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Lateral interactions effect in the kinetic Monte Carlo study of the CO_2 hydrogenation reaction on Ni(111)

Efecte de les interaccions laterals en l'estudi cinètic Monte Carlo de la reacció d'hidrogenació de CO₂ sobre Ni(111)

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IDENTIFICATION AND REFLECTION ON THE SUSTAINABLE DEVELOPMENT GOALS (ODS)

This work is a study of a reaction that produces methane from CO₂. This reaction (water-gas shift reaction) could form an energy cycle, in which from a very hazardous waste for the environment (CO₂), which comes from the combustion of fossil fuels, a new fuel is formed, which can become again a reactant of a new combustion reaction. Therefore, out of the five major areas proposed by the 2030 Agenda, this work pertains to both Planet and Prosperity. Unfortunately, this is a very unfavourable reaction energetically, so there are a large number of studies about what could be the ideal catalyst and what conditions for methane production.

Regarding the ODS, for the Planet block, this work is related to ODS 13, climate action. This is because CO_2 is one of the main gases that produces the greenhouse effect, therefore reducing emissions by industries would partly reduce the concentration of CO_2 in the atmosphere, helping to curb this harmful effect.

Moreover, with regard to the prosperity block, there are several ODS into which the work fits. First, ODS 7, affordable and clean energy. Since an energy cycle would be created, thanks to the combustion of fuels created from the methane produced, the consumption of fossil fuels would be reduced. This methane would not be enough to cover the global energy demand, unfortunately, but it would already be a step towards reducing the consumption of fossil fuels. Furthermore, it also fits into ODS 9, industry, innovation and infrastructure. This is because the studies of this reaction for methane production are based at the industrial level. A common goal they have is to minimize the large amounts of CO₂ that they can emit. In this way, it would be possible to develop a technology that would help the sustainability of the planet.

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1. SUMMARY

Several studies on the CO₂ hydrogenation reaction have been carried out in recent years. These aimed to find a way to transform the CO2 molecule into CH4, in order to reduce emissions of the dioxide into the atmosphere by creating an energetic cycle, where the residue of a combustion is transformed into a new possible fuel. In this reaction, a total of 86 elementary processes are found, which include a total of 25 different species. These different processes create a competitiveness between them, which ends up leading to the formation of CO as the main product of this reaction. In this study, simulations of this reaction catalyzed on the Ni (111) surface have been carried out by means of the kinetic Monte Carlo method, using the Zacros program in its version 3.01. Thanks to this, it has been possible to observe the complete path carried out by these reactions under different levels of pressure and temperature. Moreover, a dependence of the processes taking place on the coverage of the H species on the catalytic surface, the species with the highest average coverage of all those recorded, was observed. This fact produces an interaction between any intermediate species of the reaction when it meets an H occupying an adjacent place on the catalytic surface. This effect is called lateral interaction, and has been the main object of study of this work. In addition, it has been observed how the reaction changes when the value of the lateral interactions is modified, creating a greater attraction or repulsivity between the neighboring species. With this, significant changes have been recorded in the energy barriers of the most important processes of this reaction, the dissociation of CO₂ and CO, and the desorption of these two species.

Keywords: Lateral interactions, reverse water-gas shift reaction, Sabatier reaction, nickel (111), kinetic Monte Carlo, catalytic activity, energy barrier.

2. RESUMEN

Múltiples estudios acerca de la reacción de hidrogenación de CO₂ han sido realizados en los últimos años. Estos pretendían encontrar una manera de transformar la molécula de CO2 en CH4, con el fin de reducir las emisiones del dióxido a la atmósfera creando un ciclo energético, donde el residuo de una combustión se transforma en un nuevo posible combustible. En esta reacción, se encuentran un total 86 procesos elementales, los cuales incluyen un total de 25 especies diferentes. Estos procesos diferentes crean una competitividad entre ellos, la cual acaba derivando en la formación de CO como producto principal de esta reacción. En este estudio, se han realizado simulaciones de esta reacción catalizadas en la superficie de Ni (111) mediante el método cinético Monte Carlo, utilizando el programa Zacros en su versión 3.01. Gracias a este, se ha podido observar el camino completo que realizan estas reacciones bajo diferentes niveles de presión y temperatura. Por otra parte, se ha observado una dependencia de los procesos, que tenían lugar, hacía el recubrimiento de la especie H sobre la superficie catalítica, especie con mayor recubrimiento medio de todas las registradas. Este hecho produce una interacción entre cualquier especie intermedia de la reacción cuando se encuentra con un H ocupando un lugar adyacente en la superficie catalítica. A este efecto se le llama interacción lateral, y ha sido el objeto de estudio principal de este trabajo. Además, se ha observado qué variaciones sufre la reacción cuando se modifica el valor de las interacciones laterales, creando una mayor atracción o repulsividad entre las especies vecinas. Con esto, se han registrado cambios significativos en las barreras energéticas de los procesos más importantes de esta reacción, la disociación del CO₂ y del CO, y la desorción de estas dos especies.

Paraules clau: Interacciones laterales, reacción de desplazamiento del gas agua, reacción de Sabatier, níquel (111), Monte Carlo cinético, actividad catalítica, barrera energética.

