Interaction between (H_2; CO_2) and Cu_5Zn_8 to study the effect of catalytic properties using DFT

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The model of CuZn as a metal alloy is obtained from representative experimental data of the catalyst for the transformation of CO_2 to methanol, the surface plane (111) selected from the unit cell detecting by the position of Zn and Cu exhibits interesting regions ("A","B"). From a fundamental point of view, the interaction allows us to study the participation of Zn and Cu followed by CO_2 and H_2 for different separation distances. The molecular interaction by the energy and optimization calculations obtained results that determine important aspects to explain bond length changes of the H-H and O-C-O. Energy values identify potential areas for Zn or Cu where they exhibit attraction, repulsion, and the minimum, in molecules of H_2 and CO_2. The interaction of the hydrogen molecule with the surface in both regions shows bond length changes with a dissociative effect that reaches 0.921 Å by the direct interaction of Zn and Cu. The CO_2 interacting with Zn and Cu reaches a maximum elongation of 1,309 Å. The interaction with H_2 followed by CO_2 in the presence of the surface has physicochemical effects when increased to 3 hydrogen molecules showing the catalytic phenomenon. The calculations use a level of DFT theory with a GGA approximation and DNP base functions to describe the electronic and structural properties.

Keywords: DFT; Cu_5Zn_8; potential; H_2; CO_2.

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1. Introduction

The crude oil transformation industry whose main business is catalysts requires the use of materials obtained from research carried out with good performance to promote reaction mechanisms optimally, however, the hard work in the continuous improvement of the product poses a deep search to offer such improvement. The studies developed in the transformation of CO_2 to methanol where the applicability of methanol as a feedstock for the chemistry of chloromethane, formaldehyde, acetic acid and methyl terbutyl ether (MTBE) [1]. The methanol obtained from the transformation of CO_2 has proposed reaction mechanisms for the different products in several stages where the catalyst used has not yet found its optimal performance. The reaction mechanism for the production of methanol becomes important when considering hydrogenation on CO_2, commonly methanol is produced from natural gas or petroleum, these processes come out of the context of demand and requirement that favor the environment [2]. The transformation of CO_2 into methanol over the last few decads has shown a trend toward developing and synthesizing new catalyst. Useful materials as catalysts where activity is favorable because catalytic sites are the main promoters of the transformation of both CO and CO_2 to methanol or ethanol [3] as reaction products with the use of different types of synthesis under a diversity of chemical elements in the materials such as Cu, Zn, ZnO, Al, Al_2O_3, ZrO and their possible combinations [4-7].

The molecular design is useful to simulate a catalytic process from the atomic point of view with the identification of the reactions promoted by the material, from the calculation of the analysis of results that favor the physicochemical properties verified by the values reported experimentally by mentioning some of the surfaces, pore structure, type, as well as the shape of the catalyst, the impregnation profiles and the stress deformation considered of experimental interest. The experiments begin with the synthesis of the catalyst, followed by the characterization by spectroscopy techniques, for different combinations of elements to obtain ZnCu and ZnO/Cu the choice of surfaces such as Cu(111), ZnCu(111), ZnO/Cu(111), Cu/ZnO(0001), ZnO/Cu/ZnO(0001) and mixtures with aluminum, are considered in the search for the new material that provides optimal results in the transformation process to generate methanol. The reactions during the evolution of the process and the active sites acquire relevant importance that can be corroborated using the physical properties obtained by theoretical aspect from the analysis of the calculation. The different surfaces mentioned have the highest catalytic activity compared to Cu(110) and Cu(211). The various structural shape of surfaces where synthesized in the form of nanotubes, the reaction has an important surface interaction in these alloys CuZn in particular (Cu_5Zn_8) [8-11]. There is an experimental synthesis methodology, different from electrochemical co-reduction, which shows the easy obtaining of different alloys under a proportional diversity of Cu/Zn, showing an equivalent crystallinity and identifying

that when there is a higher proportion of Zn it is attributed to the promotion of surface oxidation and formation of ZnO when the Cu_5Zn_8 alloy is used. This alloy has a higher surface electron density where Cu shows a different activity with improved performance within the catalytic conversion process, which makes it possible to select the Cu_5Zn_8 alloy. This catalyst is more efficient and beneficial in the conversion of CO_2 to methanol compared to CuZn. The 1:1 bimetallic catalyst (CuZn) is important for its high catalytic activity, but exhibits rapid deactivation [12].

