

Cite this: *RSC Adv.*, 2017, 7, 11938

# Theoretical insight into effect of doping of transition metal M (M = Ni, Pd and Pt) on CO<sub>2</sub> reduction pathways on Cu(111) and understanding of origin of electrocatalytic activity†

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The effect of the doped transition metal M (M = Ni, Pd and Pt) on CO<sub>2</sub> reduction pathways and the origin of the electrocatalytic activity are investigated systematically by focusing on the CH<sub>4</sub> and CH<sub>3</sub>OH formation pathways based on DFT calculations associated with the computational hydrogen electrode model. Our studies show that the doping of Ni, Pd and Pt can promote CO<sub>2</sub> reduction into hydrocarbons and influence the selectivity of reduction pathways, in which the doping of Pt may be able to lead to the strongest catalytic activity. The adsorption behavior between reaction intermediates and surfaces is crucial and the interactions of intermediates with the catalysts should be moderate in order to efficiently catalyze CO<sub>2</sub> reduction into CH<sub>4</sub> and CH<sub>3</sub>OH, and avoid OH surface poisoning. The enhanced electrocatalytic activity of transition metal-doped Cu(111) surfaces may be owing to decreased overpotential and moderate electronic interactions between Cu and the doped transition metals. The doped Ni, Pd and Pt atoms can considerably decrease the overpotential and remove surface OH poisoning, in which the doped Pt can simultaneously reduce overpotential for CO formation and further reduction, and most easily remove OH, thus suggesting the best electrocatalytic activity. The moderate electron interaction between Cu and Pt and moderate upshift of the d-band center of Pt also explain why the Pt-doped Cu(111) surface has the best electrocatalytic activity for CO<sub>2</sub> reduction. Two possible descriptors can be proposed in order to scale the electrocatalytic activity of Cu-based electrocatalysts for CO<sub>2</sub> reduction, in which an ideal Cu-based electrocatalyst should be able to reduce barriers for CO formation and further reduction, and should have moderate electron interactions between Cu and the doped transition metals, and a moderate upshift of d-band center of the doped transition metals. In these ways, CO<sub>2</sub> reduction pathways can be facilitated and the yield of hydrocarbons CH<sub>4</sub> and CH<sub>3</sub>OH can be enhanced.

Received 29th December 2016  
Accepted 9th February 2017

DOI: 10.1039/c6ra28815d

rsc.li/rsc-advances

## 1. Introduction

Excessive consumption of fossil fuels has gradually led to the increasing anthropogenic emission of CO<sub>2</sub> and depletion of finite natural resources.<sup>1</sup> To mitigate over-production of CO<sub>2</sub> and prepare for a fluctuating supply of fossil fuels, efforts are being made to convert CO<sub>2</sub> into reusable hydrocarbons.<sup>2</sup> Among various approaches for conversion, electrochemical reduction of CO<sub>2</sub> is considered a potentially clean and promising technique to produce various value-added hydrocarbons at only the cost of a sustainable supply of electrical energy.<sup>3,4</sup> However, the

selectivity and faradic efficiency of the CO<sub>2</sub> electroreduction process are dependent on many factors, such as the electrode materials, the surface structures of the electrode and the type of electrolytes,<sup>5–10</sup> in which the major obstacle preventing the efficient reduction of CO<sub>2</sub> is the lack of electrode materials that can readily couple with electric energy to achieve rapid and selective cleavage of C–O bonds in CO<sub>2</sub> and formation of new bonds in the products. Towards this goal, various electrode materials and promoters have been screened experimentally and analyzed computationally to optimize their activity and selectivity for CO<sub>2</sub> reduction,<sup>10–19</sup> such as transition metals,<sup>15</sup> ionic liquids,<sup>16</sup> organometallic complexes<sup>17,18</sup> and doped graphene.<sup>19</sup> Unfortunately, present electrocatalysts for CO<sub>2</sub> reduction suffer from high overpotentials, low current densities, low selectivity or poor durability.<sup>20</sup> Among these electrocatalysts explored to date, Cu has received considerable attention because it has been demonstrated experimentally as a valid low-cost electrocatalyst for CO<sub>2</sub> reduction<sup>21,22</sup> and is the only pure

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ra28815d



elemental catalyst that produces hydrocarbons at significant faradic efficiency.<sup>20</sup> Reduction products include formate, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and other higher hydrocarbons.<sup>23–26</sup> Furthermore, theoretical study of CO<sub>2</sub> reduction on transition metals Cu, Pt, Rh, Pd, Ni, Au and Ag by Nørskov and co-authors<sup>27</sup> revealed the “volcano” type of the activity diagram, in which Cu has also the best catalytic activity and is located at the top of the diagram among these transition metals. Thus, experimental and theoretical studies all showed that Cu is the best known metal electrocatalyst for CO<sub>2</sub> reduction. However, in order to achieve high faradic efficiency, significant overpotentials are required on Cu electrodes. For example, the theoretical reversible potentials for CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> are 0.17 V and 0.08 V (*vs.* RHE), respectively, but experimentally it was observed that a very large potential of about –1.0 V is applied for CO<sub>2</sub> reduction into these hydrocarbons.<sup>28</sup> Simultaneously, the H<sub>2</sub> evolution reaction (HER) at sufficiently negative potential can reduce the faradic efficiency for CO<sub>2</sub> reduction by consuming protons and electrons. Thus, to make the CO<sub>2</sub> reduction more active and selective, properly designing new electrocatalysts is extremely urgent under the current situation.

In surface-catalyzed reactions, the surface selectivity, activity and stability can be dramatically improved through the doping of transition metals to the surface of a host, and some novel properties that are not present on the parent metal surfaces are often exhibited.<sup>29–32</sup> Thus, bimetallic Cu-based alloys with Cu-rich composition experimentally have been extensively used to improve CO<sub>2</sub> electroreduction owing to the high overpotential and low current density of the pure Cu surface, such as Cu–Ni, Cu–Zn, Cu–Cd, Cu–Sn, Cu–Pb, Cu–Au, Cu–Ag, Cu–Pd and Cu–Pt.<sup>33–40</sup> Compared to pure Cu, doping of other transition metals into Cu catalysts can modify the activation barrier for different steps, thereby leading to a reduction of overpotential and a major change of faradic efficiency. For example, Cu–Au alloy has higher faradic efficiency for CO<sub>2</sub> electroreduction than that of pure Cu,<sup>37</sup> and the experimental onset potential on the Cu–Au alloy was positively shifted, indicating that the overpotential of CO<sub>2</sub> reduction can be reduced through the doping of Au.<sup>38</sup> The Ni-doped Cu surface also displayed experimentally a superior catalytic activity with respect to the CH<sub>3</sub>OH synthesis from a mixture of CO, CO<sub>2</sub> and H<sub>2</sub> in comparison with pure Cu.<sup>39,40</sup> Such an improvement was ascribed to the capability of Ni to promote CH<sub>3</sub>OH production by activating CO<sub>2</sub> and stabilizing the intermediates owing to the higher oxygen affinity of Ni.<sup>41</sup> Recently, a Pd–Cu catalyst for CO<sub>2</sub> electroreduction was investigated.<sup>42</sup> A sharp increase of the reduction current and positive shift of potential were observed on the Pd–Cu electrode compared with those for pure Cu, indicating that the doping of Pd could effectively suppress the HER and enhance the CO<sub>2</sub> electroreduction activity. Actually, in more previous studies, both Pd single-crystal<sup>43</sup> and oxide-supported Pd catalysts<sup>44,45</sup> have also been shown to be catalytically active toward CH<sub>3</sub>OH synthesis from CO<sub>2</sub> reduction. Given that Pt is also a metal with high chemical stability and oxygen affinity, the doping of Pt could be a promising approach to improve CO<sub>2</sub> electroreduction. Thus, a Cu–Pt alloy with high Cu concentration was developed by Xiong and co-authors. The greatly improved