3. INTRODUCTION

The recent growth of the world economy has resulted in an increase in global energy demand. This has caused the atmospheric CO₂ level to rise because of a consequent augment in the use of carbon-rich fossil fuels. Therefore, the development of alternative green energy resources would be desirable, reducing the consumption of fossil fuels ^{1,2}. Unfortunately, these green energies cannot cover the global energy demand. This is the main reason why fossil fuels are still the main source of energy. Hence, one of the most interesting fields of study in chemistry nowadays is the conversion of CO₂ into new chemical products that can be used in industry: CO, CH₄, methanol and formaldehyde as main options ^[3-6]. Thus, in addition to reducing CO₂ emissions, we are generating new chemical compounds that can be used as energy sources, creating an energy cycle of great economic interest.

At this point, heterogeneous catalysis plays an essential role in the conversion of CO₂. The high thermochemical stability of CO₂ makes it difficult to achieve the catalytic conversion into fuels or hydrocarbon products. Through reacting with more reactive molecules such as H₂, the overall reaction can become less endothermic, making CO₂ conversion thermodynamically feasible ^[4]. In order to convert CO₂ into CH₄, numerous researches have been devoted to the catalytic performance of noble metals such as Rh, Ru, Pd, Pt and Ir for this reaction. It is generally accepted that Rh and Ru showed both high activity and stability in CH₄ dry reforming, while Pd, Pt and Ir were less active and more prone to deactivation ^[7,8]. However, considering the aspects of high cost and limited availability of noble metals, it is more practical, from the industrial standpoint, to develop non-noble metal catalysts which exhibit both high activity and stability. Ni-based catalysts have been widely investigated due both to their similar activity and relatively low price when compared with noble metals^[9]. Furthermore, different theoretical studies have focused on the surface of Ni (111). This is because it constitutes the most stable Ni surface and, therefore, Ni (111) facets would predominate in the large Ni nanoparticles that are present in the industrial catalysts ^[10].

In the present study we have introduced high-fidelity kinetic Monte Carlo (kMC) simulations to obtain an insight into the reaction mechanism of CO₂ hydrogenation in Ni (1 1 1) and, thus, to be able

to quantify how the lateral interactions, that these mechanisms undergo, can affect the overall reaction. Additionally, the variations that the reaction undergoes when subjected to different levels of pressure (total and partial values) and temperature will be observed. These simulations are based on the Density Functional Theory (DFT) studies presented earlier by Lozano-Reis et al. ¹⁰, where energy barriers were calculated for all elementary processes involved in CO₂ hydrogenation.

3.1. COMPUTATIONAL METHODS AND MODELS

The present reaction model involves 25 different species and a total of 86 elementary processes, used in an earlier study ^[10], as shown in Figure 1. The kMC method is the most advanced and sophisticated kinetic technique and is able to treat catalytic systems with structural complexity, extensive reaction networks and the molecular interactions that one may find in a typical heterogeneous catalytic reaction. Regarding the experimental process, this method simulates the system time evolution at the molecular level, in such a way that each elementary process has an associated transition rate ^[11,12].



Figure 1. Reaction network proposed for the CO₂ hydrogenation (left) and H₂ oxidation (right) ^[10]. Processes belonging to the RWGS reaction are: redox pathway, represented by color red, formate pathway by dark blue and carbonyl pathway by yellow. Moreover, the Sabatier reaction is composed of: the C hydrogenation pathway, by color green, HCO hydrogenation pathway, by light blue, and COH hydrogenation pathway, by orange. The black lines represent elementary steps connecting different pathways.

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3.1.1. Stochastic temporal evolution

Essentially, kMC simulation is a random walk through all the processes that can occur at each instant of time, depending on the species that are adsorbed on the lattice sites. These elementary processes, independent of each other, follow a stochastic selection method to see which one occurs. Thus, a probability $P_i(t)$ that the system is in state (configuration) i at time t can be obtained by the Master equation, where k_{ij} is the transition probability per unit time (i.e., rate constant) that the system will undergo the state transition $i \rightarrow j$ (i.e., a given elementary process). This is a lost-gain equation, which can be derived from first-principles:

$$\frac{dP_i(t)}{dt} = \sum_{j \neq i} k_{ji} P_j(t) - \sum_{j \neq i} k_{ij} P_i(t)$$
(1)

The master equation gives the evolution as a balance of probabilities accounting for the system leaving state i towards other states j or entering state i from any other state j, depending on the kinetic rate constants k_{ij}. Once the probabilities of all possible elementary processes at each instant (t) are obtained, accumulative functions are calculated, which can be expressed as a range of possibilities. After this, a uniform pseudorandom number is generated, which is compared with the accumulative functions to select the process that occurs. This procedure is updated at the end of each process to recalculate the probabilities P_i of the following process/configuration, thus generating a cycle that determines the evolution of the different steps of the reaction ^[13].