The objective of this research is carried out by molecular modeling using aggregates of atoms in periodic systems to perform single point energy and geometry optimization calculations to identify electronic properties due to the molecular interactions between (carbon-oxygen, and hydrogen) and the catalyst surface. The molecular system formed by the surface and CO_2; H_2, is used for molecular interactions where the analysis of results generates the potential energy surface (PES) [13] dependent on the intermolecular distance, knowing that the kinetic and potential energy determine the electron-electron, nucleus-electron and nucleus-nucleus interactions to evaluate the physical effect. The PES is used to identify attractive, repulsive, and minimun interaction zones by energy value, as an fundamental stage of the study affirming interaction preferences for evaluating the catalytic process by the physical effects and possible reactions due to the surface ZnCu with CO_2. The geometry optimization calculations result in changes of the electronic effect where the interaction shows the adsorption effects between the reactive molecules and the catalyst surface, identifying the strong influence of catalyst selectivity emulating the catalytic process under a DFT level allow us to understand why the participation of active sites in the transformation of CO_2 is favored, showing that interacting atoms promote variations in bond magnitude for molecules such as H_2 and CO_2 at certain intermolecular distances, showing surface activity and participation of zinc along with copper comformed active sites on surface Cu_5Zn_8. Furthermore, assuming that the synergy between the components can achieve the transformation reactions if there is an increase in the number of hydrogen molecules to carry out a hydrogenation modeling, it is finally discussed in detail.

2. Models and computational details

The molecular model representing the structure of the catalyst was built with the experimental data identifying an aggregate of atoms that simulate the system for the study of the CO_2 transformation process. A starting point is to use data obtained from a crystallographic system of the material composed of Cu and Zn in the form of 52 atom as alloy (Cu_5Zn_8), with the space group $I43m$ [14], to obtain the model of (Cu_5Zn_8)$*4$ =$Cu_{20}Zn_{32}$ with excellent stoichiometry of the unit cell. This model was designed to perform DFT calculations with periodic conditions starting from the unit cell, a surface of the supercell was generated with values in length of A: 12.3 Å, B: 12.3 Å, with a thickness of 9 Å, with a vacuum distance of 6 Å, which shows a space where H_2 and CO_2 can coexist, the latter has a distance of 2.5 Å, the value chosen to be able to have an interaction with the selected surface, which has a good stoichiometry that is favourable for interaction. The selection of the surface of the (Cu_5Zn_8) from the total volume chooses a surface section (111) [15] of the unit cell which presents 2 interesting regions where the first is a Zn in the center and its close neighbors are 6 Cu and second where the Cu is in the center and 6 Zn around it, which will allow discriminating the effects in at least two different arrangements with this surface selection to develop theoretical calculations.

The Perdew-Burke-Ernzerhof (PBE) [16] functional is important for a variety of applications in materials science, based on the results of energy and geometry optimization calculations, the fine shape is chosen in the calculations for greater accuracy [17]. A periodic three-dimensional molecular modeling system is used using the Born-Openheimer approximation. The structural nature of the particles that form clusters commonly features atomic shell systems with different energies favoring certain types of atomic bonds, and the functional PBE with exchange and correlation functionals is suitable in conjunction with local bases set function. The atoms chosen as the interaction surface are considered in the Generalized Gradient Aproximation (GGA) methodology with the basis function double numerical polarized (DNP) whose PBE functionals establish a good approximation that takes the nuclei at a possible bonding distance so that the interactions are identified for the analysis of the search for the catalytic effects produced by the modeled material.

The atomic aggregates to represent model through different quantum geometry optimization calculations by density functional theory (DFT) use a periodical system composed of Zn and Cu atoms with bonds and well-defined interatomic distances form the molecular structure of (Cu_5Zn_8), that identify morphology of arrangements without planar surfaces forming cubic structures as the most representative of the CuZn alloy structure [18]. DFT calculation of geometry optimization provided the minimum energy structure conformed by surface arrangements, and another equal aggregate was considered for the interaction between CO_2 atoms and Zn or strightforwar with Cu.

