Regular Article

The Effect of Cu Impurity on the CO-dissociation Mechanism on the Fe (100) Surface: A Full Potential DFT Study

M. Farsad[a], M.R. Elahifard[b],*, R. Behjatmanesh-Ardakani[a]

[a]_Department of Chemistry, Payame Noor University, Tehran, Iran._
[b]_Chemical Engineering Department, Faculty of Engineering, Ardakan University._

In this study, the theoretical calculations of CO dissociation were carried out on the Cu-Fe alloy surface by a full-potential method, which made more accurate results especially on the prediction of adsorption energies. This process may be governed by either a direct route or a H-assisted _via_ HCO and COH intermediates pathways. In comparison to the pure surface Fe (100), the presence of Cu atom enhanced the activation energy of direct dissociation pathway and decreased that one for H-assisted mechanism through the HCO intermediate by 0.2 eV and 0.24 eV, respectively. These effects were explained completely by the _ligand_ effect and the _ensemble_ effect corresponding to the electronic and geometrical activity of an adsorption-site on different states (initial, intermediate, and final).In this case, Cu impurity atom creates a 3-fold-Fe-hollow site instead of a 4-fold-Fe-hollow site on the surface as the _ensemble_ effect and Fe atoms near the Cu atom show more reactivity according to the _ligand_ effect. The results showed that while both methods, CO-direct dissociation and H-assisted, are feasible on Fe (100) surface, only the later one happens on Fe-Cu surface. The results of this study suggest that Fe-Cu surface with moderate trend for adsorption has a higher life expectancy compared to Fe (100) due to the higher CO-direct dissociation-activation energy to build carbide. Also, by changing the main route from direct to H-assisted, the activity of Fischer-Tropsch reaction is enhanced with lower activation energy compared to that on the Fe (100) surface.

Keywords: Fischer-Tropsch reaction, Cu-Fe alloy surface, CO dissociation; _ligand_ and _ensemble_ effects

INTRODUCTION

Fischer-Tropsch (F-T) synthesis, a principal chemical process, enables to convert syngas (a mixture of CO and H_2 producing from natural gas, coal or biomass) into hydrocarbon fuels [1-4]. It is industrially limited behind the CO strong bond which must be dissociated firstly. So, this process is extended on the catalysis surface such as iron, cobalt and ruthenium used widely for industrial purposes. Nevertheless, CO dissociation is also a key step in the mechanism of the F-T process on the catalysts which is subjected in many computational studies recently [5-11].

In general, dissociation of CO bond may occur in a direct pathway [6]:

---

*Corresponding author. E-mail: mrelahifard@ardakan.ac.ir

$$CO_{ads} + * \rightarrow C_{ads} + O_{ads} \qquad (1)$$

or _via_ formation of intermediates HCO and COH,

$$CO_{ads} + H \leftrightarrow HCO + * \rightarrow HC + O \qquad (2)$$

$$CO_{ads} + H \leftrightarrow COH + * \rightarrow C + OH \qquad (3)$$
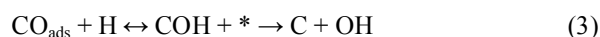
where * shows the active site. Among the catalysts, iron is introduced as an industrially active and cheap catalyst for the F-T synthesis [12].

While, Ojeda _et al._ showed that only H-assisted rout is possible on Fe (110) surface [13], Niemantsverdriet _et al._ concluded that both direct CO dissociation and H-assisted route can occur on the Fe (100) surface [14] and only the former rout is feasible on Fe (310) [15]. Due to the

stability and activity features, Fe (100) has attracted a wide attention in the theoretical research as pure or accompanied by other metals [14,16-21].

Indeed, the more intense activity of the Fe (100) catalyst leads to surface poising in a short time by carbide formation under F-T conditions. Accordingly, inserting copper impurities to the Fe surface is supposed to moderate CO adsorption and make a higher barrier for direct CO dissociation. Moreover, copper as a promoter may facilitate iron reduction and changes the product selectivity to heavier hydrocarbons [14,22-26].

Our previous result shows that CO dissociation on $Cu_{0.25}Fe_{0.75}$/Fe (100) surface is a thermodynamically possible process suggesting an appropriate surface alloy for the F-T reaction [27]. However, chemisorptions and dissociation process on alloy surfaces may be completely different from those of the corresponding elemental metals [25,28,29].

Groβ, using the concepts of the *ensemble* and the *ligand* effects, explained the activity of bimetallic catalysts [25, 26]. The term "ensemble effect" means that for occurring most of the reactions, a specified number of active sites are required [26]. The ligand effect, according to the d-band model [30,31], discussed electronic structure calculations [25] which refers to the direct chemical interactions between the components that change activity of catalysts [26].

