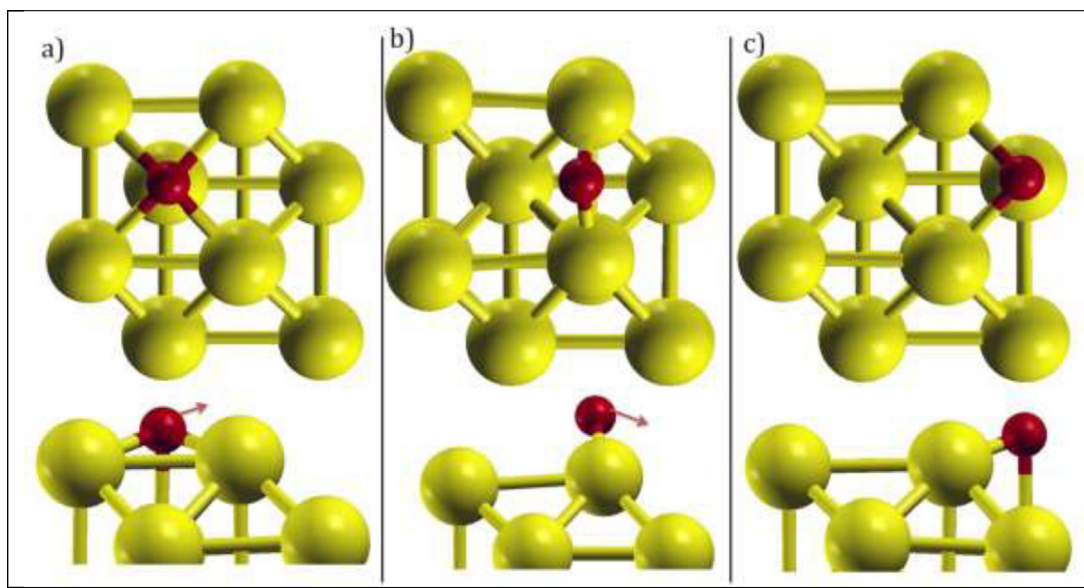
Diffusion	Hollow to hollow (eV)	C-hollow(Å)	C-bridge (Å)
C/Fe(100)	1.29	0.37	0.37
C + 2H/Fe(100)	1.46	0.37	0.37



**Fig. 3.** Diffusion energy pathway for a C atom onto Fe(100) (the solid line shows the diffusion of C onto a clean Fe surface; the dashed line shows C + 2H/Fe(100), i.e., diffusion of C onto an Fe surface coadsorbed with 0.5 ML of hydrogen).

way, a C atom is bonded to the two Fe atoms of the adjacent hollow site (Fig. 2b). The adsorption distance at a hollow site, with respect to the plane generated by the four atoms forming the surface, was calculated as 0.37 Å. A similar distance was found for the case of C diffusing through bridge sites (Table 2). This value for the





**Fig. 4.** Diffusion of C on Fe(100) with 0.5 ML of coadsorbed hydrogen: (a) the initial hollow state site, (b) the diffusion pathway on a bridge site with a higher energy value, (c) the final state on an adjacent hollow site (C atoms are shown in gray, H atoms in cyan and Fe atoms in yellow).

diffusion barrier is consistent with the results of Jiang and Carter [5], who studied the diffusion pathways of C atoms on Fe(100) and (110) and reported a surface diffusion barrier of 1.20 eV for Fe(100) and a diffusion barrier into the iron bulk of 1.60 eV. This high value of the diffusion barrier was attributed to the strength of the C-Fe bond at the hollow site on the Fe(100) surface [25]. For the diffusion of C in the presence of 0.5 ML of coadsorbed hydrogen, the diffusion barrier is increased due to the presence of hydrogen, as shown in Table 2 and Fig. 3. In the initial and final states of the diffusion of the C atom in the presence of 0.5 ML of hydrogen, the C atom is adsorbed onto adjacent hollow sites. The diffusion barrier in this case was calculated as 1.47 eV, an increase of 0.17 eV compared to the clean Fe(100) surface (Table 2 and Fig. 3).

