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Stable CO/H₂ ratio on MoP surfaces under working condition: A DFT based thermodynamics study



Surface Science

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ARTICLE INFO

Keywords: MoP Surface CO/H₂ ratio Co-adsorption DFT

ABSTRACT

By performing a systematic DFT calculation and applying the atomistic thermodynamics analysis, the adsorption configurations, stable concentrations of $nCO + mH_2$ co-adsorption on three representative MoP surfaces [(101), (001)-Mo and (001)-P] were investigated. Our results show that CO adsorbs much stronger than dissociative H_2 on (101) and (001)-Mo surfaces but competitively with dissociative H_2 on the (001)-P surface, and the hydrogen saturation coverage decreases with increasing CO pre-coverage. *Ab initio* atomistic thermodynamics analysis indicates the quite different CO and H_2 co-adsorption manners on three surfaces under syngas atmosphere, i.e., at the equilibrium co-adsorption state, the Mo/P-terminated (101) surface and the Mo-terminated (001) surface have more versatile surface CO and H_2 ratios, which are entirely different from that in the gas phase. However, the P-terminated (001) surface has only hydrogen adsorption at a wide range of conditions, which plays a role of hydrogen reservoir. Such investigations reveal that surface CO/H₂ ratio could be altered by manipulating the pressures of the gas phase and temperatures, which would be beneficial to modify the syngas conversion reactivity as well as different product distributions on solid catalyst surfaces.

1. Introduction

Due to the high electrical conductivity and activity, the study of molybdenum phosphide (MoP) as a promising non-noble-metal electrocatalyst is booming up in recent decades [1–14]. The possibility as an electrode material was also extensively explored [15–20]. Also, it has been reported that MoP possesses decent catalytic activities in many catalysis processes. For instance, it can be served as cocatalysts to improve the activity and stability of photocatalyst [21–24], be potentially used in hydro-treating of biomass [25,26] and petroleum fractions [27–33] as well as upgrading of non-edible oils [34–41].

Recently, it is found that in partial oxidation and dry reforming of methane [42–44], hydrogenation of CO_2 to methanol [45,46], hydrogenation of acetic acid [47], synthesis of higher alcohols from syngas (CO + H₂) [48] and methanation of CO [49,50] processes, MoP shows excellent catalytic performance. Especially in syngas conversion into higher alcohols, MoP presents remarkable activity and selectivity [51–54]. In such reactions, syngas indeed plays a significant role no matter as reactant, intermediates or product. Therefore, investigating the specific adsorption and activation of CO and H₂ on MoP surfaces is significant for understanding the mechanisms of these reactions.

There are extensive investigations have been reported for CO or H₂

adsorption on three low index surfaces, i.e. (100), (001) and (101) surfaces [55-60]. The mechanism of synthesis gas conversion to methane and methanol, as well as the effect of K on the reaction based on a Mo₆P₃ cluster model were studied by Zaman et al [61,62]. Very recently, based on the surface energy calculation and morphology study of MoP catalyst under experimental synthesis conditions [63], theoretical investigations have proved that CO prefers to adsorb in a molecular state with saturation coverage ranging from 4/9 to 2 monolayers (ML) on seven representative surfaces of MoP catalyst [64], while H₂ prefers to adsorb in a dissociated state with saturation coverage ranging from 1 to 4 ML [65–68]. However, it should be noted that CO and H₂ coexist under real experimental conditions. Therefore, identifying the stable CO/H2 ratio on MoP surfaces is meaningful and essential for further correlative reaction mechanism investigations. Herein, systematic DFT computations were performed to investigate the co-adsorption of CO and hydrogen on three representative MoP surfaces. The stable surface composition of CO and H under different experimental conditions were finally identified by thermodynamics method.

https://doi.org/10.1016/j.susc.2020.121738

Received 1 September 2020; Received in revised form 20 September 2020; Accepted 24 September 2020 Available online 30 September 2020

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2. Computational details

2.1. Methods

All DFT calculations were performed using the VASP (Vienna Ab initio Simulation Package) suite [69,70]. The generalized gradient approximation with the Perdew-Burke-Ernzerhof (GGA-PBE) method [71,72] in the projector augmented wave (PAW) formalism [73] was used. The cutoff energy was set to 400 eV. The energy and force tolerance were set to 10^{-4} eV and 0.02 eV/Å, respectively.

