Supporting Information for "Theoretical Insight into Effect of Doping of Transition Metal M (M = Ni, Pd and Pt) on CO_2 Reduction Pathways on Cu(111) and Understanding of Origin of Electrocatalytic Activity"

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In this paper, DFT calculations were performed to determine the intermediates for formation of CH_4 and CH_3OH from CO_2 reduction on the transition metal M (M=Ni, Pd and Pt)-doped Cu(111) surface, and the reduction pathways through various possible intermediates are investigated systematically. In the following, we will deduce the most possible pathways for CO_2 reduction into CH_4 and CH_3OH on transition metal M (M=Ni, Pd and Pt)-doped Cu(111) surface based on the reaction free energies and activation barriers analyses. Thus, the mechanistic insight into effect of doping of transition metal M (M=Ni, Pd and Pt) on CO_2 reduction into CH_4 and CH_3OH can be obtained. For comparison, the reduction pathways of CO_2 into CH_4 and CH_3OH on pure Cu(111) surface as included in our previous DFT study were also given.[1]

1. Reduction mechanism of CO_2 on the pure Cu(111) surface

Our previous DFT study[1] showed that by dissociative hydrogenation of CO_2, CO_{ads} is firstly formed on the pure Cu(111) surface, the CHO_{ads} and CH_2O_{ads} are the key intermediates towards the reduction of CO_2 into CH_4. Regardless of being the thermodynamics or kinetics, it is likely that CH_2OH_{ads} instead of CH_3O_{ads} is the intermediate for CH_4 and CH_3OH formations. Based on the activation barriers, the CH_2OH_{ads} intermediate is more easily to form CH_{2ads} intermediate and CH_3OH by hydrogenative dissociation and direct hydrogenation on pure Cu(111) surface, respectively, which may be parallel pathways. Finally, the CH_2 intermediate can lead to formation of the CH_4 by serial hydrogenation. The relatively slow steps include $CO_2(g) + H^* \rightarrow (CO + OH)^*$ and $(CO + H)^* \rightarrow CHO^*$ on the pure Cu(111) surface. Based on MEP calculation results, the optimal reaction paths for CO_2 reduction to CH_4 and CH_3OH production on the pure Cu(111) surface can be summarized in Table S1.

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Electronic supplementary information (ESI) available.

Table S1 The minimum energy paths for CO_2 reduction into CH_4 and CH_3OH and the activation barriers (E_{act}) and reaction free energies (E_{reac}) in each elementary step on the pure Cu(111) surface

Reaction paths	ΔG_{reac} (eV)	E_{act} (eV)
$CO_2(g) + H^* \rightarrow (CO + OH)^*$	0.27	1.18
$(CO + H)^* \rightarrow CHO^*$	0.86	1.06
$(CHO + H)^* \rightarrow CH_2O^*$	-0.21	0.72
$(CH_2O + H)^* \rightarrow (CH_2 + OH)^*$	0.01	1.12
$(CH_2O + H)^* \rightarrow CH_2OH^*$	0.13	0.95
$(CH_2O + H)^* \rightarrow CH_3O^*$	-1.05	1.86
$(CH_2OH + H)^* \rightarrow CH_2^* + H_2O$ (l)	-0.19	0.66
$(CH_2OH + H)^* \rightarrow CH_3OH$ (l)	-0.95	0.68
$(CH_2 + H)^* \rightarrow CH_3^*$	-0.83	0.63
$(CH_3 + H)^* \rightarrow CH_4$ (g)	-0.80	1.03

2. The possible CO_2 reduction pathways on the Ni-doped Cu(111) surface

2.1 Formation pathways of key intermediate CO on the Ni-doped Cu(111) surface

The formation of key intermediate CO is initial step during the course of CO_2 reduction. The calculated minimum energy paths (MEPs) for these possible initial steps for CO formation via direct dissociation and hydrogenative dissociation of CO_2 on the Ni-doped Cu(111) surface are shown in Fig. S1. The geometry structures of the corresponding reactants, products, and reaction intermediates are also displayed in Fig. S1. For intermediate CO formation on the Ni-doped Cu(111) surface, the reaction free energy is calculated as -0.23 eV through hydrogenative dissociation of CO_2, whereas it is -0.06 eV through CO_2 direct dissociation, which showed the former may be more favorable pathway thermodynamically for CO formation. The corresponding activation barriers for these both processes are 0.40 and 0.72 eV, respectively, indicating that hydrogenative dissociation of CO_2 into CO require lower activation barrier, which follow the same trend as the reaction free energies. Thus, both the thermodynamic and kinetic studies suggest that the more preferred pathway of CO formation may be via hydrogenative dissociation of CO_2 on the Ni-modified Cu(111) surface.

Intermediate COOH may be able to be formed during the course of CO_2 hydrogenative dissociation into CO. Thus, we perform the MEPs analysis for COOH formation and subsequent dissociation processes on the Ni-doped Cu(111) surface. As shown in Fig. S2, these both processes are all exothermic, and the corresponding reaction free energies are -0.19 and -0.59 eV, respectively, indicating that COOH formation through CO_2 hydrogenation and dissociation through dehydroxylation are thermodynamically favorable pathways on the Ni-doped Cu(111) surface. The activation barrier for COOH formation is 0.39 eV, which is approximately equal with that of CO formation through CO_2 hydrogenative dissociation. Furthermore, a very low activation barrier of *ca*. 0.16 eV is required for subsequent COOH dissociation into CO, which is almost thermo-activation process. Thereby, we can conclude that CO_2 hydrogenative dissociation into CO may be not an elementary reaction step, which may contain an intermediate COOH on the Ni-doped Cu(111) surface.

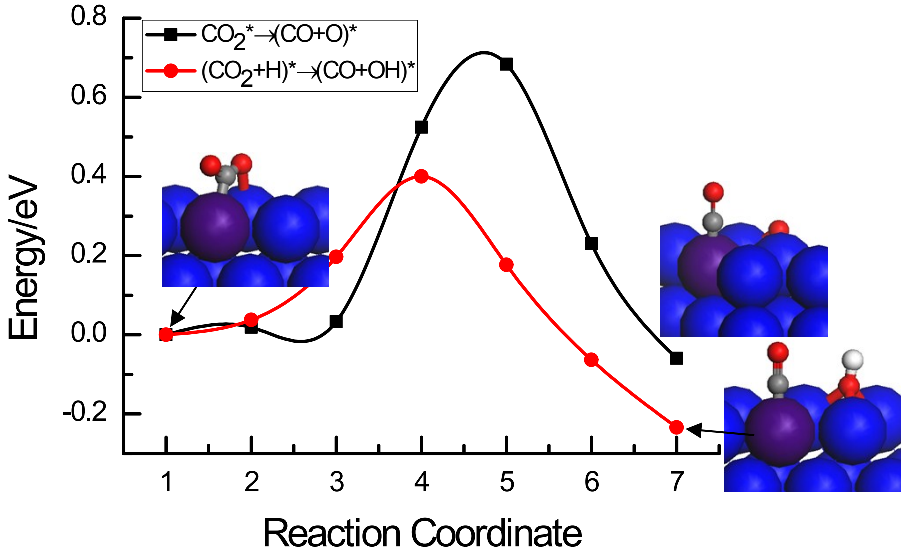

Fig. S1 MEPs of the two possible initial steps for CO formation during the course of CO_2 reduction on the Ni-doped Cu(111) surface. Carbon atoms are gray, hydrogen atoms are white, oxygen atoms are red, nickel atom is purple, and copper atoms are blue.

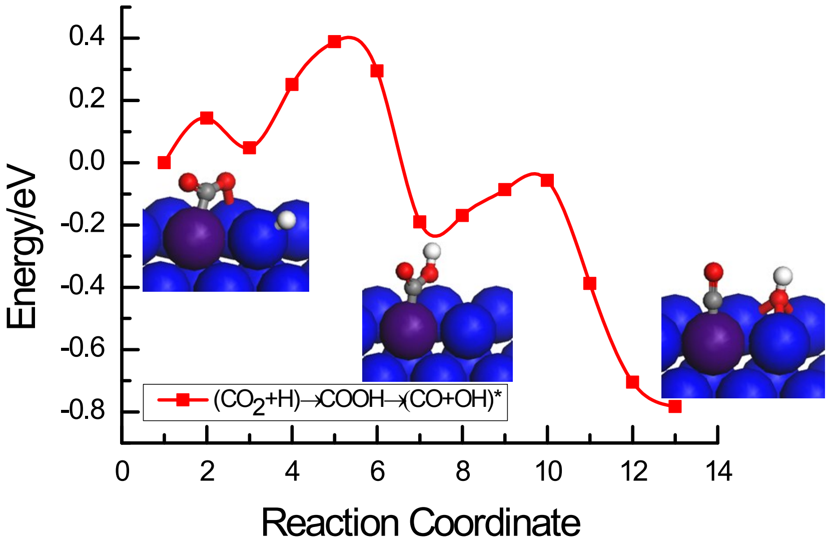

Fig. S2 MEPs for possible intermediate COOH formation and COOH subsequent reduction into CO during the course of CO_2 reduction on the Ni-doped Cu(111) surface.

On the pure Cu(111) surface, COOH is also a possible reaction intermediate during the course of CO_2

hydrogenative dissociation into CO. However, an activation barrier of 1.18 eV is required, which is considerably higher than that for the corresponding process of Ni-doped Cu(111) surface. Thus, the activation barrier for CO formation can be reduced significantly by the doping of Ni, which may be ascribed to that Ni activates the CO_2 since the chemisorbed CO_2 molecule is observed on the top sites of Ni on the surface and promotes the reduction process of CO_2.