In the same way as for C diffusion on a clean Fe(100) surface, a higher value for the energy in the diffusion pathway was observed for the bridge sites. In this case, the C atom is bonded to the Fe atoms of the bridge sites via an Fe-C-Fe bond, which temporarily increases the distance between bridge sites. Finally, the C atom is stabilized on the adjacent hollow site, and the Fe-Fe atoms return to their previous positions, as shown in Fig. 4.

By comparing the diffusion barriers on the clean surface and with coadsorbed H, it can be seen that the presence of hydrogen makes the diffusion of C more difficult. In this case, the activation barrier is comparable with the chemisorption energy, making the diffusion of C an unlikely event. The values calculated here are consistent with those of Jiang and Carter [10], who reported a diffusion energy barrier of 1.20 eV for surface C atoms in the Fe(100) bulk, and established this as an endothermic reaction that favored the carbon on the surface. In the same vein, Cinquini et al. [26] reported values for the C diffusion barriers on Ni and Ni<sub>3</sub>Pd surfaces of between 0.7 and 1.2 eV.

### 3.3. Effect of coadsorbed hydrogen on oxygen diffusion on Fe(100) surfaces

In the diffusion of O atoms, the movement of the O does not modify the positions of the Fe atoms in the same way as for C atoms. When we take an O atom adsorbed on a hollow site as the initial state, a higher energy value is found for the diffusion pathway compared to the value observed previously for the bridge site. In the case of C diffusion, an adsorption state on the bridge site is

not seen, while for the diffusion of O atoms, a local minimum is found at the bridge site (Table 3, Figs. 5 and 6).

The binding energy calculated for the O atoms at the bridge site was -6.70 eV, representing an increase of 0.03 eV compared to the value of for the adsorption of O atoms on a hollow site. The minimum energy pathway found using the NEB method shows that a bridge site is a local minimum (Fig. 6). The diffusion barrier that needs to be overcome at the hollow, in the direction towards an adjacent bridge site, is 0.33 eV. Since the bridge site is a local minimum, the energy barrier that needs to be overcome at the bridge site for diffusion to the adjacent hollow site was calculated as 0.30 eV (Table 3 and Fig. 5). It is important to note that the minimum energy pathway between bridge sites includes several stable sites at which the energy is 0.10 eV higher than in the initial state. Xing et al. [1] reported a value for the barrier to oxygen diffusion of 0.4 eV on U(100) surfaces, which is in agreement with our results. Similarly, Curnan et al. [27] reported a diffusion pathway of 0.5 eV for oxygen on Cu(011) surfaces.

In the case of an O atom on a clean Fe(100) surface, the distance from a hollow site to the plane generated by the four Fe surface atoms was calculated as 0.52 Å. Another important aspect of the coadsorption of H and O is the distance of the O atom from the plane of the surface. In this case, when an O atom diffuses between two hollow sites on a clean Fe surface, the O-Fe distance observed for the highest energy value, calculated for the minimum energy pathway, was 0.81 Å. In the presence of coadsorbed H atoms, the O-Fe distance for the highest energy value, calculated for the minimum energy path, was 1.00 Å, while the O-Fe distance from a hollow site to a clean surface was observed to be 0.82 Å, and 0.57 Å in the presence of coadsorbed H atoms (Table 3).

In the presence of H, the activation barrier to O diffusion from a hollow to a bridge site, calculated using NEB, is 0.53 eV. From a bridge to a hollow site, the activation barrier was calculated as 0.18 eV, as shown in Table 3 and Fig. 5. From these results, it can be concluded that the coadsorption of H facilitates the diffusion from a bridge to a hollow site, as shown in Fig. 6.

### 3.4. Effect of coadsorbed hydrogen in the case of hydrogen diffusion on Fe(100)

In the same way as for the O atom, the H atom prefers hollows as adsorption sites, and bridge sites exhibit local minima. For dif-