3. Results and discussion

The interaction that takes place between CO_2 and the molecular CuZn surface is initiated by energy calculation at different point to evaluate the potential by taking the values of the total energy dependent on the separation distance between the molecules within a DFT level of theory. The values of the single-point energy calculations are used to plot the trend of interest, taking into account the analysis of the energy data to evaluate the areas where there is an attractive or repulsive interaction and determine the minimum due to the effect of

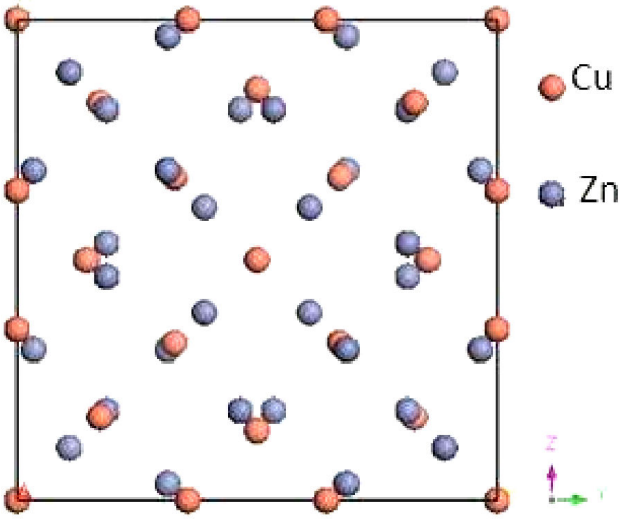

FIGURE 1. The molecular structure representative of the material (Cu_5Zn_8) with 52 atoms whose positions of the atoms in the unit cell $Cu_{20}Zn_{32}$ showing the atomic positions with stoichiometry.

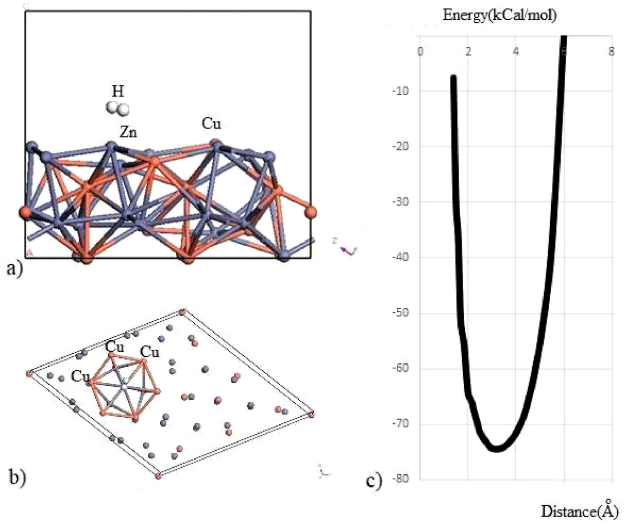

FIGURE 2. Surface of region "A" as representative of catalyst; a) Side view of H_2 and the surface of Cu_5Zn_8 at separation distance value is located; b) top view correctly identifying the region that forms a copper hexagon with Zn in the center and c) PES plot by the energy values.

the various atoms involved according to the shape of the potential. Molecules H_2, CO_2 with spatial positions parallel to the interaction surface are used to generate types of zones in the potential that are useful for the criteria of physical effects on the surface that allow identifying the sites that favor catalysis at certain separation distances. The model of the unit cell (Cu_5Zn_8) is shown in Fig. 1.

The plane with Miller indices (111) generate a surface from the unit cell of (Cu_5Zn_8) that represent the material to study and develop. The interactive effect of CO_2 and H_2 per zinc or coopper on the surface using regions ("A","B") due to interactive field the following scheme: on the one hand, the participation of Zn with 6 Cu around it will be determined, and on the other hand, the use of Cu with 6 Zn around as close neighbors, this allows to directly evaluate the effects by different schemes of a single atom and the effects of the close's neighbors.

3.1. Potential due to the interaction between (Cu_5Zn_8) and (H_2; CO_2) in the region ("A", "B")

The potential energy surface (PES) is obtained by single point energy calculations take into account interaction between alone H_2 and CO_2 with the surface (Cu_5Zn_8) for the region "A" as observed in Fig. 2. The interaction is developed in 2 regions, first, it will be to calculate where the conditions of the atomic aggregate model are shown, on the one side visualized bulk and on the top side the surface shape and graphic values show minimum relative value of the energy for interaction of -74 kcal/mol is at a separation distance of 3.0 Å, the potential plot shows that between 3.5 and 5 Å, with a difference in value of relative energy -20 kcal/mol monitoring attractive effect on H_2 favoring Zn with the 6 Cu as close neighbors.

