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# The Role of CO\* as a Spectator in CO<sub>2</sub> Electro-reduction on RuO<sub>2</sub>

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## Abstract:

*RuO<sub>2</sub> based electrocatalysts are found to be active at low over-potential towards direct electrochemical reduction of CO<sub>2</sub> to formic acid and methanol. RuO<sub>2</sub> can circumvent the thermodynamic bottleneck resulting from the scaling relations observed on metallic electrocatalyst, by employing an alternate pathway through oxygen-coordinated intermediates. Employing density functional theory based computational electrocatalysis models we show adsorbate-adsorbate interaction effects for adsorbates and reaction intermediates on the RuO<sub>2</sub>(110) surface are large and impactful to the reaction thermodynamics. We studied binding energy amendment due to adsorbate interaction (steric and electronic) with varying coverage of CO\* spectators on the catalyst surface. Implications on the reaction pathways help us rationalize differences in experimentally observed carbonaceous product mix and suppression of the hydrogen evolution reaction (HER). We show that a moderate CO\* coverage (~50%) is necessary for obtaining methanol as a product and that higher CO\* coverages leads to very low overpotential for formic acid evolution. Our analysis also clarifies the importance of the reaction condition for CO<sub>2</sub> reduction to liquid fuels utilizing RuO<sub>2</sub> based electrocatalysts.*

## 1. Introduction

The last hundred years of relentless human development have relied on fossil fuel based energy resources. To translate into a sustainable alternative course of long term growth<sup>1</sup>, expanding renewable energy resources must be tapped at the earliest possible time. This is to mitigate limitations of fossil fuel as well as the inherent environmental problems emanating from increased anthropogenic emissions of CO<sub>2</sub>. An electricity grid brimming with renewable electricity from wind and solar plants or

cars propelled by renewable energy depends on inexpensive energy conversion and storage technologies<sup>2</sup>. Electrochemical reduction of carbon dioxide to liquid fuels is an appealing approach that could alleviate much of the CO<sub>2</sub> emission challenge, solve the bottleneck of cheap energy storage and penetrate the fossil fuel dependent transport sector<sup>3</sup>.

The main challenge of direct electrochemical reduction of CO<sub>2</sub> to fuel molecules like formic acid, methanol or methane, is the absence of stable catalysts that can enable the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) at low overpotential and high selectivity over the hydrogen evolution reaction (HER)<sup>4,5</sup>. The underlying chemistry limiting the effectiveness of metallic catalysts in CO<sub>2</sub>RR to methane or methanol was recently ascertained through density functional theory based modeling of the thermodynamics of reaction steps involved<sup>6</sup>. Adsorbed CO (CO\*) is a crucial reaction intermediate in the CO<sub>2</sub>RR pathway on metallic catalysts. Strong correlation between the binding energy of key intermediates CO\* and CHO\* on metal catalyst surfaces enforces a large potential requirement for CO<sub>2</sub>RR to methane irrespective of the CO\* binding energy of the metal<sup>7</sup>. Thus, further reduction of CO\* remains a bottleneck for metal catalysts. Only copper produces mixtures of methane, ethane and formic acid at high overpotential, owing to its favorable position in the theoretical activity volcano proposed in previous work. Ruthenium oxide based electrocatalysts have been repeatedly shown<sup>8-10</sup> to produce methanol from CO<sub>2</sub> with up to 60% Faradic Efficiency (FE) at low overpotential. Formic acid has been reported<sup>11</sup> to be the other major CO<sub>2</sub>RR product on RuO<sub>2</sub> based electrocatalysts. While experimental results have been very affirmative towards good CO<sub>2</sub>RR activity, oxide catalysts have largely been overlooked amidst the recent spurt in scientific activity pertaining to electrocatalytic route to CO<sub>2</sub> reduction<sup>12-18</sup>. Our previous work on RuO<sub>2</sub>-based electrocatalysts for CO<sub>2</sub> reduction<sup>19</sup> explained that a different reaction mechanism involving HCOOH\* intermediate instead of CO\* is active on oxide electrocatalysts. We have also established<sup>20</sup> that different sets of scaling laws and resulting activity volcano leads to lower thermodynamic barriers for the CO<sub>2</sub> conversion reaction than their metal counterparts. This behavior emanates from the fundamentally different reaction path followed on oxide catalysts compared to metal catalysts. CO<sub>2</sub> activation on metals lead to COOH\* intermediate and consecutive protonation to reaction intermediates like CO\*, CHO\*/COH\*, CHOH\*/H<sub>2</sub>CO\* which tend to bind to the metal through the carbon atom<sup>21,22</sup>. On RuO<sub>2</sub> (110), CO<sub>2</sub> activation leads to OCHO\*, which is further reduced to HCOOH\*, H<sub>2</sub>COOH etc, which bind to the catalyst through oxygen atoms<sup>19</sup>. The different reaction pathway signify different scaling relations govern CO<sub>2</sub>RR on oxide surfaces<sup>20</sup>. In particular, the limitation from the CO\*/CHO\* scaling is avoided.