About the hydrogen dissociation, previous theoretical and experimental results show that H_2 is fully dissociated on the simple and noble metal easily and H_2 can undergo dissociative chemisorption. Transition-metal surfaces are usually very reactive in hydrogen dissociation with a barrier lower than 0.5 eV, which is provided by experimental conditions at normal temperature. So, the whole system was relaxed including the hydrogen atoms on the active transition-metal surfaces. The dissociative adsorption of H_2 has a small activation barrier of 0.05 eV on the Fe (100) surface. So, this step was ignored over that studies on the iron metal surface [32,33].

In this study, we investigate the CO dissociation mechanism on $Cu_{0.25}Fe_{0.75}$/Fe (100) surface and will show that while Cu impurity decreases the H-assisted CO dissociation barrier, it increases direct CO dissociation by 20% compared to the pure Fe (100) surface. This research was conducted as follows;

1. DFT consideration of a Cu-Fe alloy surface contains five layers, four Fe layers and one Cu-Fe layer with 25% Cu.
2. Studying the adsorption of (CO + H) and all intermediate compounds, *e.g.*, HCO, COH, C + OH and CH + O on the Cu-Fe alloy surface.
3. Comparing direct and H-assisted CO dissociation barriers according to the (Eq. (1)-(3)).

CALCULATION METHOD

Using FHI-aims code [34], spin-density-functional theory total-energy calculations were carried out within the full potential method. This computer program package is used to calculate impressive all-electron for any type of system. The revised form of the Perdew, Burke and Ernzerhof (rPBE) functional [35], at the generalized-gradient approximation (GGA) level, was entirely employed to calculate the exchange-correlation energy. It is confirmed that GGA (rPBE) functional may more accurately predict the adsorption energy in case of metal surface [36]. For relativistic effects, we applied the scale Zeroth-order regular approximation (ZORA) [37]. Moreover, the other parameters were adjusted as follows:

Convergence criterion for the self-consistency cycle, based on the charge density (sc_accuracy_rho) and total energy (sc_accuracy_etot) are set on 5×10^{-5} and 5×10^{-6}, respectively [34]. We found the equilibrium lattice constant for bcc-Fe bulk by 2.86 Å. in good agreement with experimental value by 2.87 Å.

To model the $Cu_{0.25}Fe_{0.75}$/Fe (100) surface, the slab method with a P (2×2) two-dimensional super cell was employed for five metal layers which included 4 atoms per metallic layer with 12 Å vacuum size. Herein, the top three layers of the slab allow to fully relax with a force convergence criterion of 0.01 eV/Å.

For the calculation of reaction barriers, a transition-state search algorithm based on the climbing-image string method [38] was applied. This technique seems to be the best choice to get a minimum-energy path and transition state, while using both limiting geometries as initial state (IS) and final state (FS). In every rout, a series of intermediate configurations which set to 8 images between IS and FS, was built up and the transition states were optimized by reducing the CI force to < 0.05 eV.

RESULTS

Adsorption Energies of all Compounds

First, to compare the accuracy of the calculation approaches, CO adsorption on the Fe (100) pure surface was considered. The most of previous theoretical research by DFT, overestimate the CO adsorption energy value for Fe (100). In this respect, Govende mentioned the adsorption energy of the CO molecule in a range between -1.9 and -2.5 eV (depending on the functional used) [39] or Zhao *et al.* reported that as -2.05 eV [40], while both of them used Vienna *ab initio* simulation Package (VASP) with PAW and PBE functionals. Niemantsverdriet *et al.* achieved better results by employing more accurate parameters in their calculations. They reported the adsorption energy of 1.53 eV for CO, which is much lower than that of other works [14]. We obtained 1.55 eV for CO adsorption which shows a good agreement with the experimental result with the range of 1.2-1.6 eV [16].

Then, after geometry optimization of $Cu_{0.25}Fe_{0.75}$/Fe (100) surface, we calculated the adsorption energy of all reactants and products for Eq. (1)-(3) on that surface. The most stable co-adsorption configuration for CO and H on a P (2 × 2) cell correspond to a tilted CO on the four-fold hollow site, similarly to that observed for the clean surface [14]. However, a different orientation is adopted by adsorbed CO on this surface, where, O atom tilts toward Fe atom near the Cu atom, which is expected relating to the ligand effect as that Fe is getting more active. In this view, the replacement of an active atom (Fe) by an inert atom (Cu), causes more reactivity of its neighboring atoms [25, 26]. So, the Fe atom near the Cu atom shows more activity than the other Fe atom. On the other hand, the presence of substitutional copper on the 4-fold-Fe- hallow site changes the active site for CO adsorption completely. So, the ensemble effects from changing the 4-fold to 3-fold-Fe-hollow site play the main role. It explains the lower CO adsorption energy on the alloy surface by -1.22 eV than pure Fe (100) surface. Here, the bond length for C-O (1.279 Å) is compared with that one on pure Fe (100) surface (1.313 Å) and CO molecule (1.128 Å). Table 1, shows the relative energies for all compounds containing one C, O, and H atoms on the alloy surface as; $H_{(\alpha)}$ + CO, $H_{(\beta)}$ + CO, $H_{(\gamma)}$ + CO, HCO, COH, HO + C, CH + $O_{(\beta)}$, CH + $O_{(\gamma)}$, C + $O_{(\beta)}$ + H and C + $O_{(\gamma)}$ + H   where, α, β, γ represent the different 3-fold hollow sites on the surface as seen in Table 1.