Commercial catalyst materials utilize Cu^{2+}, Zn^{2+}, in the complex synthesis of Cu/Zn-based precursors, where the individual processes that ultimately produce the catalyst with improved physicochemical properties and performance are considered as intermediate steps such as the formation of CuO to Cu and, similarly, ZnO to Zn so in this model Zn^{2+} was used as selected in the force fields. The potential energy curve for CO_2 decomposition has an equivalent value similar to that reported experimentally [20]. The molecular model where the potential for interaction between CO_2 and the surface of (Cu_5Zn_8) for the region "A" is evaluated, as shown in Fig. 3, the shape of the array considers a direct interaction of the carbon atom on Zn and the 2 O towards 2 of the 6 Cu in its surroundings, resulting in a minimum energy value of -150 kcal/mol for a separation distance of 3.5 Å, taking as a reference, it is identified that the energy difference with a value of -140 kcal/mol is for 4.0 and 5.0 Å (1.5 and 2.7 Å) plot of the potential presents a tendency associated with the attractive (repulsive) interaction on CO_2.

Second region evaluation of the molecular interaction for different conformation is important to compare the effects of the Zn and Cu atoms depending on their conformation, the selected region of the surface where Cu is now located in the center and 6 Zn non-coplanar and for several chosen separation distances for energy calculated and potential generated for molecular H_2 plotted. The surface of (Cu_5Zn_8) promotes an attractive (repulsive) effect after performing the analysis due to interaction effects identifying the minimum and those associated with attraction/repulsion as shown in Fig. 4 where the graph verifies that the minimum value of relative energy -180 kcal/mol, is at a separation distance between molecules of 2.0 Å, the trend of the potential shows attraction and repulsion zones. The difference in energy values is -56 kcal/mol in the interval $2.5 - 4.5$ Å, of the potential plot, showing a tendency of attraction favoring Cu with the 6 Zn as close neighbors.

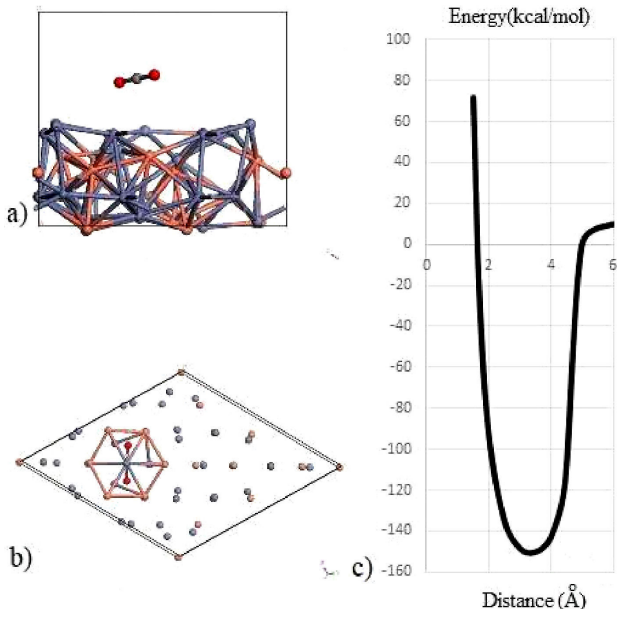

FIGURE 3. a) The side view of the interaction of CO_2 with the surface of Cu_5Zn_8 shows the bulk of atoms and CO_2, b) top view of the array with 6 Cu forming a hexagon centered on Zn where carbon interacts in the direction of Zn and O towards coppers, c) the plot of the potential generated by the energy values with a minimum value, the attractive/repulsive zone is observed.

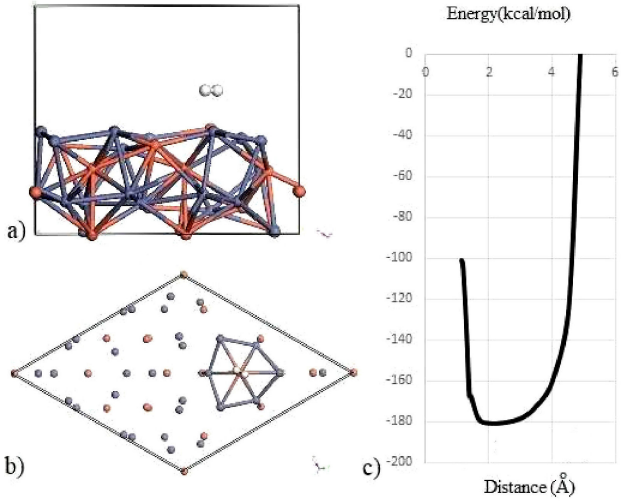

FIGURE 4. a) The side view of H_2 and the surface of Cu_5Zn_8 with the addition of atoms of the bulk on the surface and the separation of H_2 where the minimum energy is located, b) upper view where an arrangement of the centered Cu is observed forming with 6 Zn a hexagon around it, and the carbon is directed to the Cu and 2 oxygens to two of the Zn, c) Energy values describe the potential.

