Catal Lett (2009) 129:444–448
DOI 10.1007/s10562-008-9821-x

Steam Reforming of Formaldehyde on Cu(100) Surface: A Density Functional Study

Ju-Yi Bo · Shurui Zhang · Kok Hwa Lim

Received: 3 July 2008 / Accepted: 15 December 2008 / Published online: 9 January 2009

Abstract In this work we have systemically characterized the adsorption complexes of formaldehyde and its reaction intermediates to CO_2 formation on the Cu(100) surface using periodic DFT method. We found that formaldehyde reaction with surface O is thermodynamically more favorable compared with the reaction path of formaldehyde with OH.

Keywords DFT · Cu · Steam reforming · Formaldehyde

1 Introduction

Due to the concern of global warming and inevitable exhaustion of oil reserves, it is highly desirable to develop an alternative energy source to combustion engines [1]. Fuel cell, which is an electrochemical energy conversion device, has become a more environmentally friendly realistic alternative to combustion engines [2]. A hydrogen cell uses hydrogen as fuel and oxygen as oxidant, producing water as product, which does not harm environment [1]. However, difficulties of transportation and danger of handling have been caused by hydrogen's low density and large volume. Therefore, liquid fuel is preferred over gas fuel as they are more convenient and less dangerous to handle [3]. Strong efforts have been made by researchers to achieve an efficient in situ conversion of liquid fuel to hydrogen [4, 5]. A typical process for this purpose is methanol steam reforming (MSR), $CH_3OH + H_2O \rightarrow H_2 + CO_2$ on Cu-based catalysts [4, 6, 7]. On the catalyst, the formation of CO_2 is thought to be via the route of formaldehyde reacting with water related species (i.e. OH and O) via a formate type intermediate on the Cu surface [8] instead of decomposition of formaldehyde to CO [9] and then via the formation of CO_2 via the water-gas-shift reaction [10]. Although the mechanism of formaldehyde reacting with surface O to form formic acid intermediate, was previously studied using density functional (DF) cluster calculations on Cu(111) surfaces [9], it is not clear if the reacting species during steam reforming conditions is surface OH or O.

Thus in the current works, we studied the adsorption complexes of formaldehyde and its various reaction intermediates (with OH and O) on the Cu(100) surface and then look at the reaction thermodynamics of these species on the Cu(100) surface as the first step to understand the formaldehyde steam reforming reactions.

2 Computational Methods and Models

All calculations in this work used the Vienna ab initio simulation package, [11–13] with PBE [14] GGA as the exchange-correlation functional. The electron-ion interaction is described with the projector augmented wave (PAW) method [15, 16]. Brillouin zone integrations were performed using a combination of $(3 \times 3 \times 1)$ Monkhorst-Pack k-point grids [17] and generalized Gaussian smearing technique [18] and a cutoff energy of 400 eV. This energy cutoff guarantees good convergence. All atomic coordinates of the adsorbates were optimized until the force acting on each atom was less than 0.1 eV/nm.

The work was presented during the conference Catalysis for Society, Krakow, May 11-15, 2008. The paper is submitted by the conference organizers as agreed with Editor G.A. Somorjai.

J.-Y. Bo · S. Zhang · K. H. Lim (✉)
Division of Chemical and Biomolecular Engineering, School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, Jalan Bahar 637459, Singapore
e-mail: kokhwa@ntu.edu.sg

All adsorption studies were carried out on the (100) surface of Cu. We have chosen the (100) surface for its simplicity in modeling. Although real catalysts feature complex surface structures, it is nevertheless useful to study the mechanism of elementary reaction steps for idealized model surface systems, e.g. single-crystal surfaces, if only for reference purposes [19]. This modeling strategy is treated as a first step toward understanding the reactivity of more complex surfaces of the real catalysts.