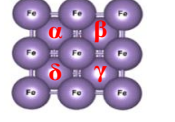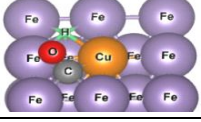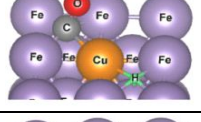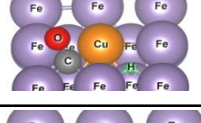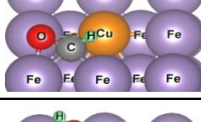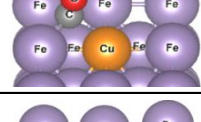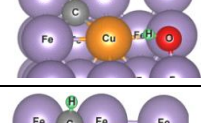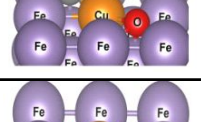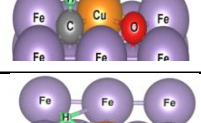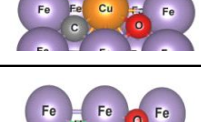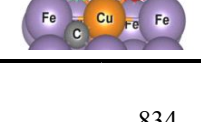Our results show that all compounds adopted a 3-fold-Fe hollow site for adsorption on the Cu-Fe alloy surface, similarly to that observed for the Fe (100) surface [14]. However, the configurations of the adsorbed COH and HCO result in H and O atoms prefer to bond with the Fe-Fe bridge site in front of the Fe-Cu bridge. Also, as 4-fold hollow site contains one cu atom as 3-fold-Fe hollow site**,** the ensemble effect decreases all adsorption energies on Cu-Fe alloy surface compared to the Fe (100) surface, *i.e.* CO, HCO, COH, H, C, O and CH species.

CO-dissociation

The direct CO-dissociation process is exothermic by -0.02 eV and the overall reaction energy is -0.9 eV, when O atom diffuses to the second nearby hollow-site (β site). The activation energy for this process is 1.29 eV, which is much larger than the direct CO dissociation on the Fe (100) surface (1.09 eV) [14]. It means that the Cu atom affects the TS more than the IS for direct CO dissociation process. Herein, the O atom located necessarily near the Cu atom in the TS and FS configuration (Fig. 1) leading to a lower stability and higher activation energy based on the ligand effect. Furthermore, according to the Arrhenius equation the rate constant difference for direct CO dissociation on Fe (100) and Cu-Fe/Fe (100) surfaces increases exponentially by lowering the temperature.

In the H-assisted routes, (Eq. (2),(3)) the formation of HCO and COH are endothermic process by 0.60 and 0.92 eV, respectively. Then, they are followed by a subsequent dissociation step leading to the CH and OH formation (second steps of Eqs. (2), and (3)) which are exothermic process, with reaction energies of -0.79 eV and -1.34 eV, respectively. Compared to the results of the Fe (100) surface, by +0.56 and +0.94 eV as reaction energies of HCO and COH formations, it is concluded that while the Cu atom indisposes the surface to HCO formation, it makes a better site for COH species. Regarding the configuration of the adsorbed HCO, H atom must be located near the Cu-Fe bridge which is less active than Fe-Fe bridge site due to the ligand effect. Conversely, in the adsorbed COH, H atom is located near the Fe-Fe bridge site of alloy surface with larger activity *vs*. Fe-Fe site in pure Fe (100) surface [27].