The equation $E_{ads} = E(X/slab) - E(X) - E(slab)$ is used to calculate the adsorption energy (E_{ads}) of one X adsorbate. E(X/slab), E(X) and E(slab) represent the total energy of the slab with one X adsorption, X molecule in the gas phase and the bare surface, respectively. A negative $E_{\rm ads}$ value indicates an exothermic adsorption process. Therefore, the more negative E_{ads} , the more stable adsorption. The differential adsorption energy (ΔE_{ads}) was defined as $\Delta E_{ads} = E(X_{n+1}/slab) - E(X_n/slab)$ slab) -E(X), where n + 1 and n are the numbers of adsorbed X species. A breakthrough point where ΔE_{ads} change to positive was used to identify the saturation coverage. On the Y species pre-covered surface, the formula changes to $E_{ads} = E(X&Y/slab) - E(X) - E(Y/slab)$ and $\Delta E_{ads} = E(X_{n+1}\&Y/slab) - E(X_n\&Y/slab) - E(X)$, respectively. The energetics including zero-point energy correction were used for the following discussion. Ab initio atomistic thermodynamics [74-80] was introduced to consider the effects of temperature and pressure on the surface ratio of co-adsorption species. The detailed description of the method is given in the Supplementary Information section (SI). The monolayer (ML) coverage was defined by the ratio of the adsorbed X adsorbates to outmost surface P atoms for (001)-P termination or Mo atoms for other terminations.

2.2. Models

The WC-type MoP bulk crystal structure was used for calculation, and the obtained lattice constant is a = b = 3.239 Å, c = 3.193 Å, agree well with the experimental report (a = b = 3.223 Å and c = 3.191 Å) [81]. For studying CO and H₂ co-adsorption, three representative surfaces with different surface features were chosen, i.e., the most stable MoP(101) surface with Mo/P mixed termination and the least stable MoP(001) surface with Mo or P terminations. The *p* (3×3) supercell with ten atomic layers in total was chosen to simulate the (001)-P surface, and the first four atomic layers were allowed to relaxation, denoted by $p(3 \times 3)$ -10L/R4. For (001)-Mo and (101) surfaces, $p(3 \times 3)$ -8L/R4 and $p(2 \times 3)$ -8L/R4 supercells were used, respectively. To avoid strong interactions between slabs, a vacuum layer of 15 Å was constructed. For all three surfaces, a $3 \times 3 \times 1$ Mon-khorst–Pack k-point sampling was employed.

3. Results and discussion

3.1. Single CO or H_2 adsorption

The surface structures of the three chosen terminations are presented in Fig. 1. The circled letters mark the possible adsorption sites. **T**, **B**, **H** represent top, bridge and hollow site, respectively. As shown in Fig. 1, on the (101) surface, there are one **T** site, one **B** site and one **H** site. The most stable adsorption site of CO on this surface is **T** site with $E_{ads} = -1.84 \text{ eV}$ [64]. CO interact with one surface Mo atom through C atom and the Mo-C distance is 2.01 Å. Molecular H₂ could adsorb at the top of surface Mo atoms (-0.54 eV), and the dissociation process is barrierless (0.02 eV) but highly exothermic (-1.41 eV) [68]. The most stable adsorption site of single H atom on the (101) surface is **B** site with $E_{ads} = -0.73 \text{ eV}$, and the two Mo-H bonds are 1.88, 1.89 Å, respectively. On both (001)-Mo and (001)-P surfaces, there are one **T** site, one **B** site, one fcc hollow site (**H1**) and one hcp hollow site (**H2**). On the (001)-Mo surface, CO locates at the **B** site is most stable with



Fig. 1. The top and side views of the MoP(101), MoP(001)-Mo and MoP(001)-P surface structures and possible adsorption sites (Mo atoms/blue, P atoms/pink).