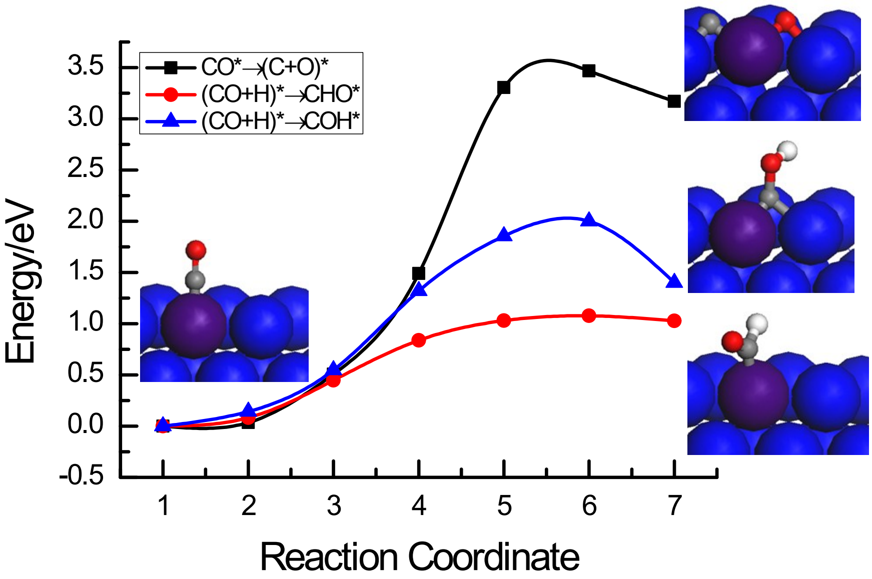

Fig. S3 MEPs of formation processes of C, CHO and CHO through CO dissociation and hydrogenation on the Ni-modified Cu(111) surface.

2.2 Reduction pathways of key intermediate CO on the Ni-doped Cu(111) surface

Three possible reactions pathways are considered for CO further reduction on the Ni-doped Cu(111) surface, namely, direct dissociation via C-O bond cleavage into adsorbed C and O atoms, hydrogenation into form an adsorbed formyl (CHO), and hydrogenation into form an adsorbed hydroxymethylidyne (COH). The thermodynamic analyses show that these three possible reaction pathways are all endothermic processes, in which CO direct dissociation is the most endothermic process thermodynamically with a reaction free energy of 3.17 eV, whereas the reaction free energy is the least positive, *ca.* 1.03 eV for CHO intermediate formation through CO hydrogenation. The thermodynamic results show that the most favorable pathway for CO further reduction on the Ni-doped Cu(111) surface is CHO formation via hydrogenation. Based on the MEPs analyses in Fig. S3, the activation barriers for the corresponding pathways are 3.58, 2.04 and 1.08 eV, respectively, in which the highest activation barrier is required for CO direct dissociation, and the activation barrier for intermediate CHO formation is nearly 1.0 eV lower than COH formation. On this basis, we are able to conclude that the most favorable reaction pathway in CO further reduction is CO hydrogenation into CHO on the Ni-doped Cu(111) surface.

2.3 Further reduction of intermediate CHO on the Ni-doped Cu(111) surface

On the Ni-doped Cu(111) surface, there may be exist four possible pathways for intermediate CHO further reduction, including direct dissociation into adsorbed CH and O through C-O bond cleavage, and C and OH through C-H and C-O bonds breaking, hydrogenation into form adsorbed intermediates CH_2O and CHOH. As shown in Fig. S4, among the four possibilities of CHO further reduction, only CHO hydrogenation into CH_2O has negative reaction free energy (*ca*. -0.04 eV), whereas other three pathways are all endothermic processes, suggesting thermodynamically that CH_2O formation pathway is the most favorable. Simultaneously, the kinetic analyses from MEPs also show that the lowest activation barrier is required for intermediate CHO hydrogenation into CH_2O (*ca*. 0.28 eV). The activation barriers are 1.52, 2.31, and 0.95 eV, respectively for direct dissociation into CH+O and C+OH, and hydrogenation into CHOH. Therefore, we can conclude that CH_2O should be a key intermediate during the course of CO_2 reduction into hydrocarbons on the Ni-doped Cu(111) surface.

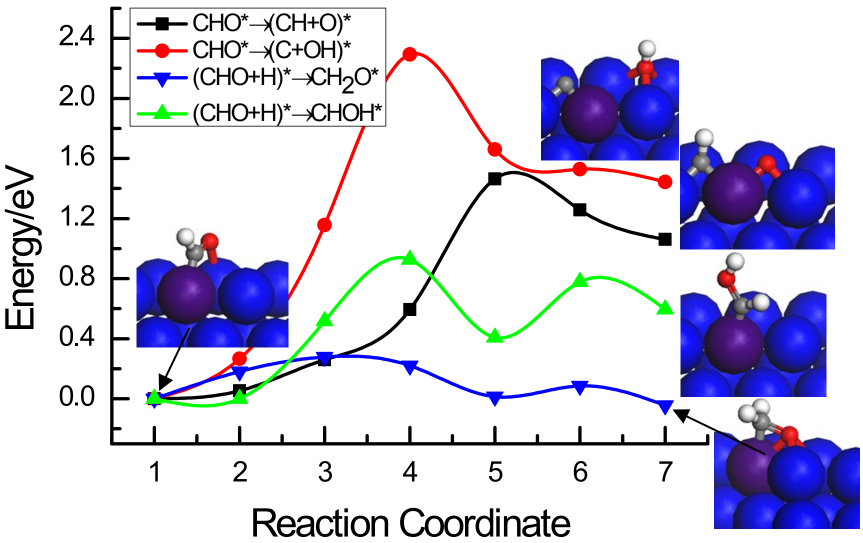

Fig. S4 MEPs of four possibility of CHO further reduction on the Ni-doped Cu(111) surface.

2.4 Subsequent reduction pathways of CH_2O on the Ni-doped Cu(111) surface

For intermediate CH_2O further reduction on the Ni-doped Cu(111) surface, it may undergo direct dissociation into adsorbed CH_2 and O, direct hydrogenation into adsorbed intermediates CH_3O and CH_2OH, and hydrogenative dissociation into adsorbed CH_2 and OH. The calculated reaction free energies for direct dissociation through C-O bond breaking and hydrogenative dissociation into CH_2 are 0.67 and 0.06 eV, respectively, while for formation of adsorbed CH_3O and CH_2OH through direct hydrogenation they are -0.60 and -0.08 eV, respectively. This seems to show thermodynamically that CH_3O formation via CH_2O direct hydrogenation is the most preferable pathway among four possibilities. Based on the MEPs studies, the activation barriers are 0.93, 0.24, 0.27, and 0.24 eV for these four possible pathways, respectively, as shown in Fig. S5. Thereinto, CH_3O and CH_2OH formation, and CH_2O hydrogenative dissociation into CH_2 have nearly equal and lower activation barriers than CH_2O direct dissociation. Therefore, although the reaction free energy for CH_2OH formation is less exothermic than CH_3O formation, and it is even slightly endothermic for CH_2O hydrogenative dissociation into CH_2, CH_3O and CH_2OH formation through direct hydrogenation, and CH_2 formation through hydrogenative dissociation are all more favorable reaction pathways kinetically on the Ni-doped Cu(111) surface. They may be parallel pathways after alloying Cu with Ni.

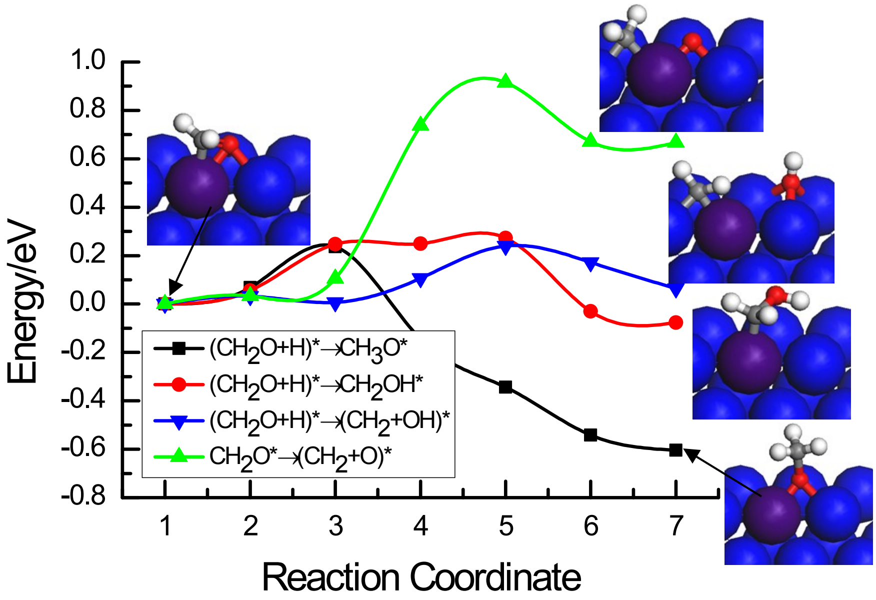

Fig. S5 MEPs of CH_3O, CH_2OH, and CH_2 formations through direct hydrogenation, hydrogenative dissociation, and direct dissociation of CH_2O on the Ni-doped Cu(111) surface.