Table 1. Geometry Structures and Relative Energies of all Coumponds on the Pure Fe (100) and $Cu_{0.25}Fe_{0.75}$/Fe (100) Alloy Surfacs. The C-O Bond Length is only Presented for Compounds on the $Cu_{0.25}Fe_{0.75}$/Fe (100) Surface

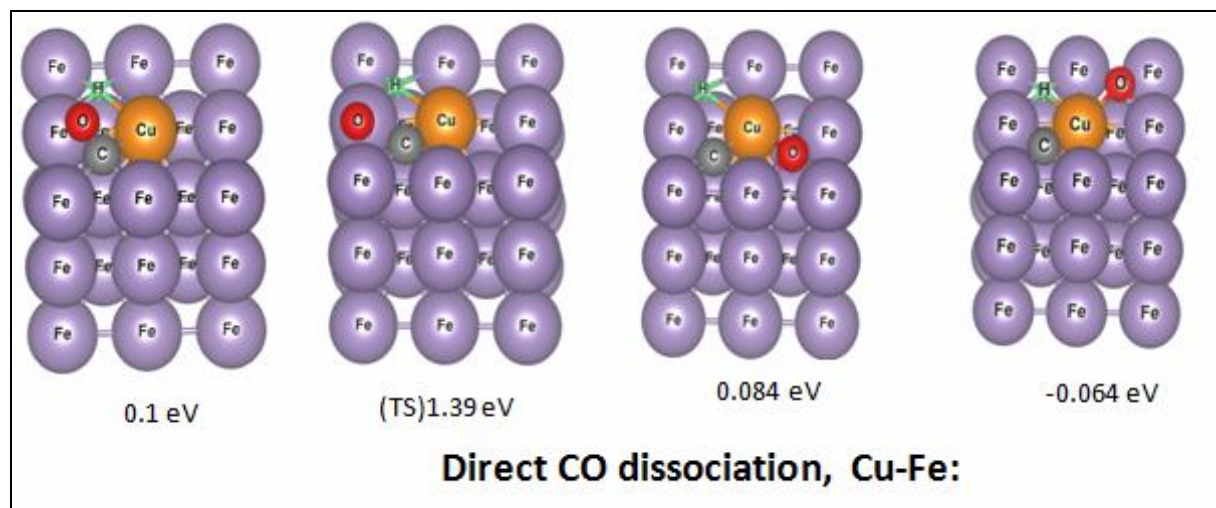| Species		Relative Energy		$d_{co}(A^o)$
		Cu-Fe	Fe(100)	Cu-Fe
H(α)+CO		0.1	0.13	1.279
H(β)+CO		0	0	1.294
H(γ)+CO		0.06	0.16	1.276
HCO		0.66	0.72	1.382
COH		0.98	1.1	1.44
HO+C		-0.36	–	–
CH+O(β)		-0.9	–	–
CH+O(γ)		-0.13	-1	–
C+O(γ)+H		0.09	-0.24	–
C+O(β)+H		-0.64	-0.29	–

Fig. 1. Adsorbate structures for direct CO dissociation on $Cu_{0.25}Fe_{0.75}$/Fe (100) alloy surface.

Fig. 2. Adsorbate structures for H-assisted CO dissociation *via* HCO formation on the $Cu_{0.25}Fe_{0.75}$/Fe (100) alloy surface.

Both of the reaction energies for the OH and CH formation are more positive than those on the Fe (100) surface by 0.15 eV and 0.1 eV, respectively [14], which may be explained with the same discussion to the direct CO dissociation process, *i.e.* the O species move to the region near the Cu atom.

The energy barrier for HCO formation is 0.73 eV, a value lower than that one on Fe (100) by 0.78 eV [14] (Fig.