3.1.2. Determining the rate constants of an elementary process

Many kMC simulations in the past have used approximate rate constants in the definition of transition probabilities, some of them employing logical guesses based on experimental constants, and others fitting rate constants to experimental data, or even using arbitrary values with no tie to the true reaction. These approximations have limitations, while more systematic and accurate parameterization can be achieved using first-principles data in conjunction with statistical mechanical frameworks such as Transition State Theory (TST). Using the TST method, the kinetic constant is calculated by considering the probability of the system visiting the transition state, and averaging over the speeds with which it is traveling towards the product state. The final result for the TST rate constant k_{TST} is ^[14]:

$$k_{TST}(T) = \frac{K_B T}{h} \frac{K_B T}{P^0} \frac{Q^{\ddagger}}{Q_{reac1} \cdot Q_{reac2}} e^{-\Delta E^{0 \neq}/K_B T} \text{ (e.g. ,for a bimolecular process)}$$
(2)

where h denotes Planck's constant, K_B is the Boltzmann constant, P^0 is 1 bar, $\Delta E^{0\neq}$ is the energy barrier including zero-point energy correction and Q_i is the molecular partition function for the transition state (Q[‡]) and for the reactants (Q_{reac1} and Q_{reac2}). This molecular partition function contains the contributions of electronic, nuclear, vibrational, rotational and translational degrees of freedom:

$$Q = q_{elec} \cdot q_{nuc} \cdot q_{vib} \cdot q_{rot} \cdot q_{trans}$$

(3)

Moreover, the energy barrier is often strongly dependent on the locations of spectator adsorbed species within the local neighbourhood of the reactants and/or products. Such a dependence arises due to lateral interactions exerted by the spectators to the reactants/products species, which may stabilize or destabilize initial, transition and final states. In this way, the lateral interactions can act in an attractive way, decreasing the value of $\Delta E^{0\neq}$, or on the other hand, in a repulsive way, causing an increase in $\Delta E^{0\neq}$.

Therefore, lateral interactions not only affect a process itself but also its reverse one, and hence its reaction energy (ΔE_{rxn}^0):

$$\Delta E_{rxn}^{0} \left(\boldsymbol{\theta} \right) = \Delta E_{fwd}^{0\neq} \left(\boldsymbol{\theta} \right) - \Delta E_{rev}^{0\neq} \left(\boldsymbol{\theta} \right)$$
(4)

which is the difference between forward and reverse energy barriers of an elementary event for any arrangement of spectators in the neighbourhood of the reaction, for a given configuration σ (i.e., coverage). Furthermore, using the Brønsted–Evans–Polanyi relation (BEP) ^[15], the forward energy barrier can be expressed for any configuration σ , in terms of the energy barrier $\Delta E_{fwd}^{0\neq}(0)$ and reaction energy $\Delta E_{rxn}^{0}(0)$, both at the zero-coverage limit ($\theta = 0$):

$$\Delta E_{fwd}^{0\neq}(\boldsymbol{\theta}) = max\left(0, \Delta E_{rxn}^{0}(\boldsymbol{\theta}), \Delta E_{fwd}^{0\neq}(0) + \omega \cdot \left(\Delta E_{rxn}^{0}(\boldsymbol{\theta}) - \Delta E_{rxn}^{0}(\boldsymbol{\theta})\right)\right)$$
(5)

The reverse energy barrier can be obtained with a similar equation.

In this work, the effect of lateral interactions for the hydrogenation reaction of CO₂ at different values of pressure and temperature will be studied. This will allow robust predictions to be made about how the system will evolve under different conditions.

4. OBJECTIVES

The main goal of this work is the study of the effect of lateral interactions in the kinetic Monte Carlo study of the CO_2 hydrogenation reaction on Ni (111). This study will be carried out using the Zacros program, in which it will be possible to simulate the reaction to different conditions in order to see its evolution for each one.

5. EXPERIMENTAL SECTION

In this work, Zacros code (version 3.01) has been used for the experimental section. Thanks to this software, it has been possible to simulate and record, at the molecular level, each elementary process that occurs in the CO₂ hydrogenation reaction. For these simulations, the hexagonal symmetry of the Ni (111) surface has been mimicked using a lattice model consisting of a twodimensional hexagonal periodic grid of 8 x 8 points. In this lattice, each adsorbed molecule can interact with its 6 near neighbours in the hexagonal lattice. The effect of these lateral interactions will be studied, observing how these modify the production of the reaction by making them more attractive or repulsive.

Moreover, DFT calculations made by Lozano-Reis et al. published in ACS catalysis ¹⁰ have been used in this work. These calculations are about the adsorption energies of the intermediate species at their most favourable sites and the reaction energies and energy barriers for both forward and backward processes. On the other hand, some small errors were found and corrected in the values of the lateral interactions of this earlier publication. These corrected values are the ones that have been used as a reference for the study.

From here, a total of different 192 simulations have been made in order to study the following effects. First, it was observed whether the lateral interactions really influenced the production of the reaction at different pressure and temperature values. For this purpose, a simulation without lateral interactions was compared with another simulation with the corrected values. Once it was observed that there was an effect of lateral interactions, the values of the most important lateral interactions observed were modified. The lateral interactions to be modified were chosen by observing that the processes most frequently performed in the simulations were always the same. These lateral interactions were CO₂-H, H-H, CO-H and O-H. Simulations were performed for each of these lateral interactions in case they were more attractive, and also in case they were more repulsive. In addition, for each simulation, all the processes carried out were recorded, so that the Turnover Frequency (TOF) and the average coverages for each simulation could be calculated. Also, the energy barriers of the most significant processes were recorded along with the neighbouring adsorbed species each time the elementary process in question was carried out.

6. SIMULATIONS WITH AND WITHOUT LATERAL INTERACTIONS

Firstly, kMC simulations were performed without lateral interactions for different pressure and temperature values, thus creating an ideal model in which neighbouring species did not affect the elementary processes occurring at each instant of time. At the end of these simulations, a record of all the processes that had occurred was obtained, in addition to another record where the molecules that had been adsorbed at each instant could be observed. From these documents, it was possible to calculate the TOF of the reaction and an average coverage of H, CO, O, CO₂ and OH species. These results are shown in Figure 2.