2.5 Subsequent reduction pathways of CH_3O and CH_2OH on the Ni-doped Cu(111) surface

Based on the above thermodynamic and kinetic analysis, CH_3O and CH_2OH may be reaction intermediates during the course of CO_2 reduction into hydrocarbons on the Ni-doped Cu(111) surface. The CH_3O further reduction is examined firstly. There may be exist three possibilities, including CH_3O direct dissociation into adsorbed CH_3+O through C-O bond cleavage, hydrogenation into CH_3OH, and hydrogenative dissociation into CH_4 and CH_3+OH. The consideration of CH_4 formation through hydrogenative dissociation is due to previous theoretical study on the Cu(211) surface from Nørskov and coauthors thermodynamically suggested that CH_4 can be produced by CH_3O hydrogenation.[2] Based on our present thermodynamic analyses, the calculated reaction free energy for CH_4 formation through CH_3O hydrogenative dissociation is -0.32 eV, whereas the reaction free energies of 0.39, 0.32 and 0.31 eV are required for CH_3+O, CH_3+OH and CH_3OH formations, respectively. This seems to suggest that CH_3O hydrogenative dissociation into CH_4 is also preferable pathway on the Ni-doped Cu(111) surface, as demonstrated thermodynamically in Nørskov and coauthors' work. However, our present kinetic studies show that an activation barrier of 0.90 eV is required for hydrogenative dissociation into CH_4, which are higher than that of CH_3O direct hydrogenation into CH_3OH (*ca*. 0.68 eV), as shown in Fig. S6. In the mean time, high activation barriers of 0.95 and 1.96 eV for CH_3O direct and hydrogenative dissociation into CH_3+O and CH_3+OH are also required. Thus, direct hydrogenation into CH_3OH should be the most preferred reaction pathway among CH_3O further reduction on the Ni-doped Cu(111) surface due to relatively lower activation barrier.

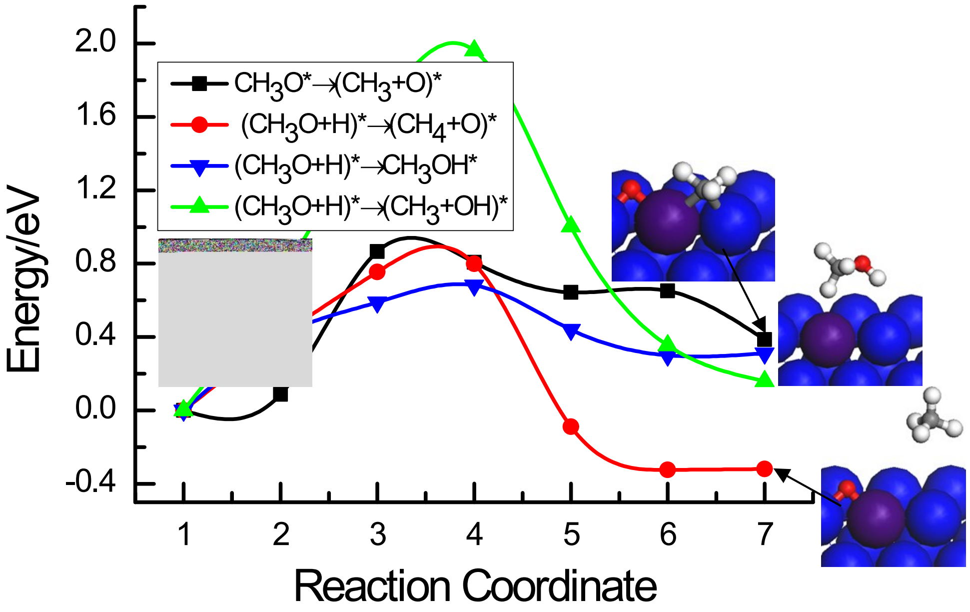

Fig. S6 MEPs of CH_3, CH_4, and CH_3OH formation through CH_3O direct dissociation, hydrogenative dissociation, and direct hydrogenation on the Ni-doped Cu(111) surface.

For intermediate CH_2OH further reduction, there possible reaction pathways are considered, such as direct dissociation into adsorbed CH_2 through C-O bond breaking, hydrogenative dissociation into adsorbed CH_2, and direct hydrogenation into CH_3OH. The reaction free energies of -0.03, -0.13, and -0.61 eV are required for these three reaction pathways, respectively, in which the most exothermic pathway is CH_3OH formation through direct hydrogenation. This indicates thermodynamically that CH_3OH formation is the most favorable among these three possibilities on the Ni-doped Cu(111) surface. Simultaneously, it is also observed in Fig. S7 that CH_3OH formation through CH_2OH direct hydrogenation has the lowest activation barrier (*ca*. 0.16 eV) than CH_2 formation through direct and hydrogenative dissociation with activation barriers of 0.95 and 0.58 eV, respectively. Thus, the intermediate CH_2OH tends to form CH_3OH by direct hydrogenation after alloying Cu with Ni, which is relatively more facile in contrast with CH_2 formation.

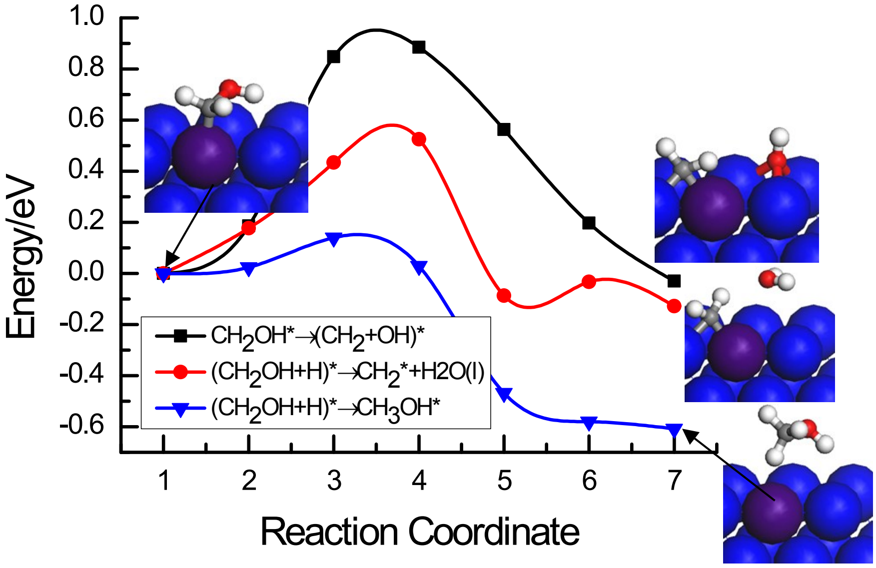

Fig. S7 MEPs of CH_3OH and CH_2 formation through direct hydrogenation, hydrogenative dissociation, and direct dissociation of CH_2OH on the Ni-doped Cu(111) surface.

2.6 CH_4 formation pathways on the Ni-doped Cu(111) surface

Since CH_3 and CH_4 formation through the direct and hydrogenative dissociation of CH_3O on the Ni-doped Cu(111) surface is more difficult than the formation of CH_2 based on the above thermodynamic and kinetic analyses, the final CH_4 production is possibly to be formed by intermediate CH_2 serial hydrogenation. Four possible formation pathways of CH_2 have been shown above including CH_2O direct and hydrogenative dissociation, CH_2OH direct and hydrogenative dissociation. The lowest activation barrier (*ca.* 0.24 eV) is required by CH_2O hydrogenative dissociation into CH_2, thereby this pathway is the most favorable for CH_2 formation on Ni-modified Cu(111) surface. The MEPs of CH_4 formation through intermediate CH_2 serial hydrogenation is shown in Fig. S8. The reaction free energies are calculated as -0.55 and -0.59 eV for CH_3 formation through CH_2 hydrogenation and CH_4 formation through CH_3 hydrogenation, respectively. These two pathways are all strong exothermic processes, suggesting thermodynamically that they are easily to occur. The calculated activation barriers for the corresponding processes are 0.30 and 0.21 eV, respectively, which are very low and can be overcome at ambient temperature.

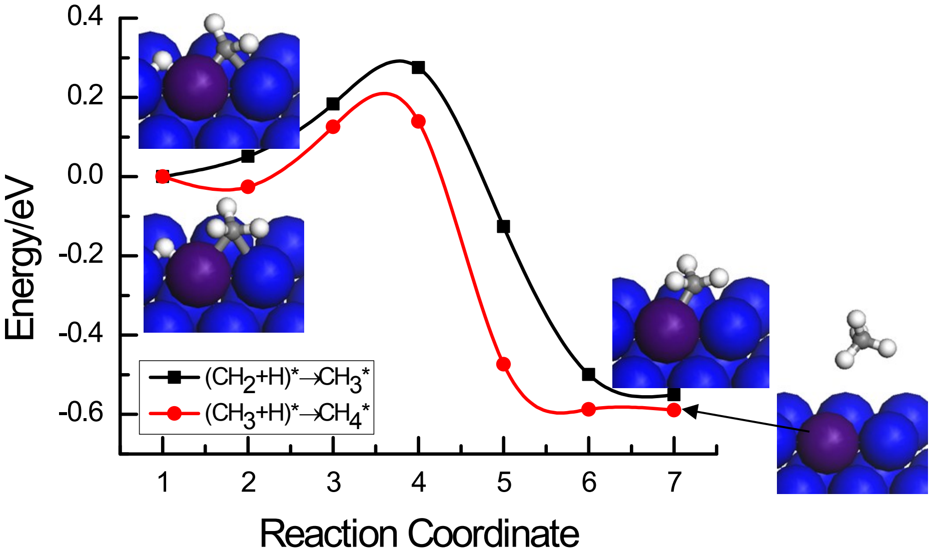

Fig. S8 MEPs of hydrocarbons CH_3 and CH_4 formation through CH_2 serial hydrogenation on the Ni-doped Cu(111) surface.

