NRC·CNRC

NRC Publications Archive
Archives des publications du CNRC

Comment on “Density functional theory and 3D-RISM-KH molecular theory of solvation studies of CO_2 reduction on Cu-, Cu_2O-, Fe-, and Fe_3O_4-based nanocatalysts”

Gusarov, Sergey

For the publisher’s version, please access the DOI link below./ Pour consulter la version de l’éditeur, utilisez le lien DOI ci-dessous.

Publisher’s version / Version de l'éditeur:
https://doi.org/10.1007/s00894-021-04974-z
Journal of Molecular Modeling, 27, 12, pp. 1-4, 2021-11-06

NRC Publications Archive Record / Notice des Archives des publications du CNRC :
https://nrc-publications.canada.ca/eng/view/object/?id=315f16cd-23ec-4ebf-b0ed-ff5166259151
https://publications-cnrc.canada.ca/fra/voir/objet/?id=315f16cd-23ec-4ebf-b0ed-ff5166259151

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at
https://nrc-publications.canada.ca/eng/copyright
READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L’accès à ce site Web et l’utilisation de son contenu sont assujettis aux conditions présentées dans le site
https://publications-cnrc.canada.ca/fra/droits
LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D’UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n’arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

National Research Council Canada | Conseil national de recherches Canada

Canada

Comment on "Density functional theory and 3D-RISM-KH molecular theory of solvation studies of CO_2 reduction on Cu-, Cu_2O-, Fe-, and Fe_3O_4-based nanocatalysts"

Sergey Gusarov

sergey.gusarov@nrc-cnrc.gc.ca; gusarov@ualberta.ca

Nanotechnology Research Centre, National Research Council of Canada, 11421 Saskatchewan Drive, Edmonton, Alberta T6G 2M9, Canada

Abstract

Recently, A. Kovalenko et al. reported the computational study of molecular structure and energetics of CO_2+H_2 reduction reaction on Cu-, Cu_2O-, Fe-, and Fe_3O_4-based nanocatalysts in J. Mol. Model., 26, 267 (2020). Authors claim that they developed and tested the multiscale modeling description of this process by combining the periodical boundary condition density functional theory (PBC DFT) and molecular theory of solvation. However, due to inappropriate selection of intermediate strictures, in particular, the unfavorite structure of CO* adsorbed on Cu-, Cu_2O-, Fe-, and Fe_3O_4- nanoparticles, and some inconsistency in preparation of initial structures by DFT approach there are serious concerns about the correctness and quality of the presented results. In addition, by this comment, I would like to help other researchers working on the development of new catalysts for electrochemical reduction of CO_2 to avoid further misunderstandings following from this study.

Keywords: DFT, RISM, reduction reaction

Introduction

The electrochemical CO_2 reduction in which carbon dioxide is converted back into a usable fuel attracts a lot of attention in industrial and academic research as it offers a smart pathway for sustainable carbon dioxide consumption. [1]. However, in order to efficiently break the strong carbon-oxygen bond the development of the new catalysts with high effectiveness and selectivity is required. This increases the need for the detailed understanding of possible pathways of the reaction and their energetics which in turn rises the role of computation modeling as an important tool providing a valuable inside into the area [2-5].

To date there is a large number of research devoted to the theoretical study of catalytic properties of different surfaces, nanoparticles and hybrid systems, (e.g., see reviews [6, 7]) but regardless of the necessity of further computational investigations of numerous pathways, the initial steps of the reaction are well described [4-9]. The adsorption of CO_2 and following formation of CO on the catalytic surface are between the most important steps in different pathways of electrochemical CO_2 reduction. They are sufficiently represented in the literature [2,10,11] including works [12-17] referenced and used by A. Kovalenko et al. as the pathways for their modeling of the electrochemical CO_2 conversion in [18].

Comments

Unfortunately, the step presented by authors in Figures 2d, 3d, 4d and 5d [18] does not correspond to any intermediate steps of CO_2+H_2 reduction reaction suggested till now, including the works referenced by A. Kovalenko in [18]. Moreover, because the induced charges and optimal geometries of systems mentioned above were used in the following 3D-RISM calculations, the free energies presented in Table 1 and Figure 6 [18] correspond to the meaningless structures.

Also, the parameters of DFT calculations used in [18] are questionable. For example, the Cu_{21} cluster (as well as other Cu_2O-, Fe-, and Fe_3O_4 clusters) which authors called a "slab" is modeled by periodical boundary density functional theory (PBC DFT), however the shorter distance between clusters in neighbouring periodical cells is about 13 Å which exclude their interaction. Despite this, the authors use a large number of k-vectors (10x10x10) which make sense only for 3D periodical systems.