To model these surfaces, a 4-layer slab was used with adsorbates binding on one side of the slab. This 4-layer slab model represents an acceptable compromise between accurate representation of a real metallic surface and computational economy. The unit cell consists of 9 Cu atoms per layer and thus enable us to consider low surface coverage of 1/9. The slabs are separated by a vacuum spacing of ~ 1 nm. For adsorption studies, we studied the adsorption characteristics of H, O, CO, CO_2, OH, HCOO and COOH, H_2CO and H_2COO and HCOOH on three high symmetrical sites (top, bridge, and hollow) on the Cu(100) surfaces.

The adsorption energy of adsorption complexes was then calculated from the equation: $E_B = E_{ad/sub} - (E_{ad} + E_{sub})$, where $E_{ad/sub}$ is the total energy of the slab model covered with the adsorbate, and E_{ad} and E_{sub} are the total energies of the adsorbate in the gas phase and of the clean substrate, respectively. From this definition, a positive value implies a release of energy or a favorable adsorption.

3 Results and Discussion

Our calculated bulk optimized Cu lattice constant is 3.63 Å, in agreement with previous reported result of 3.63 Å using the PW91 functional [4]. Adsorbed complexes of H, O, OH, CO, CO_2, COOH, H_2CO, H_2COO, H_2COOH, HCOO and HCOOH on the bulk terminated Cu(100) surface have been studied.

3.1 Atomic Hydrogen H

The adsorption energies, E_B of atomic H on the top, bridge and hollow sites were calculated to be −169, −213 and −226 kJ mol^{-1}, respectively. This agree with the trend reported in previous theoretical studies on the Cu(111) surface using periodic slab [4] and cluster models [20]. The results of adsorption energies on both surfaces are presented in Table 1. The difference in adsorption energy of our current works and previous theoretical results is about 10 kJ mol^{-1}. This is within our expectation as different surface models and GGA (PW91 vs. PBE) were used for the two calculations.

Table 1 Comparison of adsorption energies of the most stable adsorption complexes of H, O, OH, CO, CO_2, COOH, H_2CO, H_2COO, H_2COOH, HCOO, and HCOOH on Cu(100) and Cu(111) surfaces

	Cu(100)	Cu(111)
H	−226(h)	−237[a] (h)
O	−480(h)	−465[a] (h)
OH	−306(h)	−309[b] (h)
CO	−86(b)	−83[a] (h)
COOH	−192[c](b)	
HCOO	−291(b)	−313[d] (b)
H_2COO	−360(b)	−415[e] (b)
H_2COOH	−268(b)	

Parentheses denote adsorption sites, h–hollow, b–bridge, t–top

[a] Ref. [4]

[b] Ref. [16]

[c] Binding via C and O atoms, otherwise through two O atoms

[d] Cluster model, Ref. [27]

[e] Cluster model, Ref. [32]

3.2 Atomic Oxygen O

The adsorption energies E_B on the top, bridge and hollow sites were −304, −407 and −480 kJ mol^{-1}, respectively. Therefore, the most stable adsorption position of atomic oxygen is at hollow site. Comparatively, the E_B for atomic O are more exothermic than those for atomic H. This is due to the fact that atomic O has more valence electrons to interact with the surface. This results in a stronger interaction and more exothermic E_B for O. Previous theoretical studies of atomic O adsorption on Cu(111) surface [4] reveal that the adsorption energies at top site and hollow site on Cu(111) are −294 and −465 kJ mol^{-1}, respectively in agreement with our expectation as the Cu atoms on Cu(100) surface is less coordinated and binds stronger to the O atom.

3.3 Hydroxyl Group OH

Different starting geometries where the molecular axis of OH is orientated normal and parallel to the Cu(100) surface were studied. After geometric optimization, the OH geometries always end up with O binding to the surface. When OH group adsorbs on the Cu(100) surface, the O atom interacts with Cu surface and form a bond with the surface Cu atoms. In gas phase, the O–H bond distance is 0.99 Å. It is shortened to 0.97 Å upon adsorption on Cu(100) surface, similar to the case of OH adsorption on Pd (111) surface [21]. The interaction between OH and the

Cu surface are mainly due to charge transfer from Cu to OH [22] and hence lead to a shortening of the O–H bond as the OH acquire the negative charge. The E_B for top, bridge and hollow sites are −220, −279 and −306 kJ mol^{-1}, respectively. These are in agreement with previous reports that OH favors higher coordination sites [23] with reported E_B of 232, 294 and ~ 309 kJ mol^{-1} for top, bridge and hollow sites on the Cu(111) surface [8].