3. The possible CO_2 reduction pathways on the Pd-doped Cu(111) surface

3.1 The possible initial step of CO_2 reduction on the Pd-doped Cu(111) surface

The calculated minimum energy paths (MEPs) for possible initial steps of CO_2 reduction into CO and COOH via direct dissociation, hydrogenative dissociation and hydrogenation on the Pd-doped Cu(111) surface are shown in Fig. S9. For intermediates CO and COOH formation on the Pd-doped Cu(111) surface, the reaction free energies are calculated as 0.31 and 0.51 eV through hydrogenative dissociation and hydrogenation of CO_2, respectively, whereas it is 1.02 eV through CO_2 direct dissociation, which showed hydrogenative dissociation into CO and hydrogenation into COOH may be more favorable pathways thermodynamically. The corresponding activation barriers for these three processes are 0.83, 0.72 and 2.09 eV, respectively, indicating that hydrogenative dissociation into CO and hydrogenation of CO_2 into COOH require lower activation barriers, in which the activation barrier for COOH formation is slightly lower than that of CO formation. Furthermore, a low activation barrier of *ca*. 0.42 eV is required with a reaction free energy of -0.19 eV for subsequent COOH dissociation into CO, as shown in Fig. S10. Thereby, we can conclude that CO_2 hydrogenative dissociation into CO is not an elementary reaction step, intermediate COOH may be able to be formed during the course of CO_2 hydrogenative dissociation into CO on the Pd-doped Cu(111) surface.

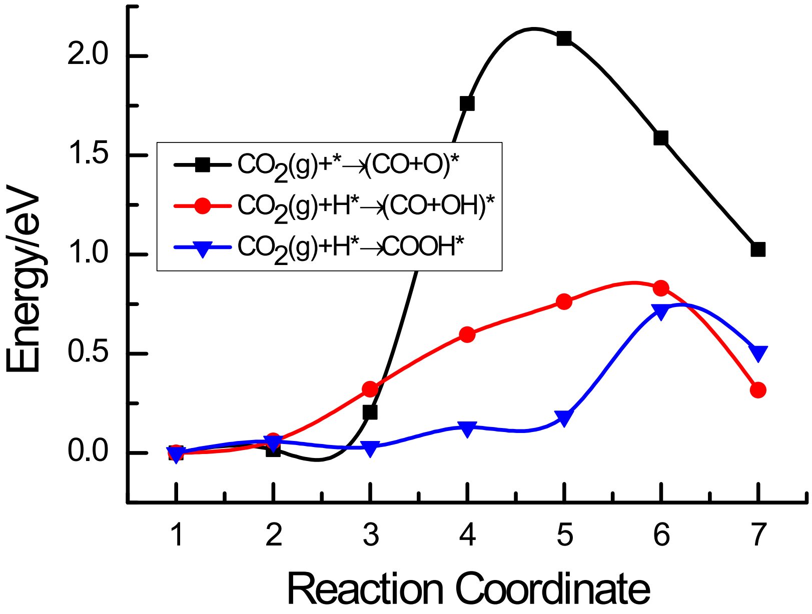

Fig. S9 MEPs of the possible initial steps for CO_2 reduction into CO and COOH intermediates on the Pd-doped Cu(111) surface.

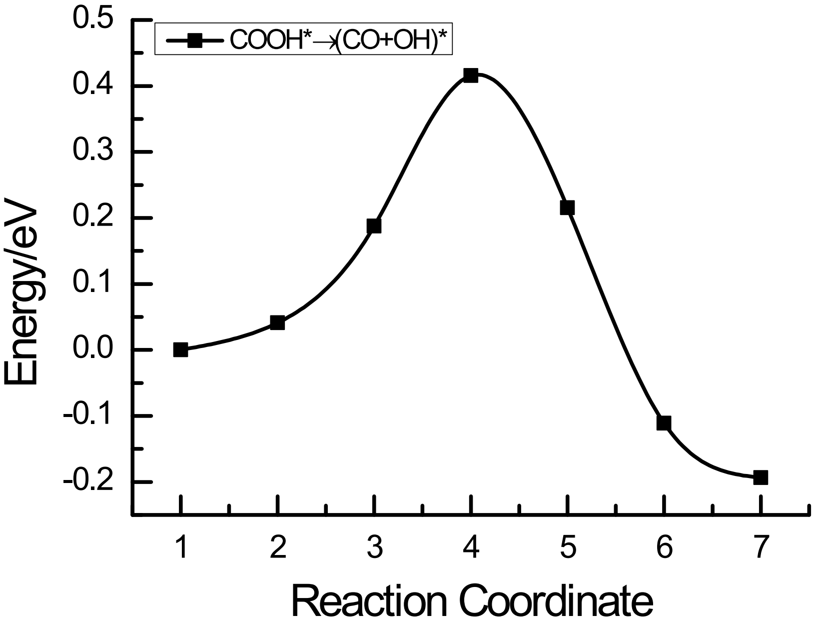

Fig. S10 MEPs for possible intermediate COOH reduction into CO during the course of CO_2 reduction on the Pd-doped Cu(111) surface.

3.2 Reduction pathways of key intermediate CO on the Pd-doped Cu(111) surface

Three possible reactions pathways are considered for CO further reduction on the Pd-doped Cu(111) surface, namely, direct dissociation via C-O bond cleavage into adsorbed C and O atoms, hydrogenation into form an adsorbed formyl (CHO), and hydrogenation into form an adsorbed hydroxymethylidyne (COH). The thermodynamic analyses show that these three possible reaction pathways are all endothermic processes, in which CO direct dissociation is the most endothermic process thermodynamically with a reaction free energy of 3.55 eV, whereas the reaction free energy is the least positive, *ca*. 0.52 eV for CHO intermediate formation through CO hydrogenation. The thermodynamic results show that the most favorable pathway for CO further reduction on the Pd-doped Cu(111) surface is CHO formation via hydrogenation. Based on the MEPs analyses in Fig. S11, the activation barriers for the corresponding pathways are 4.04, 1.19 and 0.87 eV, respectively, in which the highest activation barrier is required for CO direct dissociation, and the activation barrier for intermediate CHO formation is nearly 0.32 eV lower than COH formation. On this basis, we are able to conclude that the most favorable reaction pathway in CO further reduction is CO hydrogenation into CHO on the Pd-doped Cu(111) surface.

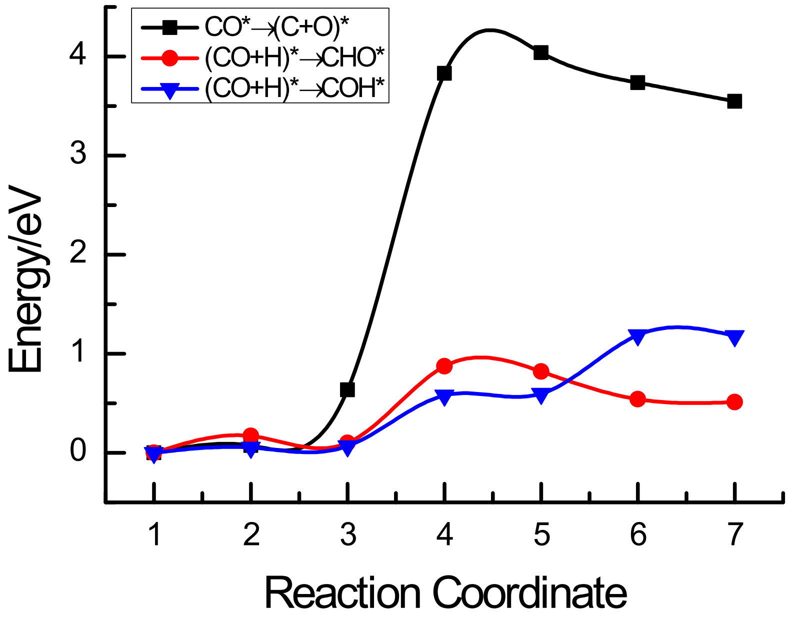

Fig. S11 MEPs of formation processes of C, CHO and CHO through CO dissociation and hydrogenation on Pd-modified Cu(111) surface.

3.3 Further reduction of intermediate CHO on the Pd-doped Cu(111) surface

Four possible pathways for intermediate CHO further reduction are considered on the Pd-doped Cu(111) surface, including direct dissociation into adsorbed CH and O through C-O bond cleavage, and C and OH through C-H and C-O bonds breaking, hydrogenation into form adsorbed intermediates CH_2O and CHOH. As shown in Fig. S12, among the four possibilities, only CHO hydrogenation into CH_2O has negative reaction free energy (*ca*. -0.25 eV), whereas other three pathways are all endothermic processes, suggesting thermodynamically that CH_2O formation pathway is the most favorable. Simultaneously, the kinetic analyses from MEPs also show that the lowest activation barrier is required for intermediate CHO hydrogenation into

CH_2O (*ca*. 0.10 eV). The activation barriers are 2.10, 2.65, and 0.68 eV for direct dissociation into CH + O and C + OH, and hydrogenation into CHOH, respectively. Therefore, we can conclude that CH_2O should be a key intermediate during the course of CO_2 reduction into hydrocarbons on the Pd-doped Cu(111) surface.