chemical stability and superior electrocatalytic activity towards CO<sub>2</sub> reduction were exhibited owing to the presence of Pt.<sup>36</sup> Moreover, the alloying of Cu with Pt can lower the decomposition activation energy of formate by up to 13%.<sup>46</sup> In the recent theoretical studies on CO<sub>2</sub> reduction, density functional theory (DFT) was employed by Liu and co-authors to investigate the CH<sub>3</sub>OH synthesis reaction from CO<sub>2</sub> reduction on transition metals-doped Cu(111) surfaces.<sup>47</sup> The overall CH<sub>3</sub>OH yield was increased by the doped Ni, Pd and Pt compared with pure Cu, suggesting that the doping of Ni, Pd and Pt is able to promote the CH<sub>3</sub>OH production of the Cu(111) surface. Using DFT calculations associated with the standard hydrogen electrode model,<sup>48,49</sup> Hirunsit and co-authors performed a systematic thermodynamic investigation for CO<sub>2</sub> electroreduction into CH<sub>4</sub> and CH<sub>3</sub>OH on Cu-based electrocatalysts with a Cu-rich composition of Cu<sub>3</sub>X (X is Ag, Au, Co, Ni, Pd, Pt, Rh and Ir). The investigation exhibited that a considerably different electrocatalytic activity was produced and hydrocarbon selectivity was changed compared with those on the pure Cu surface, in which on the mostly Cu-based alloy catalysts CH<sub>4</sub> is more energetically favorable to be yielded than CH<sub>3</sub>OH, and CH<sub>3</sub>OH was found to be more favorable than CH<sub>4</sub> production on Cu<sub>3</sub>Pd and Cu<sub>3</sub>Pt surfaces. On most surfaces the potential-limiting step is the CO protonation with the exception of on Cu<sub>3</sub>Au and Cu<sub>3</sub>Co surfaces. Most recently, the activation of CO<sub>2</sub> on transition metal TM (TM = Fe, Co, Ni, Ru, Rh, Pd, Ag, Os, Ir, Pt and Au)-doped Cu(111) and Cu(100) surfaces was investigated with a dopant coverage of 1/9 ML by Qiu and co-authors using first-principle DFT calculations combined with a slab model.<sup>50,51</sup> The studies predicted that Co, Ru and Os may be potential dopants to enhance the chemisorption of CO<sub>2</sub> on both TM-doped Cu surfaces. However, previous experimental and theoretical studies only showed that the doped transition metals could reduce the thermodynamic overpotential of CO<sub>2</sub> reduction and activate CO<sub>2</sub> molecules. The exact CO<sub>2</sub> electroreduction mechanisms and origin of electrocatalytic activation on Cu-based electrocatalysts still remain unclear, especially kinetic analysis of the elementary reaction steps and the relationship between the kinetic barriers and adsorption ability of the reaction intermediates. Essentially, the doping of transition metals can change the CO<sub>2</sub> reduction pathways and reduce the activation barriers, thereby leading to the reduced overpotential and enhanced catalytic activity. A general understanding of the adsorption behavior, reaction mechanism and atomic-level origin of the electrocatalytic activity of Cu-based catalyst bimetallic surfaces will help us discover more efficient catalysts for a given reaction.

Based on the above analysis, Ni, Pd and Pt atoms as potential dopants may be able to enhance CO<sub>2</sub> reduction into hydrocarbons on the Cu surface. Furthermore, Cu, Ni, Pd and Pt have the same face-centered cubic structure, which gives them a crystallographic match. Thus, the activation barriers of key steps can be maneuvered through the miscible bimetallic combinations of Cu with Ni, Pd and Pt, thereby resulting in improved surface catalytic activity and selectivity. Focusing on the CH<sub>4</sub> and CH<sub>3</sub>OH formation pathways, the effect of the doped transition metal M (M = Ni, Pd and Pt) on the CO<sub>2</sub> reduction pathways and



the origin of the electrocatalytic activity are investigated systematically based on DFT calculations associated with the computational hydrogen electrode model. The (111) facet is chosen owing to its high selectivity for CH<sub>4</sub> production. The major goal of this work is to examine the effects of the doped Ni, Pd and Pt atoms on the CO<sub>2</sub> reduction pathways, surface electrocatalytic activity and selectivity in comparison with pure Cu catalyst. Some key factors that influence surface electrocatalytic activity, such as OH surface poisoning, the limiting potential, potential-limiting step and electronic interactions between Cu and Ni, Pd and Pt, are also demonstrated. The development of more superior electrocatalysts requires an essential understanding of these effects.

## 2. Computational method and modeling

All DFT calculations were implemented through the PWSCF codes included in the Quantum ESPRESSO distribution,<sup>52</sup> while figures of the chemical structures were produced by the XCRYSDEN graphical package.<sup>53–55</sup> The exchange–correction interactions were treated by using the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE).<sup>56</sup> The nuclei and core electrons were described by ultrasoft pseudo-potentials.<sup>57</sup> The transition metal M (M = Ni, Pd and Pt)-doped Cu electrodes modeled by three-layer (111) slabs with a 2 × 3 supercell were used to perform the calculations of the all stable geometry structure of various adsorption and co-adsorption intermediates, which has been shown to be thick enough to well describe the CO<sub>2</sub> reduction. The calculated equilibrium lattice constant of Cu was 3.66 Å, which was in good agreement with experimental and theoretical values (3.62 and 3.66 Å, respectively).<sup>58,59</sup> During the geometry optimization, the bottom two atomic layers in the transition metal M (M = Ni, Pd and Pt)-doped Cu(111) slabs were kept fixed, whereas the top one layer and the adsorbates were relaxed to geometry configurations with the lowest energy. A vacuum region of 16 Å was used along the z-direction to avoid any periodic interactions. For the 2 × 3 supercell, the surface Brillouin zone was sampled by using a 4 × 3 × 1 uniformly shifted *k*-mesh. The Kohn–Sham orbitals were expanded in a plane-wave basis set, and the plane-wave cutoff energy was optimized at 26 Ry. The smearing technique of Methfessel and Paxton was used to treat the Fermi-surface effects with a value of smearing parameter of 0.02 Ry.<sup>60</sup> The convergence criteria for the total energy and Cartesian force components acting on each atom were set to within 10<sup>−5</sup> Ry and below 10<sup>−3</sup> Ry Bohr<sup>−1</sup>, respectively. Additionally, it has been shown that dopants Pd and Pt prefer to stay in the surface of Cu(111), while Ni is in favor of the bulk.<sup>61</sup> However, based on the experiments conducted by Chorkendorff and coauthors,<sup>39,40</sup> the active adsorbents are able to pull the Ni atom out to the surface under hydrocarbon synthesis conditions, such as CO. Thus, our present study did not include the segregation of Ni into the bulk. The doping range of dopants on the Cu-based electrocatalyst surfaces from *ca.* 1/9 to 1/4 has been studied in the previous experimental and theoretical studies,<sup>35,36,47,50,51,62</sup> and

the surface with dopant coverage of *ca.* 1/6 ML has superior electrocatalytic activity towards CO<sub>2</sub> reduction. Thus, only one surface Cu atom was substituted by a dopant (Ni, Pd and Pt) atom in each periodic supercell in the present study, corresponding to a dopant coverage of 1/6 ML. Selecting dopant coverage of 1/6 ML is also in order to compare with our previous studies on a pure 2 × 3 Cu(111) surface.<sup>63</sup>

The minimum energy paths (MEPs) for each step of the CO<sub>2</sub> reduction into hydrocarbons were determined by the climbing-image nudged elastic band (CI-NEB) method.<sup>64,65</sup> The image of highest energy approximated the transition state of the optimized reaction coordinate, and the transition state images from the CI-NEB calculations were optimized by the quasi-Newton method, which minimizes the forces to find the saddle point. For each intermediate point in the MEPs, geometry optimization was also performed.

## 3. Results and discussion

### 3.1 The optimal reaction pathways of CO<sub>2</sub> reduction

The calculated results of CO<sub>2</sub> reduction into CH<sub>4</sub> and CH<sub>3</sub>OH on the pure Cu(111) surface were reported in our previous work<sup>63</sup> and are summarized in the ESI† again to complete the systematic comparison. Various possible pathways obtained by minimum energy pathway (MEP) analysis during the course of CO<sub>2</sub> reduction on transition metal M (M = Ni, Pd and Pt)-doped Cu(111) are also demonstrated in the ESI.† Based on the MEP analyses of the elementary reaction steps, it can be concluded that CO, CHO and CH<sub>2</sub>O are key reaction intermediates during the course of CO<sub>2</sub> reduction into hydrocarbons on Ni-, Pd- and Pt-doped Cu(111) surfaces, in which CO is firstly formed through CO<sub>2</sub> dissociative hydrogenation, and the COOH intermediate is involved during the course of CO formation. On the Ni-doped Cu(111) surface, formation of intermediates CH<sub>3</sub>O, CH<sub>2</sub>OH and CH<sub>2</sub> through further CH<sub>2</sub>O hydrogenation and hydrogenative dissociation are all favorable reaction pathways, which may be parallel pathways in the CO<sub>2</sub> reduction mechanism based on the MEP analyses. CH<sub>3</sub>OH formation more easily occurs through CH<sub>2</sub>OH hydrogenation in CH<sub>3</sub>O and CH<sub>2</sub>OH further reduction on the Ni-doped Cu(111) surface. Simultaneously, CH<sub>2</sub> that is produced through CH<sub>2</sub>O hydrogenative dissociation also leads to CH<sub>4</sub> formation. Notably, CH<sub>2</sub>OH hydrogenation into CH<sub>3</sub>OH formation and CH<sub>2</sub> serial hydrogenation into CH<sub>4</sub> require very low activation barriers on the Ni-doped Cu(111) surface, which can be all overcome by the thermoactive process at ambient temperature. Thus, we conclude that CH<sub>4</sub> and CH<sub>3</sub>OH may be able to be formed during CO<sub>2</sub> reduction simultaneously on the Ni-doped Cu(111) surface. The MEP analyses on the Pd-doped Cu(111) surface show that CH<sub>2</sub>O direct hydrogenation into CH<sub>3</sub>O is the most favorable pathway among all possibilities of further CH<sub>2</sub>O reduction. The most preferred reaction pathway among further CH<sub>3</sub>O reduction is CH<sub>3</sub>O hydrogenative dissociation into CH<sub>3</sub> on the Pd-doped Cu(111) surface. Thus, CH<sub>4</sub> can be formed through CH<sub>3</sub> hydrogenation. On the Pt-doped Cu(111) surface, direct hydrogenation of CH<sub>2</sub>O to form CH<sub>3</sub>O and CH<sub>2</sub>OH intermediates are the most favorable pathways. Thus, CH<sub>3</sub>O and CH<sub>2</sub>OH may be



reaction intermediates in CO<sub>2</sub> reduction on the Pt-doped Cu(111) surface. The MEP analyses show that CH<sub>3</sub> and CH<sub>3</sub>OH can be formed easily through CH<sub>3</sub>O hydrogenative dissociation and CH<sub>2</sub>OH hydrogenation, respectively. Simultaneously, a CH<sub>2</sub> intermediate can be also formed through CH<sub>2</sub>OH hydrogenative dissociation. Intermediates CH<sub>2</sub> serial hydrogenation and CH<sub>3</sub> hydrogenation possibly result in the formation of the final CH<sub>4</sub> product. Thus, we can conclude that CH<sub>4</sub> and CH<sub>3</sub>OH in CO<sub>2</sub> reduction on the Pt-doped Cu(111) surface are also possible products. Based on thermodynamic and kinetic analyses, (CO + H)\* → CHO\* is the slowest step on these three surfaces. The optimal reaction pathways of CO<sub>2</sub> reduction on the pure and transition metal M (M = Ni, Pd and Pt)-doped Cu(111) surfaces are summarized in Fig. 1.