Figure 2. Event frequency of the CO₂ hydrogenation reaction for four different operating conditions without lateral interactions: (a) T = 573.15 K, P H₂ = 0.8 bar, P CO₂ = 0.2 bar; (b) T = 673.15 K, P H₂ = 0.8 bar, P CO₂ = 0.2 bar; (c) T = 573.15 K, P H₂ = 8 bar, P CO₂ = 2 bar; (d) T = 673.15 K, P H₂ = 8 bar, P CO₂ = 2 bar.

As can be seen, in this model without lateral interactions, the reaction follows the reverse of watergas shift reaction through the redox pathway. There are also some formate and carbonyl pathway processes recorded, but these are not relevant as they end up reversing. Here it is clearly observed that as the pressure and/or temperature values increase, the TOF of the reaction increases in the same way. In addition, the difference between the forward and reverse reaction frequencies of CO₂ adsorption corresponds to the number of CO₂ dissociation processes that have taken place. Thus, it follows that all the dissociated CO₂ forms CO, which desorbs and yields the TOF of the reaction. In this way, and as seen below, this will be the main pathway that the reaction will take in any given condition. Furthermore, an average coverage of adsorbed species has been calculated (Table 1).

Average coverage	T = 573.15 K P _T = 1 bar	T = 673.15 K P _T = 1 bar	T = 573.15 K P _T = 10 bar	T = 673.15 K P _T = 10 bar
Өн	31.7 ± 0.3 %	6.9 ± 0.2 %	60.3 ± 0.3 %	35.6 ± 0.3 %
θco	0.0481 ± 0.0007 %	0.0094 ± 0.0002 %	0.178 ± 0.0005 %	0.0306 ± 0.0005 %
θο	0.0180 ± 0.0003 %	0.0417 ± 0.0006 %	0.0363 ± 0.0006 %	0.0363 ± 0.0006 %
θ _{CO2}	0.545 ± 0.006 %	0.675 ± 0.006 %	0.852 ± 0.006 %	0.690 ± 0.006 %
ө _{он}	0 ± 0 %	0.073 ± 0.001 %	0.0028 ± 0.0001 %	0.0613 ± 0.0009 %

Table 1. Average coverage values of some adsorbed species during the simulations under different working conditions without lateral interactions.

As can be seen, practically the only species that has a significant adsorption percentage is H. It varies as expected according to the known laws of physics. As the temperature increases, an increase in energy is granted, which allows it to more easily overcome the energy barrier of the desorption process, hence, the higher the temperature, the lower the coverage. On the other hand, as the pressure increases, there is a greater number of H_2 molecules that dissociate, which makes H adsorption larger. Both physical effects have been observed in all the coverage records of all species in the simulations performed.

Once these results were obtained, a simulation was performed with the corrected values of the ACS Catalysis data of Lozano-Reis et al. ¹⁰, in which the lateral interaction of CO₂ with a nearby H acquired a more attractive value than it really is. Therefore, this lateral interaction was corrected to its real value (i.e., from -0.114 eV to -0.003 eV). The results shown in Figure 3 were obtained for these simulations with all lateral interactions included, for the same pressure and temperature conditions.



Figure 3. Event frequency of the CO₂ hydrogenation reaction under four different operating conditions including corrected lateral interactions: (a) T = 573.15 K, P H₂ = 0.8 bar, P CO₂ = 0.2 bar; (b) T = 673.15 K, P H₂ = 0.8 bar, P CO₂ = 0.2 bar; (c) T = 573.15 K, P H₂ = 8 bar, P CO₂ = 2 bar; (d) T = 673.15 K, P H₂ = 8 bar, P CO₂ = 2 bar; (d) T = 673.15 K, P H₂ = 8 bar, P CO₂ = 2 bar; (d) T = 673.15 K, P H₂ = 8 bar, P CO₂ = 2 bar; (d) T = 673.15 K, P H₂ = 8 bar, P CO₂ = 2 bar; (d) T = 673.15 K, P H₂ = 8 bar, P CO₂ = 2 bar; (d) T = 673.15 K, P H₂ = 8 bar, P CO₂ = 2 bar; (d) T = 673.15 K, P H₂ = 8 bar, P CO₂ = 2 bar; (d) T = 673.15 K, P H₂ = 8 bar, P CO₂ = 2 bar; (d) T = 673.15 K, P H₂ = 8 bar, P CO₂ = 2 bar; (d) T = 673.15 K, P H₂ = 8 bar, P CO₂ = 2 bar; (d) T = 673.15 K, P H₂ = 8 bar, P CO₂ = 2 bar.

Together, the respective average coverages are shown in Table 2.

Average coverage	T = 573.15 K P _T = 1 bar	T = 673.15 K P⊤ = 1 bar	T = 573.15 K P _T = 10 bar	T = 673.15 K P⊤ = 10 bar
θ _Η	12.50 ± 0.08 %	16.5 ± 0.1 %	17.60 ± 0.03 %	15.38 ± 0.09 %
θ _{co}	0 ± 0 %	0 ± 0 %	0.123 ± 0.002 %	0.080 ± 0.001 %
θο	0.073 ± 0.001 %	0.320 ± 0.004 %	0.082 ± 0.001 %	0.321 ± 0.004 %
θ _{CO2}	0.836 ± 0.006 %	0.0641 ± 0.006 %	0.576 ± 0.006 %	0.841 ± 0.006 %
θ _{он}	0.0132 ± 0.0002 %	0.0400 ± 0.0006 %	0.0087 ± 0.0001 %	0.0312 ± 0.0004 %

Table 2. Average coverage values of some species during the simulations under different working conditions including lateral interactions.