The surface when interacting with CO_2 for the "B" region, several separation distances are considered in calculating the energy value at each point it is used to plot the potential, finding a minimum relative energy value at -890 kcal/mol with separation distance of 3 Å, the attractive interaction zone as in the previous cases is 3.0 to 4.5 Å the energy difference in this interval is -220 kcal/mol as shown in Fig. 5. At this stage, it can be said that the surface is favored to perform an attractive interaction where the interacting molecules are chemisorbed and according to the energy values are located where the reactions can have a greater effect due to the type of conformation and atomic arrangement.

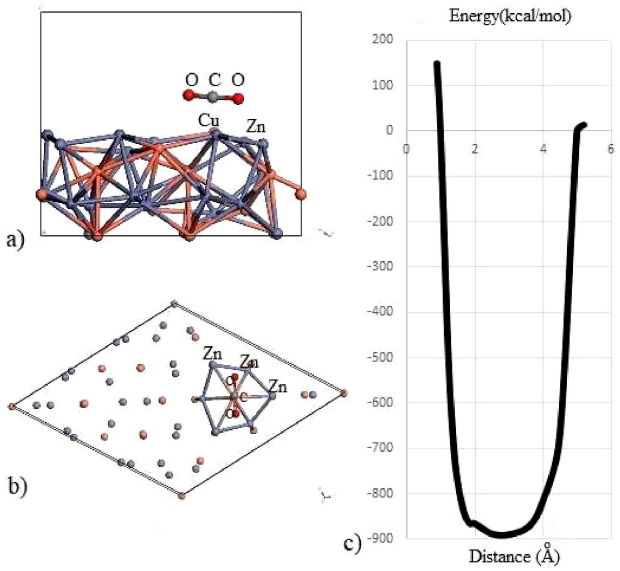

FIGURE 5. a) The side view of the CO_2 and the surface of the Cu_5Zn_8 make up the bulk of atoms on the surface locating the separation distance of the CO_2 for the minimum energy value, b) the upper view where the carbon is directed towards Cu and the oxygens towards 2 of the 6 Zn that form a hexagon type and c) Potential formed by the energy values in the graph.

The surface regions of the catalyst "A" and "B" with a single hydrogen molecule with a single CO_2 can allow the detection of the physical effect of the interaction by identifying if a reaction occurs due to modifications in the molecular structure of the CO_2. The results of various geometry optimization calculations placing the hydrogen molecule in different positions above and to the sides of the CO_2 and the intermediate position between the surface and the CO_2, in all cases show repulsive interactions without showing any reaction of the hydrogen molecule with the CO_2 and the surface, the most relevant is that the carbon atom formed a bond with the Cu and the oxygens forming a O-C-O angle at all times until convergence.

3.2. The interaction between (Cu_5Zn_8) and (H_2; CO_2) in the region ("A", "B") by geometry optimization

The energy values obtained for each of the potentials in each graph present a minimum value and their repulsion-attraction zones, selecting the repulsive interaction zone to perform the geometry optimization calculations and arrive at the minimum energy value to obtain its convergence by monitoring the formation or dissociation generated due to the interaction. The left (right) zone of the potential is established as the repulsive (attractive) zone to assess whether there is a dissociative effect by the interaction of H_2 and CO_2 molecules with the surface. The model take into account the initial point as