The presence of spectator species on the catalyst surface can enhance or poison electrocatalyst activity, as have been studied theoretically and experimentally<sup>23-27</sup>. Despite the COOH\* intermediate being much less stable than the OCHO\* intermediate, a small amount of COOH\* might form on CO<sub>2</sub> activation. Further

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3 reduction is expected to leave adsorbed CO\* from this contingent reaction<sup>11</sup>. CO\*  
4 spectators interact with other adsorbed reaction intermediates and alter their binding  
5 energy. We have observed that spectator CO\* species can have large effect on H\*  
6 binding free energy, potentially promoting/poisoning HER<sup>20</sup>. Similar behavior has  
7 been observed for metallic catalysts<sup>28</sup>. We expect similar effect can be present for  
8 OH\* binding free energy as well. Intermediates formed during CO2RR to methanol  
9 on the RuO<sub>2</sub> catalyst surface are bound to the surface by oxygen atoms, and their  
10 binding energy is correlated with the OH\* binding energy. Thus a strong effect of  
11 CO\* spectators on the onset potential for methanol production and selectivity over  
12 HER is expected. Shift in the reaction site of CO2RR due to blockade of more  
13 favorable sites by CO\* spectator can have very large effect on the thermodynamics  
14 of elementary reaction steps. For example, under reducing conditions the RuO<sub>2</sub>(110)  
15 surface can have both strong binding bridge sites and weak binding coordinated  
16 unsaturated (cus) sites available for intermediates. If all bridge sites (br) are  
17 occupied by spectator CO\* species, then the reaction can only proceed through cus  
18 sites. To create a categorical understanding of CO\* spectators on the CO2RR  
19 pathway on RuO<sub>2</sub>(110) surface, we study the possible reaction intermediate and  
20 paths to formic acid, methanol and methane in the presence of different  
21 concentrations of CO\* spectators as well as variation in the br/cus sites occupied by  
22 spectator CO\*. This work displays that weakening and strengthening of binding  
23 energies is of surprising importance towards both onset potential and possibly also  
24 the product selectivity for CO2RR on RuO<sub>2</sub>. The outcome from this study is  
25 especially important to the understanding and development of oxide-based CO<sub>2</sub>RR  
26 electrocatalyst, which may break the scaling relations. We show that high CO\*  
27 coverage can render RuO<sub>2</sub> based catalysts very effective at formic acid evolution  
28 and lower selectivity towards HER, while a moderate coverage improves on  
29 methanol selectivity. Our results might give a clue to the widely varied product  
30 composition obtained from CO2RR with RuO<sub>2</sub> based electrocatalysts and highlight  
31 the importance of spectator coverage for successful CO2RR using RuO<sub>2</sub>.  
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## 44 2. Computational details

45 We utilize VASP<sup>29</sup> package for density functional theory (DFT) based simulation of  
46 model catalyst surfaces with adsorbed reaction intermediates. Standard PBE-PAW  
47 potentials as distributed with VASP 5.3 are used with 500 eV wavefunction cutoff.  
48 Previous comparison study on convergence of chemisorption energy on RuO<sub>2</sub>  
49 surface from VASP (PAW) and Wien2K (all electron) indicated that 400 eV cutoff is  
50 sufficient for routine calculations. 600 eV cutoff for standard PAW can provide  
51 accuracy of up to 10 meV<sup>30</sup>. Higher energy cutoff for this work is irrelevant as errors  
52 in the order of 0.1 eV is expected in GGA level theory<sup>31</sup>. Here newly developed  
53 BEEF-vdW<sup>32</sup> exchange correlation functional is utilized. Our lattice parameter  
54 estimates are a=4.537 Å and c=3.135 Å for RuO<sub>2</sub>, which agrees well with  
55 experimental data<sup>33</sup>. Following our previous studies<sup>19,20</sup> the supercell representing  
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3 the catalyst surface RuO<sub>2</sub>(110) consists of a four layer thick slab with lower two  
4 layers fixed at atomic positions identical to bulk RuO<sub>2</sub>. The bridge site is considered  
5 vacant due to reducing environment during CO<sub>2</sub>RR (Figure SI1). This model has  
6 two bridge and two cus sites available for reaction intermediates and spectator CO\*  
7 molecules. During simulation, we use a 4x4x1 k-point mesh and 16 Å of vacuum in  
8 the z-direction and Gaussian electronic smearing. Optimization of atomic positions  
9 are done until forces on atoms in top two layers and adsorbates are lower than 0.003  
10 eV/Å. Vibrational modes for adsorbed molecules are also analyzed to enable finite  
11 temperature free energy estimates by approximating adsorbate degrees of freedom  
12 as independent quantum mechanical harmonic oscillators (Table SI1).

13 Adsorbate binding free energies are estimated w.r.t. gas phase free energies (Table  
14 SI2) of hydrogen, water and CO<sub>2</sub><sup>20</sup>. Systematic DFT-errors in total energy evaluation  
15 are corrected for H<sub>2</sub> (0.1 eV), CO<sub>2</sub> (0.3 eV), formic acid (0.15 eV) and COOH\* (0.15  
16 eV) following the approach by Christensen et al.<sup>34</sup>. A stabilization of formic acid in  
17 solution<sup>35</sup> from deprotonation in neutral electrolyte (-0.19 eV) is also taken into  
18 account, and the experimentally observed reaction product concentrations were  
19 used for free energy estimation of methanol<sup>9</sup>, formic acid and methane<sup>11</sup> free  
20 energies. The reaction thermodynamics calculations are susceptible to variation in  
21 reactant/product concentration in the electrolyte. High concentration of methanol in  
22 electrolyte leads to increased free energy (up to 0.2 eV) and release of methanol  
23 might become difficult. The low vapor pressure of formic acid means small variation  
24 in free energy from higher concentration. Thus, effects of concentration are minimal  
25 for formic acid evolution.