### 3.2 Comparison of CO<sub>2</sub> reduction pathways among pure and Ni-, Pd- and Pt-doped Cu(111)

The reaction free energies and activation barriers for the optimal CO<sub>2</sub> reduction pathways into CH<sub>4</sub> and CH<sub>3</sub>OH production are listed in Tables 1 and 2 on the pure and transition metal Ni-, Pd- and Pt-doped Cu(111) surfaces.

Based on the data in Tables 1 and 2, potential energy diagrams for formation of CH<sub>4</sub> and CH<sub>3</sub>OH through CO<sub>2</sub> reduction on the pure and transition metal Ni-, Pd- and Pt-doped Cu(111) surfaces are given in Fig. 2–5, respectively. We observed that the activation barriers of CO formation through

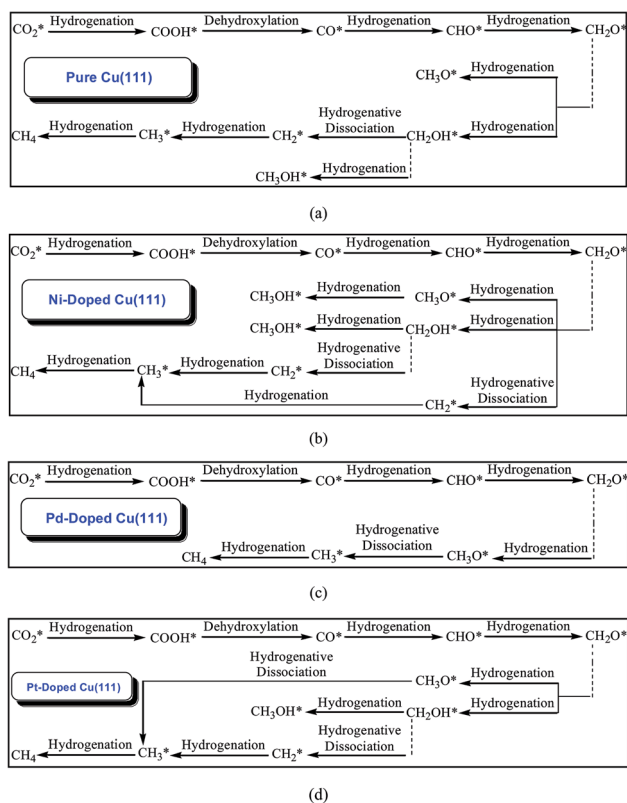


Fig. 1 The optimal reaction pathways of CO<sub>2</sub> reduction into CH<sub>4</sub> and CH<sub>3</sub>OH on: (a) pure Cu(111); (b) Ni-doped Cu(111); (c) Pd-doped Cu(111); and (d) Pt-doped Cu(111).

initial CO<sub>2</sub> reduction are considerably decreased by the doping of Ni, Pd and Pt, which is the rate-determining step of CO<sub>2</sub> reduction on the pure Cu(111) surface (*ca.* 1.18 eV). Thus, the doping of Ni, Pd and Pt can activate CO<sub>2</sub> and enhance the surface activity of Cu catalysts for CO<sub>2</sub> reduction. Therefore, CO formation requires significantly lower activation barriers on Ni and Pt-doped Cu(111) surfaces (*ca.* 0.40 and 0.65 eV), whereas an activation barrier of 0.83 V is required after doping of Pd (see Fig. S1, S19 and S16†), which may be attributed to chemisorbed CO<sub>2</sub> molecule being observed after doping of Ni and Pt by binding C atom at Ni and Pt sites, whereas only physisorbed

Table 1 The optimal CO<sub>2</sub> reduction pathways into hydrocarbons CH<sub>4</sub> and CH<sub>3</sub>OH and the reaction free energies ( $E_{\text{reac}}$ ) and activation barriers ( $E_{\text{act}}$ ) for each elementary step on the pure and Ni-doped Cu(111) surfaces<sup>a</sup>

Reaction paths	Pure Cu(111)		Ni-doped Cu(111)	
	$\Delta G_{\text{reac}}$ (eV)	$E_{\text{act}}$ (eV)	$\Delta G_{\text{reac}}$ (eV)	$E_{\text{act}}$ (eV)
CO <sub>2</sub> (g) + H* → (CO + OH)*	0.27	1.18	-0.23	0.40
(CO + H)* → CHO*	0.90	1.06	1.03	1.08
(CHO + H)* → CH <sub>2</sub> O*	-0.20	0.72	-0.04	0.28
(CH <sub>2</sub> O + H)* → (CH <sub>2</sub> + OH)*	0.01	1.12	0.06	0.24
(CH <sub>2</sub> O + H)* → CH <sub>2</sub> OH*	0.13	0.95	-0.60	0.27
(CH <sub>2</sub> O + H)* → CH <sub>3</sub> O*	-1.05	1.86	-0.08	0.24
(CH <sub>2</sub> OH + H)* → CH <sub>2</sub> * + H <sub>2</sub> O (l)	-0.19	0.66	-0.13	0.58
(CH <sub>2</sub> OH + H)* → CH <sub>3</sub> OH (l)	-0.95	0.68	-0.61	0.16
(CH <sub>2</sub> + H)* → CH <sub>3</sub> *	-0.83	0.63	-0.55	0.30
(CH <sub>3</sub> + H)* → CH <sub>4</sub> *	-0.80	1.03	-0.59	0.21

<sup>a</sup> The asterisk (\*) indicates that the species is adsorbed on the surface. The zero point energies (ZPE) for all species, which are obtained by the present DFT calculations, are included in the reaction free energy. For instance, for the reaction step of (CO + H)\* → CHO\*, the reaction free energy is calculated according to “ $E(\text{CHO}^*) - E(\text{CO} + \text{H})^* + \text{ZPE}(\text{CHO}^*) - \text{ZPE}(\text{CO}^*) - \text{ZPE}(\text{H}^*)$ ”.

Table 2 The optimal CO<sub>2</sub> reduction pathways into hydrocarbons CH<sub>4</sub> and CH<sub>3</sub>OH and the reaction energies ( $E_{\text{reac}}$ ) and activation barriers ( $E_{\text{act}}$ ) for each elementary step on Pd- and Pt-doped Cu(111) surfaces

Reaction paths	Pd-doped Cu(111)		Pt-doped Cu(111)	
	$\Delta G_{\text{reac}}$ (eV)	$E_{\text{act}}$ (eV)	$E_{\text{reac}}$ (eV)	$\Delta G_{\text{reac}}$ (eV)
CO <sub>2</sub> (g) + H* → (CO + OH)*	0.31	0.83	0.07	0.65
(CO + H)* → CHO*	0.51	0.87	0.41	0.84
(CHO + H)* → CH <sub>2</sub> O*	-0.25	0.10	-0.02	0.35
(CH <sub>2</sub> O + H)* → (CH <sub>2</sub> + OH)*	0.24	0.52	0.26	0.82
(CH <sub>2</sub> O + H)* → CH <sub>2</sub> OH*	-0.12	0.68	-0.35	0.59
(CH <sub>2</sub> O + H)* → CH <sub>3</sub> O*	-0.80	0.06	-0.62	0.17
(CH <sub>2</sub> OH + H)* → CH <sub>2</sub> * + H <sub>2</sub> O (l)	-0.01	0.33	0.10	0.60
(CH <sub>2</sub> OH + H)* → CH <sub>3</sub> OH (l)	-0.86	0.30	-0.53	0.34
(CH <sub>3</sub> O + H)* → CH <sub>3</sub> OH (l)	-0.10	1.86	-0.17	1.36
(CH <sub>3</sub> O + H)* → (CH <sub>3</sub> + OH)*	0.01	0.29	-0.12	0.63
(CH <sub>2</sub> + H)* → CH <sub>3</sub> *	-0.83	0.35	-0.95	0.33
(CH <sub>3</sub> + H)* → CH <sub>4</sub> *	-1.01	0.23	-0.82	0.70



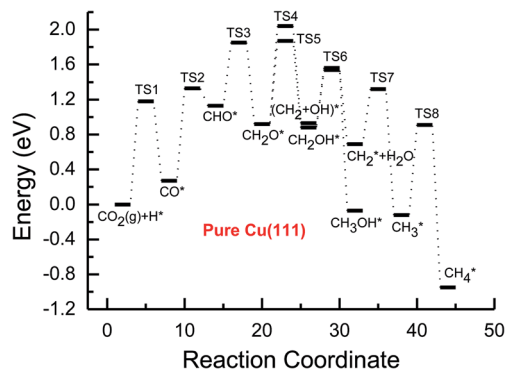


Fig. 2 Potential energy diagrams for the CH<sub>4</sub> and CH<sub>3</sub>OH formation through CO<sub>2</sub> reduction on the pure Cu(111) surface. TS stands for transition state.