3.4 Carbon Monoxide CO

CO binds to the metallic surface through its carbon atom [20]. The E_B at top site, bridge and hollow sites are −83, −86 and −79 kJmol^{-1}, respectively. Previous theoretical studies on Cu(111) [4] reported E_B of −69 kJ mol^{-1} (top), −83 kJ mol^{-1} (fcc) and −80 kJ mol^{-1} (hcp) in agreement with our present study.

3.5 Carbon Dioxide CO_2

CO_2 being a close shell molecule is difficult to be activated and hence, its binds weakly to the Cu(100) surface with essentially zero adsorption energies. Experimental studies on Cu(100) surface reported E_B of −25 to −30 kJ mol^{-1} for different surface coverages, showing that CO_2 is indeed weakly bounded to the Cu surface [24]. Adsorption of CO_2 on Cu(110) surface has also been studied by XPS and UPS [25] and it was reported that no CO_2 adsorption was observed on clean Cu(110) surface.

3.6 Formaldehyde H_2CO

All atoms in formaldehyde are fully coordinated and thus there is little driving force for it to interact with the Cu surface. Previously, it was reported that formaldehyde binds to the Cu(111) surface in the top-bridge-top configuration with BE of −11 kJ mol^{-1} [4]. On the Cu(100) surface, we found similar trend that H_2CO binds weakly to the Cu(100) surface in the top-bridge-top configuration with BE of −16 kJ mol^{-1}.

3.7 Carboxyl Group COOH

COOH can interacts with Cu(100) surface via its two oxygen atoms. At the bridge site, COOH interacts with the Cu surfaces with O–Cu bond distances of 2.07 Å and 2.16 Å and $E_B = -76$ kJ mol^{-1}. At the hollow site, COOH interacts with the Cu(100) surface with E_B of −59 kJ mol^{-1}, slightly weaker than the bridge site as seen with the elongation of O–Cu bond distances of ~ 0.05 –2.16 Å and 2.23 Å. In addition, COOH can also interact with the surface via both the C and O atoms (see Fig. 1a). This adsorption complex ($E_B = -192$ kJ mol^{-1}) is more stable than the formal adsorption complex by more than 100 kJ mol^{-1} where two O atoms are bonded to the surface. This is because in the current case, C atom is not fully coordinated and hence allow strong binding to the surface compared to the formal case, in consistent with previous finding on the Pd and Pt surfaces [26].

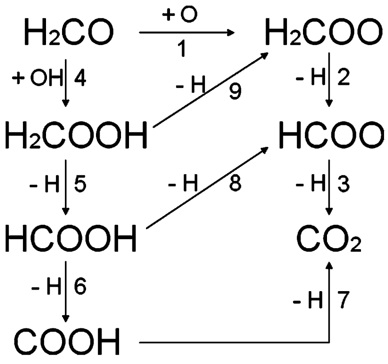

Fig. 1 Top and Side views of the most stable adsorption complexes of a) COOH, b) HCOO, c) H_2COO and d) H_2COOH on the Cu(100) surface. *Light gray sphere*–H atom, *dark gray sphere*–C atom, *red color sphere*–O *and blue sphere*–Cu