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33 Vibrational modes of adsorbate molecules are used to estimate zero-point energy,  
34 heat capacity and entropic contributions to the free energy at room temperature  
35 using the harmonic oscillator model as implemented in atomistic simulation  
36 environment (ASE). Usage of the reversible hydrogen electrode (RHE) scale for  
37 electrochemical potential helps simplify onset potential estimation by considering  
38 reversible formation of a proton/electron pair from a hydrogen molecule as zero V-  
39 RHE at any given pH. Accordingly, the analysis becomes pH independent except for  
40 the free energy of formic acid in solution. We have employed the computational  
41 hydrogen electrode (CHE) model<sup>36</sup> to determine the thermodynamics of the  
42 electrochemical reaction steps involving single electron/proton transfer. The free  
43 energy of an adsorbate formed at the  $n^{\text{th}}$  proton transfer step if lowered by  $nU$  eV  
44 when a potential of  $U$  vs. RHE (V-RHE) is applied. Under the assumptions of the  
45 CHE model, for a particular, elementary proton transfer step, requiring an increase in  
46 binding free energy can be made free energy neutral by applying a negative  
47 potential, equivalent to the increase in free energy at 0 V-RHE. Hence, an analysis of  
48 relative binding energies of adsorbates formed at different electron transfer steps  
49 (Table 1) at 0 V-RHE allows us to investigate modifications in CO<sub>2</sub>RR pathway and  
50 onset potential as well as selectivity over HER due to adsorbate interactions with  
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Table 1: Adsorbate/product cases examined at electron transfer step from  $0e^-$  to  $8e^-$ 

$0e^-$	$1e^-$	$2e^-$	$3e^-$	$4e^-$
*	OCHO*, H*, COOH*	HCOOH*, CO*+H <sub>2</sub> O(l), HCOOH(aq), H <sub>2</sub> (aq)	H <sub>2</sub> COOH*	H <sub>3</sub> CO*+OH*, H <sub>2</sub> CO+ H <sub>2</sub> O(l), O*+CH <sub>3</sub> OH(aq)
$5e^-$	$6e^-$	$7e^-$	$8e^-$	
H <sub>3</sub> CO*+ H <sub>2</sub> O(l), H <sub>2</sub> COH*+ H <sub>2</sub> O(l), OH*+CH <sub>3</sub> OH(aq)	O*+CH <sub>4</sub> (aq)+ H <sub>2</sub> O(l), CH <sub>3</sub> OH*+ H <sub>2</sub> O(l), CH <sub>3</sub> OH(aq)+H <sub>2</sub> O(l)	OH*+CH <sub>4</sub> (aq) + H <sub>2</sub> O(l)	CH <sub>4</sub> (aq)+ H <sub>2</sub> O(l)	

### 3. Results and discussion

#### 3.1. Spectator coverage

With four adsorption sites in the simulation model (Figure SI1), CO\* coverage can be 0%, 25%, 50%, 75% or 100%, respectively. Each CO\* spectator in the simulation model amounts to 25% added CO\* coverage. With full CO\* coverage, CO<sub>2</sub>RR or HER cannot advance due to unavailability of active sites, unless CO\* is first reduced. Two different types of active site being present and considering symmetry of the relative positions of the CO\* adsorbates, 25% and 75% coverage can be realized in two different ways, while 50% coverage leads to four different representations (Figure SI2). All such different CO\* coverages are inspected for their relative thermodynamic stability (Figure SI3). Visual representations are provided in Figure SI2.

On the bare surface, the 1st CO\* adsorption at the bridge site is favorable compared to cus site by 0.18 eV (Figure SI3). With respect to the CO molecule, the binding free energy of CO\* at the bridge site of the bare surfaces is -1.34 eV. Two cus sites and one bridge site are accessible for catalysis at 25% CO\* coverage. With 50% CO\* coverage, putting all adsorbates in the bridge site is the most stable configuration. All other cus configurations with 50% CO\* coverage are less stable by 0.28 eV. The adsorption free energy for the two 50% CO\* coverage configurations with a combination of bridge and cus occupancy are less stable than the all bridge configuration by 0.08 eV (while neighboring bridge and cus sites have CO\* (bridge+cus-near in SI3)) and 0.1 eV (occupied bridge and cus sites are far apart (bridge+cus-far in SI3)). With both bridge sites covered by CO\*, catalysis can only occur on the cus sites available (Figure SI2). On the other hand, if CO at 50% CO\* coverage occupies both bridge and cus sites, there are still bridge and cus sites available for CO<sub>2</sub>RR. At 75% CO\* coverage, the adsorbate configuration with CO\*

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3 on 2\*bridge+cus sites is more stable than CO\* on bridge+2\*cus by 0.2 eV (Figure  
4 SI3). These two configurations are fundamentally different, as the first allows  
5 catalysis through the cus sites and the latter requires the reaction to take place at the  
6 bridge site (Figure SI2). Due to repulsive CO\*-CO\* interactions, the incremental  
7 binding free energy for CO\* decreases with CO\* coverage (Figure SI3). The  
8 incremental binding free energy for four CO\* molecules considering the most stable  
9 configurations are -1.34 eV, -0.93 eV, -0.75 eV, and -0.46 eV, respectively. Thus the  
10 driving force for further CO\* adsorption is smaller at high CO\* coverage. It is striking  
11 that at 0 V-RHE and 75% CO\* coverage, OH\* binds slightly stronger to the empty  
12 fourth site than CO\* (by 0.02 eV). Thus OH\* can displace the 4<sup>th</sup> CO\*.  
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17 The CO\* spectator coverage at experimental conditions can also be limited due to  
18 reduction of CO\* to CHO\* or COH\*, lowering the CO\* coverage. CHO\* is more  
19 stable than COH\* on the RuO<sub>2</sub> (110) surface by 0.22 eV to 0.45 eV for different CO\*  
20 coverages. At 0 V-RHE, the reduction of one of CO\* to CHO\* is energetically uphill  
21 by 1.34 eV, 0.63 eV, 0.73 eV, and 0.03 eV for CO\* coverage of 25%, 50%, 75%, and  
22 100%, respectively. This indicates, that complete poisoning of the catalyst surfaces  
23 is not favorable. On the contrary, CO\* spectators will not be removed by reduction  
24 even with application of moderate reducing potential if the coverage is low (~25%).  
25 50% and 75% CO\* coverage might be observed under CO<sub>2</sub>RR conditions, due to  
26 kinetic barriers of CO\* protonation and transient evolution of CO from CO<sub>2</sub>RR. Slow  
27 transport of CO away from the catalyst will eventually leave the catalyst surface with  
28 high CO\* coverage<sup>37</sup> as might be the case in a previous experimental study<sup>11</sup>.  
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33 Previous studies by Popic et al. and Qu et al. employing pure ruthenium oxide  
34 electrocatalyst<sup>9,10</sup> have not reported any CO detected as a product. We deduce that  
35 these experimental results observing methanol as the primary product, might have a  
36 catalyst surface with low to medium CO\* coverage if only a very small quantity of CO  
37 is produced and stays bound to the active site<sup>9,10</sup>. On the contrary, experiments by  
38 Spataru et al.<sup>11</sup> observe hydrogen and formic acid as dominant products along with  
39 methanol, methane and CO. It can be contemplated that the presence of CO at 30 to  
40 200 ppm<sup>11</sup> in the solution comes from CO escaping the catalyst surface when a high  
41 CO\* coverage is reached.  
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### 48 3.2. Hydroxylation with CO\* spectator