To illustrate the instability of structures presented in Figures 2d, 3d, 4d and 5d [18] the interaction of CO with the system containing twenty-one copper atoms similar to used by A. Kovalenko was modeled by the same software package OpenMX [19] with the same basis set, electronic temperature and box size (20Å×20Å×20Å) [18]. The only cut-off energy was changed to fit the recommended range (200 Ryd) [20] to increase the accuracy of calculations.

As the authors do not provide the information about using dispersion correction and magnetic properties of Cu_{21}, the presented calculations were performed for different combinations of these parameters (see Table 1 and Figure 1). Many works (e.g. [21]) suggest to use the D3 in combination with PBE functional to get more accurate results for the adsorption of CO on metallic structures. As it can be seen from the table the effect of including the dispersion correction is mostly affect the adsorption energies defined as:

$$E_{ads} = -[E_{total} - (E_{adsorbate} + E_{adsorbent})] . \quad (1)$$

Apparently, the authors kept the geometry of the "slab" fixed during the optimization of CO, so the presented calculations were performed for both the fixed and relaxed Cu_{21} cluster. Two initial positions of the CO molecule oriented by Carbon (Figure 1a) and by Oxygen (Figure 1f) to the "slab" were used in the computations.

The relaxed structures resulting from the first initial orientation (Figure 1a) are presented in Figures 1b-1e. They have a stable covalent bond (~ 1.83 Å) between C and Cu atoms. Oppositely, in the case of CO-reversed initial orientation (Figure 1f), the CO molecule was repelled from the cluster (Figures 1g-1j) to the distance of about 2.9 Å, thus excluding the covalent bond formation. The corresponding energies and distances are listed in Table 1.

Whenever the Cu_{21} cluster was relaxed too (Figure 2), the CO molecule formed the stable C-Cu covalent bond for both initial orientations (Figures 1a and 1f) which clearly shows the instability of structures in Figures 2d, 3d, 4d and 5d presented in [18]. The copper cluster significantly changed its shape which does not allow to fully separate the adsorption and redistribution energies. This also shows that the system selected in [18] cannot correctly represent the "2-atom vacancy Cu_{21} slab nanocatalyst" [18] due to the strong stress forces appearing on the surface of Cu_{21} cluster.

Another important point is that the combination of 3D-RISM [23] and PBC DFT used in [18] is not self-consistent. That means that "the partial charges and geometries obtained from running the OpenMX software package" are calculated in a vacuum and so do not contain the effect of solvent. Further, these parameters are used in the molecular theory of solvation calculations which makes resulting free energies (Table 1 [18]) less accurate. At the same time, there is the freely available self-consistent combination of 3D-RISM with PBC DFT [24] implemented into the Quantum Espresso package [25]. It was already used to model properties of the Pt(111)/electrolyte electrochemical interface [26].

Conclusions

In principle, the self-consistent combination of PBC DFT and 3D-RISM is perspective way to study of the intermediate products of electrochemical reduction of CO_2 to hydrocarbon fuels, however, the work presented by A. Kovalenko et al. [18] contains some faults in system preparation as well as in the application of periodical density functional theory which does not allow to recommend it as the reference work for this approach.

Declarations

Funding: National Research Council Canada, Clean Energy Program

Conflicts of interest: author declares no competing interests

Availability of data and material: OpenMX output files available upon request

Code availability: OpenMX 3.9, BIOVIA Discovery Studio 2020

Authors' contributions: Sergey Gusarov: analysis, calculations, writing manuscript

References

1. Lewis NS, Nocera DG (2006). Proc. Natl. Acad. Sci. U. S. A. 103:15729–15735
2. Hussain J, Jonsson H, and Skulason E (2018) ACS Catal. 8:5240−5249
3. He J, Wu C, Li Y, and Li C (2021) J. Mater. Chem. A 9:19508
4. Liu C, Lourenço M, Hedström S, Cavalca F, Diaz-Morales O, Duarte HA, Nilsson A, Pettersson L (2017) J. Phys. Chem. C 121:25010−25017
5. Lee J, Kattel S, Jiang Z, Xie Z, Yao S, Tackett B, Xu W, Marinkovic N and Chen J (2019) Nat. Comm. 10:3724-3731
6. Ramírez-Valencia L, Bailón-García E, Carrasco-Marín F and Pérez-Cadenas A (2021) Catalysts 11:351-417
7. Nguyen DL, Kim Y, Hwang YJ, Won DH (2019) Carbon Energy 2:72–98
8. Nitopi S, Bertheussen E, Scott SB, Liu X, Engstfeld AK, Horch S, Seger B, Stephens IE, Chan K, Hahn C, Nørskov JK, Jaramillo TF, and Chorkendorff I (2019) Chem Rev. 119:7610-7672
9. Maxime Bossche M, Rose-Petruck C, and Jónsson H (2021) J. Phys. Chem. C 125:13802−13808
10. Kortlever R, Shen J, Schouten K, Calle-Vallejo F, and Koper M (2015) J. Phys. Chem. Lett. 6:4073−4082