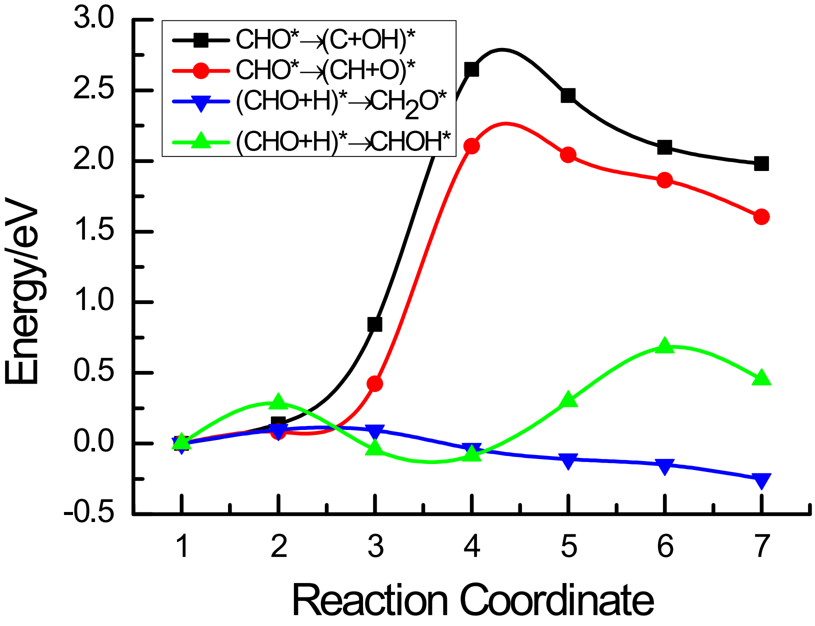

Fig. S12 MEPs of four possibility of CHO further reduction on the Pd-doped Cu(111) surface.

3.4 Subsequent reduction pathways of CH_2O on the Pd-doped Cu(111) surface

For intermediate CH_2O further reduction on the Pd-doped Cu(111) surface, it may undergo direct dissociation into adsorbed CH_2 and O, direct hydrogenation into adsorbed intermediates CH_3O and CH_2OH, and hydrogenative dissociation into adsorbed CH_2 and OH. The calculated reaction free energies for direct dissociation through C-O bond breaking and hydrogenative dissociation into CH_2 are 1.00 and 0.24 eV, respectively, while for formation of adsorbed CH_3O and CH_2OH through direct hydrogenation they are -0.80 and -0.12 eV, respectively. This shows thermodynamically that CH_3O formation via CH_2O direct hydrogenation is the most preferable pathway among four possibilities. Based on the MEPs studies, the activation barriers are 1.58, 0.52, 0.06, and 0.68 eV for these four possible pathways, respectively, as shown in Fig. S13. Thereinto, CH_3O formation requires the lowest activation barriers, which is a non-activated process. Therefore, thermodynamic and kinetic studies all show that CH_3O formation through CH_2O direct hydrogenation is the most favorable pathways among four possibilities on the Pd-doped Cu(111) surface.

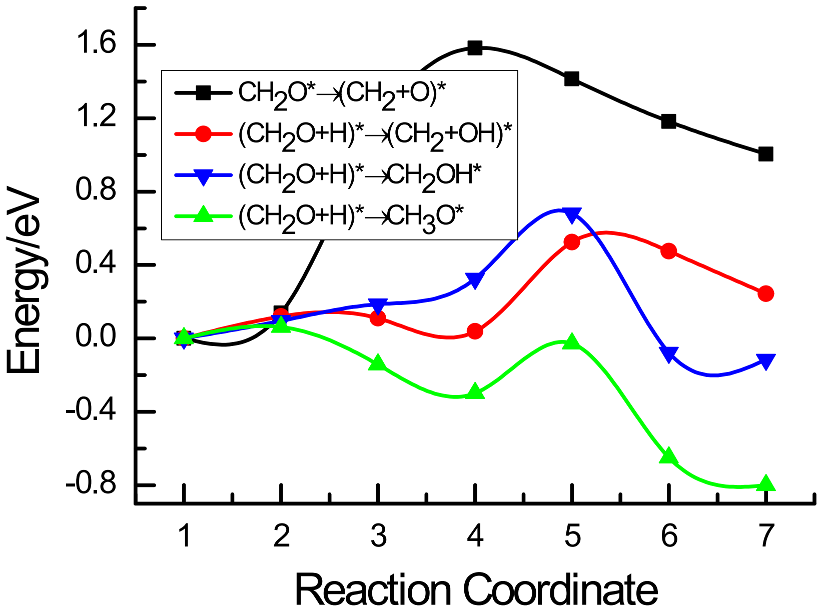

Fig. S13 MEPs of CH_3O, CH_2OH, and CH_2 formations through direct hydrogenation, hydrogenative dissociation, and direct dissociation of CH_2O on the Pd-doped Cu(111) surface.

3.5 Subsequent reduction pathways of CH_3O on the Pd-doped Cu(111) surface

The CH_3O further reduction is examined. There may be exist four possibilities, including CH_3O direct dissociation into adsorbed CH_3+O through C-O bond cleavage, hydrogenation into CH_3OH, and hydrogenative dissociation into CH_4 and CH_3+OH. Based on our present thermodynamic analyses, the calculated reaction free energy for CH_4 formation through CH_3O hydrogenative dissociation is -0.16 eV, whereas the reaction free energies of 0.53, 0.01 and -0.10 eV are required for CH_3 + O, CH_3 + OH and CH_3OH formations, respectively. This seems to suggest that CH_3O hydrogenative dissociation into CH_4 is also preferable pathway on the Pd-doped Cu(111) surface. However, our present kinetic studies show that an activation barrier of 2.81 eV is required for hydrogenative dissociation into CH_4, which are significantly higher than that of CH_3O hydrogenative dissociation into CH_3+OH (*ca.* 0.29 eV), as shown in Fig. S14. In the mean time, high activation barriers of 1.68 and 1.86 eV for CH_3O direct dissociation and hydrogenation into CH_3+O and CH_3OH are also required. Thus, hydrogenative dissociation into CH_3 should be the most preferred reaction pathway among CH_3O further reduction on the Pd-doped Cu(111) surface due to significantly lower activation barrier.

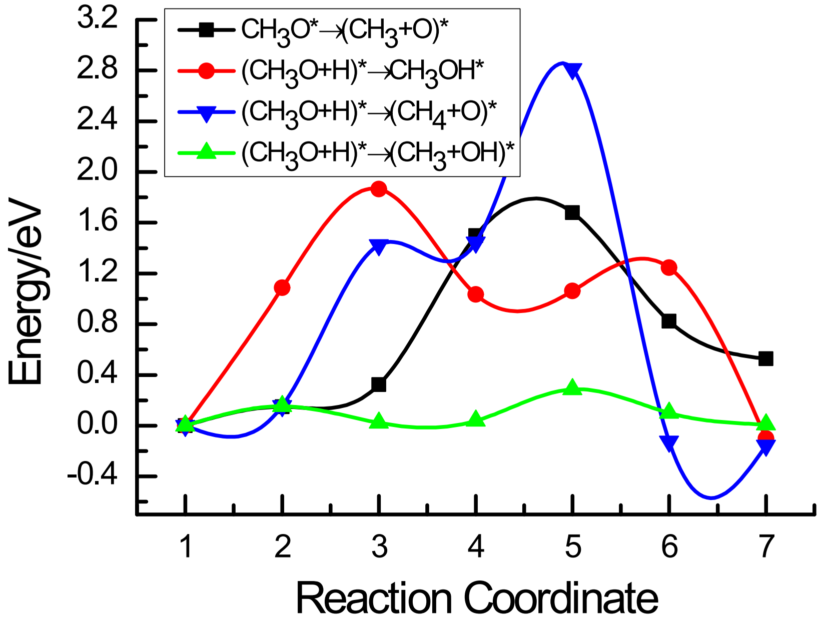

Fig. S14 MEPs of CH_3, CH_4, and CH_3OH formation through CH_3O direct dissociation, hydrogenative dissociation, and direct hydrogenation on the Pd-doped Cu(111) surface.

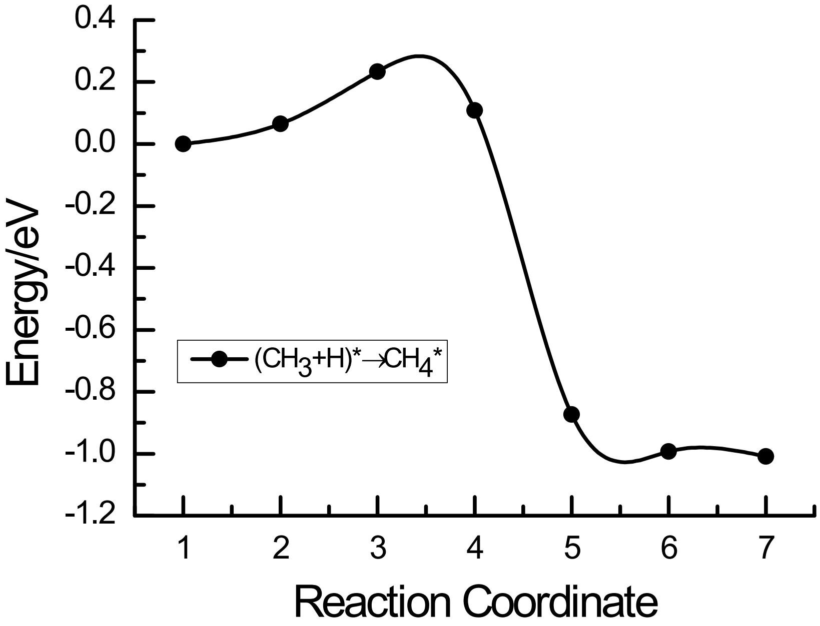

Fig. S15 MEPs of hydrocarbon CH_4 formation through CH_3 hydrogenation on the Pd-doped Cu(111) surface.