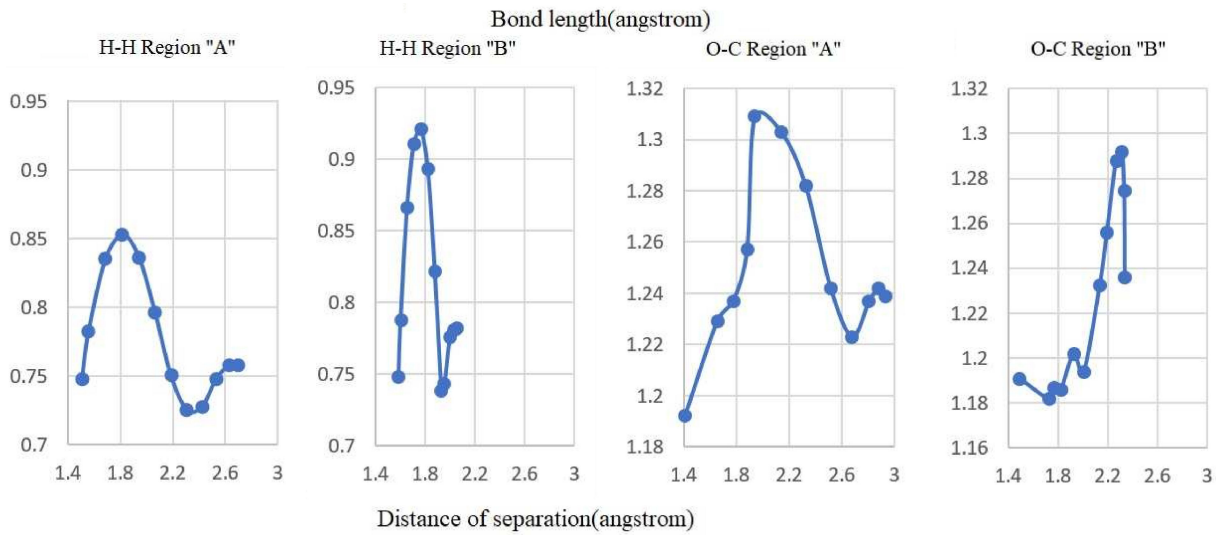

FIGURE 6. The graphs show the length of the hydrogen bond interacting with the surface in the regions ("A", "B"), as well as the carbon dioxide, observing the changes in the bond as the beginning of a dissociation of the hydrogen molecule and carbon-oxygen.

TABLE I. The values of separation distance and bond length shown in columns 1-2 for H-H in region "A"; and 3-4 H-H region "B".

Distance (Å)	Bond length (Å)	Distance (Å)	Bond length (Å)
1.503	0.748	1.588	0.748
1.554	0.783	1.605	0.788
1.685	0.836	1.656	0.866
1.814	0.853	1.710	0.911
1.938	0.837	1.766	0.921
2.061	0.797	1.821	0.893
2.183	0.751	1.876	0.822
2.304	0.726	1.930	0.738
2.420	0.728	1.953	0.743
2.528	0.748	1.997	0.776
2.624	0.758	2.031	0.781
2.694	0.758	2.052	0.782

TABLE II. The values of separation distance and bond length shown in columns 1-2 for O-C in region "A"; and 3-4 O-C in region "B".

Distance (Å)	Bond length (Å)	Distance (Å)	Bond length (Å)
1.412	1.192	1.489	1.191
1.656	1.229	1.721	1.182
1.778	1.237	1.770	1.187
1.882	1.257	1.821	1.186
1.940	1.309	1.924	1.202
2.143	1.303	2.005	1.194
2.326	1.282	2.134	1.233
2.515	1.242	2.190	1.256
2.677	1.223	2.263	1.288
2.807	1.237	2.310	1.292
2.883	1.242	2.329	1.275
2.930	1.239	2.334	1.236

separation distance of 1.50 Å, determining the energy values at each point, the molecular behavior, and the structural changes by the interaction necessary to obtain a dissociation of the H_2 molecule and CO_2 as shown in Fig. 6.

The bond length values for H-H and O-C in Table I and Table II respectively, are plotted in Fig. 6, variation values analyze for 2 columns correspond to the interaction of the hydrogen molecule with the surface in the "A" region, showing that the H-H elongation values are from 0.748 to 0.853 Å showing dissociative tendency or the maximum is at 1.814 Å in the direction of the Zn atom adding effect of the Cu. Columns 3 and 4 show that the H-H bond in the "B" region ranges from 0.748 to 0.921 Å equivalent dissociative effect where the maximum is 1.766 Å in the direction of the Cu atom with effect by Zn around. Table II present the case of CO_2 in region "A", the values obtained are reported in columns 1 and 2, ranging from 1.192 to 1.309 Å with the maximum at a separation distance of 1.94 Å, where the carbon atom is in the direction of the zinc. The last part of columns 3 and 4 correspond to the interaction of CO_2 with the surface in the "B" region where the values of the $O-C$ bond vary from 1.191 to 1.292 Å with the maximum for separation distance of 2.31 Å from the Cu atom. The results show an attractive interaction of Zn with the oxygens of the CO_2, as shown in previous results [19]. The attractive interaction, as evidenced by the PES, and geometry optimization calculations corroborate that the Zn is favorable with oxygen, as well as the Cu is favorable with carbon.