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50 CO<sub>2</sub> is often reduced in aqueous electrolytes. Hydroxylation of active sites is  
51 energetically downhill and spontaneous at the bridge site of RuO<sub>2</sub> (110) surface  
52 (Figure 1). Any available bridge site is expected to be hydroxylated at 0 V-RHE. OH\*  
53 needs to be removed from the active site for CO<sub>2</sub>RR to proceed. Thus OH\* removal  
54 can become a thermodynamic limiting step. Interactions between CO\* and OH\* are  
55 attractive for 25% to 50% CO\* coverage, making OH\* binding is stronger in presence  
56 of CO\* spectators (Figure 1).  
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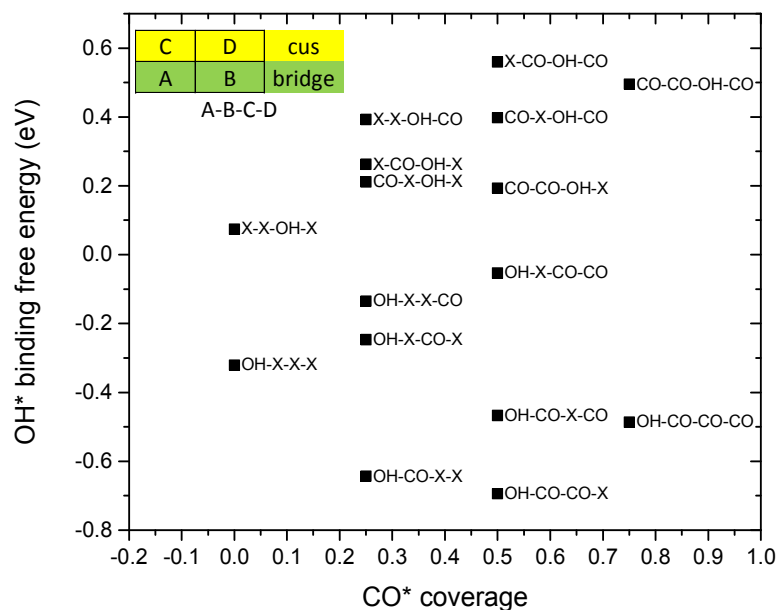


Figure 1:  $\text{OH}^*$  binding energy as a function of  $\text{CO}^*$  coverage and spatial distribution of  $\text{CO}^*$  adsorbates. As depicted in the inset, the distribution of  $\text{OH}^*$  and  $\text{CO}^*$  at the two bridge and two cus sites consecutively are used as label, where X denotes an unoccupied site.

Investigations of the adsorbate binding free energy on the  $\text{RuO}_2$  (110) surface at bridge and cus sites reveal that oxygen coordinated adsorbates like  $\text{OH}^*$  bind significantly stronger to the bridge sites compared to cus sites (Figure 1). The relative preference for bridge sites is less pronounced for  $\text{CO}^*$  (Figure S13). The binding energy for  $\text{OH}^*$  at different  $\text{CO}^*$  spectator configurations and binding sites are presented in Figure 1 showing favored bridge site binding of  $\text{OH}^*$  over cus site binding. For example, the binding energy of  $\text{OH}^*$  at bridge and cus sites are -0.32 eV and +0.08 eV, respectively, while these values for  $\text{CO}^*$  is -1.34 eV and -1.16 eV (w.r.t. CO molecule). This observation helps to understand the distribution of spectating  $\text{CO}^*$  in bridge and cus sites under reaction conditions. Key CO<sub>2</sub>RR intermediates on oxide surfaces like  $\text{OCHO}^*/\text{HCOOH}^*/\text{H}_2\text{COOH}^*$ , etc., are all O-coordinated. If a mixture of  $\text{CO}^*$  and O-coordinated intermediates are present on the catalyst surface, CO<sub>2</sub>RR intermediates would preferentially occupy the bridge sites and the bi-dentate coordination will be preferred over mono-dentate binding. For example, three  $\text{CO}^*$  and one  $\text{OH}^*$  adsorbate can be distributed such that  $\text{OH}^*$  can occupy a bridge site or it can occupy a cus site. The configuration with  $\text{OH}^*$  in bridge site has ~1 eV lower free energy than the configuration with  $\text{OH}^*$  in cus site (Figure 1). This is critical in effective CO<sub>2</sub>RR catalysis on the  $\text{RuO}_2$  (110) surface.