3.8 Formate HCOO

Both oxygen atoms of the HCOO interact with copper surface at the bridge site and form bonds with the distances of ~2.01 Å with Cu(100). While at the hollow site, O–Cu bond distance is slightly elongated to 2.06 Å showing weaker interaction at this site. The E_B calculated for bridge and hollow sites are −291 and −272 kJ mol^{-1}, respectively. Previous calculations of HCOO adsorption on the (100) and (111) surfaces of Cu cluster with B3LYP functional showed that it prefers the bridge site with $E_B = -313$ kJ mol^{-1} [27]. This is in agreement with our current work bearing in mind the differences in surface model (cluster vs. slab), and functional (B3LYP vs. PBE). The previous reported theoretical O–Cu bond distance of 2.01 Å [27] and experimental report of O–Cu distance of 1.98 ± 0.04 Å [28] are in perfect agreement with our current calculated O–Cu bond distance of 2.01 Å. In addition, previous reported theoretical C–O bond distance, 1.27 Å [27] and experimental report of C–O bond distance of 1.27 ± 0.04 Å [29, 30] on Cu(111) also agree well with our present computed value of 1.27 Å.

3.9 Dioxymethylene H_2COO

Similar to HCOO, H_2COO binds to the surface via its two O atoms. The calculated E_B at bridge site is −360 kJ mol^{-1} showing essentially no preference of adsorption sites. H_2COO binds stronger to the surface compare to HCOO, because both the O atoms in H_2COO

are unsaturated radicals compares to the O atoms in formate where one O atom is fully coordinated (doubled bonded to C) and the other is an unsaturated radical. Upon adsorption on Cu(100) surface, the C–O bond distances is elongated from the 1.34 Å (gas phase) to 1.39 Å. Here, we observed that O–Cu distance is 1.87 Å, shorter that those found for HCOO, in consistence with the higher adsorption energies found for H_2COO compared to HCOO. Previous reported E_B of H_2COO adsorption on different bridge sites of the (111) surface of Cu_{30} cluster model using B3LYP functional, were −367 and 404 kJ mol^{-1} [31] and 342 and 415 kJ mol^{-1}[32], in agreement with our current computed E_B of −360 kJ mol^{-1} bearing in mind the different surface model and exchange-correlation functional used.

3.10 H_2COOH Methylene Glycol Radical

With one H attached to the O of H_2COO, H_2COOH interacts weaker to the Cu surfaces as one O atom in OH interacts weaker with the Cu surface via its lone pair of electrons as indicated by the Cu–O and Cu–OH bond distances of 2.05 and 2.26 Å, respectively. This E_B for H_2COOH is −268 kJ mol^{-1} at the bridge sites. The adsorption energy of the most stable H_2COOH adsorption complexes is comparable to HCOO because the O atoms in H_2COOH and HCOO are similar where one O atom is unsaturated radical and the other fully coordinated (C–O–H vs. C=O).

3.11 Formic Acid HCOOH

While H_2COOH process an unsaturated O atom, HCOOH is fully coordinated and hence there is little driving force to interact with the Cu surface. Indeed, HCOOH essentially does not bind to the surface with near zero adsorption energies and no activation of its various molecular bonds. This is in consistence with various experimental observations that formic acid has high diffusivity and reported to be weakly held on the catalyst surface [33, 34].

4 Reaction Energy

Reaction energies of possible transformation of formaldehyde to CO_2 (see Fig. 2) are reported in Table 2. It is believed that formaldehyde reacts with water related species (O or OH, reaction 1 and 4 in Table 2) to form formic acid type of intermediates before decomposing to CO_2. The path where formaldehyde reacting with surface O (reaction 1) to produce H_2COO has been previously studied [35] and was found to be thermodynamically favorable [20]. This intermediate H_2COO was also observed by infra-red spectroscopy on silica supported copper catalysts [36]. The proposed mechanism was based on TPD experiment for the H_2CO/O adsorption complexes on Cu(110) [37, 38]. Here this was found the reaction to be exothermic, by −51 kJ mol^{-1}. Subsequent decomposition of H_2COO to HCOO and H (reaction 2) is highly exothermic, $\Delta E =$ −114 kJ mol^{-1} indicating high thermodynamic driving forces for this reaction path. The decomposition of HCOO to CO_2 is an endothermic reaction, $\Delta E = 58$ kJ mol^{-1}