**Table 3**

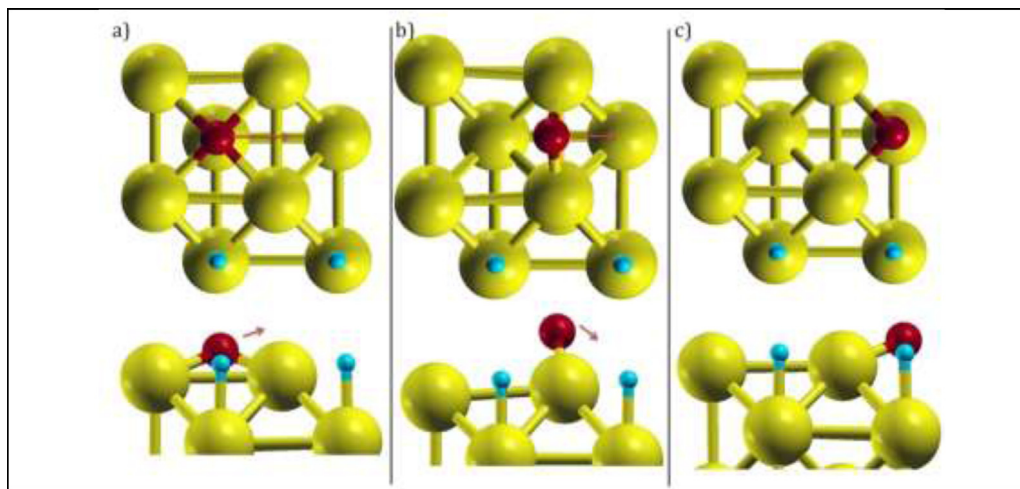
Diffusion barriers and distances of O atoms from the plane formed by the four atoms of the hollow site and for the two Fe atoms at the bridge site for Fe(100).

Diffusion	Hollow to bridge (eV)	Bridge to hollow (eV)	O-bridge (Å)	O-hollow (Å)
O/Fe(100)	0.33	0.30	0.81	0.52
O + 2H/Fe(100)	0.53	0.18	1.00	0.57

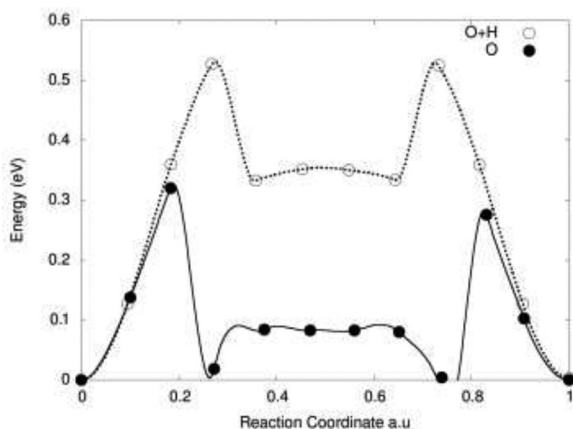
**Table 4**

Diffusion barriers and distances of the H atom from the plane generated by the four atoms of the hollow sites, and for the two Fe atoms at the bridge sites in Fe(100).

Diffusion	Hollow to bridge (eV)	Bridge to hollow (eV)	O-bridge (Å)	O-hollow (Å)
H/Fe(100)	0.11	0.05	0.68 Å	0.36 Å
H + 2H/Fe(100)	0.15	0.06	–	–



**Fig. 5.** Diffusion of an oxygen atom on an Fe(100) surface: (a) initial state on a hollow site, (b) diffusion at a bridge site, and (c) final state at the adjacent hollow site (the O atom is shown in red, and the Fe atoms in yellow).



**Fig. 6.** Pathway for oxygen diffusion on Fe(100) surfaces (the solid line shows diffusion on a clean Fe(100) surface, and the dashed line shows diffusion in the presence of 0.5 ML of coadsorbed H).

fusion from a bridge to a hollow site, an H atom requires 0.05 eV. In the bridge sites, the hydrogen atoms exhibit an H-Fe distance of 0.68 Å with respect to the hollow sites, while the H-Fe distance was observed to be 0.36 Å from the plane of the surface (see Fig. 7 and Table 4). The energy barrier calculated for the minimum energy path using NEB was 0.11 eV, from a hollow site to a bridge site on a clean Fe(100) surface (Fig. 8).

The coadsorbed hydrogen has no effect on the H-Fe distance for hollow or bridge sites. The H-Fe energies were 0.68 Å and 0.36 Å

for the hollow and bridge sites, respectively, on a clean surface with coadsorbed H (Figs. 7 and 8, and Table 4).