3.6 CH_4 formation pathways on the Pd-doped Cu(111) surface

Since the hydrogenative dissociation of CH_3O into form CH_3 on the Pd-doped Cu(111) surface is the most facile based on the above thermodynamic and kinetic analyses, the final CH_4 production is possibly to be formed by intermediate CH_3 hydrogenation. The MEPs of CH_4 formation through intermediate CH_3 hydrogenation is shown in Fig. S15. The reaction free energy is calculated as -1.01 eV for CH_4 formation through CH_3 hydrogenation. This pathway is strong exothermic processes, suggesting thermodynamically that it is easily to occur. The calculated activation barrier for the corresponding process is 0.23 eV, which is a thermo-activated process and can be overcome at ambient temperature.

4. The possible CO_2 reduction pathways on the Pt-doped Cu(111) surface

4.1 The possible initial step of CO_2 reduction on the Pt-doped Cu(111) surface

The calculated minimum energy paths (MEPs) for possible initial steps of CO_2 reduction into CO and COOH through direct dissociation, hydrogenative dissociation and hydrogenation on the Pt-doped Cu(111) surface are shown in Fig. S16. For intermediates CO and COOH formation on the Pt-doped Cu(111) surface, the reaction free energies are calculated as 0.07 and 0.25 eV through hydrogenative dissociation and hydrogenation of CO_2, respectively, whereas it is 0.40 eV through CO_2 direct dissociation, which showed hydrogenative dissociation into CO and hydrogenation into COOH may be more favorable pathways thermodynamically. The corresponding activation barriers for these three processes are 0.65, 0.52 and 0.88 eV, respectively, indicating that hydrogenative dissociation into CO and hydrogenation of CO_2 into COOH require relatively lower activation barriers, in which the activation barrier for COOH formation is slightly lower than that of CO formation. Furthermore, a low activation barrier of *ca*. 0.37 eV is required with a reaction free energy of -0.33 eV for subsequent COOH dissociation into CO, as shown in Fig. S16. Thus, we can conclude that CO_2 hydrogenative dissociation into CO is not an elementary reaction step, intermediate COOH may be able to be formed during the course of CO_2 hydrogenative dissociation into CO on the Pt-doped Cu(111) surface.

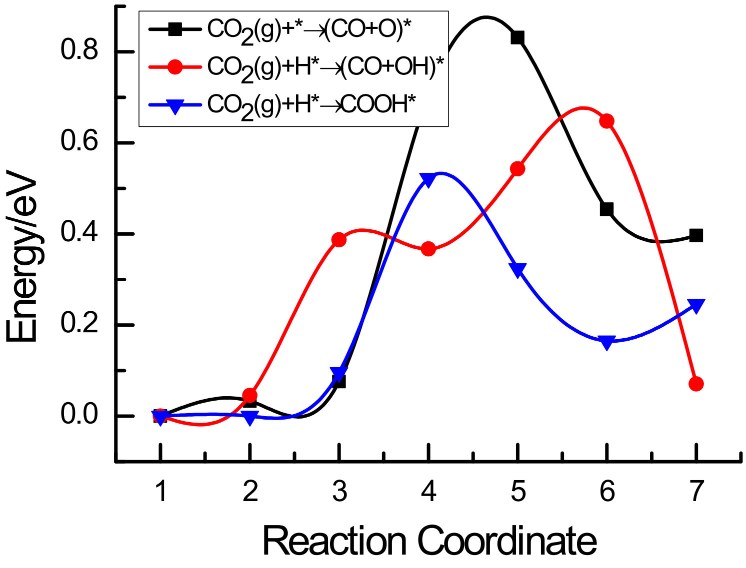

Fig. S16 MEPs of the possible initial steps for CO_2 reduction into CO and COOH intermediates on the Pt-doped Cu(111) surface.

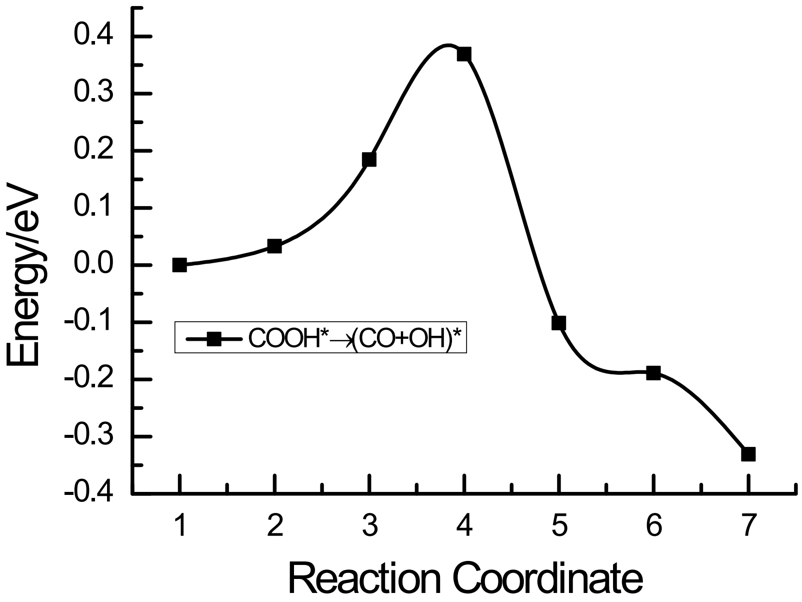

Fig. S17 MEPs for possible intermediate COOH reduction into CO during the course of CO_2 reduction on the Pt-doped Cu(111) surface.

4.2 Reduction pathways of key intermediate CO on the Pt-doped Cu(111) surface

Three possible reactions pathways are considered for CO further reduction on the Pt-doped Cu(111) surface, namely, direct dissociation via C-O bond cleavage into adsorbed C and O atoms, hydrogenation into form an adsorbed CHO, and hydrogenation into form an adsorbed COH. The thermodynamic analyses show that these three possible reaction pathways are all endothermic processes, in which CO direct dissociation is the most endothermic process thermodynamically with a reaction free energy of 3.75 eV, whereas the reaction free energy is the least positive, *ca*. 0.41 eV for CHO intermediate formation through CO hydrogenation. Thus, the thermodynamic results show that the most favorable pathway for CO further reduction on the Pt-doped Cu(111) surface is CHO formation through hydrogenation. Based on the MEPs analyses in Fig. S18, the activation barriers for the corresponding pathways are 4.45, 1.51 and 0.84 eV, respectively, in which the highest activation barrier is required for CO direct dissociation, and the activation barrier for intermediate CHO formation is nearly 0.67 eV lower than COH formation. On this basis, we are able to conclude that the most favorable reaction pathway in CO further reduction is CO hydrogenation into CHO on the Pt-doped Cu(111) surface.

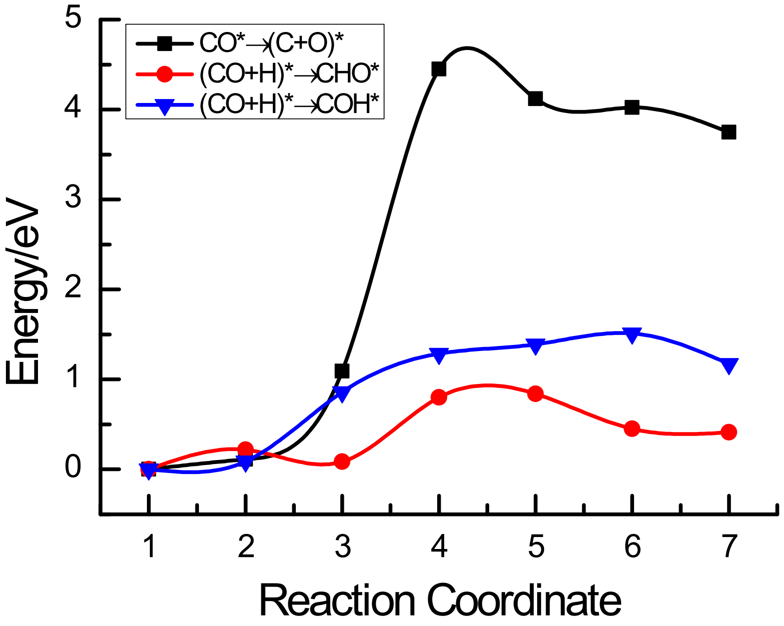

Fig. S18 MEPs of formation processes of C, CHO and CHO through CO dissociation and hydrogenation on the Pt-doped Cu(111) surface.

4.3 Further reduction of intermediate CHO on the Pt-doped Cu(111) surface

Four possible pathways for intermediate CHO further reduction are considered on the Pt-doped Cu(111) surface, including direct dissociation into adsorbed CH and O through C-O bond cleavage, and C and OH through C-H and C-O bonds breaking, hydrogenation into form adsorbed intermediates CH_2O and CHOH. Among the four possibilities, only CHO hydrogenation into CH_2O has negative reaction free energy (*ca.* -0.02 eV), CHO hydrogenation into CHOH is slightly endothermic (*ca.* 0.37 eV), whereas other two pathways are all strong endothermic processes, as shown in Fig. S19, suggesting thermodynamically that CH_2O and CHOH formation pathway may be the most favorable. Furthermore, the kinetic analyses from MEPs also show that CHO hydrogenation into CH_2O and CHOH have nearly equal activation barriers (*ca.* 0.35 and 0.40 eV), which are the lowest among four possibilities. The activation barriers are 2.62 and 2.90 eV for direct dissociation into CH+O and C+OH, respectively. Therefore, it can be concluded that intermediates CH_2O and CHOH may be able to be formed during the course of CO_2 reduction into hydrocarbons on the Pt-doped Cu(111) surface, which may be parallel pathways.