11. Nie X, Luo W, Janik M, Asthagiri A (2014) 312:108-122
12. Li C, Kanan MW (2012). J. Am. Chem. Soc. 134:7231–7234
13. Feaster JT, Shi C, Cave ER, Hatsukade T, Abram DN, Kuhl KP, Hahn C, Nørskov JK, Jaramillo TF (2017). ACS Catal. 7:4822–4827
14. Choi S, Sang B-I, Hong J, Yoon KJ, Son J-W, Lee J-H, Kim B-K, Kim H (2017). Sci. Rep. 7:41207–41210
15. Kuhl KP, Hatsukade T, Cave ER, Abram DN, Kibsgaard J, Jaramillo TFJ (2014). Am. Chem. Soc. 136:14107–14113
16. Kuhl KP, Cave ER, Abram DN, Jaramillo TF (2012). Energy Environ. Sci. 5:7050–7059
17. Hatsukade T, Kuhl KP, Cave ER, Abram DN, Jaramillo TF (2014) Phys. Chem. Chem. Phys. 16:13814–13819
18. Kovalenko A, Neburchilov V (2020) J. Mol. Model. 26:267-276
19. Ozaki T, Kino H. (2004) Phys Rev B. 72(4):045121-045128
20. T. Ozaki, (2020), User's manual of OpenMX Ver. 3.9, http://www.openmx-square.org/openmx_man3.9
21. Davis J, Baletto F, and Johnston RL (2015) J. Phys. Chem. A 119(37):9703–9709
22. BIOVIA Discovery Studio (2020) Dassault Systems, San Diego, CA, USA
23. Kovalenko A (2013). Pure Appl Chem 85:159–199
24. Nishihara S, Otani M (2017) Phys. Rev. B 96:115429-115434
25. Giannozzi P et al. (2009) J. Phys.: Condens. Matter. 21:395502-395520
26. Tesch R, Kowalski P, and Eikerling MH (2021) J. Phys.: Condens. Matter 33:444004-444017

Distance, Å				
	Magnetic Cu_{21}		Non-Magnetic Cu_{21}	
	R(Cu_{21}-CO)	R(Cu_{21}-OC)	R(Cu_{21}-CO)	R(Cu_{21}-OC)
DFT-D3	1.83142	2.97017	1.83900	2.96940
DFT	1.83222	2.85480	1.83296	2.97138
Adsorption Energy, *eV*				
	Magnetic Cu_{21}		Non-Magnetic Cu_{21}	
	E(Cu_{21}-CO)	E(Cu_{21}-OC)	E(Cu_{21}-CO)	E(Cu_{21}-OC)
DFT-D3	1.06942	0.24926	1.21227	0.18068
DFT	1.20111	0.12626	1.16927	0.12136

Table 1. C-Cu and O-Cu interatomic distances and adsorption energies for the relaxed systems presented in Figure 1 (b-e, g-j) calculated by optimization of the initial states in Figure 1a (Cu_{21}-CO) and Figure 1f (Cu_{21}-OC).