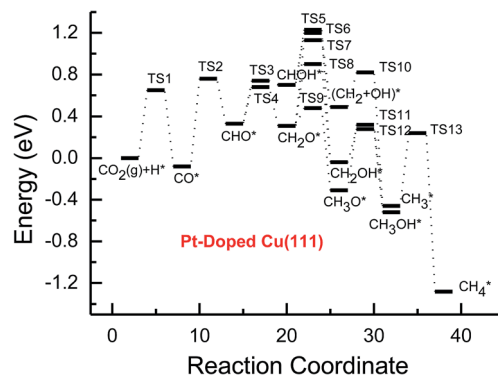


Fig. 5 Potential energy diagrams for CH<sub>4</sub> and CH<sub>3</sub>OH formation through CO<sub>2</sub> reduction on the transition metal Pt-doped Cu(111) surface.

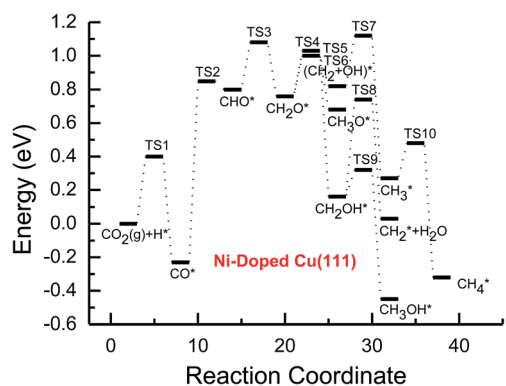


Fig. 3 Potential energy diagrams for CH<sub>4</sub> and CH<sub>3</sub>OH formation through CO<sub>2</sub> reduction on the transition metal Ni-doped Cu(111) surface.

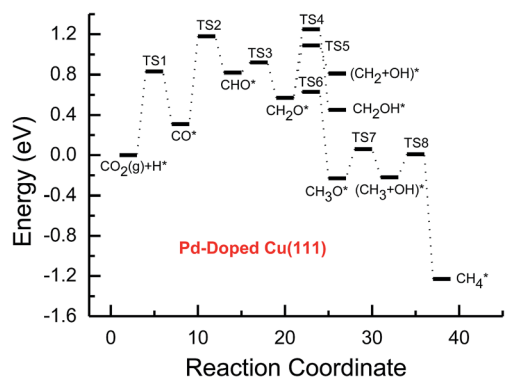


Fig. 4 Potential energy diagrams for CH<sub>4</sub> and CH<sub>3</sub>OH formation through CO<sub>2</sub> reduction on the transition metal Pd-doped Cu(111) surface.

CO<sub>2</sub> was observed on the Pd-doped Cu(111) surface. For further CO reduction, CO hydrogenation into CHO was shown to be the preferred reaction pathway on the Ni-, Pd- and Pt-doped Cu(111) surfaces, as obtained on the pure Cu(111) surface.<sup>63</sup> Our previous study and the work from Mei and co-authors<sup>63,66</sup> have shown that CO prefers to desorb from Cu rather than to

undergo further hydrogenation into CHO, which is in favor of dissociation back to CO and H. For example, CO hydrogenation to form CHO needs to overcome an activation barrier of 1.06 eV on the pure Cu(111) surface, whereas the inverse process only requires an activation barrier of 0.16 eV. The corresponding pathway has nearly equal activation barriers on the Ni-doped Cu(111) surface and the pure Cu(111) surface (1.06 eV vs. 1.08 eV), and a very low activation barrier for CHO dissociation back to CO was required (*ca.* 0.10 eV). Both steps may hinder CH<sub>4</sub> and CH<sub>3</sub>OH formation in CO<sub>2</sub> reduction on the pure and Ni-doped Cu(111) surfaces. In fact, a large amount of CO was observed experimentally on Cu for CH<sub>3</sub>OH synthesis.<sup>67</sup> Based on our present calculations, the doping of Pd and Pt helps to improve the corresponding hydrogenation process. The activation barriers are 0.87 and 0.84 eV for CO hydrogenation after the doping of Pd and Pt, which are 0.19 and 0.22 eV lower than the corresponding barrier on the pure Cu(111) surface, respectively. Moreover, the activation barriers for CHO dissociation back to CO are increased on Pd- and Pt-doped Cu(111) surfaces (see Fig. S11 and S18<sup>†</sup>), which are 0.10 and 0.27 eV higher than the corresponding barriers on the pure Cu(111) surface, respectively. Improvement of further CO reduction may be attributed to the stronger CO adsorption. The adsorption energy of CO is 0.13 and 0.48 eV stronger after doping of Pd and Pt than that on the pure Cu(111) surface, respectively, *i.e.* the CO intermediate can be stabilized. Our present studies also show that the CO molecule can be stabilized by the doping of Ni. However, CO adsorption is stronger than that on the pure Cu(111) surface by 0.80 eV after doping of Ni, which is significantly higher than that on the Pd- and Pt-doped Cu(111) surfaces, thereby leading to a relatively poor improvement for further CO reduction into CHO. Although the doped Ni atom cannot significantly improve the further CO reduction into CHO, it makes CO formation the most facile to occur. According to our calculations, CO prefers to adsorb on the top sites of Ni, Pd and Pt. In comparison, the energetically most favorable site for CO adsorption is the fcc-hollow site on the pure Cu(111) surface.<sup>63</sup>

Subsequent further CHO reduction into the CH<sub>2</sub>O intermediate is the most favorable pathway among various possibilities on the pure and Ni-, Pd- and Pt-doped Cu(111) surfaces (see



Fig. S4, S12 and S19<sup>†</sup>). The activation barriers of 0.28, 0.10 and 0.35 eV are required for this pathway, respectively, which are significantly lower than that on the pure Cu(111) surface (*ca.* 0.72 eV). Simultaneously, it can be found that the CHO intermediate may be formed on the Pt-doped Cu(111) surface since CH<sub>2</sub>O and CHO formation through CHO hydrogenation have nearly equal activation barriers (*ca.* 0.35 and 0.40 eV). We also observed that the further reduction of CHO is energetically comparable to CHO dissociation back to CO after the doping of Ni, Pd and Pt. Thus, although the doping of Ni has a poor improvement for further CO reduction, it considerably improves the further CHO reduction into key intermediate CH<sub>2</sub>O. The significantly lower activation barriers after the doping of Ni, Pd and Pt may be owing to the stronger CHO adsorption. CHO prefers to bind at Ni, Pd and Pt sites through a C atom after the doping of Ni, Pd and Pt, which is 0.67, 0.29 and 0.68 eV more stable than that on the pure Cu(111) surface, respectively. Thus, the CHO intermediate is able to be stabilized and further CHO reduction can be promoted by the doping of Ni, Pd and Pt atoms.

On the Ni-doped Cu(111) surface, CH<sub>2</sub>O hydrogenation into CH<sub>3</sub>O and CH<sub>2</sub>OH, and hydrogenative dissociation into CH<sub>2</sub> may be parallel pathways since they have very low and almost equal activation barriers. The barriers for the corresponding pathways are 0.24, 0.27 and 0.24 eV, respectively. Only CH<sub>3</sub>O formation is the most preferred pathway in further CH<sub>2</sub>O reduction on the Pd-doped Cu(111) surface with a very low activation barrier of 0.06 eV, which is a non-activated process, as shown in Fig. S13.<sup>†</sup> On the Pt-doped Cu(111) surface, CH<sub>3</sub>O and CH<sub>2</sub>OH formations through CH<sub>2</sub>O hydrogenation are the most favorable pathways among four possibilities owing to the relatively lower activation barriers (0.21 and 0.59 eV), as shown in Fig. S20.<sup>†</sup> However, considerably higher activation barriers are required on the pure Cu(111) surface for further CH<sub>2</sub>O reduction compared with that on Ni-, Pd- and Pt-doped Cu(111), and the most favorable reduction pathway is hydrogenation of CH<sub>2</sub>O into CH<sub>2</sub>OH with an activation barrier of 0.95 eV. The significantly lower barriers may be owing to the doping of Ni, Pd and Pt stabilizing the CH<sub>2</sub>O intermediate, which adsorbs on the Ni-, Pd- and Pt-doped Cu(111) surfaces through the C atom directly interacting with Ni, Pd and Pt and O atoms interacting with Cu and transition metal M (M = Ni, Pd and Pt). In comparison, the adsorption of CH<sub>2</sub>O intermediate on the Ni-, Pd- and Pt-doped Cu(111) surfaces is 0.55, 0.19 and 0.31 eV more stable than that on pure Cu(111), respectively. On the Pt-doped Cu(111) surface, CH<sub>2</sub> and CH<sub>2</sub>OH may be able to be formed through CHO hydrogenative dissociation and direct hydrogenation owing to almost identical activation barriers (*ca.* 0.53 and 0.54 eV). However, CHO dissociation back into CHO only requires a very low activation barrier of *ca.* 0.04 eV, as shown in Fig. S4 and S19,<sup>†</sup> which is a non-activated process. Thus, although CHO can be formed on the Pt-doped Cu(111) surface, its further reduction may not be able to occur.