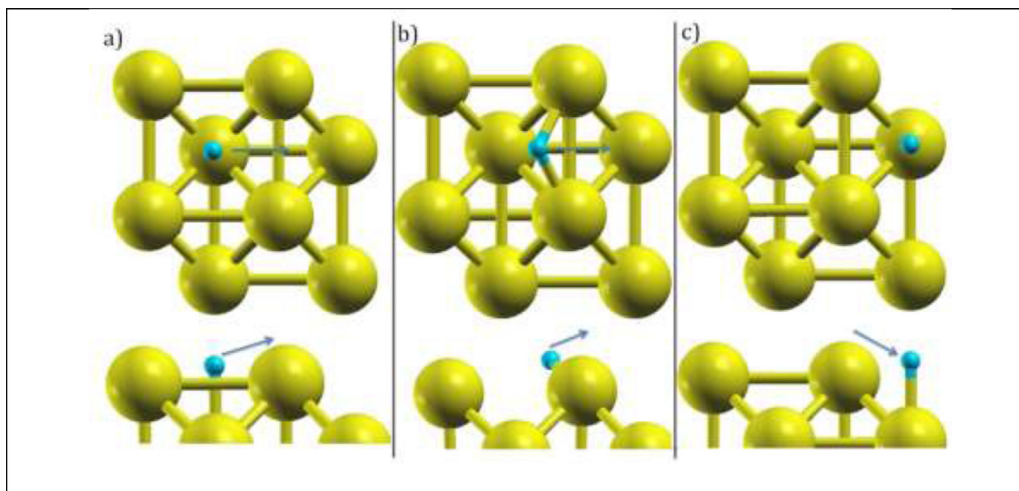
The main difference between clean and H coadsorbed Fe(100) surfaces is the increase in the energy barrier. For a clean surface, the energy barrier calculated using NEB for the diffusion from hollow to bridge sites was 0.11 eV, and the energy barrier on H-coadsorbed Fe(100) was 0.15 eV. From a bridge to a hollow, the energy barriers were 0.05 eV and 0.06 eV for clean and H-coadsorbed surfaces, respectively (Fig. 9 and Table 4).

Ferrin and Kandoi [7] report the diffusion of H from the surface to the sub-surface of the H layer on several (100) transition metal surfaces. In the case of Fe, the value was reported to be 0.14 eV for surface diffusion and 0.22 eV for the diffusion of H atoms from the surface to the bulk.

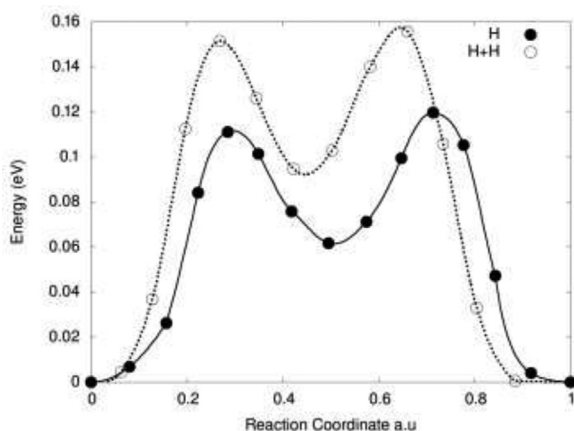
The values presented here are in agreement with previous values reported by Del V Gomez et al. [2], where the barriers to the diffusion of H on metal surfaces were reported as 0.2 and 0.4 eV for Pt and Au, respectively. Kristinsdóttir and Skúlason [15] reported values for the diffusion of H on metal surfaces of around 0.15 eV.

#### 4. Diffusion coefficients for C, O and H on Fe(100) surfaces

The diffusion of adsorbates on metal surfaces is a key aspect of the description of these reactions on surfaces. Although there are no perfectly ordered surfaces at the atomic level, a parameterization of the surface is convenient for use in our model. In this case, we will take well-defined adsorption sites where the adsorbates occupy specific low energy sites, at which the adsorbates are



**Fig. 7.** Diffusion of a hydrogen atom on an Fe(100) surface: (a) initial state at a hollow site, (b) diffusion to a bridge site; (c) final state at an adjacent hollow sites (the H atom is shown in cyan, and the Fe atoms in yellow).