Figure 3 shows that the effects of temperature and pressure on TOF follow the same pattern as in Figure 2. It is also observed that by adding the lateral interactions, the TOF of the reactions has decreased. This decrease in TOF is due to the direct effect that lateral interactions have on each process given in the reaction. These interactions, as described above, stabilize or destabilize configurations of nearby species on the lattice, giving rise to a new value for the energy barrier of each process, and thus modifying the overall kinetics of the reaction. By contrast, at 10 bar and 573.15 K we observe the opposite. The reason is given mainly by the large amount of H atoms adsorbed at these conditions without lateral interactions. The high H₂ pressure at 573.15 K causes a larger H adsorption than desorption, resulting in a large number of diffusion processes of this species, which creates a competitive effect with the RWGS reaction, decreasing the TOF.

7. EFFECT OF THE MOST IMPORTANT LATERAL INTERACTIONS

A series of lateral interactions have been chosen based on the processes observed and the species adsorbed in the first simulations. These are: CO₂ - H, CO - H, H - H and O - H. As seen previously, the species that adsorbs the most is the H, so all the lateral interactions studied are based on this species. Thus, both more attractive and more repulsive values have been adopted for these interactions. Subsequently, additional simulations have been considered for each simulation, obtaining the results shown below.

7.1. EFFECT OF CO₂ - H INTERACTION

In the following simulations, the results obtained in Figure 3 ($LI_{CO2-H} = -0.003 \text{ eV}$) were compared with those obtained from different values of the CO₂-H lateral interaction. To start with, simulations were performed with the values published in ACS catalysis ($LI_{CO2-H} = -0.114 \text{ eV}$), since the only substantial erroneous value was that of this lateral interaction. Subsequently, simulations were performed with a value of this lateral interaction more attractive ($LI_{CO2-H} = -0.214 \text{ eV}$) and one more repulsive ($LI_{CO2-H} = 0.097 \text{ eV}$), as shown in Figure 4.



Figure 4. Event frequency of the CO_2 hydrogenation reaction four different values of the lateral interaction CO_2 - H at 573.15 K and P H₂ = 0.8 bar, P CO₂ = 0.2 bar: (a) LI _{CO2-H} = -0.003 eV; (b) LI _{CO2-H} = 0.097 eV; (c) LI _{CO2-H} = -0.114 eV; (d) LI _{CO2-H} = -0.214 eV.

We observe that when the lateral interaction becomes more attractive, the TOF of the reaction tends to increase. This is an effect observed in all simulations performed for these changes in the CO₂ - H lateral interaction at different pressure and temperature values. However, this is not what was expected to be obtained, since by making a lateral interaction more attractive, it stabilizes the state it affects, increasing the effective energy barrier for that process. Because of this, the first idea before seeing the results was that the TOF would decrease as the lateral interaction took on more negative values. This is because the reaction and its TOF do not depend on only one process, and although the lateral interaction greatly affects CO₂ dissociation, other competitive processes are also affected. This effect will be studied in more detail in the next section. Additionally, the corresponding average coverage values have been presented in Table 3 for all lateral interaction values.

Average coverage	LI _{CO2-н} = -0.003 eV	LI _{CO2-н} = 0.097 eV	LI _{CO2-н} = -0.114 eV	LI _{CO2-н} = -0.214 eV
θ _Η	12.50 ± 0.08 %	12.22 ± 0.07 %	12.94 ± 0.07 %	13.97 ± 0.08 %
θco	0±0%	0.0235 ± 0.0005 %	0.0363 ± 0.0006 %	0.158 ± 0.002 %
θο	0.073 ± 0.001 %	0.093 ± 0.001 %	0.253 ± 0.005 %	0.599 ± 0.009 %
θ _{CO2}	0.836 ± 0.006 %	0.762 ± 0.006 %	0.654 ± 0.006 %	2.10 ± 0.05 %
Ө ОН	0.0132 ± 0.0002 %	0.0087 ± 0.0001 %	0 ± 0 %	0.0203 ± 0.0003 %

Table 3. Average coverage value of some species during the simulations for different values of the CO₂-H lateral interaction, at 573.15 K and P H₂ = 0.8 bar, P CO₂ = 0.2 bar.

In contrast to those observed in the TOFs, Table 3 shows that as the lateral interaction becomes more attractive, stabilizing the CO_2 - H configuration, the average coverages of these two species increases, as expected. This effect is observed in all simulations performed with these values of the lateral interaction at different pressure and temperature values, except for the case of LI_{CO2-H} = -

0.214 eV at 573.15 and 10 bar. In this case, the results for TOF and coverages were different. Thus, a much lower TOF was obtained (Figure 5). In addition, an average H coverage value of 37.55% and a CO_2 coverage value of 56.99% were obtained. This is mainly because this value of the lateral interaction turns out to be too attractive for the system at this pressure, a situation of higher adsorbed H species. This results in the configuration of CO_2 with neighbouring H being too stable, producing no new process, only remaining adsorbed on the lattice. However, when simulations are performed at 673.15 K, the system obtains an increase in energy due to the temperature increment, which causes the reaction to return to the patterns shown above.