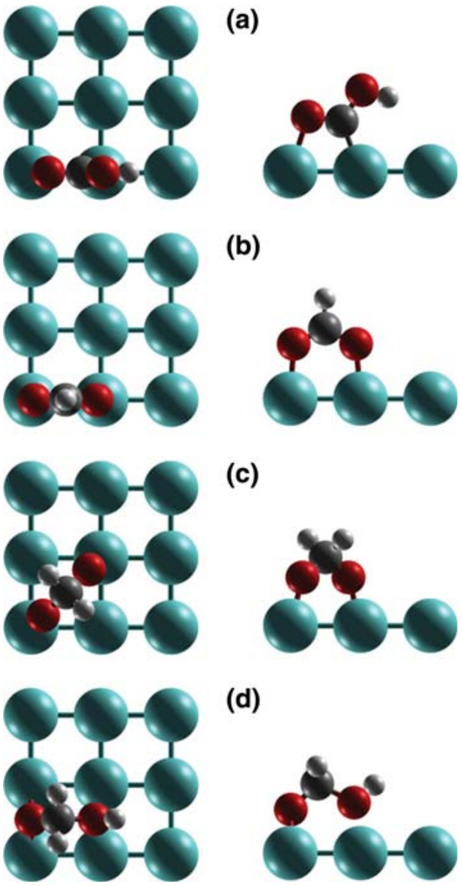

Fig. 2 Proposed reaction network for formaldehyde steam reforming on Cu(100) surface

Table 2 Calculated $\Delta_{rxn}E$ (kJ mol^{-1}) for the various steps in the proposed reaction network for Cu(100) surface

No.	Reaction	Reaction energy
1	$H_2CO + O \rightarrow H_2COO$	−51
2	$H_2COO \rightarrow H + HCOO$	−114
3	$HCOO \rightarrow CO_2 + H$	58
4	$H_2CO + OH \rightarrow H_2COOH$	−76
5	$H_2COOH \rightarrow HCOOH + H$	42
6	$HCOOH \rightarrow COOH + H$	1
7	$COOH \rightarrow CO_2 + H$	−3
8	$HCOOH \rightarrow HCOO + H$	−61
9	$H_2COOH \rightarrow H_2COO + H$	96

where the heat can be compensated from the earlier two decomposition paths (1 and 2).

H_2CO can also react with surface OH with reaction energies of -76 kJ mol^{-1}, to form H_2COOH indicating the possibility of this reaction path. As surface OH was found to be more abundant than surface O on the Cu(111) surface under steam reforming conditions [16]. Subsequent decomposition reaction via the C–H or O–H bond breaking path are endothermic, $\Delta E = 42$ kJ mol^{-1} (reaction path 5) and 96 kJ mol^{-1} (reaction 9), respectively. The C–H bond breaking reaction of H_2COOH can be driven by the exothermic subsequent O–H bond breaking reaction (path 8) where HCOOH is decomposed to HCOO and H with $\Delta E = -61$ kJ mol^{-1}. On the other hand, further decomposition of H_2COO is exothermic, $\Delta E = -114$ kJ mol^{-1} (reaction 2).

Here, we found that the overall reaction paths to CO_2 from formaldehyde reaction with surface O (reactions 1) and OH are both exothermic, $\Delta E = -107$ and -36 kJ mol^{-1}, respectively, indicating the thermodynamically, formaldehyde prefers to react with surface O. For reaction paths involving the HCOO intermediate, the likely rate determining step would be the C–H bond breaking of HCOO as the reaction is endothermic, 58 kJ mol^{-1} (reaction 3) while for reaction involving the COOH intermediate would be the C–H bond breaking reaction of H_2COOH with endothermic reaction energy of 42 kJ mol^{-1} (reaction 5).

5 Conclusions

In this work we have systemically characterized the adsorption of formaldehyde and its reaction intermediates to CO_2 formation on the Cu(100) surface using periodic DFT. We found that formaldehyde, formic acid and CO_2 bind very weakly to the surface with essentially very low adsorption energies. For atomic O and H atoms on the surface, they are rather mobile on the surfaces with rather flat potential energy surface. HCOO, H_2COO intermediates prefers to bind to the surface using both their O atoms with high adsorption energies of ~ 300 kJ mol^{-1}. We found that formaldehyde reaction with surface O is thermodynamically more favorable compared with formaldehyde reaction with OH.