**Fig. 8.** Minimum energy pathway for H diffusion on a clean Fe(100) surface and an Fe(100) surface with 0.5 ML of coadsorbed H (the solid line shows the diffusion on a clean Fe(100) surface, and the dashed line shows diffusion in the presence of 0.5 ML of coadsorbed H).

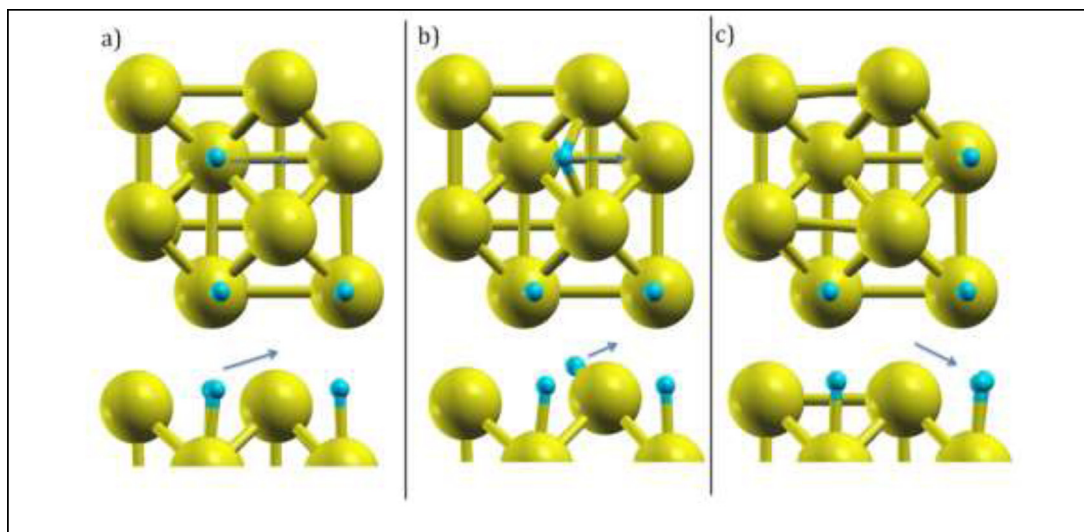
normally chemisorbed. Although the surface is ordered, the movement of an adsorbate on the metal surface can be considered to be stochastic, and for simplicity, this will be assumed to be a two-dimensional movement. Based on these simplifications, it can be shown that the root mean square of the displacement is proportional to both the observation time and to the trace diffusion coefficient, denoted by  $D^*$  [28,29]. In general, for adsorbate diffusion, the mean square of the displacement is expressed as

$$\langle r^2 \rangle = 4tD^* \quad (2)$$

where  $\langle r^2 \rangle$  is the root mean square of the displacement,  $t$  is the observation time and  $D^*$  is the diffusion coefficient, expressed as follows:

$$D^* = \frac{na^2\nu}{4} e^{\left(\frac{-E_d}{kT}\right)} \quad (3)$$

In this equation, the coordination number  $n$  is  $n = 4$ , as it is a (100) surface;  $a$  is the distance between adsorption sites;  $\nu$  is the frequency (attempts per unit time) of the displacements; and  $E_d$  is the diffusion energy calculated in the previous section for the adsorbates C, O and H. As can be seen from Eq. (2), in order to



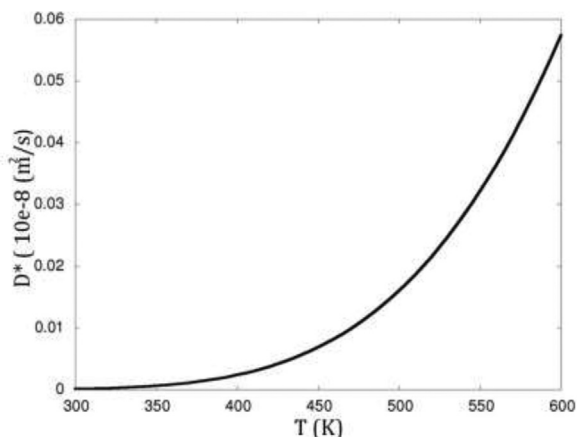
**Fig. 9.** Diffusion of hydrogen atoms on Fe(100) surfaces with 0.5 ML of coadsorbed H: (a) initial state at a hollow site, (b) diffusion to a bridge site, (c) final state at an adjacent hollow site (H atoms are shown in cyan and Fe atoms in yellow).