Figure 5. Event frequency of the CO₂ hydrogenation reaction with a value of Ll_{CO2}-H = -0.214 at 573.15 K and 10 bar.

7.2. EFFECT OF CO - H INTERACTION

In the following simulations, the results obtained in Figure 3 ($LI_{CO-H} = 0.054 \text{ eV}$) were compared with those obtained from different values of the CO-H lateral interaction. In order to compare correctly, a more repulsive value of this lateral interaction ($LI_{CO-H} = 0.154 \text{ eV}$) and a more attractive value ($LI_{CO-H} = -0.046 \text{ eV}$) have been taken. Thus, the frequencies and TOF are shown in Figure 6.



Figure 6. Event frequency of the CO₂ hydrogenation reaction for two different values of the CO - H lateral interaction at 573.15 K and P H₂ = 0.8 bar, P CO₂ = 0.2 bar: (a) LI _{CO - H} = 0.154 eV; (b) LI _{CO - H} = -0.046 eV.

Here we observe the same effect as in the previous case, the TOF tends to increase as the CO - H lateral interaction becomes more attractive. This is also because competitive processes are equally affected by lateral interaction. The corresponding average coverage values have been presented in Table 4.

Average coverage	LI _{CO-H} = 0.154 eV	LI _{CO-H} = - 0.046 eV
θ _Η	12.86 ± 0.06 %	12.32 ± 0.07 %
θ _{co}	0.0074 ± 0.0001 %	0.169 ± 0.002 %
θο	0.0408 ± 0.0006 %	0.186 ± 0.003 %
θ _{CO2}	0.836 ± 0.006 %	0.837 ± 0.006 %
θ _{OH}	0±0%	0.0171 ± 0.0003 %

Table 4. Average coverage value of some species during the simulations for different values of the CO - H lateral interaction, at 573.15 K and P H₂ = 0.8 bar, P CO₂ = 0.2 bar.

In this part, no significant difference in coverage has been observed for different values of the lateral interaction in question.

7.3. EFFECT OF H - H INTERACTION

In the following simulations, the results obtained in Figure 3 ($LI_{H-H} = 0.27 \text{ eV}$) were compared with those obtained from different values of the CO-H lateral interaction. In order to compare correctly, a more repulsive value of this lateral interaction ($LI_{H-H} = 0.40 \text{ eV}$) and a more attractive value ($LI_{H-H} = 0.14 \text{ eV}$) have been considered. Thus, the results are shown in Figure 7.



Figure 7. Event frequency of the CO₂ hydrogenation reaction for two different values of the H-H lateral interaction at 573.15 K and P H₂ = 0.8 bar, P CO₂ = 0.2 bar: (a) LI H-H = 0.40 eV; (b) LI H-H = 0.14 eV.

In these simulations, at different values of the H-H lateral interaction, minimal differences are observed in the TOF values obtained, which may even include the possible statistics error of the calculation. Furthermore, the calculated average coverages are shown in Table 5.

Average coverage	LI _{H-H} = 0.40 eV	LI _{H-H} = 0.14 eV
θ _Η	13.41 ± 0.07 %	13.58 ± 0.08 %
θco	0.0094 ± 0.0001 %	0.0279 ± 0.004 %
θο	0.102 ± 0.002 %	0.110 ± 0.0002 %
θ _{CO2}	0.813 ± 0.006 %	0.815 ± 0.006 %
θ _{ОН}	0.0112 ± 0.0002 %	0.0057 ± 0.0001 %

Table 5. Average coverage values of some species during the simulations for different values of the H-H lateral interaction, at 573.15 K and P H_2 = 0.8 bar, P CO₂ = 0.2 bar.

These data, both for the effects observed in Figure 7 and for the coverages in Table 5, have been recorded for all simulated pressure and temperature values. Thus, we can state that the H-H lateral interaction does not have a significant effect on the RWGS reaction. This, to some degree, is surprising, since hydrogen is one of the reactants in this reaction, as well as being the molecule with the highest adsorption rate.

7.4. EFFECT OF O - H INTERACTION

In the following simulations, the results obtained in Figure 3 ($LI_{O-H} = 0.118 \text{ eV}$) were compared with those obtained from different values of the O-H lateral interaction. In order to compare correctly, a more repulsive value of this lateral interaction ($LI_{O-H} = 0.218 \text{ eV}$) and a more attractive value ($LI_{O-H} = 0.018 \text{ eV}$) have been taken. Thus, the corresponding following results are shown in Figure 8.



Figure 8. Event frequency of the CO₂ hydrogenation reaction for two different values of the O-H lateral interaction at 573.15 K and P H₂ = 0.8 bar, P CO₂ = 0.2 bar: (a) LI $_{0-H}$ = 0.218 eV; (b) LI $_{0-H}$ = 0.018 eV.

The same effect is observed as in Figure 4 and 6. For more attractive values of the lateral interaction, the TOF increases. This effect is observed for all simulations at different pressure and temperature values. Furthermore, the corresponding average coverages are presented in Table 6.