2). It means that the Cu atom shows a different effect on TS and FS for HCO formation process by reducing (increasing) the activation energy (formation energy). The following step (HCO → HC + O) has an activation energy of 0.52 eV, which is much smaller than that on the Fe (100) surface (0.64 eV), might be due to the unfavorable HCO adsorption site. The overall activation energy for H-assisted dissociation from HCO intermediate is 1.1 eV with 0.2 eV
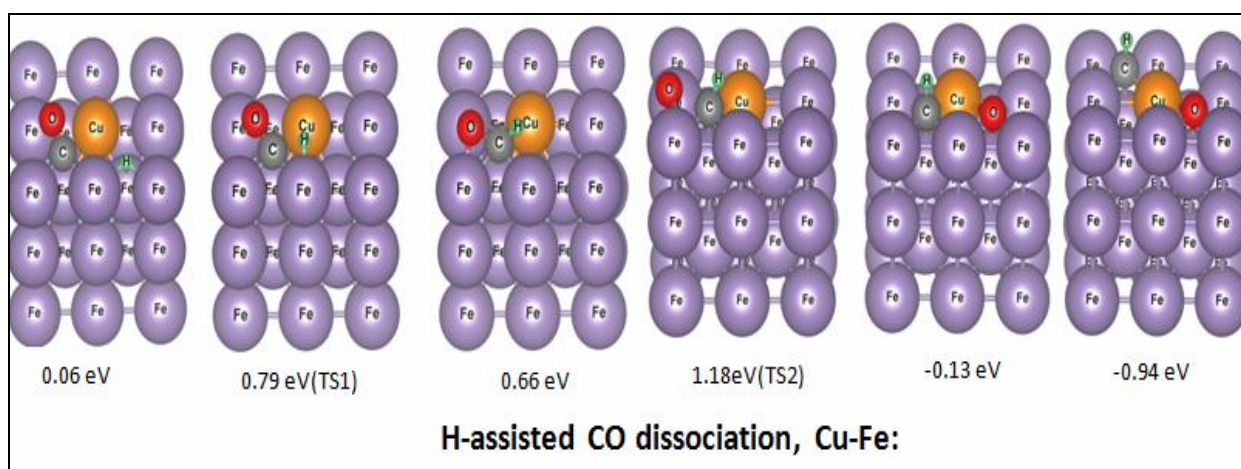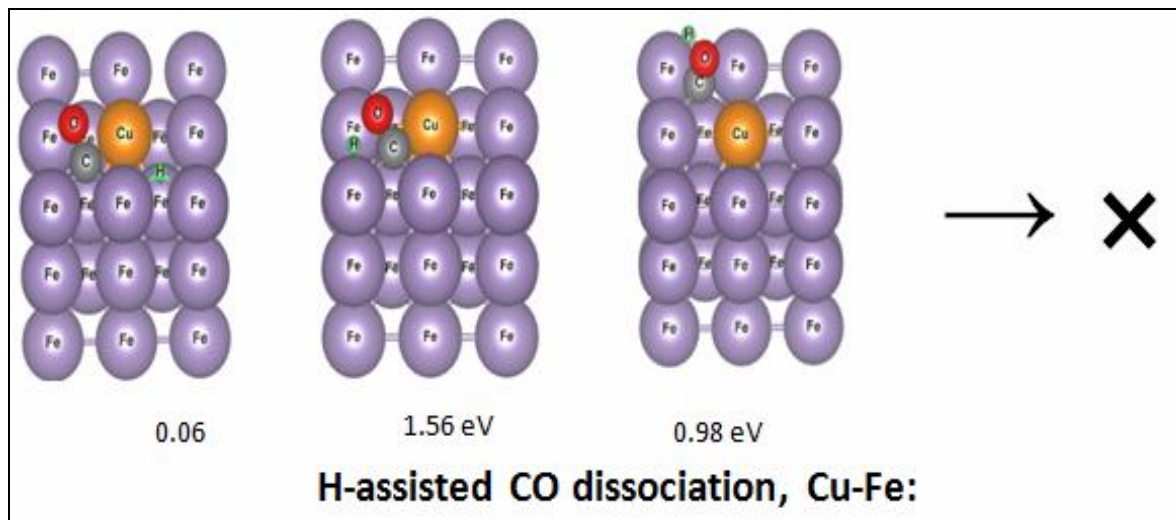
Fig. 3. Adsorbate structures for H-assisted CO dissociation *via* COH formation on the $Cu_{0.25}Fe_{0.75}/Fe$ (100) alloy surface.
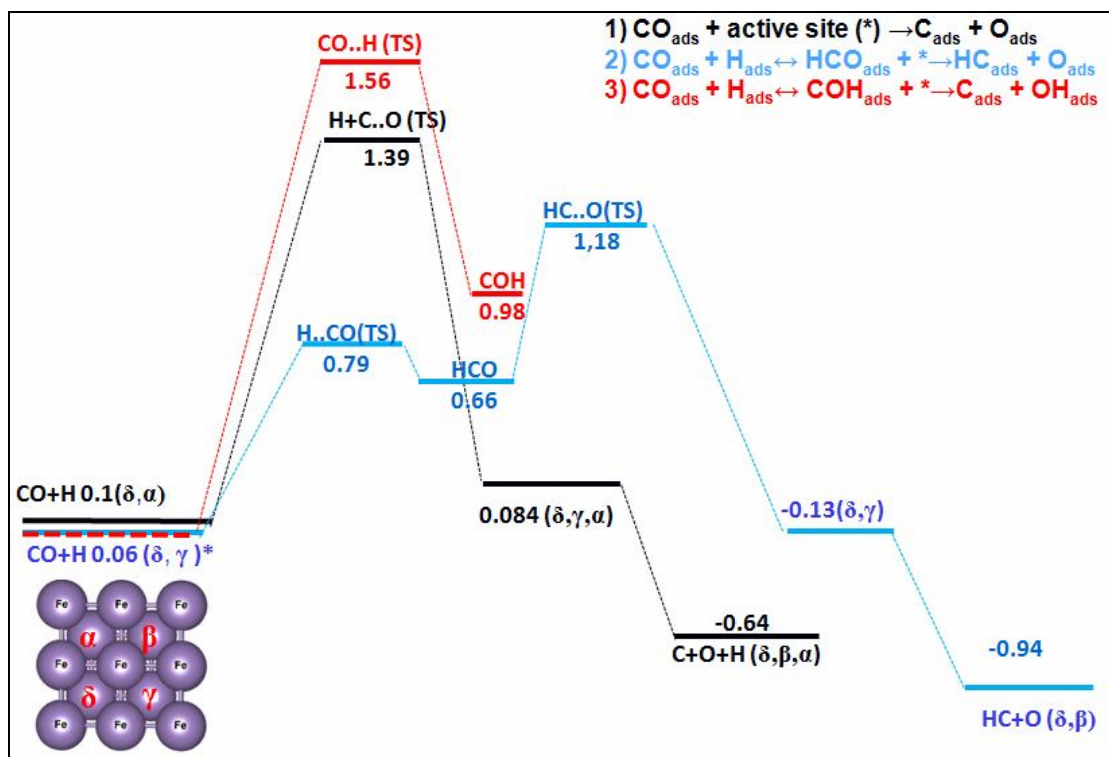