Further reduction of CH<sub>2</sub>OH intermediate into CH<sub>3</sub>OH is more favorable to occur with an activation barrier as low as 0.16 eV on the Ni-doped Cu(111) surface, which is significantly more facile in contrast with CH<sub>3</sub>O further reduction, as shown

in Fig. S6 and S7.<sup>†</sup> Thus, CH<sub>3</sub>OH can be formed easily by CH<sub>2</sub>OH hydrogenation after the doping of Ni atom. CH<sub>3</sub>O hydrogenative dissociation into the CH<sub>3</sub> intermediate is the most preferred pathway in further CH<sub>3</sub>O reduction on the Pd- and Pt-doped Cu(111) surfaces with relatively lower activation barriers of 0.29 and 0.63 eV, respectively. On the Pt-doped Cu(111) surface, CH<sub>3</sub>OH and CH<sub>2</sub> can be also formed easily through hydrogenation and hydrogenative dissociation in further reduction of CH<sub>2</sub>OH with relatively lower activation barriers of 0.34 and 0.60 eV, respectively. Thus, the doping of Pt may lead to simultaneous formation of CH<sub>2</sub>, CH<sub>3</sub> and CH<sub>3</sub>OH, as shown in Fig. S22 and S23.<sup>†</sup> Our previous studies also suggested that CH<sub>3</sub>OH and CH<sub>2</sub> were formed on the pure Cu(111) surface through further reduction of CH<sub>2</sub>OH with activation barriers of 0.68 and 0.66 eV, respectively.<sup>63</sup> However, the doping of Ni and Pt leads to a significant decrease of the activation barriers for CH<sub>3</sub>OH formation. Thus, further CH<sub>2</sub>OH reduction can be improved through the doped Ni and Pt atoms, whereas the doping of Pd promotes CH<sub>3</sub>O formation and further reduction, leading to enhanced CH<sub>4</sub> and CH<sub>3</sub>OH yields. Further reduction of CH<sub>3</sub>O was not considered on the pure Cu(111) surface owing to the significantly higher activation barrier of CH<sub>3</sub>O formation. The significant promotion effect on further CH<sub>2</sub>OH reduction may be owing to the stronger CH<sub>2</sub>OH adsorption after doping of Ni and Pt atoms. The binding of CH<sub>2</sub>OH is 0.39 and 0.51 eV more stable than that on the pure Cu(111) surface, and it prefers to bind at the top site of the Ni and Pt atoms by C atom on the Ni- and Pt-doped Cu(111) surfaces. Compared with that on the pure Cu(111) surface, CH<sub>3</sub>O on the Ni-doped Cu(111) surface is 0.05 eV more stable. However, CH<sub>3</sub>O is 0.09 and 0.25 eV less stable after the doping of Pd and Pt than that on the pure Cu(111) surface, which may explain why the CH<sub>3</sub> intermediate can be formed through hydrogenative dissociation of CH<sub>3</sub>O after doping of Pd and Pt.

Based on the above analyses, CH<sub>4</sub> production possibly occurs through serial CH<sub>2</sub> hydrogenation on the Ni- and Pt-doped Cu(111) surfaces or direct CH<sub>3</sub> hydrogenation on the Pd- and Pt-doped Cu(111) surfaces. The activation barriers for CH<sub>2</sub> hydrogenation into CH<sub>3</sub> and CH<sub>3</sub> hydrogenation into CH<sub>4</sub> are 0.30 and 0.21 eV, 0.35 and 0.23 eV, 0.33 and 0.70 eV on Ni, Pd- and Pt-doped Cu(111) surfaces (see Fig. S8, S15 and S24<sup>†</sup>), respectively, which are notable lower than that for the corresponding pathways on the pure Cu(111) surface (0.63 eV and 1.03 eV, respectively). Based on our present calculations, the doping of Ni and Pt helps to stabilize CH<sub>2</sub> and CH<sub>3</sub> intermediates and enhance the corresponding hydrogenation processes, in which CH<sub>2</sub> and CH<sub>3</sub> are 0.43 and 0.22 eV, 0.18 and 0.23 eV more stable after doping of Ni and Pt, respectively. Although CH<sub>3</sub> is 0.07 eV less stable on the Pd-doped Cu(111) surface, the doping of Pd still can improve further CH<sub>3</sub> reduction into CH<sub>4</sub>. This may be attributed to different electronic interactions among Ni and Pd, Ni and Pt, which will be confirmed by subsequent electronic structure analysis. Additionally, OH can be formed during the course of CO<sub>2</sub> reduction into CH<sub>4</sub> and CH<sub>3</sub>OH on the pure and Ni-, Pd- and Pt-doped Cu(111) surfaces, which may lead to poisoning of surface active sites. Thus, the OH removal to form H<sub>2</sub>O is an important step for CO<sub>2</sub>



reduction. The activation barriers for OH removal are 1.09, 0.68, 0.56 and 0.21 eV on pure and Ni-, Pd- and Pt-doped Cu(111) surfaces, respectively, as shown in Fig. 6. We observe that the doping of Ni, Pd and Pt atoms significantly decreases the activation barriers of OH removal, which is 0.41, 0.53 and 0.88 eV lower than the corresponding barrier on pure Cu(111), respectively. Therefore, the reduced value of the activation barrier after the doping of Ni atom is lower than that on the Pd- and Pt-doped Cu(111) surfaces. The significant improvement of OH removal on the Pd- and Pt-doped Cu(111) may be owing to the weaker OH adsorption, in which the adsorption of OH is 0.16 and 0.26 eV less stable than that on the pure Cu(111) surface, respectively, whereas the doping of Ni makes OH adsorption 0.08 eV stronger. Thus, the doping of metals with less affinity toward OH, such as Pd and Pt, improves the OH removal step and proves to be more efficient than pure Cu and high OH affinity metal Ni.

On this basis, the effect of the doped Ni, Pd and Pt atoms on the selectivity of the reaction pathways and reduction production can be revealed. The doped Ni, Pd and Pt atoms changed the rate-determining step of CO<sub>2</sub> reduction, which is (CO<sub>2</sub> + H)\* → (CO + OH)\* on the pure Cu(111) surface, whereas it is changed into (CO + H)\* → CHO\* after the doping of Ni, Pd and Pt. The activation barriers of rate-determining steps are also

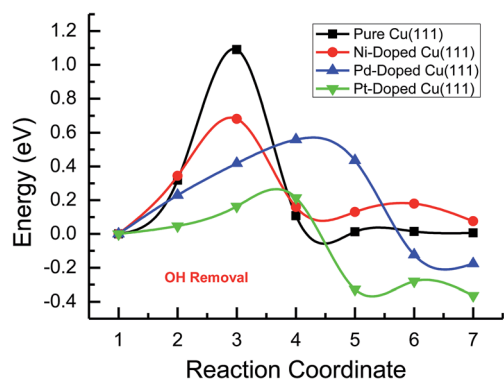


Fig. 6 The minimum energy pathways of OH removal to form H<sub>2</sub>O on pure and Ni-, Pd- and Pt-doped Cu(111) surfaces.

reduced, which are 0.10, 0.31 and 0.34 eV lower than that of the corresponding process on the pure Cu(111) surface, respectively. Simultaneously, we observed that the activation barriers in overall optimal pathways for CO<sub>2</sub> reduction into CH<sub>4</sub> and CH<sub>3</sub>OH are 1.88, 1.12, 1.18 and 0.90 eV on the pure and Ni-, Pd- and Pt-doped Cu(111) surfaces, respectively, as shown in Fig. 2–5, in which the barriers are considerably decreased compared with that on pure Cu(111) and the doping of Pt may be able to lead to the strongest catalytic activity owing to the most reduced value. Therefore, higher CH<sub>4</sub> and CH<sub>3</sub>OH yields can be expected on the Ni-, Pd- and Pt-doped Cu(111) surfaces. The higher reactivity of Ni-, Pd- and Pt-doped Cu(111) surfaces is also consistent with the previous experimental observations.<sup>36,39–42</sup> The adsorption behavior of intermediates may be able to determine CO<sub>2</sub> reduction activity based on the above discussion. The most stable adsorption sites and adsorption energies for the possible intermediates involved in CO<sub>2</sub> reduction into CH<sub>4</sub> and CH<sub>3</sub>OH on the pure and Ni-, Pd- and Pt-doped Cu(111) surfaces are given in Table 3. It is clear that the doping of Ni, Pd and Pt atoms can stabilize the relatively weaker adsorbed C- and O-containing intermediates on the pure Cu(111) surface, such as CO, CHO and CH<sub>2</sub>O, where C and O atoms directly interact with the doped Ni, Pd and Pt atoms, thereby resulting in easier formation and reduction of CO, CHO and CH<sub>2</sub>O in spite of the doped Ni atom not notably improving further CO reduction into CHO owing to excessively strongly adsorbed CO. However, the stronger adsorbed intermediates, such as CH<sub>3</sub>O and OH, are destabilized by the doped Pd and Pt atoms in comparison with pure Cu(111), which make CH<sub>3</sub>O formation and further reduction able to occur on the Pd- and Pt-doped Cu(111) surfaces and OH removal be easier. Owing to the high carbon and oxygen affinity of Ni, all intermediates can be stabilized by the doped Ni atom in CO<sub>2</sub> reduction and the Ni-doped Cu(111) surface has the strongest adsorption ability among the Ni-, Pd- and Pt-doped Cu(111) surfaces, whereas the doping of Pd and Pt leads to the weakest and moderate adsorption of most intermediates, respectively, which may explain why Pt-doped Cu(111) surfaces have the best catalytic activity for CO<sub>2</sub> reduction. Thus, it is concluded that moderate adsorbed intermediates on the Cu-based electrocatalyst surfaces will favor CO<sub>2</sub> reduction.