Average coverage	LI = 0.218 eV	LI = 0.018 eV
θ _Η	12.67 ± 0.08 %	12.42 ± 0.06 %
θ _{co}	0.0153 ± 0.0002 %	0.0101 ± 0.0002 %
θο	0.109 ± 0.0006 %	0.0.0625 ± 0.0009 %
θ _{CO2}	0.672 ± 0.006 %	0.734 ± 0.006 %
θ _{OH}	0±0%	0±0%

Table 6. Average coverage value of some species during the simulations for different values of the O-H lateral interaction, at 573.15 K and P $H_2 = 0.8$ bar, P CO₂ = 0.2 bar.

In this part, no significant difference in coverages has been observed for different values of the lateral interaction in question.

8. ENERGY BARRIERS

The question to see can be how the energy barriers change with each modification of the lateral interactions and hence the overall kinetics of the reaction has been studied.

Thanks to the Zacros program, with a few small modifications to the input, it was possible to record for each process the effective energy barrier that occurred as a result of neighbouring species exerting a lateral interaction. Thus, energy barriers were recorded for the most important processes: CO₂ dissociation, H₂O formation, HCOO formation, OH formation, CO₂ desorption (when the lateral CO₂ - H interaction was modified) and CO desorption (when the lateral CO - H interaction was modified). The idea of recording the HCOO barrier was initially interesting in order to be able to reason why the reaction does not continue to evolve to different pathways other than CO formation and subsequent CO desorption. Unfortunately, for most of the simulations, this process hardly occurred, and in some simulations, it did not occur at all. Therefore, we have not been able to draw any

conclusions from these simulations. Furthermore, the energy barrier obtained for the most important processes with lateral interactions ($\Delta E^{0\neq}(\theta)$) has been compared with the energy barrier for the processes without lateral interactions ($\Delta E^{0\neq}(0)$). These values without lateral interactions (i.e., DFT energy barriers) were published by Lozano-Reis et al. ¹⁰ in ACS catalysis, and are also shown in table 7 for comparison.

Surface process	ΔE ^{0≠} (0) (eV)
CO ₂ dissociation	0.86
H ₂ O formation	1.25
HCOO formation	1.06
OH formation	1.28
CO ₂ desorption	0.14
CO desorption	1.58

Table 7. Energy barriers for processes without lateral interactions expressed in eV, including zero-point energies.

8.1. Energy barriers for different values of the CO_2 - H interaction

With these modifications, the following changes in the energy barrier of CO₂ dissociation and CO₂ desorption have been observed. For the rest of the processes studied, the energy barrier has barely been modified, obtaining the same value for the great majority of the processes recorded. Additionally, this value coincides with the energy barrier without lateral interaction.

Thus, the results for the processes that have undergone modifications are shown in Figure 9 and 10.



Figure 9. Energy barriers of CO₂ dissociation for four different values of the CO₂ - H lateral interaction at 573.15 K and P H₂ = 0.8 bar, P CO₂ = 0.2 bar: (a) LI $_{CO_2 - H} = -0.003$ eV; (b) LI $_{CO_2 - H} = -0.097$ eV; (c) LI $_{CO_2 - H} = -0.114$ eV; (d) LI $_{CO_2 - H} = -0.214$ eV. The value of the energy barrier without lateral interactions for this process (0.86 eV) is shown in green.



Figure 10. Energy barriers of CO₂ desorption for four different values of the CO₂ - H lateral interaction at 573.15 K and P H₂ = 0.8 bar, P CO₂ = 0.2 bar: (a) LI _{CO2-H} = -0.003 eV; (b) LI _{CO2-H} = 0.097 eV; (c) LI _{CO2-H} = -0.114 eV; (d) LI _{CO2-H} = -0.214 eV. The value of the energy barrier without lateral interactions for this process (0.14 eV) is shown in green.

This pattern, together with the average value of the energy barrier, is repeated for all pressure and temperature values, except for the above-mentioned case of $LI_{CO2-H} = -0.214$ eV at 573.15 K and 10 bar (Figure 11).



Figure 11. Energy barrier of CO_2 dissociation (on the left) and CO_2 desorption (on the right) for $LI_{CO2-H} = -0.214$ eV, at 573.15 K and P H₂ = 8 bar, P CO₂ = 2 bar: The value of the energy barriers without lateral interactions for these processes (0.86 eV and 0.14, respectively) are shown in green.

Figure 11 shows how the energy barrier of these two processes has greatly increased. This has caused both processes to be much more expensive to perform, which is why the TOF of these simulations at these conditions is significantly lower. In addition, another effect observed and caused by this is the very high average CO_2 coverage at these conditions, being trapped once adsorbed by the large energy barriers to overcome to react or desorb. However, thanks to the results in Table 9 and 10, it has been possible to better understand the reason why the TOF increases when the CO_2 - H lateral interaction is more attractive, and not the other way around. For this purpose, the kinetic constant was calculated using the TST formula with the energy barrier including the lateral interactions ($\Delta E^{0\neq}(\theta)$). Subsequently, a ratio (r_i) between the kinetic constant for the dissociation process and the kinetic constant for the desorption process was calculated at the same temperature. In this way, the number of times that one process occurs in relation to the other can be determined. Thus, the ratios for the different values of Ll_{CO2} - H at 573.15 K and 1 bar are shown in Table 8.