Fig. 4. Relative energy of states and CO dissociation. *The inset clarifies the nomenclature for the different 4-fold hollow sites occupied by components.

smaller than direct CO dissociation on the Cu-Fe alloy surface. It means that the former process would have a rate constant around 10^3 times higher at 250 °C. However, on Fe (100) surface, H-assisted dissociation shows more activation energy than direct CO dissociation with 0.27 eV [14], expressing a large effect of Cu atom on the catalytic reactivity of Fe (100).

H-assisted CO dissociation from COH intermediate (Eq. (3)) by hydrogenation of the oxygen-end of the CO molecule and then dissociating into OH and C may also proceed (Fig. 3). Herein, a problem is the different orientation of CO bond for the adsorbed CO and COH species, *i.e.* a tilted configuration versus upright form. It leads to a more endothermic reaction and activation energy for COH formation process. The energy barrier of this process is 1.5 eV which canceled the CO dissociation via the COH intermediate to take place on Cu-Fe alloy surface. Overall, as seen in Fig. 4, CO dissociation through HCO intermediate would be dominantly favored especially under the higher H_2 pressure and lower temperature, suggesting that the Cu-Fe alloy surface enlarges the catalytic longevity in the F-T process.

CONCLUSIONS

We present the theoretical DFT calculation using a full potential method to consider the first step of the F-T synthesis (CO dissociation) *via* both direct and H-assisted mechanisms on the $Cu_{0.25}Fe_{0.75}$/Fe (100) alloy surface. Our results supports that the substitution of 25% Fe atoms by Cu atoms causes the opposite effect on those routs by increasing (decreasing) the activation energy of CO-direct (H-assisted) dissociation in comparison with that on the Fe (100) pure surface. Herein, Cu impurity decreases the CO adsorption energy by 0.33 eV and enhances the activation energy of the CO-direct dissociation by 0.2 eV. However, it alters the activation energy of H-assisted CO dissociation via HCO intermediates from 1.36 eV on Fe (100) surface to 1.1 eV on $Cu_{0.25}Fe_{0.75}$/Fe (100) alloy surface. All effects of Cu impurity on Fe (100) activity may be explained using ensemble and ligand effects which are referred to the geometrical and electronic properties, respectively. While the ensemble effect plays the dominant role for adsorption process, where the most stable site (4-Fe fold hollow site)

disappears as a consequence of alloy formation, the ligand effect determines the higher activation energy for direct CO-dissociation.

REFERENCES

[1] Röper, M., Fischer-Tropsch synthesis, in: Catalysis in C1 Chemistry. Springer, 1983, p. 41-88.

[2] Steynberg, A., Introduction to fischer-tropsch technology. *Stud. Surf. Sci. Catal.* **2004**, *152*, 1-63, DOI: 10.1016/S0167-2991(04)80458-0.

[3] Storch, H. H.; Anderson, R. A.; Golumbic, N., The Fischer-Tropsch and Related Syntheses. Wiley, New York, 1951.

[4] Davis, B. H., Fischer-Tropsch synthesis: relationship between iron catalyst composition and process variables. *Catal. Today.* **2003**, *84*, 83-98, DOI: 10.1016/S0920-5861(03)00304-3.

[5] Dry, M. E., Fischer-Tropsch synthesis over iron catalysts. *Catal. Lett.* **1990**, *7*, 241-251, DOI: 10.1007/BF00764506.

[6] Shetty, S.; Jansen, A. P.; van Santen, R. A., Direct versus hydrogen-assisted CO dissociation. *J. Am. Chem. Soc.* **2009**, *131*, 12874-12875, DOI: 10.1021/ja9044482.