 $E_{ads} = -2.43 \text{ eV}$ [64]. CO bridging two surface Mo atoms and the two Mo-C bonds are 1.99, 2.28 Å, respectively. A Mo-O bond (2.34 Å) also formed due to the tilted CO configuration. Molecular H₂ could form stable adsorption (-0.71 eV) at T site, but the dissociation barrier is also very low (0.04 eV), therefore H₂ also prefers the dissociative adsorption with $E_{ads} = -1.79 \text{ eV}$ [68]. H atom adsorbs at H1 site with $E_{ads} = -0.95$ eV is most stable, and the average distance of three Mo-H bonds is 2.02 Å. On the P-termination of (001) surface, the most stable configuration of CO adsorption is at the H2 site with $E_{ads} = -0.95 \text{ eV} [64]$. CO interact with three surface P atoms and one underneath Mo atom, the Mo-C distance is 2.22 Å, and the average P-C distance is 1.98 Å. H₂ only forms weak and physical adsorption and has very low dissociation barrier (0.08 eV), the dissociative adsorption has $E_{ads} = -1.37$ eV [68]. The most stable configuration of H adsorption is at the T site with $E_{ads} = -$ 0.68 eV, and the P-H distance is 1.42 Å. The detailed structures of CO, H and dissociative H₂ adsorption on the three surfaces are shown in Fig. S1.

It is clearly showed that the adsorption of CO is much stronger than dissociative H_2 on (101) and (001)-Mo surfaces, indicating CO pre-adsorption is thermodynamically more favored. However, on the (001)-P surface, CO adsorbs stronger than one single H atom but weaker than dissociative H_2 . To identify the most stable co-adsorption state on (001)-P surface, CO pre-adsorption and H-pre-adsorption were both considered. Only the most stable co-adsorption states were discussed in the later part.

3.2. CO and H_2 co-adsorption on the MoP(101) surface

Table 1 listed the co-adsorption energies of *n*CO pre-covered (101) surface with mH_2 (including dissociative and molecular state), and all the related adsorption configurations of *n*CO + 2*m*H were given in Fig. S2-S11. On the clean (101) surface, the saturation coverage for CO and

Table 1

Differential H_2 dissociative adsorption energies (eV) on the *n*CO pre-covered MoP(101) surface.

	0CO	1CO	2CO	3CO	4CO	5CO	6CO	7CO	8CO	9CO
0H 2H 4H 6H 8H 10H 12H 14H	-1.43 -1.31 -1.16 -0.14 -0.27 -0.34 -0.04	-1.84 -1.40 -1.18 -0.76 -0.19 -0.28 -0.24 -0.08	-1.81 -1.26 -1.07 -0.47 -0.25 -0.25 -0.18 -0.04	-1.61 -1.20 -0.91 -0.40 -0.25 -0.27 -0.11	-1.62 -1.11 -0.81 -0.28 -0.29 -0.22	-1.54 -1.04 -0.66 -0.32 -0.26	-1.60 -0.86 -0.58 -0. 33	-0.69 -0.73 -0.36	-0.57 -0.49 -0.12	-0.42 -0.33
14H	-0.04	-0.08	-0.04							

hydrogen is 3/2ML (9CO) and 7/3 ML (14H), respectively. When the coverage of hydrogen below 2 ML, there are only H atoms on the surface. However, molecular H₂ appears when coverage increasing. Apparently, the differential adsorption energy and the saturation coverage of H₂ decrease with the increasing CO pre-coverage. According to the computed differential adsorption energies of H₂, it is possible to adsorb less than 14H atoms on 1CO and 2CO pre-covered surfaces, i.e., the saturation coverage of hydrogen is 7/3 ML (14H). On 3CO pre-covered surface, the saturation coverage of hydrogen decreases to 2 ML (12H). On 4CO pre-covered surface, the saturation coverage of hydrogen decreases to 5/3 ML (10H). On 5CO pre-covered surface, the saturation coverage of hydrogen decreases to 4/3 ML (8H). Then, the saturation coverage of hydrogen further decreases to 1 ML (6H) on 6CO precovered surface, 2/3 ML (4H) on 7CO or 8CO pre-covered surfaces, and 1/3 ML (2H) on 9CO pre-covered surface. It should be mentioned that on the pure or nCO (n=1-5) pre-covered surfaces, molecular H₂ could co-exist with H atoms on the surface at high coverage, but the molecular H₂ just weakly adsorbed (less than 0.25 eV) and easy to desorb (Fig. S3-S7).