Acknowledgments J. Bo and S. Zhang acknowledge support from SCBE FYP's project. This work was supported by NTU's grants SUG 43/06 and M58120000.

References

1. Ross DK (2006) Vacuum 80:1084
2. Holladay JD, Wang Y, Jones E (2004) Chem Revs 104:4767
3. Ha S, Larsen R, Masel RI (2005) J Power Sources 144:28
4. Chen Z-X, Neyman KM, Lim KH, Roesch N (2004) Langmuir 20:8068
5. Neyman KM, Lim KH, Chen Z-X, Moskaleva LV, Bayer A, Reindl A, Borgmann D, Denecke R, Steinrück HP, Rösch N (2007) Phys Chem Chem Phys 9:3470
6. Trimm DL, Önsan ZI (2001) Catal Rev 43:31
7. Foo ASY, Lim KH (2008) Catal Lett. doi:10.1007/s10562-008-9653-8
8. Lim KH, Moskaleva LV, Rösch N (2006) Chem Phys Chem 7:1802
9. Lim KH, Chen Z-X, Neyman KM, Rösch N (2006) J Phys Chem B 110:14890
10. Iwasa N, Takezawa N (2003) Top Catal 22:215
11. Kresse G, Furthmüller J (1996) Phys Rev B 54:11169
12. Kresse G, Hafner J (1996) Phys Rev B 47:104205
13. Kresse G, Furthmüller J (1999) Comp Mat Sci 6:15
14. Perdew JP, Burke K, Ernzerhof M (1996) Phys Rev Lett 77:3865
15. Blöchl PE (1994) Phys Rev B 50:17953
16. Kresse G, Joubert D (1999) Phys Rev B 59:1758
17. Monkhorst HJ, Pack JD (1976) Phys Rev B 13:5188
18. Methfessel M, Paxton AT (1989) Phys Rev B 40:3616
19. Somorjai GA (1994) Introduction to surface chemistry and catalysis. Wiley, New York
20. Gomes JRB, Gomes JANF (2001) Surf Sci 471:59
21. Chao Y, Chen Z-X (2006) Surf Sci 600:4572
22. Pettersson LGM, Agren H, Vahtras O, Carravetta V (1995) J Chem Phys 103:8713
23. Gomes JRB, Gomes JANF, Illas F (1999) Surf. Sci. 443:165
24. Rasmussen PB, Taylor PA, Chorkendorff I (1992) Surf. Sci. 269–270:352
25. Krause J, Borgmann D, Wedler G (1996) Surf. Sci 347:1
26. Yue CMY, Lim KH (2008) Catal Lett. doi:10.1007/s10562-008-9741-9
27. Gomes JRB, Gomes JANF (1999) Surf. Sci. 432:279
28. Woodruff DP et al (1988) Surf Sci 201:275
29. Stohr J, Outka DA, Madix RJ, Dobler U (1985) Phys Rev Letts 54:1256
30. Outka D, Madix RJ, Stohr J (1985) Surf Sci 164:235
31. Gomes JRB, Gomes JANF (2000) Surf Sci 446:283
32. Gomes JRB, Gomes JANF (1999) Electrochemica Acta 45:653
33. Ying DHS, Madix RJ (1980) J Catal 61:48
34. Bowker M, Rowbotham E, Leibsle FM, Haq S (1996) Surf Sci 349:97
35. Bowker M, Madix RJ (1981) Surf Sci 102:542
36. Clarke DB, Lee DK, Sandoval MJ, Bell AT (1994) J Catal 150:81
37. Wachs IE, Madix RJ (1979) Surf Sci 84:375
38. Barteau MA, Bowker M, Madix MJ (1980) Surf Sci 94:303