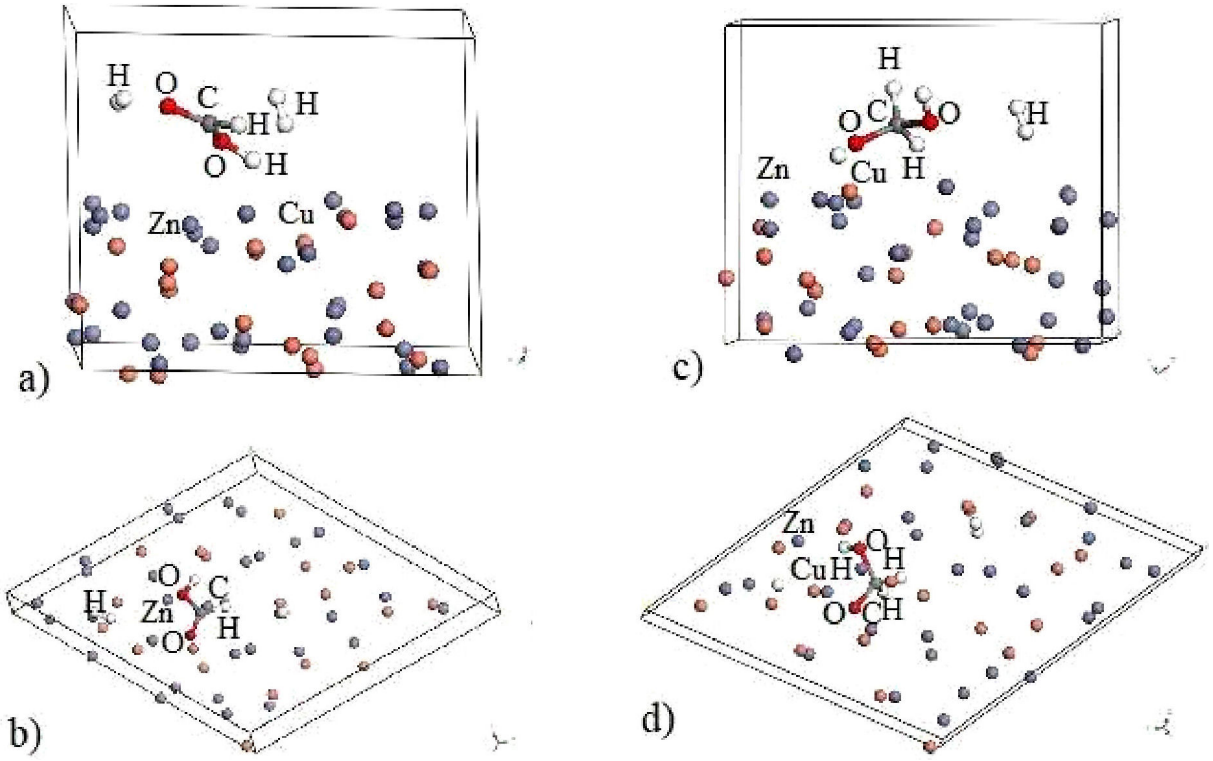

FIGURE 7. In a) and b) the lateral and upper view of the linear molecule CO_2 is shown with the 3 hydrogen molecules forming bonds with H-O and C-H-O in the "A" regions; for region "B" it is observed in c) and d) a double bond of two hydrogens with carbon and one hydrogen with oxygen the other hydrogen are dispersed.

3.3. Physicochemical effect of hydrogen on the interaction between the surface of (Cu_5Zn_8) and ($3(H_2)$; CO_2) in both regions ("A", "B") by optimization

The catalytic effects must consider the proton transfer from the molecular hydrogen together with the dissociation of the oxygen - carbon, for this the interaction between (H_2 and CO_2) and the surface by selecting the hydrogen molecule as a possible promoter to identify the phenomenon of physicochemical. The PES gives us evaluation criteria of the study to obtain important interaction zones under different degrees of freedom explored in both regions in particular CO_2 [20].