**Table 5**

Parameters obtained for the diffusion coefficients for carbon, oxygen and hydrogen.

Species	$a$ [m]	$k_d$ [N/m]	$\nu$ [1/seg.]	$E_d$ [eV]
C	$2.85 \times 10^{-10}$	18	$6.76 \times 10^{12}$	1.46
O		9.2	$4.18 \times 10^{12}$	0.33
H		4.0	$1.10 \times 10^{13}$	0.11

**Fig. 10.** Diffusion coefficient for an oxygen atom on Fe(100) as a function of temperature, from Eq. (3).

obtain the complete coefficient of diffusion for each adsorbate, we need to calculate the frequency of the displacements,  $\nu$ . Although the value of  $\nu$  can be approximated using transition state theory or more sophisticated theoretical tools, in our case we used a simple approximation previously reported by Giménez et al. [28,29]. This approach preserves sufficient characteristics to enable us to draw clear conclusions and interpretations of the behavior of the system. Any potential around the minimum as appears to be harmonic for small oscillations. In the same way, the initial state of each adsorbate in a hollow site represents a minimum of the energy at the surface. As each adsorbate diffuses toward the next adsorption site, the energy begins to increase with a parabolic form. The initial part of the diffusion barrier can be approximated to a parabola in each case, allowing us to obtain  $k_d$  (Table 5). The parabolas formed for the initial part of the diffusion by a graph of energy versus the diffusion coordinates can be related to the behavior of energy in a simple harmonic oscillator, where the energy is given by

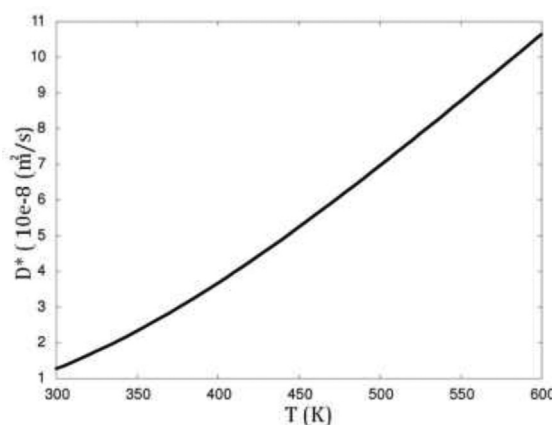
$$E = \frac{k_d x^2}{2} \quad (4)$$

where

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k_d}{m}} \quad (5)$$

Here in Eq. (4),  $x$  represents the diffusion pathway points, and  $m$  in Eq. (5) represents the mass of adsorbed atom. By performing a second-order regression of the points calculated for the diffusion process,  $k_d$  is obtained from Eq. (4) and replaced in Eq. (5) to obtain the diffusion frequency of involved atoms  $\nu$ , as shown in Table 5.

When these parameters are applied to Eq. (3), the variation in the diffusion coefficient for each adsorbate as a function of temperature can be found. In the case of C, it was found that the value of the diffusion coefficient was very low and therefore negligible i.e., less than  $1 \times 10^{-12} \text{ m}^2/\text{s}$ . It can therefore be concluded that carbon does not undergo superficial diffusion at the temperatures examined in this case (300–600 K). On the other hand, it can be seen from Fig. 10 that a low diffusion coefficient was found for oxygen

**Fig. 11.** Diffusion coefficient for a hydrogen atom on a Fe(100) surface as a function of the temperature, from Eq. (3).

at temperatures between 300 and 450 K, which indicates that this adsorbed species is not very active at low temperatures and becomes progressively activated above 450 K.

Between 450 and 600 K and above, the diffusion coefficient of oxygen increases rapidly, and between 300 K and 600 K, the diffusion coefficient increases by a factor of 590. In the case of hydrogen, we see a much higher activity; this is as expected, due to its low diffusion barrier and its high pre-exponential frequency. In the same temperature range, the diffusion of hydrogen on the surface is up to hundred times greater than for oxygen (Fig. 11).