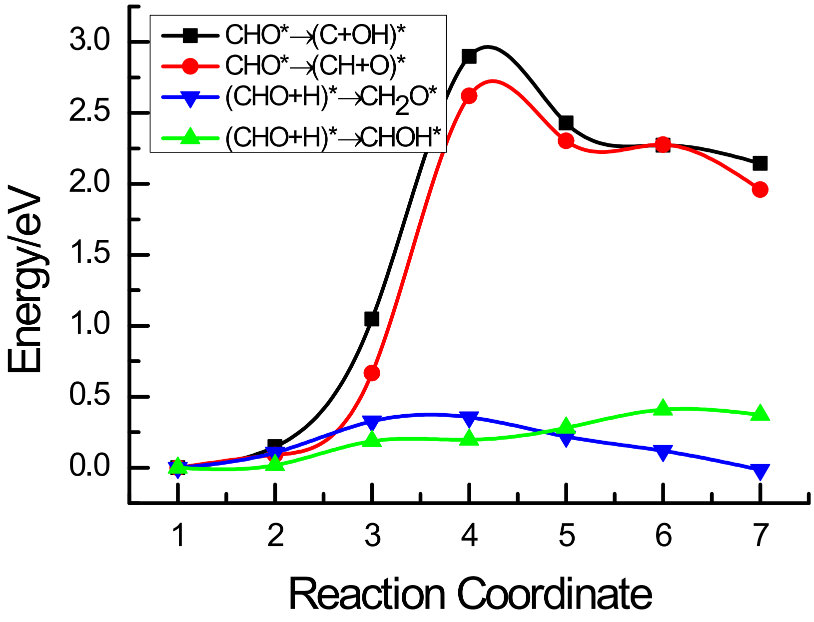

Fig. S19 MEPs of four possibility of CHO further reduction on the Pt-doped Cu(111) surface.

4.4 Subsequent reduction pathways of CH_2O and CHOH on the Pt-doped Cu(111) surface

Based on the above analyses, CH_2O and CHOH are all possible reaction intermediates on the Pd-doped Cu(111) surface. For intermediate CH_2O further reduction, it may undergo direct dissociation into adsorbed CH_2+O, direct hydrogenation into adsorbed intermediates CH_3O and CH_2OH, and hydrogenative dissociation into adsorbed CH_2+OH. The calculated reaction free energies for direct dissociation through C-O bond breaking and hydrogenative dissociation into CH_2 are 1.15 and 0.26 eV, respectively, while for formation of adsorbed CH_3O and CH_2OH through direct hydrogenation they are -0.62 and -0.35 eV, respectively. This shows thermodynamically that CH_3O and CH_2OH formations through CH_2O direct hydrogenation are the most preferable pathways among four possibilities. Based on the MEPs studies, the activation barriers are 1.60, 0.82, 0.21 and 0.59 eV for these four possible pathways, respectively, as shown in Fig. S20. Thereinto, CH_3O and CH_2OH formations require relatively lower activation barriers. Therefore, thermodynamic and kinetic studies all show that CH_3O and CH_2OH formations through CH_2O direct hydrogenation are the most favorable pathways among four possibilities on the Pt-doped Cu(111) surface.

Three possibilities are considered for intermediate CHOH further reduction, including direct dissociation into adsorbed CH+OH, direct hydrogenation into adsorbed CH_2OH, and hydrogenative dissociation into adsorbed CH_2+OH. The calculated reaction free energies for direct dissociation and hydrogenative dissociation into CH_2 are 0.46 and -0.21 eV, respectively, while for formation of adsorbed CH_2OH through direct hydrogenation, it is -0.69 eV. This shows thermodynamically that CH_2OH formation through CHOH direct hydrogenation is the most preferable pathway among three possibilities. Based on the

MEPs studies, the activation barriers are 1.03, 0.54 and 0.53 eV for these three possible pathways, respectively, as shown in Fig. S21, in which CHOH hydrogenative dissociation into CH_2 and hydrogenation into CH_2OH have relatively lower activation barriers, and they are approximately equal. Therefore, the results show that CH_2 and CH_2OH formations through CHOH hydrogenative dissociation and direct hydrogenation are the most favorable pathways among three possibilities on the Pt-doped Cu(111) surface. However, we note that CHOH dissociation back into CHO requires a very low activation barrier of 0.04 eV, which is significantly lower than that of CHO further reduction and is a non-activated process. Thus, CHOH may be not a stable reaction intermediate.

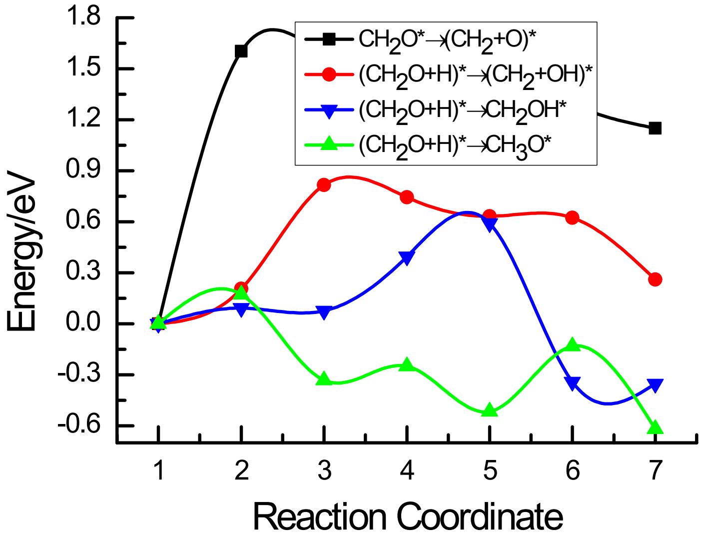

Fig. S20 MEPs of CH_3O, CH_2OH and CH_2 formations through direct hydrogenation, hydrogenative dissociation, and direct dissociation of CH_2O on the Pt-doped Cu(111) surface.

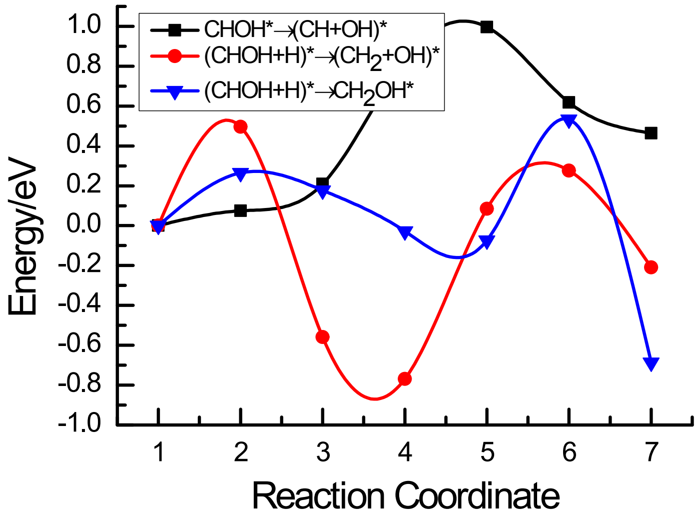

Fig. S21 MEPs of CH_2OH, CH_2 and CH formations through direct hydrogenation, hydrogenative dissociation, and direct dissociation of CHOH on the Pt-doped Cu(111) surface.

4.5 Subsequent reduction pathways of CH_3O and CH_2OH on the Pt-doped Cu(111) surface

Based on the above thermodynamic and kinetic analysis, CH_3O and CH_2OH may be reaction intermediates during the course of CO_2 reduction into hydrocarbons on the Pt-doped Cu(111) surface. The CH_3O further reduction is examined firstly. There may be exist three possibilities, including CH_3O direct dissociation into adsorbed CH_3+O through C-O bond cleavage, hydrogenation into CH_3OH and hydrogenative dissociation into CH_4 and CH_3+OH. Based on our present thermodynamic analyses, the calculated reaction free energy for CH_4 formation through CH_3O hydrogenative dissociation is -0.24 eV, whereas the reaction free energies of 0.65, -0.12 and -0.17 eV are required for CH_3+O, CH_3+OH and CH_3OH formations, respectively. This seems to suggest that CH_3O hydrogenative dissociation into CH_4 is also preferable pathway on the Pt-doped Cu(111) surface. However, our present kinetic studies show that an activation barrier of 1.22 eV is required for hydrogenative dissociation into CH_4, which is significantly higher than that of CH_3O hydrogenative dissociation into CH_3+OH (*ca.* 0.63 eV), as shown in Fig. S22. In the mean time, high activation barriers of 1.23 and 1.36 eV for CH_3O direct and hydrogenation into CH_3+O and CH_3OH are also required. Thus, hydrogenative dissociation into CH_3 should be the most preferred reaction pathway among CH_3O further reduction on the Pt-doped Cu(111) surface due to the lowest activation barrier.