Furthermore, some interesting phenomenon was found for the adsorption configurations of pure CO or H_2 and their co-adsorption on the (101) surface. For example, for the pure CO adsorption, the first 6CO preferentially occupy the six **T** sites and the rest 3CO occupy three **B** sites to reach the saturation of 9CO. For the pure H adsorption, however, the first 6H atoms preferentially occupy the six **B** sites and the rest H atoms or H_2 molecules occupy the six **T** sites to reach the saturation of 14H. In this case, CO and H will take quite different adsorption sites at *n*CO (*n*=1-6) pre-covered surfaces, which means that CO adsorption does not affect the adsorption configurations of the first six H atoms, but further adsorption of H atoms was limited by the residual **T** sites. On the *n*CO (*n*=7-9) pre-covered surface, H atoms can only occupy the **B** sites, and the coverage of adsorbed H atoms was equal to 12-n.

3.3. CO and H_2 co-adsorption on the MoP(001)-Mo surface

On the clean (001)-Mo surface, the saturation coverage for CO and hydrogen is 1ML (9CO) with all CO on the T sites and 26/9 ML (26H) with 9H on the H1 sites and the rest H or H₂ on the T sites, respectively. When the coverage of hydrogen more than 11/9 ML, molecular H₂ appears, i.e., the dissociative and molecular state of H₂ could co-exist at high coverage (Fig. S12). The structures and co-adsorption energies of adsorbed mH₂ on nCO pre-covered (001)-Mo surface were summarized in Fig. S13–S21 and Table 2. Similarly, the hydrogen coverage also decreases with the increase of CO pre-coverage. According to the computed differential H₂ adsorption energies, the 1CO pre-covered surface can have 22H (22/9ML) adsorption (22H + 1CO), 2CO precovered surface can have 20H (20/9ML) adsorption (20H + 2CO), 3CO

Table 2

Differential H₂ dissociative adsorption energies (eV) on the *n*CO pre-covered MoP(001)-Mo surface.

	0CO	1CO	2CO	3CO	4CO	5CO	6CO	7CO	8CO	9CO
0H		-2.43	-2.39	-2.37	-2.21	-2.01	-1.50	-1.35	-1.57	-1.62
2H	-1.83	-1.77	-1.71	-1.62	-1.57	-1.39	-1.18	-1.47	-1.16	-1.12
4H	-1.66	-1.61	-1.47	-1.27	-1.15	-1.02	-0.96	-0.91	-0.97	-0.86
6H	-1.56	-1.38	-1.25	-0.95	-0.61	-0.51	-0.64	-0.56	-0.59	-0.60
8H	-1.29	-1.16	-0.73	-0.44	-0.35	-0.30	-0.31	-0.34	-0.48	-0.20
10H	-0.82	-0.37	-0.28	-0.35	-0.31	-0.28	-0.30	-0.26	-0.20	
12H	-0.25	-0.35	-0.28	-0.31	-0.29	-0.28	-0.18	-0.27		
14H	-0.30	-0.25	-0.32	-0.34	-0.30	-0.31	-0.31			
16H	-0.19	-0.32	-0.27	-0.30	-0.36	-0.20				
18H	-0.22	-0.24	-0.36	-0.35	-0.14					
20H	-0.20	-0.32	-0.32							
22H	-0.02	-0.31								
24H	-0.19									
26H	-0.22									