Table 3 The most stable adsorption sites and adsorption energies ( $E_{\text{ads}}$ ) for the possible intermediates involved in CO<sub>2</sub> reduction into CH<sub>4</sub> and CH<sub>3</sub>OH on pure and Ni-, Pd- and Pt-doped Cu(111) surfaces

Species	Cu(111)		Ni-doped Cu(111)		Pd-doped Cu(111)		Pt-doped Cu(111)	
	Sites	$E_{\text{ads}}$ (eV)	Sites	$E_{\text{ads}}$ (eV)	Sites	$E_{\text{ads}}$ (eV)	Sites	$E_{\text{ads}}$ (eV)
COOH	Bridge	-1.56	Bridge	-1.95	Bridge	-1.69	Bridge	-2.03
CO	fcc	-0.80	Top	-1.59	Top	-0.93	Top	-1.28
CHO	fcc	-1.25	Top	-1.93	Top	-1.54	Top	-1.93
CH <sub>2</sub> O	fcc	-0.05	fcc	-0.60	fcc	-0.24	fcc	-0.36
CHOH	fcc	-2.50	Top	-3.02	fcc	-2.60	Top	-2.95
CH <sub>2</sub> OH	fcc	-0.90	fcc	-1.29	fcc	-1.11	fcc	-1.41
CH <sub>3</sub> O	fcc	-2.28	fcc	-2.33	fcc	-2.19	hcp	-2.03
CH <sub>2</sub>	fcc	-2.94	fcc	-3.37	fcc	-2.90	fcc	-3.12
CH <sub>3</sub>	fcc	-1.36	fcc	-1.58	Top	-1.29	Top	-1.59
OH	fcc	-3.16	fcc	-3.24	hcp	-3.00	hcp	-2.90



### 3.3 Origin of catalytic activity

#### 3.3.1 The limiting potential and potential-limiting step.

The Ni-, Pd- and Pt-doped Cu(111) surfaces may be able to decrease the overpotentials of CO<sub>2</sub> electroreduction, which can be linked directly to the proton and electron transfer to adsorbed intermediates being strongly bonded to the surface and determines the catalytic activity of the electrocatalysts. Thus, potential dependent reaction free energies and limiting potentials are obtained in order to ascertain the origin of the overpotential and electrocatalytic activity using the computational hydrogen electrode (CHE) model proposed by Nørskov and co-authors.<sup>68</sup> The mechanistic details are elucidated in the ESI.† A thermodynamic equilibrium potential of 0.17 V vs. RHE for hydrocarbons formation is used to calculate the reaction free energies if we assume CO<sub>2</sub> reduction to be in equilibrium and neglect ohmic losses. This model could provide an elegant way to calculate the potential-dependent reaction free energies for each step under electrochemical conditions by avoiding the explicit treatment of solvated protons. The potential where the reaction free energy is zero is referred to as the limiting potential, which serves as an estimate of the onset potential for each intermediate; the most endothermic reaction step in the reaction pathways is referred to as the potential-limiting step.

The calculated limiting potentials (*E*) and reaction free energies ( $\Delta G_{\text{reac}}$ ) at 0.17 V vs. RHE in CO<sub>2</sub> electroreduction to CH<sub>4</sub> and CH<sub>3</sub>OH on pure and Ni-, Pd-, and Pt-doped Cu(111) surfaces are listed in Tables 4 and 5. We found that the potential-limiting step is CHO formation (CO\* + H<sup>+</sup> + e<sup>-</sup> → CHO\*) with the most positive reaction free energy at 0.17 V vs. RHE on the pure and Ni-, Pd- and Pt-doped Cu(111) surfaces, requiring limiting potentials of -0.60, -0.72, -0.44 and -0.40 V vs. RHE by the CHE model, respectively. It can be observed that the limiting potentials are positively shifted after the doping of Pd and Pt atoms, whereas it is more negative after

**Table 5** The limiting potentials (*E*) and reaction free energies ( $\Delta G_{\text{reac}}$ ) at 0.17 V vs. RHE (thermodynamic equilibrium potential) in CO<sub>2</sub> electroreduction to CH<sub>4</sub> and CH<sub>3</sub>OH on the Pd- and Pt-doped Cu(111) surfaces

Possible reduction steps	Pd-doped Cu(111)		Pt-doped Cu(111)	
	<i>E</i> (V)	$\Delta G_{\text{reac}}$ (eV)	<i>E</i> (V)	$\Delta G_{\text{reac}}$ (eV)
(a) CO <sub>2</sub> * + H <sup>+</sup> + e <sup>-</sup> → (CO + OH)*	-0.11	0.28	0.82	-0.65
(b) CO* + H <sup>+</sup> + e <sup>-</sup> → CHO*	-0.44	0.61	-0.40	0.57
(c) CHO* + H <sup>+</sup> + e <sup>-</sup> → CH <sub>2</sub> O*	0.35	-0.18	0.08	0.09
(d) CH <sub>2</sub> O* + H <sup>+</sup> + e <sup>-</sup> → (CH <sub>2</sub> + OH)*	-0.08	0.25	-0.16	0.33
(e) CH <sub>2</sub> O* + H <sup>+</sup> + e <sup>-</sup> → CH <sub>3</sub> O*	0.97	-0.80	0.69	-0.52
(f) CH <sub>2</sub> O* + H <sup>+</sup> + e <sup>-</sup> → CH <sub>2</sub> OH*	0.25	-0.08	0.43	-0.26
(g) CH <sub>2</sub> OH* + H <sup>+</sup> + e <sup>-</sup> → CH <sub>3</sub> OH (l)	0.93	-0.76	0.62	-0.45
(h) CH <sub>2</sub> OH* + H <sup>+</sup> + e <sup>-</sup> → CH <sub>2</sub> * + H <sub>2</sub> O (l)	0.11	0.06	0.00	0.17
(i) CH <sub>3</sub> O* + H <sup>+</sup> + e <sup>-</sup> → CH <sub>3</sub> OH (l)	0.21	-0.04	0.36	-0.19
(j) CH <sub>3</sub> O* + H <sup>+</sup> + e <sup>-</sup> → (CH <sub>3</sub> + OH)*	0.01	0.16	0.32	-0.15
(k) CH <sub>2</sub> * + H <sup>+</sup> + e <sup>-</sup> → CH <sub>3</sub> *	1.03	-0.86	1.11	-0.94
(m) CH <sub>3</sub> * + H <sup>+</sup> + e <sup>-</sup> → CH <sub>4</sub> *	1.14	-0.97	0.84	-0.67
(n) OH* + H <sup>+</sup> + e <sup>-</sup> → H <sub>2</sub> O (l)	0.36	-0.19	0.48	-0.31

the doping of Ni atom, implying that the doped Pd and Pt atoms can decrease the overpotential of this pathway. The strongest CO adsorption on the Ni-doped Cu(111) surface may induce the protonation to be potentially limited, resulting in a relatively high overpotential for CHO formation. The formation of CHO is also the rate-determining step in CO<sub>2</sub> reduction on the Ni-, Pd- and Pt-doped Cu(111) surfaces based on the above kinetic analyses, and its activation barriers are lower after the doping of Pd and Pt atoms, and slightly higher after the doping of Ni atom, compared with that on the pure Cu(111) surface. Although the doped Ni atom leads to more negative limiting potential (-0.72 V) and more positive reaction free energy (0.89 eV) for CHO formation, it can notably shift the limiting potential and reaction free energy to more positive (1.11 V) and more negative values (-0.94 eV) for CO formation (CO<sub>2</sub>\* + H<sup>+</sup> + e<sup>-</sup> → (CO + OH)\*), respectively, in which the formation of CO has a slightly negative limiting potential of -0.07 V and a positive reaction free energy of 0.24 eV on the pure Cu(111) surface. The above kinetic studies also show that the activation barrier of CO formation is significantly decreased by the doping of Ni atom. Thus, the decreased overpotential for CO formation can be concluded after the doping of Ni. As shown in Table 5, the doping of Pt atom also can significantly shift the limiting potential of CO formation to a more positive value and make the reaction free energy more negative, thus leading to decrease of the overpotential. However, the limiting potential and reaction free energy of CO formation after the doping of Pd are almost unchanged compared with that on the pure Cu(111) surface. These may be owing to chemisorbed CO<sub>2</sub> being observed on Ni- and Pt-doped Cu(111) surfaces and only physisorbed CO<sub>2</sub> is formed on the Pd-doped Cu(111) surface. Simultaneously, the limiting potentials of OH removal are also shifted positively after the doping of Ni, Pd and Pt, which are 0.06, 0.24 and 0.36 V more positive than that on the pure Cu(111) surface, respectively, leading to the reduction of the overpotential. Therefore,