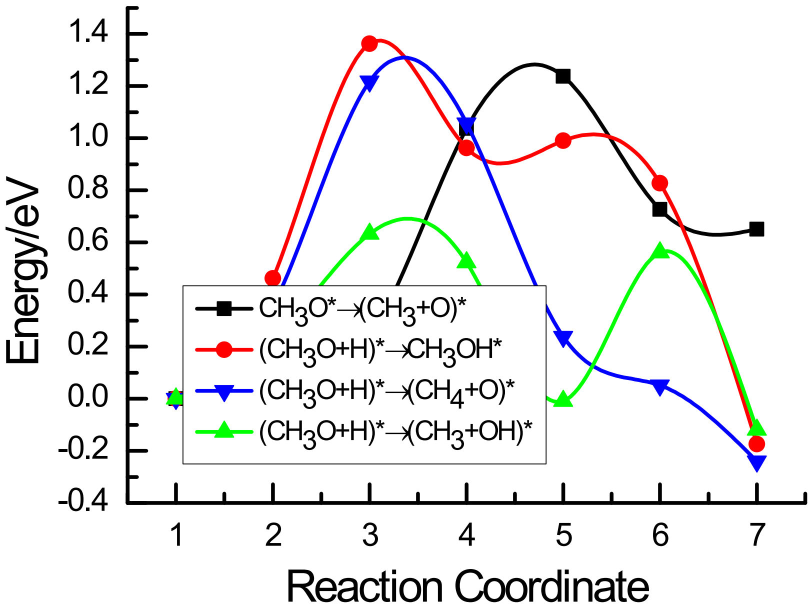

Fig. S22 MEPs of CH_3, CH_4 and CH_3OH formation through CH_3O direct dissociation, hydrogenative dissociation, and direct hydrogenation on the Pt-doped Cu(111) surface.

For intermediate CH_2OH further reduction on the Pt-doped Cu(111) surface, there possible reaction pathways are considered, such as direct dissociation into adsorbed CH_2 through C-O bond breaking, hydrogenative dissociation into adsorbed CH_2, and direct hydrogenation into CH_3OH. The reaction free energies of 0.58, 0.10, and -0.53 eV are required for these three reaction pathways, respectively, in which only CH_3OH formation is exothermic pathway. This indicates thermodynamically that CH_3OH formation is the most favorable among these three possibilities on the Pt-doped Cu(111) surface. Simultaneously, it is also observed in Fig. S23 that CH_3OH formation through CH_2OH direct hydrogenation has the lowest activation barrier (*ca.* 0.34 eV) than CH_2 formation through direct and hydrogenative dissociation with activation barriers of 1.06 and 0.60 eV, respectively. Thus, the intermediate CH_2OH tends to form CH_3OH by direct hydrogenation on the Pt-doped Cu(111) surface, which is relatively more facile in contrast with CH_2 formation.

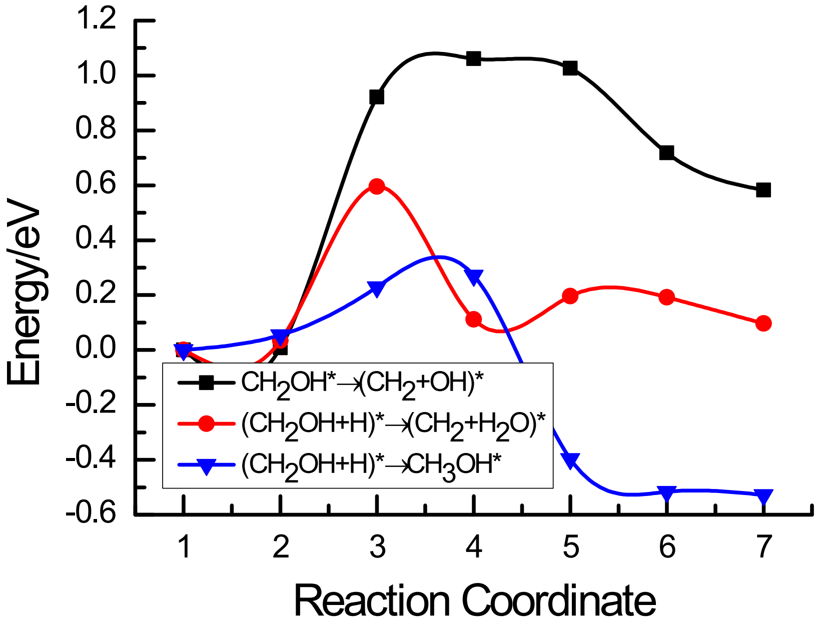

Fig. S23 MEPs of CH_3OH and CH_2 formation through direct hydrogenation, hydrogenative dissociation, and direct dissociation of CH_2OH on the Pt-doped Cu(111) surface.

4.6 CH_4 formation pathways on the Pt-doped Cu(111) surface

Based on the above thermodynamic and kinetic analyses, the final CH_4 production is possibly to be formed by intermediate CH_2 serial hydrogenation and CH_3 hydrogenation. Two possible formation pathways of CH_2 have been shown above through CHOH hydrogenative dissociation and CH_2OH hydrogenative dissociation since they have nearly equal activation (*ca.* 0.53 and 0.60 eV) on the Pt-doped Cu(111) surface. CH_3 can be formed through CH_3O hydrogenative dissociation. The MEPs of CH_4 formation through intermediate CH_2 serial hydrogenation is shown in Fig. S24. The reaction free energies are calculated as -0.95 and -0.82 eV for CH_3 formation through CH_2 hydrogenation and CH_4 formation through CH_3

hydrogenation, respectively. These two pathways are all strong exothermic processes, suggesting thermodynamically that they are easily to occur. The calculated activation barriers for the corresponding processes are 0.18 and 0.70 eV, respectively.

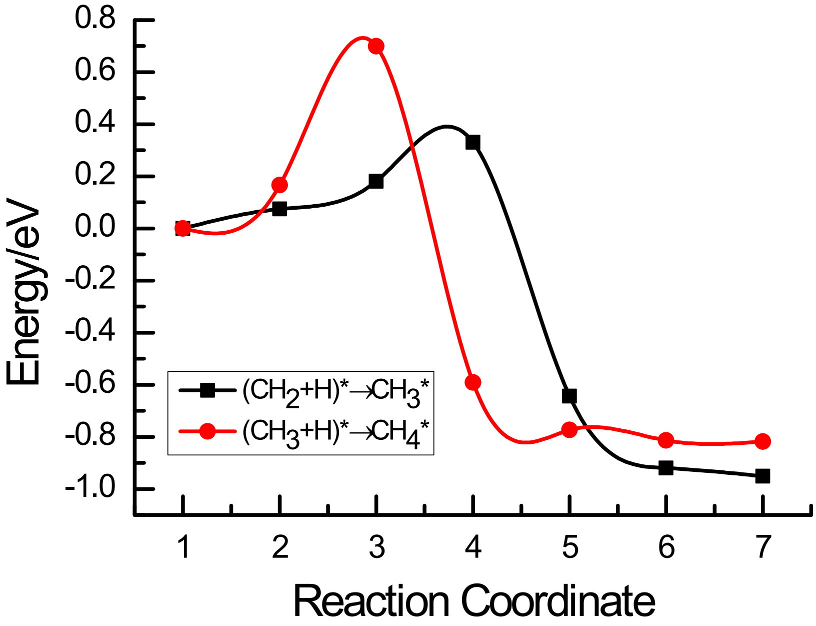

Fig. S24 MEPs of hydrocarbons CH_3 and CH_4 formation through CH_2 serial hydrogenation on the Pt-doped Cu(111) surface.

5. Mathematical details about computational hydrogen electrode model[3]

In this technique, zero voltage is defined based on the reversible hydrogen electrode (RHE), in which the reaction

$$\mathrm{H}^{+} + \mathrm{e}^{-} \leftrightarrow \frac{1}{2}\mathrm{H}_2$$

is defined to be in equilibrium at zero voltage, at all values of pH, at all temperatures, and with H_2 at 101325 Pa pressure. Therefore, in the computational hydrogen electrode (CHE) model, the chemical potential of a proton-electron pair, $\mu(\mathrm{H}^{+})+\mu(\mathrm{e}^{-})$ is equal to half of the chemical potential of gaseous hydrogen ($\frac{1}{2}\mu(\mathrm{H}_2)$) at a potential of 0 V. In this way, the chemical potential of proton-electron pair can be calculated simply by calculating the chemical potential of gas-phase H_2. The chemical potential of the proton-electron pair can be adjusted as a function of the applied potential by the standard relation between chemical and electrode potential, $\Delta G = -\mathrm{e}E$, where e is the elementary positive charge and E is the applied bias. Since the RHE is defined to be at 0 V at all pH values, a pH correction is not needed. Thus, the total chemical potential of the proton-electron pair as a function of applied potential, at all temperature and pH values, can be calculated as

$$\mu(\mathrm{H}^+) + \mu(\mathrm{e}^-) = \frac{1}{2}\mu(\mathrm{H}_{2(\mathrm{g})}) - \mathrm{e}E$$

As an example, to calculate the free energy change from adsorbed CHO to adsorbed CH_2O, the free energy change of the below chemical reaction needs to be calculated:

$$\mathrm{CHO^*} + (\mathrm{H}^+ + \mathrm{e}^-) \rightarrow \mathrm{CH_2O^*}$$

Where an asterisk (*) indicates that the species is adsorbed on the copper surface. The free energy change of this reaction would thus be:

$$\begin{aligned}\Delta G &= \mu(\mathrm{CH_2O^*}) - \mu(\mathrm{CHO^*}) - [\mu(\mathrm{H}^+) + \mu(\mathrm{e}^-)] \\ &= \mu(\mathrm{CH_2O^*}) - \mu(\mathrm{CHO^*}) - [\frac{1}{2}\mu(\mathrm{H}_{2(\mathrm{g})}) - \mathrm{e}E]\end{aligned}$$

Thus, the CHE model allows the potential (*E*) to be explicitly contained within the free energy change of each step.

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