From the results reported above, it can be observed that in all temperature ranges, H is the most active species in terms of diffusion, and this influences the formation of all surface species. It can therefore be concluded that the formation of oxygenated species,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  is greater at high temperatures, due to the activation of oxygen diffusion on the surface. The increase in the diffusion of both O and H with respect to temperature is of great interest. The behavior observed here is in agreement with the experimental results reported by Dry et al. [30] and Rhode et al. [31], where the production of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  increased in Fischer-Tropsch synthesis on Fe surfaces as a function of the temperature. Dry et al. [30] investigated a temperature range from 225 to 265 °C (498–538 K), in which the production of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  increased with temperature. In the same way, the results reported by Rhode et al. [31] showed the same behavior for the formation of  $\text{H}_2\text{O}$  at temperatures between 30 and 220 °C (303–493 K). Based on the results obtained in this work that support previously published experimental values, a mechanism for the formation of hydrogenated chains can be inferred. The formation of the initial species CH,  $\text{CH}_2$  and  $\text{CH}_3$  occurs due to the diffusion of superficial hydrogen. As shown in this section, H is the species that diffuses the most on the surface of Fe (100), while C does not undergo diffusion and the diffusion of O is activated at temperatures above 450 K.

## 5. Conclusions

In the present work, we studied the diffusion of carbon, oxygen, and hydrogen species on the surface of Fe(100). We also analyzed the effect of hydrogen coadsorption on the diffusion pathway of the same species. The binding energies of C, O and H atoms on a clean surface and an H-coadsorbed surface showed that the presence of hydrogen decreased the strength of the binding between the C and O atoms and the Fe(100) surface, from  $-9.05$  to  $-8.21$  eV for C, and from  $-6.73$  to  $-6.57$  eV for O. This effect arises because hydrogen takes a charge density from the Fe atoms. In the case of an H-coadsorbed surface, the effect is reversed, and the

adsorption energy increases from  $-2.24$  to  $-2.31$  eV. The values for the diffusion barriers for each atom adsorbed onto the surface and the variation in these values due to the coadsorption of hydrogen showed that the presence of hydrogen causes an increase in the diffusion barrier in all cases. For C atoms, the barrier increases from  $1.29$  to  $1.46$  eV, while for O atoms, it increases from  $0.33$  eV along the pathway from hollow to bridge sites to  $0.30$  for a transition from bridge to hollow sites. On the other hand, in the presence of H, the diffusion barrier for oxygen was  $0.53$  eV from hollow to bridge sites and  $0.18$  eV from bridge to hollow sites. This indicates that hydrogen favors the adsorption of oxygen onto hollow sites. The diffusion barrier for hydrogen from hollow to bridge sites on clean Fe(100) surfaces was  $0.11$  eV, and from bridge to hollow sites, it was  $0.05$  eV. In the H presence, the diffusion barriers for the same pathways were  $0.15$  and  $0.06$  eV, respectively. The calculation of the diffusion frequency for C, O and H atoms present the values of  $6.67 \times 10^{12}/s$ ,  $4.18 \times 10^{12}/s$ , and  $1.10 \times 10^{13}/s$ , respectively. From these values, it can be seen that hydrogen as the most active species on the surface. This is confirmed by the value of the diffusion coefficient calculated as a function of the temperature. For C and O, mobility was activated above  $1200$  and  $450$  K, respectively, while H was active over the entire range of temperatures studied. Our results for the diffusion barriers are consistent with previous observations and provide a valuable understanding of the mechanism underlying this phenomenon, since at high temperatures, there is a greater production of oxygenated species. An important conclusion from this study is that the activity on the surface is mainly due to the diffusion mechanisms of hydrogen atoms.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

### Acknowledgments

The authors gratefully acknowledge financial support from the Dirección Nacional de Investigaciones and La Facultad de Ciencias of the Universidad Nacional de Colombia, and Mincienas under the program "CONVOCATORIA PROGRAMA DE ESTANCIAS POST-DOCTORALES EN ENTIDADES DEL SNCTel 2019".

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