or 4CO pre-covered surfaces can have 18H (18/9ML) adsorption (18H + 3-4CO), 5CO pre-covered surface can have 16H (16/9ML) adsorption (16H + 5CO), 6CO pre-covered surface can have 14H (14/ 9ML, 14H + 6CO) adsorption, 7CO pre-covered surface can have 12H (12/9ML, 12H + 7CO) adsorption, 8CO pre-covered surface can have 10H (10/9ML, 10H + 8CO) adsorption, and 9CO pre-covered surface can have 8H atoms (8/9ML, 8H + 9CO). Notably, extra 8H atoms are still possible to adsorb on the CO saturated surface. Despite of these energetic changes, the co-adsorbed H atoms normally occupy the H1 and T sites, which are same to that on the clean surface. Similar to that of (101) surface, molecular H₂ could co-exist with H atoms on the nCO (n = 1-8) pre-covered surfaces at high coverage, and H₂ normally occupy the **T** sites. The results indicate that the location of H atoms is only dependent on the limitation of the available free sites, while does not affect by the pre-covered CO molecules. However, the co-adsorbed H atoms slightly affect the adsorption configurations of CO. As shown in Fig. S13-S19, the B-sited CO turns to T-sited as H-coverage increases.

3.4. CO and H_2 co-adsorption on the MoP(001)-P surface

On the bare (001)-P surface, the saturation coverage of CO is 4/9ML (4CO), and under this saturation coverage, one CO occupies the H2 site, three CO occupy the B sites. However, the saturation coverage of hydrogen is 1ML (9H) with all H atoms at the T sites. Table 3 and Fig. S22-S25 listed the structures and co-adsorption energies of dissociative adsorbed mH2 on nCO pre-covered (001)-P surface. Similar to that of (101) and (001)-Mo surfaces, the hydrogen coverage decreases from 1ML to 2/9ML with the increase of CO pre-coverage. As shown in Table 3, the possible group of pre-covered *n*CO and saturated H atoms are 6H + CO, 4H + 2CO, 4H + 3CO and 2H + 4CO. Furthermore, the co-adsorbed CO has no effect on the adsorption configurations of H atoms, but the co-adsorbed H atoms result in the change of CO adsorption from H2 site to B site, as shown in Fig. S22-S25. It also should be mentioned that due to the very weak physical adsorption of molecular H₂ on this surface (0.02-0.04 eV), only adsorption of H atom is favored. Considering the strong P-H interaction, the possibility of PH₃ formation was explored. Based on our calculation, the process of removing one P-H species from 1H adsorbed or H saturated (001)-P surface and producing one PH₃ molecule is highly endothermic (2.09 or 1.95 eV). Therefore, we suppose that under low temperature, the (001)-P surface is stable under H₂ atmosphere, even in high H₂ pressure.

3.5. Surface CO/H_2 ratio at given temperature and pressure

Based on the *n*CO + 2*m*H co-adsorption energies and structures obtained by our DFT calculations, the surface CO/H₂ ratio and the effects of temperature (T) and pressure (*p*) were studied by applying the atomistic thermodynamics. Since desorption and reaction of CO and H₂ are inevitable at high temperatures, only 0-500K temperature range was considered. For studying the effect of total pressure, the partial pressure of CO and H₂ (p_{CO}/p_{H2}) was set to be 1/1. The corresponding phase diagrams were shown in Fig. 2. In each phase diagram, the regions with different color represent different stable surface composition under given conditions.

As shown in Fig. 2, the stable surface composition presents

Table 3

Differential H₂ dissociative adsorption energies (eV) on the *n*CO pre-covered MoP(001-P) surface.