Reaction path thermodynamics shows that bridge site CO<sub>2</sub>RR is not only energetically preferred but also has lower thermodynamic onset potential. For example, at 75% CO\* coverage, OCHO\* is unlikely to form at the cus site (binding free energy of +0.95 eV) but bridge site occupation as a mono-dentate adsorbate is feasible (binding free energy of -0.13 eV). The preferred CO\* spectator configurations important for CO<sub>2</sub>RR at 0%, 25%, 50%, 75% CO\* coverage are given in Figure 2 (a)-(d). Other free bridge sites and cus sites can be occupied by CO<sub>2</sub>RR/HER adsorbates as portrayed in Figure 2(e)-(i). OCHO\* and H<sub>2</sub>COOH\* adsorbate binds as bi-dentate adsorbate if adjoining bridge and cus sites are not occupied by CO\* spectators (Figure 2 (e) and (h)). These adsorbates are mono-dentate at high CO\* coverage (Figure 2 (f)). Adsorbates like H<sub>2</sub>CO\* (Figure 2(j)) and HCOOH\* (Figure 2 (g)) are always mono-dentate but reaction intermediate can consist of a pair of adsorbate like H<sub>3</sub>CO\*+OH\* (Figure 2(i)). The priority of O-atom coordinated CO<sub>2</sub>RR intermediates at bridge site is not valid for HER and HER can proceed even at cus site, while bridge sites are hydroxylated. Therefore, HER thermodynamic analysis is done for variety of spectators.

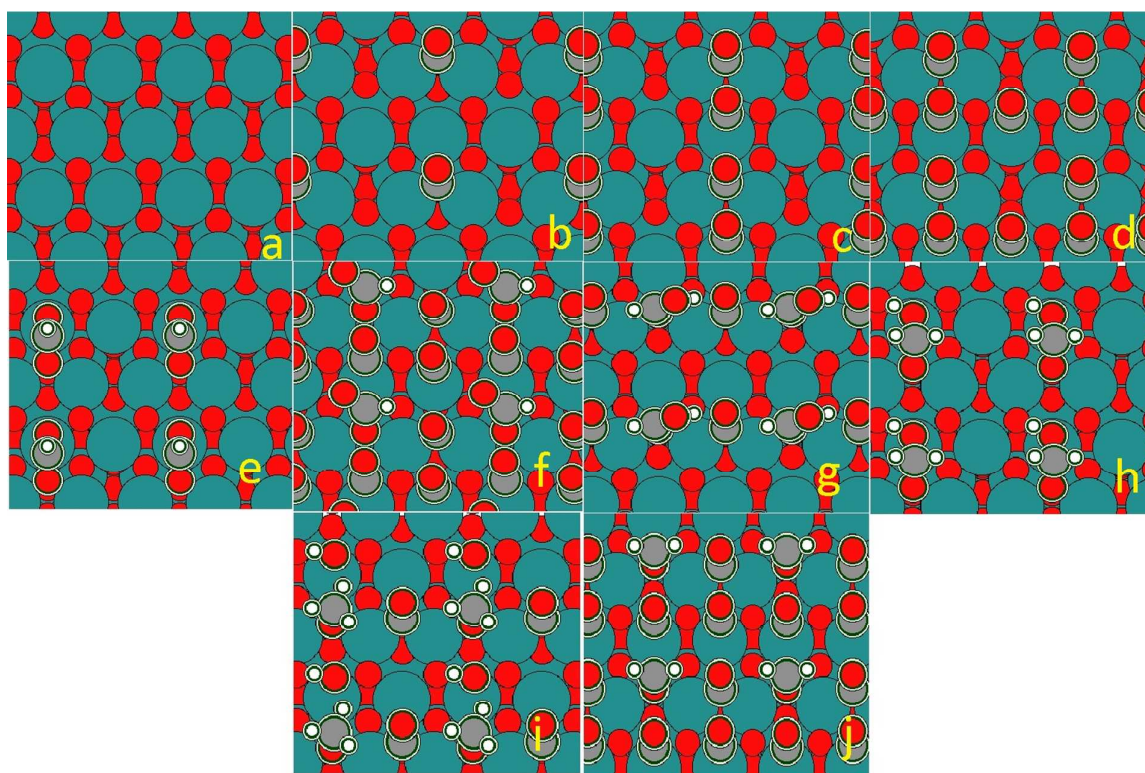


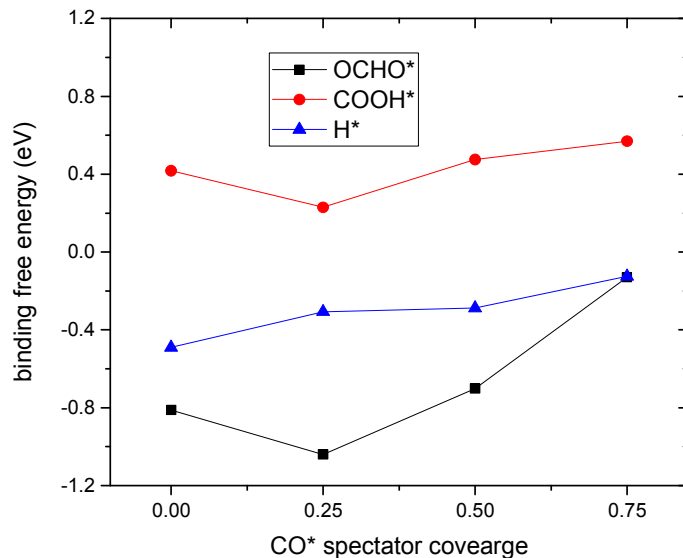
Figure 2: Simulated RuO<sub>2</sub>(110) surface with two bridge sites and two cus sites available. Bridge sites are coordinated to two ruthenium atoms, and cus sites are on top of ruthenium atoms. (a) all sites empty. (b) one bridge site have CO\*. (c) one bridge site and one cus site have CO\*. (d) one bridge site and two cus sites have CO\*. (e) bi-dentate OCHO\* bound through one bridge and one cus site. (f) OCHO\* in mono-dentate configuration in bridge site with three CO\* spectators occupying all