**Table 4** The limiting potentials (*E*) and reaction free energies ( $\Delta G_{\text{reac}}$ ) at 0.17 V vs. RHE (thermodynamic equilibrium potential) in CO<sub>2</sub> electroreduction to CH<sub>4</sub> and CH<sub>3</sub>OH on the pure and Ni-doped Cu(111) surfaces

Possible reduction steps	Pure Cu(111)		Ni-doped Cu(111)	
	<i>E</i> (V)	$\Delta G_{\text{reac}}$ (eV)	<i>E</i> (V)	$\Delta G_{\text{reac}}$ (eV)
(a) CO <sub>2</sub> * + H <sup>+</sup> + e <sup>-</sup> → (CO + OH)*	-0.07	0.24	1.11	-0.94
(b) CO* + H <sup>+</sup> + e <sup>-</sup> → CHO*	-0.60	0.77	-0.72	0.89
(c) CHO* + H <sup>+</sup> + e <sup>-</sup> → CH <sub>2</sub> O*	0.45	-0.28	0.32	-0.15
(d) CH <sub>2</sub> O* + H <sup>+</sup> + e <sup>-</sup> → (CH <sub>2</sub> + OH)*	0.38	-0.21	0.10	0.07
(e) CH <sub>2</sub> O* + H <sup>+</sup> + e <sup>-</sup> → CH <sub>3</sub> O*	1.26	-1.09	0.76	-0.59
(f) CH <sub>2</sub> O* + H <sup>+</sup> + e <sup>-</sup> → CH <sub>2</sub> OH*	0.23	-0.06	0.07	0.10
(g) CH <sub>2</sub> OH* + H <sup>+</sup> + e <sup>-</sup> → CH <sub>3</sub> OH (l)	1.19	-1.02	0.76	-0.59
(h) CH <sub>2</sub> OH* + H <sup>+</sup> + e <sup>-</sup> → CH <sub>2</sub> * + H <sub>2</sub> O (l)	0.43	-0.26	0.40	-0.23
(i) CH <sub>3</sub> O* + H <sup>+</sup> + e <sup>-</sup> → CH <sub>3</sub> OH (l)	0.17	0.00	0.07	0.10
(j) CH <sub>3</sub> O* + H <sup>+</sup> + e <sup>-</sup> → (CH <sub>3</sub> + OH)*	0.24	-0.07	0.22	-0.05
(k) CH <sub>2</sub> * + H <sup>+</sup> + e <sup>-</sup> → CH <sub>3</sub> *	1.05	-0.88	0.84	-0.67
(m) CH <sub>3</sub> * + H <sup>+</sup> + e <sup>-</sup> → CH <sub>4</sub> *	1.07	-0.90	0.86	-0.69
(n) OH* + H <sup>+</sup> + e <sup>-</sup> → H <sub>2</sub> O (l)	0.12	0.05	0.18	-0.01



the Pt-doped Cu(111) surface with the weakest OH adsorption has the most positive limiting potential and the most negative reaction free energy, which is in agreement with the above kinetic analyses, suggesting that the doped metals with less affinity toward OH could decrease surface OH poisoning and enhance the catalytic activity. Thus, the best electrocatalytic activity of the Pt-doped Cu(111) surface for CO<sub>2</sub> reduction may be able to be attributed to the simultaneous reduction of overpotential for CO formation and further reduction, and the easiest OH removal.

**3.3.2 The analysis of electronic structure.** The adsorption behavior and reduction mechanism may be able to be determined by electronic interactions between the Cu(111) surface and the doped transition metals M (M = Ni, Pd and Pt). The analyses of electronic structures facilitate the understanding the origin of catalytic activity of the transition metal Ni-, Pd- and Pt-doped Cu(111) surfaces toward CO<sub>2</sub> reduction. Thus, in order to determine the origin of the catalytic activity and understand the electron transfer between the transition metal M (M = Ni, Pd and Pt) and the Cu(111) surface, we performed local density of states (LDOS) analysis of pure and Ni-, Pd- and Pt-doped Cu(111) surfaces in the present study since it can describe the number of electron at Fermi energy level that are available to be occupied. A high LDOS at the Fermi energy level means that there are many electrons available for occupation. Fig. 7 and 8 give the LDOS of the pure and Ni-, Pd- and Pt-doped Cu(111) surfaces. For comparison, the LDOS of pure Ni, Pd and Pt are

also included. The results show that the doping of Ni, Pd and Pt leads to an obvious change of the s state of Cu at the Fermi energy level compared with that of the pure Cu(111) surface, in which s orbitals of Cu in Ni- and Pt-doped Cu(111) have relatively lower LDOS, as shown in Fig. 7(a), implying that more electrons in the s states of Cu are transferred after the doping of Ni and Pt. The LDOS of the d orbital of Cu in the pure and Ni-, Pd- and Pt-doped Cu(111) are almost unchanged, as shown in Fig. 7(b), suggesting that electron transfer may not occur in the d state of Cu. Thus, the observed significantly lower LDOS of the s states of Cu in Ni- and Pt-doped Cu(111) means that more electrons are transferred, thereby leading to stronger adsorption of reaction intermediates in CO<sub>2</sub> reduction on Ni- and Pt-doped Cu(111) surfaces than that on the Pd-doped Cu(111) surface (Table 3).

In the mean time, we also observed that the s and d states of Ni, Pd and Pt in Ni-, Pd- and Pt-doped Cu(111) are changed significantly near the Fermi energy level compared with those of pure Ni, Pd and Pt, as shown in Fig. 8(a) and (b). The considerably higher LDOS near the Fermi energy level shows that electrons in the s state of Cu are transferred into the s and d states of Ni, Pd and Pt. The highest LDOS in the d states of Ni in Ni-doped Cu(111) may imply that the most electron transfer and strongest interactions occur between Cu and Ni. Thus, the present studies explain why the reaction intermediates have the strongest adsorption on the Ni-doped Cu(111) surface. The relatively weaker interaction between Cu and transition metals Pd and Pt may result in weaker adsorption of intermediates.

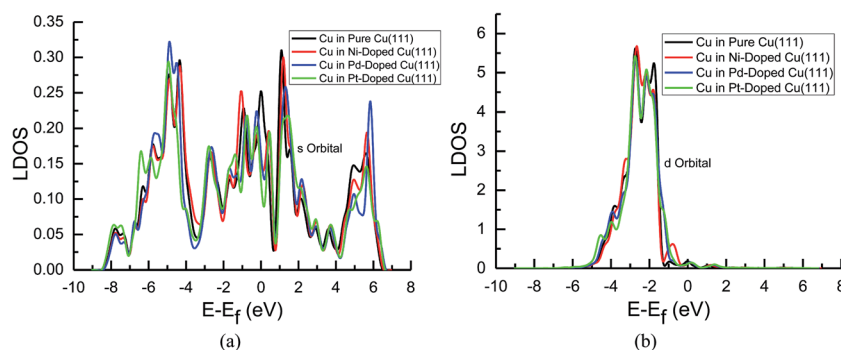


Fig. 7 Local density of states of pure and transition metals Ni-, Pd- and Pt-doped Cu(111) surfaces: (a) s orbital of Cu and (b) d orbital of Cu.

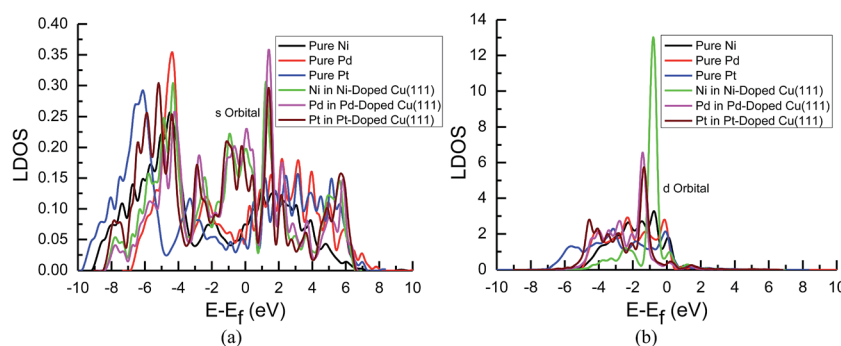


Fig. 8 Local density of states of pure and transition metals Ni-, Pd- and Pt-doped Cu(111) surfaces: (a) s orbitals of Ni, Pd and Pt; and (b) d orbitals of Ni, Pd and Pt.