LI _{со2-н} (eV)	r = k _{dis} /k _{des}
- 0.003	3.8533 · 10-7
0.097	3.1963 · 10 ⁻⁷
- 0.114	5.5575 · 10 ⁻⁷
- 0.214	3.6414 · 10 ⁻⁷

Table 8. Ratios between kinetic constants for different LI CO₂-H values at 573.15 and P H₂ = 0.8 bar, P CO₂ = 0.2 bar.

Thanks to the results shown in Table 8, it can be observed how many CO_2 dissociation processes occur respect CO_2 desorption processes. For the first three results, the relationship between ratio and TOF is direct, higher ratio equals higher TOF. This is because, although the CO_2 - H state is stabilized making the lateral interaction more attractive, there are other competitive processes that are also being affected, such as CO_2 desorption. Thus, fewer of the competitive processes are occurring, increasing the possibility of the dissociation process, which gives a rise to the TOF of the reaction. However, the case of LI = -0.214 is particular, as it has the highest TOF and low ratio relative to the others. This is because there are a large number of H diffusion processes, and by moving with such a high frequency these are easily dislodged from a neighbouring CO_2 position, allowing the production of the processes. That is, for this value of LI, the process depends, to a greater extent in relation to the rest of the values, on the coverage of H and the diffusion of this species.

8.2. ENERGY BARRIERS FOR DIFFERENT VALUES OF THE CO - H INTERACTION

On this occasion, only changes in CO₂ dissociation and CO desorption have been recorded. The results are shown in Figures 12 and 13.



Figure 12. Energy barriers of CO_2 dissociation for two different values of the CO-H lateral interaction at 573.15 K and P H₂ = 0.8 bar, P CO₂ = 0.2 bar: (a) LI CO-H = 0.154 eV; (b) LI CO-H = -0.046 eV. The value of the energy barrier without lateral interactions for this process (0.86 eV) is shown in green.



Figure 13. Energy barriers of CO desorption under two different values of the CO-H lateral interaction at 573.15 K and P H₂ = 0.8 bar, P CO₂ = 0.2 bar: (a) LI _{CO-H} = 0.154 eV; (b) LI _{CO-H} = -0.046 eV. The value of the energy barrier without lateral interactions for this process (1.58 eV) is shown in green.

These changes in the CO - H lateral interaction modify the stability of this state, affecting CO₂ dissociation in a direct way, since CO is a product of this process. However, as in the previous case,

the TOF depends on many other competitive processes, such as diffusions, hence, although the lateral interaction is more attractive, the TOF sees an increase.

8.3. ENERGY BARRIERS FOR DIFFERENT VALUES OF THE H - H INTERACTION

For the different values of this lateral interaction, no changes have been observed in the energy barrier of any of the processes studied, giving as a result in each simulation practically the same values as without interaction, as shown in Table 7. Thus, in these simulations, the TOF is highly dependent on all the competitive processes that have occurred.

8.4. ENERGY BARRIERS FOR DIFFERENT VALUES OF THE O - H INTERACTION

As in section 8.3, no substantial changes in energy barriers have been recorded at different values of this lateral interaction. Thus, in these simulations, the TOF is also highly dependent on all the competitive processes that have occurred

9. CONCLUSIONS

In this work, it has been observed that the CO₂ hydrogenation reaction on Ni (111) is unlikely to produce CH₄ under the temperature and pressure conditions studied. The route to produce CO and H₂O (through RWGS reaction) is the most energetically favourable pathway, with the major part of the elementary processes passing through this route. However, although as well some elementary processes are observed in another routes, they evolve back again through their reversible processes. One solution to be able to observe methane production is the change of the catalyst. Performing all the kMC simulations again but with another metal catalyst (e.g., Ru) could be suitable for this purpose.

First, different kMC simulations with and without lateral interactions, show that the effect of the increase of temperature or pressure, produces a rise of the TOF. Moreover, it has been observed that there is a real effect of these interactions on the yield of the reaction. In general, for simulations including lateral interactions, the TOF tends to decrease with respect to simulations without lateral interactions, at the same T and P conditions. However, there is a possible exception for 573.15 K and 10 bar; under these conditions and without lateral interactions, the average coverage of H has

increased by a large amount, resulting in a large number of competitive processes such as diffusions of this species on the catalytic surface. This has resulted in a decrease of the TOF at these conditions.

Furthermore, the study of the $CO_2 - H$, CO - H, H - H and O - H lateral interactions, modifying their values, show only some effects for $CO_2 - H$ and CO - H. Thus, more attractive lateral interactions produce larger TOFs in both cases. However, at large pressure and low temperatures a decrease of the TOF is observed because there is a poisoning of the lattice due to the large coverage of CO_2 and H.

The analysis of the energy barriers depending on the lateral interactions (i.e., coverage) shows that mainly for $CO_2 - H$ and CO - H lateral interactions, for more attractive values of the lateral interaction, the value energy barrier shifts towards higher values, which means a higher energetic cost for the progress of the process, which should imply a lower TOF. However, the TOF increases because, for more attractive values of the lateral interaction, more CO_2 dissociation processes occurred with respect to its desorption. Therefore, it was the competitiveness of these reactions that could increase the TOF.

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11. ACRONYMS

- BEP: Brønsted-Evans-Polanyi relation
- DFT: Density Functional Theory
- LI: Lateral Interactions
- kMC: Kinetic Monte Carlo
- ODS: Objectius de Desenvolupament Sostenible
- RWGS: Reverse Water-Gas Shift Reaction
- TST: Transition State Theory