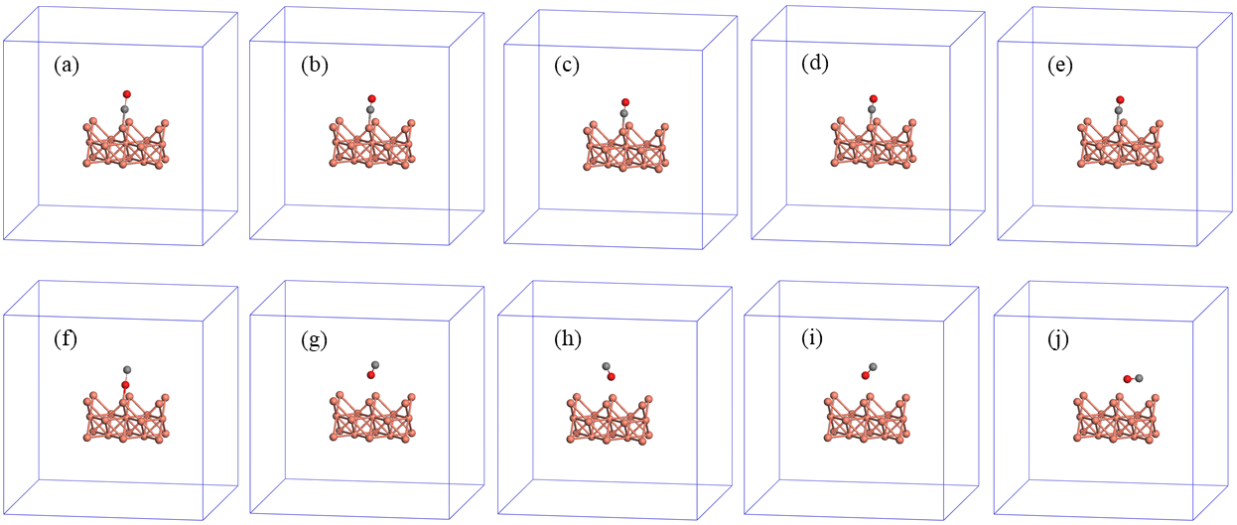

Figure 1. Initial (carbon oriented *a* and oxygen oriented *f*) and corresponding CO-Cu_{21} optimized structures (*b-e* for carbon oriented and *g-j* for oxygen oriented initial), calculated for magnetic (*c*,*e*,*h*,*j*) and non-magnetic (*b*,*d*,*g*,*i*) Cu_{21}, with (*d*,*e*,*i*,*j*) and without (*b*,*c*,*g*,*h*) D3 dispersion correction. Prepared using BIOVIA Discovery Studio 2020 [22].

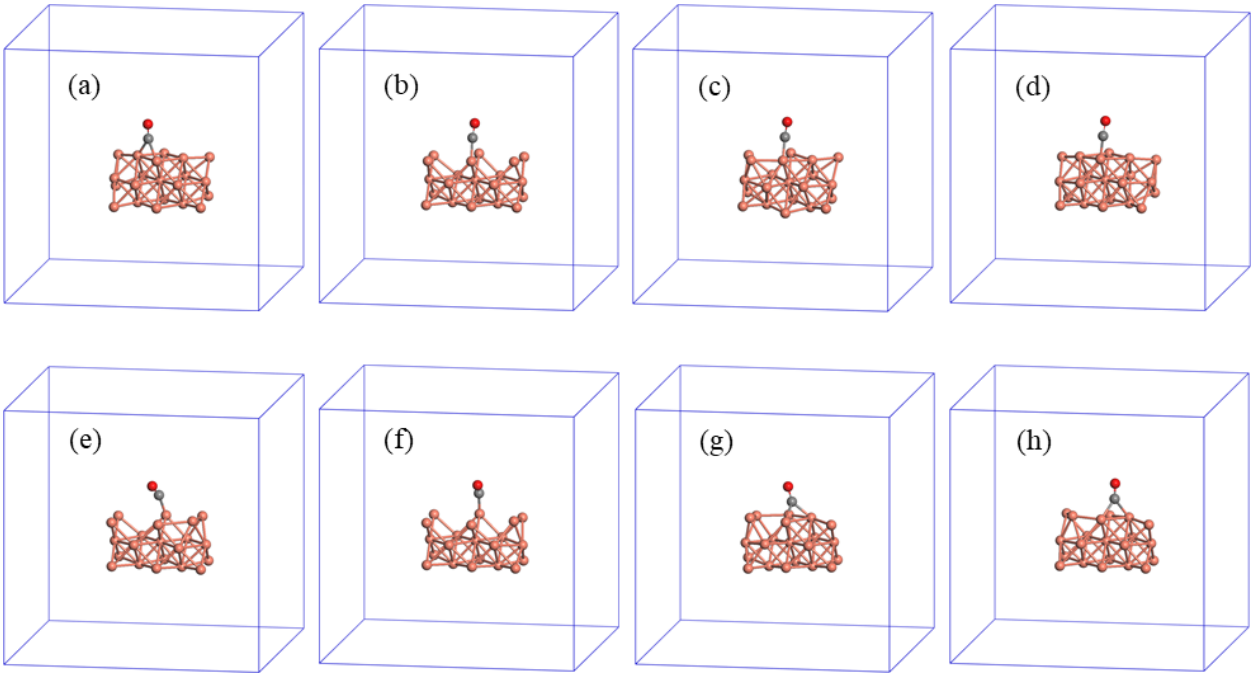

Figure 2. The structures obtained similarly to Figure 1 b-e, g-j with additional optimization of Cu_{21} cluster. Prepared using BIOVIA Discovery Studio 2020 [22].