	0CO	1CO	2CO	3CO	4CO
0H 2H 4H 6H 8H	-1.38 -1.40 -1.08 -0.44	-0.95 -1.20 -1.07 -0.60	-0.61 -1.16 -0.62	-0.36 -0.82 -0.22	-0.29 -0.44

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Fig. 2. Phase diagrams of stable nCO + 2mH co-adsorption coverage at different temperatures and total pressures ($p_{CO} = p_{H2} = p/2$) on MoP(101) surface (a), MoP (001)-Mo surface (b) and MoP(001)-P surface (c), respectively.

interesting differences on the three surfaces. At $p_{CO}/p_{H2} = 1/1$ and different total pressures, on the (101) surface, the stable surface composition changes gradually from the initial 9CO + 2H to 6CO + 6H/6CO + 4H/6CO + 2H/6CO/4CO/2CO/CO with increasing temperature. On the (001)-Mo surface, the stable surface composition changes from the initial 9CO + 8H gradually to 9CO + 6H/9CO + 4H/9CO + 2H/9CO(7CO + 2H)/5CO + 2H co-adsorption, and then to 5CO/4CO/3CO adsorption with increasing temperature. However, on the (001)-P surface, there is only hydrogen adsorbed on the surface, and the surface coverage gradually decreases from 8H to 6H/4H with increasing temperature.

Applying the situation under plausible total pressure (p = 1 atm, $p_{\rm H2} = p_{\rm CO} = 0.5$ atm) and the moderate temperature (i.e. 200K) as an example for direct comparison, the (101) surface has CO and hydrogen co-adsorption on the surface, and the equilibrium coverage is 6CO + 6H. The (001)-Mo surface has 9CO+6H co-adsorption. In contrast, the (001)-P surface only has hydrogen adsorption on the surface, and the equilibrium coverage is 8H. Based on the above discussion, it can be found that under the syngas conversion reaction condition, the Mo/P terminated (101) surface and (001)-Mo surface have more versatile surface CO/H₂ ratio and therefore higher opportunity to produce new species. In contrast, the (001)-P surface prefers hydrogen adsorption only, which could be a hydrogen reservoir. This also indicates that the different roles of MoP surfaces in the complex CO hydrogenation reaction mechanisms. Closer inspections of Fig. 2 also reveal that the surface CO/H₂ ratio is totally different from that in the gas phase. For instance, the ratio of CO and H₂ in the gas phase (p_{CO}/p_{H2}) at 200K is 1/ 1, but the surface ratio is 2/1 on the (101) surface, 3/1 on the (001)-Mo surface and 0/1 on the (001)-P surface, respectively. In summary, the surface CO/H₂ ratio could be tuned by manipulating the pressures of the gas phase and temperatures, which would be beneficial to modify the selectivity of syngas conversion on solid catalyst surfaces.

4. Conclusion

The co-adsorption of molecular CO and dissociative H_2 on the three representative MoP surfaces, i.e. (101), (001)-Mo and (001)-P surfaces were systematically studied by density functional theory calculation. It is found that CO adsorbs much stronger than dissociative H_2 on (101) and (001)-Mo surfaces but competitively with dissociative H_2 on the (001)-P surface, and the hydrogen saturation coverage decreases with increasing CO pre-coverage. Furthermore, the pre-adsorbed CO molecules have ignored effects on the adsorption configurations of H species because of their differences in favorable adsorption sites. However, the co-adsorbed H species slightly affect the CO adsorption configurations with increasing H coverage.

Ab initio atomistic thermodynamics analysis indicates that these three surfaces have different syngas adsorption properties. At the equilibrium co-adsorption state, the Mo/P-mixed (101) surface and the Mo-terminated (001) surface have more versatile surface CO/H₂ ratio, which is quite different from that in the gas phase. However, the Pterminated (001) surface has only hydrogen adsorption at a wide range of conditions, which plays a role of hydrogen reservoir. Our results clearly reveal that surface CO/H₂ ratio could be tuned by manipulating the pressures of the gas phase and temperatures, which would be beneficial to modify the syngas conversion reactivity as well as different product distributions on solid catalyst surfaces.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

This work was financially supported by the National Natural Science Foundation of China (No. 21903049 and No. U1510103), the Fund for Shanxi "1331 Project" Engineering Research Center (PT201807) and Shanxi "1331 Project" Key Innovative Research Team (1331KIRT). The support from the Shanghai Supercomputing Center and the Supercomputing Center of Shanxi University is greatly acknowledged.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi: 10.1016/j.susc.2020.121738.

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