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3 other sites. (g)  $\text{HCOOH}^*$  at the bridge site with  $\text{CO}^*$  in the other bridge site. (h)  
4  $\text{H}_2\text{COOH}^*$  in bi-dentate configuration. (i)  $\text{H}_3\text{CO}^*+\text{OH}^*$  intermediate with one bridge  
5 site  $\text{CO}^*$  spectator (j)  $\text{H}_2\text{CO}^*$  in bridge site with two cus site and one cus site  $\text{CO}^*$   
6 spectators. The actual unit cell in simulation is given in Figure S11.  
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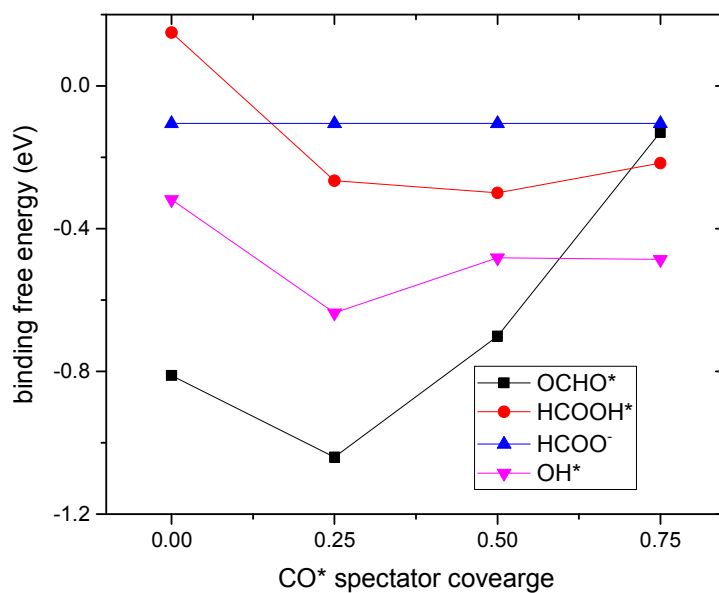
### 10 11 3.3. $\text{CO}_2$ activation: $\text{OCHO}^*$ vs $\text{COOH}^*$

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14 From a purely thermodynamic point of view, the free energy diagrams identifies  
15 which reaction intermediate is most favorable at a particular electron transfer step.  
16 For example, if  $\text{OCHO}^*$  is more stable than  $\text{COOH}^*$  at 0 V-RHE, it will remain the  
17 preferred intermediate at an applied reducing potential (Figure 3(a)). A proton  
18 transfer to  $\text{CO}_2$  molecules in the solvated phase creates both the intermediates. The  
19 free energy is lowered by the equal amount due to an applied reducing potential.  
20  $\text{OCHO}^*$  is a bi-dentate adsorbate if adjacent sites are available. At 0% and 25%  $\text{CO}^*$   
21 coverage,  $\text{OCHO}^*$  binds through one bridge and one cus site (Figure 2(e)). Presence  
22 of  $\text{CO}^*$  in an adjacent bridge site strengthens the  $\text{OCHO}^*$  binding at low (25%)  $\text{CO}^*$   
23 coverage compared to bare catalyst surface (Figure 3(a)). At 50%  $\text{CO}^*$  coverage,  
24  $\text{OCHO}^*$  can bind through one bridge and one cus site or through two cus sites  
25 depending upon the  $\text{CO}^*$  distribution. On a bare surface,  $\text{OCHO}^*$  occupying the  
26 bridge+cus sites have a binding free energy of -0.81 eV. It is interesting to note that  
27 the configuration with bridge+cus distribution of  $\text{CO}^*$  spectators continue to be the  
28 more stable than bridge+bridge configuration when  $\text{OH}^*$  or  $\text{OCHO}^*$  are present on  
29 the surface. It can be argued that at a level of 50% coverage,  $\text{CO}_2\text{RR}$  will occur  
30 through a combination of bridge and cus sites and  $\text{OCHO}^*$  stays bi-dentate. 75%  
31  $\text{CO}^*$  coverage compel  $\text{OCHO}^*$  to be mono-dentate (Figure 2(f)), reducing the binding  
32 free energy significantly. Albeit, the 2\*cus+bridge configuration of  $\text{CO}^*$  adsorbates  
33 lets  $\text{OCHO}^*$  adsorb at the bridge site, which is significantly more favorable than the  
34 cus site adsorption. Thus, in the presence of  $\text{OCHO}^*$ , the 2\*cus+bridge configuration  
35 of the  $\text{CO}^*$  spectators is more stable.  
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43 It should be noted that trends in  $\text{COOH}^*$  and  $\text{OCHO}^*$  binding free energy at different  
44  $\text{CO}^*$  adsorbate configuration are similar and maintain their relative position in the  
45 free energy diagram. Figure 3(a) shows that  $\text{OCHO}^*$  intermediate is much stronger  
46 bound to the active site than  $\text{COOH}^*$ , regardless of spectator coverage.  
47 Consequently, the  $\text{CO}_2\text{RR}$  pathway proceed preferentially through  $\text{OHCO}^*$  and other  
48 O-coordinated adsorbates at all  $\text{CO}^*$  coverages. The other (unwanted) intermediate  
49 after the 1<sup>st</sup> proton transfer step is  $\text{H}^*$  (Figure 3(a)).  
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(a)



(b)

Figure 3: Effect of CO\* coverage on binding energy of (a) intermediates formed by the 1<sup>st</sup> proton transfer\*/OCHO\*/COOH\*; (b) HCOOH\* and OH\* at the available bridge site (or bridge+cus site for OCHO\*) and free energy for deprotonated formic acid in solution.