The reactions involved in the process to propose reaction mechanisms that explain the transformation of CO_2 with preadsorbed surface atomic H present different formate intermediate trajectories during the transformation and are identified during the process to confirm that physicochemical changes occur in the interaction between molecules. Several controversies have been raised claiming that they may not be the active intermediates but rather stable spectators, and direct CO_2 decomposition has also been suggested.

The physicochemical effect of hydrogen is relevant within the interaction scheme between the surface (Cu_5Zn_8) and ($3(H_2)$, CO_2) by geometry optimization to be able to evaluate the reaction $CO_2+3(H_2)\rightarrow CH_3OH+H_2O$ which presents a different effect with the Zn than with the Cu when it interacts, previous results when it is the Cu bonds to the carbon forming an angle with the 2 oxygens. The phenomenon of chemisorption is favored when 3 hydrogen molecules are involved by placing them on the sides and above the CO_2, observing as a result the effect of the surface when identifying the hydrogenation of the CO_2. In this type of interaction is when a chemical reaction is observed in different events, such as those reported in other researchs [21-23].

The catalytic effect is observed with the increase in the number of hydrogens to 3, firstly, when the carbon atom targets the zinc, the reaction promoted is identified that only one hydrogen molecule dissociates to generate the C-H and O-H bonds with prior dissociation of the CO_2 as shown in Figs. 7a) and 7b). Equivalent calculation without surface ocurre when considered model without surface obtained the same reaction. In another calculation, now Cu is in the direction of CO_2 where the reaction for 3 hydrogen molecules is H-C-H and O-H, at this point the catalyst dissociated 2 hydrogen molecules and promoted bonds with CO_2 prior dissociation as a result of the interaction, as shown in Figs. 7c) and 7d).

4. Conclusions

The regions ("A", "B") evaluated by the PES, in both cases by the results it is possible to determine the physical effects by the type of atomic conformation, indicating by the energy values that there is attractive interaction for H_2, showing that the shape of the potential with are equivalent when determining the phenomenon of chemisorption for the 2 regions, high-

lighting that the depth is greater in the region "A" which justifies that there is greater in order to give preference to Zn over hydrogen than Cu, in an equivalent form for CO_2, the graph of the potential also shows the existence of chemisorption for both regions, but now the one with the greatest depth is the "B" region, which indicates that the Cu atom is responsible. The trend of the potential values shows that the interaction of interest to identify the dissociations was obtained by all electron type optimization calculations, observing in the results small elongations promoted by the surface both by hydrogen molecule and by CO_2 by the interaction with the surface. In the case of CO_2, it is observed in the evaluation by the potentials, it has a depth 4 times greater than the "A" region, which corroborates that the effect of Cu is associated with the "B" region, which shows that it presents an extreme quimisortion that captures the carbon atom, which is verifiable by PES and optimization calculation, showing to capture regions by the graph of the energy values, since the evolution of CO_2 the carbon does not following in direction of Zn is observed to move and place itself on top of one of the 6 Cu. The importance of the active sites is demonstrated by the interactions between H_2 and CO_2 molecules within the evaluated surface regions, as determined by the results on the elongation of the O-C and H-H bonds that promotes catalysis within the transformation process of hydrogenated CO_2. Through the interaction around the active sites, the participation of the Cu-Zn material is determined to show the areas of catalytic interest, which are reflected in the energy values (PES), and it is verified by the physicochemical effects of hydrogen that show the formation reactions as the beginning of the possible reaction mechanisms proposed during the transformation process by the interaction between the surface of Cu_5Zn_8, claiming that it is the promoter of catalysis with hydrogen molecules and carbon dioxide molecules. The active sites that promote catalysis in the transformation of hydrogenated CO_2 through the interaction around them are evaluated, identifying their participation to show the areas of catalytic interest, which are reflected in the energy values (PES), in addition to the possible reaction mechanisms proposed during the transformation process when there is interaction between the surface of Cu_5Zn_8, which serves as a catalysis promoter with hydrogen molecules and carbon dioxide. The results are favorable to identify the effects of both copper and zinc in the interaction with a system of atoms in combination where it is stated that copper is the main promoter of capturing CO_2 molecules and through the effect of combined stresses of the alloy the transfer of hydrogen ions to oxygen is promoted to initiate the process of reaction mechanisms with this material. It is appropriate and importantly describes what the acid site does and promotes as a combination of effects between zinc and copper with hydrogen and carbon dioxide.

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