The d-band center of surface atoms,  $\epsilon_d$ , is a key parameter that influences surface adsorption characteristics,<sup>69,70</sup> and its upshift and downshift can be used to judge the catalytic activity of the electrocatalysts.<sup>71–73</sup> The shift of the d-band center into a lower energy level (downshift) corresponds to the weaker adsorption of reaction intermediates, whereas the shift into a higher energy level (upshift) corresponds to the stronger adsorption. Thus, the d-band centers of surface atoms were calculated in pure and Ni-, Pd- and Pt-doped Cu(111), which is the first moment of the projected d-band density of states on the surface atoms referenced to the Fermi energy level. The corresponding values for surface atoms are listed in Table 6. It was found that there is a slight and considerably upshift of the d-band center of surface Cu and Ni atoms (*ca.* 0.02 and 0.74 eV) in Ni-doped Cu(111) compared with that of the pure metal surfaces, respectively, whereas that of surface Cu atoms is not changed after the doping of Pd and Pt atoms. The relatively lower upshift of the d-band center of the surface Pt atom in Pt-doped Cu(111) is also observed (*ca.* 0.20 eV). However, the d-band center of the surface Pd atom is downshifted significantly in Pd-doped Cu(111) (*ca.* -0.34 eV) compared with that of pure Pd. Thus, we conclude that the doping of Ni and Pd can lead to the strongest and weakest adsorption of reaction intermediates on the Ni and Pd-doped Cu(111) surfaces, respectively. Furthermore, the significant upshift of the d-band center of the surface Ni atom and the strongest interaction between CO and the Ni-doped Cu(111) surface may also be able to explain why further CO reduction has the most positive activation barrier and the most negative limiting potential on the Ni-doped Cu(111) surface among the Ni-, Pd- and Pt-doped Cu(111) surfaces, whereas the significant downshift of the d-band center of the surface Pd atom in Pd-doped Cu(111) explains why only physisorbed CO<sub>2</sub> is observed, which even leads to slightly more negative limiting potential for CO formation in comparison with that on pure Cu(111). Accordingly, we infer that the dopant Pt with moderate upshift of the d-band center is the most capable of enhancing the electrocatalytic activity of Cu catalysts for CO<sub>2</sub> reduction, which confirms the above thermodynamic and kinetic studies.

Based on our present calculations, CO formation and further reduction are key reaction steps during the course of CO<sub>2</sub>

reduction into hydrocarbons. CO<sub>2</sub> reduction on the Cu catalyst can be promoted and higher hydrocarbons yield may be able to be expected by the doping of transition metals. On the basis of the above discussion, two possible descriptors can be proposed in order to scale the electrocatalytic activity of Cu-based alloy catalysts for CO<sub>2</sub> reduction. One is activation barriers of CO formation and further reduction. The transition metal-doped Cu-based alloy electrocatalysts with lower activation barriers for CO formation and further reduction will exhibit better catalytic activity for CO<sub>2</sub> reduction. For example, the barriers of CO formation are decreased by the doped Ni, Pd and Pt atoms, and those of further CO reduction on the Pd- and Pt-doped Cu(111) surfaces are also reduced. The chemisorbed CO<sub>2</sub> on Cu-based electrocatalyst surfaces will favor the formation of the key intermediate CO, *i.e.* the doping of Ni and Pt lead to the formation of chemisorbed CO<sub>2</sub> and make CO formation easier. The moderately adsorbed CO on Cu-based electrocatalyst surfaces can avoid CO desorption and poisoning on surface active sites, thereby being in favor of further CO reduction, *i.e.* the Ni-doped Cu(111) surface has excessively strong CO adsorption, resulting in the highest barrier and the most negative limiting potential for further CO reduction among pure, Ni-, Pd- and Pt-doped Cu(111) surfaces. Another is the electronic structure of the transition metals-doped Cu-based electrocatalysts. The moderate interactions between Cu and transition metals and the moderate upshift of the d-band center of the doped transition metals in transition metal-doped Cu(111) will favor CO<sub>2</sub> reduction, which can lead to moderate adsorption of intermediates. For example, the Ni-doped Cu(111) surface with the strongest interaction between Cu and Ni and the most upshift of the d-band center of the Ni atom, and Pd-doped Cu(111) surface with the downshift of the d-band center of Pd atom have relatively poorer electrocatalytic activity for CO<sub>2</sub> reduction than the Pt-doped Cu(111) surface. Thus, an ideal Cu-based alloy electrocatalyst toward CO<sub>2</sub> reduction should be able to reduce activation barriers for CO formation and further reduction, and should have moderate electron interactions between Cu and the doped transition metals, and a moderate upshift of the d-band center of the doped transition metals. In these ways, CO<sub>2</sub> reduction pathways can be facilitated and the yield of hydrocarbons CH<sub>4</sub> and CH<sub>3</sub>OH can be enhanced.

Table 6 The DFT calculated d-band center,  $\epsilon_d$  of surface atoms in pure and Ni-, Pd- and Pt-doped Cu(111)

Surface atoms		$\epsilon_d$ (eV)	$\Delta\epsilon_d^a$ (eV)
Pure Cu		-2.52	—
Pure Ni		-1.79	—
Pure Pd		-2.02	—
Pure Pt		-2.69	—
Ni-doped Cu(111)	Cu	-2.50	0.02
	Ni	-1.05	0.74
Pd-doped Cu(111)	Cu	-2.52	0.00
	Pd	-2.36	-0.34
Pt-doped Cu(111)	Cu	-2.52	0.00
	Pt	-2.49	0.20

<sup>a</sup>  $\Delta\epsilon_d$  represents difference of the d-band center,  $\epsilon_d$  of surface atoms between surface atoms in Ni-, Pd- and Pt-doped Cu(111) and pure surface atoms.

## 4. Conclusions

In our present paper, the effect of the doped transition metal M (M = Ni, Pd and Pt) on CO<sub>2</sub> reduction pathways and the origin of the electrocatalytic activity are investigated systematically by focusing on the CH<sub>4</sub> and CH<sub>3</sub>OH formation pathways based on DFT calculations of the key adsorbates associated with the computational hydrogen electrode model. Our studies show that the doping of Ni, Pd and Pt can promote CO<sub>2</sub> reduction and influence the selectivity of the reduction pathways and products, in which the doping of Pt may be able to lead to the strongest catalytic activity. The adsorption behavior of intermediates may be able to determine the CO<sub>2</sub> reduction activity. The destabilization of the stronger adsorbed intermediates to



CH<sub>3</sub>O by the doped Pd and Pt atoms make CH<sub>3</sub>O formation and further reduction occur, thus the selectivity of reduction pathways is revealed. Owing to high carbon and oxygen affinity of Ni, all intermediates can be stabilized by the doped Ni atom. The Ni-doped Cu(111) surface has the strongest adsorption ability among the Ni-, Pd- and Pt-doped Cu(111) surfaces, whereas the doping of Pd and Pt leads to the weakest and moderate adsorption of most intermediates, respectively, which may explain why Pt-doped Cu(111) surfaces have the best catalytic activity for CO<sub>2</sub> reduction. Thus, it is concluded that moderate adsorbed intermediates on the Cu-based electrocatalyst surfaces will favor CO<sub>2</sub> reduction.

The enhanced electrocatalytic activity of the transition metal-doped Cu(111) surfaces may be owing to the decrease of the overpotential and electronic interactions between Cu and the transition metals. Further reduction of CO into CHO is the potential-limiting step on the pure and Ni-, Pd- and Pt-doped Cu(111) surfaces. The doping of Pd and Pt atoms can reduce the overpotential of CHO formation, whereas the doped Ni makes it slightly higher in comparison with pure Cu(111). The overpotential of CO formation is notably decreased after the doping of Ni, which is the rate-determining step on pure Cu(111). The significantly reduced overpotential for CO formation is also observed on the Pt-doped Cu(111). However, a slightly increased overpotential is obtained on the Pd-doped Cu(111) for CO formation. Simultaneously, the Pt-doped Cu(111) surface has the lowest overpotential for OH removal, suggesting that the doped metals with less affinity toward OH could enhance the catalytic activity. Thus, the doped Pt can simultaneously reduce the overpotential for CO formation and further reduction and most easily remove OH. The electronic structures analyses show that there is a moderate interaction between Cu and Pt and a moderate upshift of the d-band center of Pt. These analyses confirm why the Pt-doped Cu(111) surface has the best electrocatalytic activity for CO<sub>2</sub> reduction.

Two possible descriptors can be proposed in order to scale the electrocatalytic activity of Cu-based electrocatalysts for CO<sub>2</sub> reduction. One is activation barriers of CO formation and further reduction. The transition metal-doped Cu-based electrocatalysts with lower barriers will exhibit better catalytic activity for CO<sub>2</sub> reduction. The chemisorbed CO<sub>2</sub> on the Cu-based electrocatalyst will favor the formation of the key intermediate CO. The moderate adsorbed CO on the Cu-based electrocatalyst can avoid CO desorption and poisoning on surface active sites, thereby being in favor of further reduction of CO. Another is the electronic structure of the Cu-based electrocatalysts. The moderate interactions between Cu and the doped transition metals and the moderate upshift of the d-band center of the doped transition metals will be in favor of CO<sub>2</sub> reduction. Thus, an ideal Cu-based electrocatalyst should be able to reduce barriers for CO formation and further reduction, and should have moderate interactions between Cu and the doped transition metals, and a moderate upshift of d-band center of the doped transition metals. In these ways, CO<sub>2</sub> reduction pathways can be facilitated and the yield of hydrocarbons CH<sub>4</sub> and CH<sub>3</sub>OH can be enhanced.

## Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (Grant No. 21303048), the Outstanding Youth Foundation of the Education Department of Hunan Province (Grant No. 16B178), the Hunan Provincial Natural Science Foundation of China (Grant No. 13JJ4101), the Construct Program of the Key Discipline in Hunan Province (Applied Chemistry), the Doctoral Start-up Fund of Hunan University of Arts and Science, the Hunan Provincial College Students Inquiry Learning and Innovative Pilot Projects (Grant No. 201510549007) and the Innovation Project of Hunan University of Arts and Science (Grant No. YB1509 and YB1612).

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