### 3.4. Selectivity of CO<sub>2</sub>RR vs. HER

The spectator adsorbate interaction between CO\* and H\* is repulsive and H\* binding weakens with higher CO\* coverage (Figure 3(a)). Substantially weaker binding of H\* than OCHO\* facilitate selectivity of CO<sub>2</sub>RR over HER<sup>20</sup>. For CO\* coverages 0-50%, OCHO\* is stronger bound to the catalyst surface than H\* by 0.31-0.73 eV (Figure 2 (a)). The binding free energy difference is over 1 eV for a coverage of 50% CO\* occupying all the bridge sites (Figure SI4). Because H\* is a prerequisite for HER, we thus find the best selectivity for CO<sub>2</sub>RR at 50% CO\* coverage. For high (75%) CO\* coverage, owing to the aforementioned destabilization of OCHO\*, H\* is equally probable to form (Figure 3(a)) at bridge sites (binding energy difference of 4 meV between H\* and OCHO\*). For 75% coverage and cus site adsorption, H\* is remarkably favored by 0.32 eV over OCHO\* at cus sites (Figure SI5). At high CO\* coverage, RuO<sub>2</sub> electrocatalysts should therefore show less selectivity towards CO<sub>2</sub>RR and evolve significant amounts of hydrogen.

RuO<sub>2</sub>(110) bridge sites, when vacant, are hydroxylated in aqueous solution due to negative binding free energy of OH\* at the bridge site at 0 V-RHE (Figure 1). Hydroxylation of cus sites is not energetically favorable at 0 V-RHE and HER can proceed at the cus site. For 0% CO\* coverage and hydroxylated bridge sites, the H\* binding free energy at the cus site is +0.33 eV, i.e. HER requires a reducing potential of -0.33 V-RHE (Table 2). However, the OH\* removal potential for clean RuO<sub>2</sub>(110) surface bridge site is -0.32 V-RHE. Once OH\* is removed, on an otherwise empty surface, the H\* binding free energy at the cus site is +0.22 eV. H\* binding at cus site (with H\* spectators at all bridge site) is +0.41 eV. The surface coverage, onset potential and the reaction site might vary, but these binding free energies suggest that at very low CO\* coverage, only HER is active at reducing potential up to -0.32 V-RHE utilizing both bridge and cus sites. Schematics of few such spectator configurations (within the 2x2-model catalyst surface) for HER mechanism and predicted onset potentials are provided in Table 2.

Table 2: Calculated thermodynamic onset potential [V-RHE] for HER at bridge and cus sites with different spectator species on RuO<sub>2</sub> (110); yellow represents a cus site and green represents a bridge site. OH, CO, H are possible spectators and X is the absence of any of them. \* is the site considered for HER.

Configurations															
cus	X	*		CO	*		X	*		X	*		CO	*	
bridge	OH	OH		CO	OH		H	H		CO	X		CO	X	
HER onset [V-RHE]	-0.33			-0.56			-0.41			-0.26			-0.22		
cus	X	*		*	X		X	X		*	X		OH	*	
Bridge	OH	CO		X	X		CO	*		CO	CO		OH	OH	
HER onset [V-RHE]	-0.39			-0.22			-0.31			-0.41			-0.56		
cus	X	X		CO	X		CO	*		CO	CO				
Bridge	*	X		CO	*		CO	CO		*	CO				
HER onset [V-RHE]	-0.49			-0.29			-0.63			-0.13					

Easy availability of CO<sub>2</sub> in solution phase can prevent HER by formation of OCHO\* in 2\*cus or bridge+cus bi-dentate configuration due to higher stability than H\* (Figure 3(a)). The binding free energy of OCHO\* in weak binding cus site (2\*cus configuration) with bridge sites filled by OH\* is -0.71 eV, and when bridge sites are filled with a mixture of OH\* and CO\*, the OCHO\* binding free energy is -0.70 eV. In comparison, H\* binding is +0.33 eV and +0.39 eV for similar bridge site spectator configuration, respectively.