[7] Ponec, V.; Van Barneveld, W. A., Role of chemisorption in Fischer-Tropsch synthesis. *Ind. Eng. Chem. Res.* **1979**, *18*, DOI: 10.1021/i360072a009.

[8] Chorkendorff, I.; Niemantsverdriet, J., Concepts of modern catalysis and kinetics. 2003. in. Wiley-VCH, 1997.

[9] Ma, S.; Jiao, Z.; Zhang, X.; Dai, X., Alkali metal induced effects on coadsorbed carbon monoxide on Co (0001): A density functional theory study. *Comput. Theor. Chem.* **2013**, *1009*, 55-59, DOI: 10.1016/j.comptc.2012.12.028.

[10] Hou, X. J.; Li, H.; He, P., Theoretical investigation for adsorption of CO_2 and CO on MIL-101 compounds with unsaturated metal sites. *Comput. Theor. Chem.* **2015**, *1055*, 8-14, DOI: 10.1016/j.comptc.2014.12.017.

[11] Chen, R.; Chen, Z.; Ma, B.; Hao, X.; Kapur, N.; Hyun, J.; Cho, K.; Shan, B., CO adsorption on Pt (111) and Pd (111) surfaces: A first-principles based

lattice gas Monte-Carlo study. *Comput. Theor. Chem.* **2012**, *987*, 77-83, DOI: 10.1016/j.comptc.2011.07.015.

[12] Fajín, J. L.; Cordeiro, M.; Gomes, J. R., Fischer-Tropsch synthesis on multicomponent catalysts: What can we learn from computer simulations?. *Catalysts.* **2015**, *5*, 3-17, DOI: 10.3390/catal5010003.

[13] Ojeda, M.; Nabar, R.; Nilekar, A. U.; Ishikawa, A.; Mavrikakis, M.; Iglesia, E., CO activation pathways and the mechanism of Fischer–Tropsch synthesis. *J. Catal.* **2010**, *272*, 287-297, DOI: 10.1016/j.jcat.2010.04.012.

[14] Elahifard, M. R.; Jigato, M.P.; Niemantsverdriet, J., Direct *versus* hydrogen-assisted CO dissociation on the Fe (100) Surface: a DFT study. *Chem. Phys. Chem.* **2012**, *13*, 89-91, DOI: 10.1002/cphc.201100759.

[15] Elahifard, M. R.; Jigato, M. P.; Niemantsverdriet, J. H., *Ab initio* calculations of the direct and hydrogen-assisted dissociation of CO on Fe (310). *Chem. Phys. Lett.* **2012**, *534*, 54-57, DOI: 10.1016/j.cplett.2012.03.031.

[16] Sorescu, D. C.; Thompson, D. L.; Hurley, M. M.; Chabalowski, C. F., First-principles calculations of the adsorption, diffusion, and dissociation of a CO molecule on the Fe (100) surface. *Phys. Rev. B.* **2002**, *66*, 035416, DOI: 10.1103/PhysRevB.66.035416.

[17] Bromfield, T. C.; Curulla Ferré, D.; Niemantsverdriet, J., A DFT study of the adsorption and dissociation of CO on Fe (100): Influence of surface coverage on the nature of accessible adsorption states. *Chem. Phys. Chem.* **2005**, *6*, 254-260, DOI: 10.1002/cphc.200400452

[18] Blyholder, G.; Lawless, M., A theoretical study of the site of CO dissociation on Fe (100). Surf. *Sci.* **1993**, *290*, 155-162, DOI: 10.1016/0039-6028(93)90597-D.

[19] Meehan, T. E.; Head, J. D., A theoretical comparison of CO bonding on the Fe (100) surface. *Surf. Sci.* **1991**, *243*, L55-L62, DOI: 10.1016/0039-6028(91)90334-O.

[20] Pavo, A.; Braga, M.; Taft, C.; Hammond, B.; Lester Jr, W., Theoretical study of the CO interaction with the Fe (100) surface. *Phys. Rev. B.***1991**, *44*, 1910, DOI: 10.1103/PhysRevB.44.1910.

[21] Aray, Y.; Rodriguez, J., Study of CO adsorption on the Fe (100) surface using the Laplacian of the electronic charge density. *Surf. Sci.* **1998**, *405*, L532-L541, DOI: 10.1016/S0039-6028(98)00147-2.

[22] Vink, T.; Gijzeman, O. L. J.; Geus, J., CO interaction with Fe (100): Effects of carbon and oxygen adlayers on co adsorption isotherms. *Surf. Sci.* **1985**, *150*, 14-23, DOI: 10.1016/0039-6028(85)90207-9.

[23] Gijzeman, O.; Vink, T.; Van Pruissen, O.; Geus, J., Adsorption of CO on Fe, Cu, and Cu-Fe surface alloys. *J. Vac. Sci. Technol. A.* **1987**, *5*, 718-721, DOI: 10.1116/1.574280.

[24] Bukur, D. B.; Mukesh, D.; Patel, S. A., Promoter effects on precipitated iron catalysts for Fischer-Tropsch synthesis. *Ind. Eng. Chem. Res.* **1990**, *29*, DOI: 10.1021/ie00098a008.

[25] Groß, A., Reactivity of bimetallic systems studied from first principles. *Top. Catal.* **2006**, *37*, 29-39, DOI: 10.1007/s11244-006-0005-x.

[26] Groß, A., Tailoring the reactivity of bimetallic overlayer and surface alloy systems. *J. Phys. Condens. Matter.* **2009**, *21*, 084205, DOI: 10.1088/0953-8984/21/8/084205.

[27] Elahifard, M.; Fazeli, E.; Joshani, A.; Gholami, M., *Ab initio* calculations of the CO adsorption and dissociation on substitutional Fe-Cu surface alloys relevant to Fischer-Tropsch Synthesis: bcc-(Cu) Fe (100) and fcc-(Fe) Cu (100). *Surf. Interface. Anal.* **2013**, *45*, 1081-1087, DOI: 10.1002/sia.5228.

[28] Christensen, A.; Ruban, A.; Stoltze, P.; Jacobsen, K. W.; Skriver, H. L.; Nørskov, J. K.; Besenbacher, F., Phase diagrams for surface alloys. *Phys. Rev. B.* **1997**, *56*, 5822, DOI: 10.1103/PhysRevB.56.5822.

[29] Demirci, E.; Carbogno, C.; Groß, A.; Winkler, A., Adsorption of CO on Ni/Cu (110) bimetallic surfaces. *Phys. Rev. B.* **2009**, *80*, 085421, DOI: 10.1103/PhysRevB.80.085421.

[30] Hammer, B.; Nørskov, J., Electronic factors determining the reactivity of metal surfaces. *Surf. Sci.* **1995**, *343*, 211-220, DOI: 10.1016/0039-6028(96)80007-0.

[31] Groß, A., Adsorption at nanostructured surfaces from first principles. *J. Comput. Theor. Nanosci.* **2008**, *5*, 894-922, DOI: 10.1166/jctn.2008.2533.

[32] Harris, J., Dissociation of hydrogen on metal surfaces. *Langmuir.* **1991**, *7*, 2528-2533, DOI: 10.1021/la00059a022.

[33] Abbasi, A.; Sardroodi, J. J., Theoretical investigation of the adsorption behaviors of CO and CO_2 molecules on the nitrogen-doped TiO_2 anatase nanoparticles: Insights from DFT computations. *JTCC.* **2017**, *16*, 1750005, DOI: 10.1007/s11244-012-9796-0.

[34] Blum, V.; Gehrke, R.; Hanke, F.; Havu, P.; Havu, V.; Ren, X.; Reuter, K.; Scheffler, M., *Ab initio* molecular simulations with numeric atom-centered orbitals. *Comput. Phys. Commun.* **2009**, *180*, 2175-2196, DOI: 10.1016/j.cpc.2009.06.022.

[35] Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865, DOI: 10.1103/PhysRevLett.77.3865.

[36] Abild-Pedersen, F.; Andersson, M., CO adsorption energies on metals with correction for high coordination adsorption sites-A density functional study. *Surf. Sci.* **2007**, *601*, 1747-1753, DOI: 10.1016/j.susc.2007.01.052.

[37] Van Lenthe, E.; Snijders, J.; Baerends, E., The zero-order regular approximation for relativistic effects: The effect of spin-orbit coupling in closed shell molecules. *J. Chem. Phys.* **1996**, *105*, 6505-6516, DOI: 10.1063/1.472460.

[38] Weinan, E.; Ren, W.; Vanden-Eijnden, E., Simplified and improved string method for computing theminimum energy paths in barrier-crossing events. *J. Chem. Phys.* **2007**, *126*, 1641033, DOI: 10.1063/1.2720838.

[39] Govender, A. A., Towards a mechanism for the Fischer-Tropsch synthesis on Fe (100) using density functional theory. Technische Universiteit Eindhoven, 2010, p. 1-20.

[40] Zhao, Y.; Li, S.; Sun, Y., CO Dissociation Mechanism on Cu-Doped Fe (100) Surfaces, *J. Phys. Chem. C* **2013**, *117*, 24920-24931, DOI: 10.1021/jp408932y.