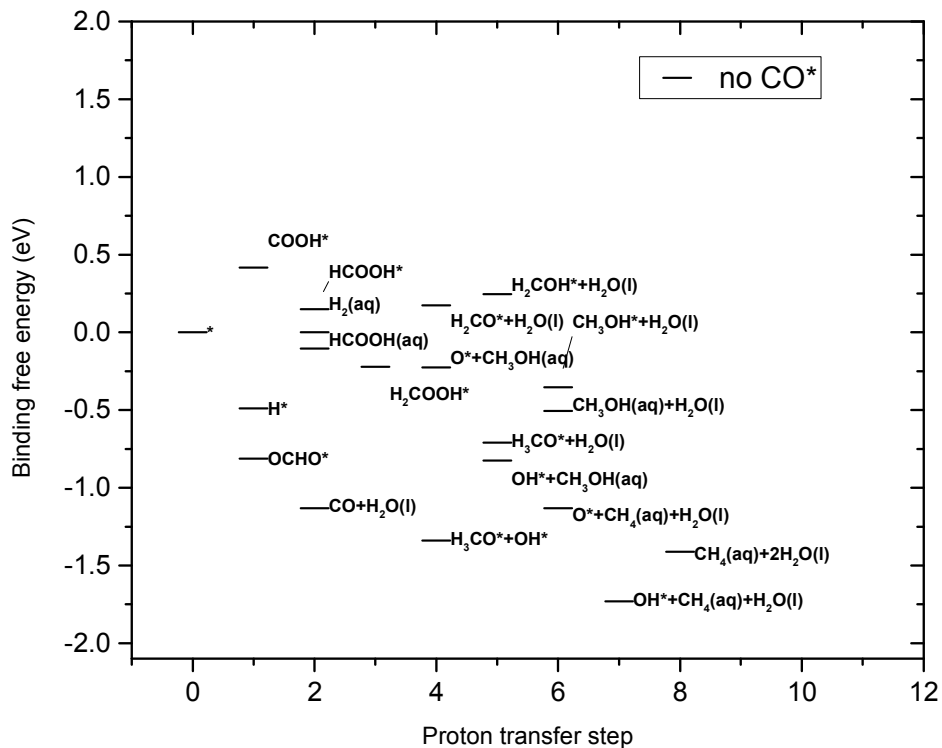
For 25% CO\* coverage, the attractive adsorbate-adsorbate interaction between CO\* and OH\* at bridge sites makes OH\* removal from bridge much more difficult (-0.64 V-RHE). Again bi-dentate OCHO\* is very stable with a binding free energy of -1.04 eV at 25% CO\* coverage. The H\* binding free energy at the cus site (OH\* and CO\* being present at bridge sites) is +0.39 eV, cancelling significant HER activity. A similar argument for subdued HER activity holds for 50% CO\* coverage (all the bridge site occupied (Figure S14)), where all cus sites are available for adsorption. H\* and OCHO\* have binding free energy of +0.41 eV and -0.69 eV respectively (Table S14). On the other hand, in the more favorable configuration, the CO\* adsorbates are distributed between bridge and cus sites and the other bridge site is occupied by OH\*. H\* binding free energy at the cus site is +0.56 eV but the bridge OH\* removal is estimated at -0.48 V-RHE. H\* binding free energy at a free bridge site with 50% CO\* coverage is -0.29 eV and that at cus site is +0.26 eV. Consequently, HER can progress through bridge or cus sites at ~-0.3 V-RHE (Table 2) except when OCHO\* forms occupying both the bridge and cus site. This analysis shows that up to 50%

CO\* coverage is expected to allow little HER activity if OCHO\* forms rapidly. For the 2\*bridge+cus CO\* configuration (75% coverage), H\* binding is very weak (+0.63 eV), while for 2\*cus+bridge configuration, H\* binding free energy is near ideal at +0.03 eV but hydroxylation of active site block HER above -0.48 V-RHE.

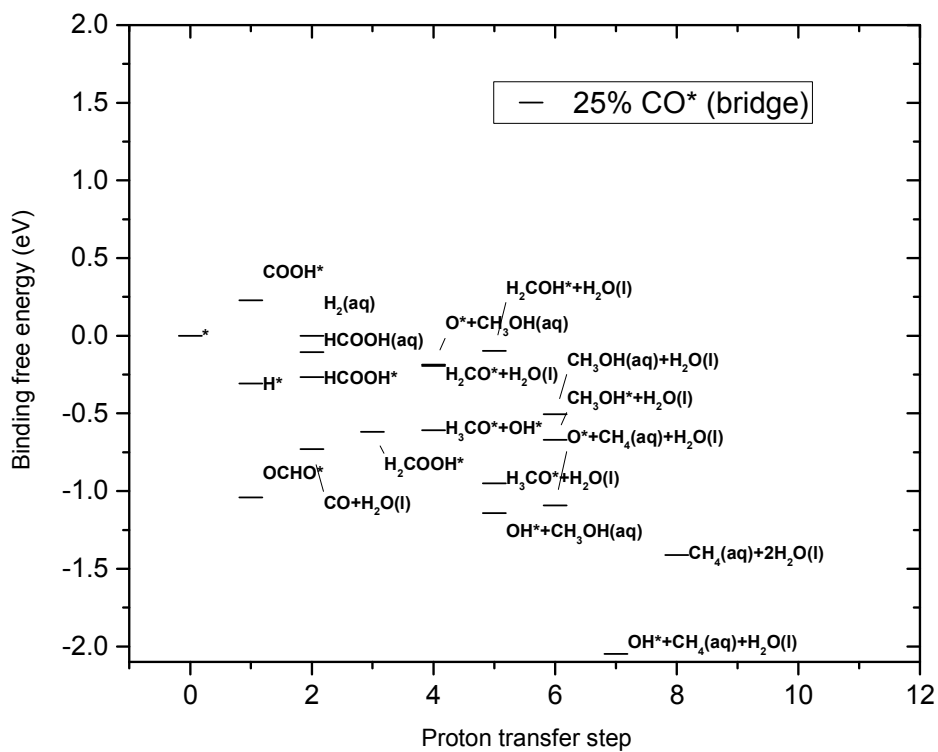
### 3.5. Impact of CO\* coverage on CO<sub>2</sub>RR intermediate binding

Six of the CO\* coverage configurations (Figure SI2) are picked for analysis of the CO<sub>2</sub>RR reaction mechanism – 0% CO\* coverage, 25% CO\* coverage (bridge site), 50% CO\* coverage (all bridge sites), 50% CO\* coverage (neighboring bridge and cus sites), 75% CO\* coverage (2\*bridge+cus sites), 75% CO\* coverage (bridge+2\*cus sites). Multisite adsorbates like H<sub>3</sub>CO\* + OH\*, which occupy two bridge sites in absence of CO\* spectator and a combination of bridge+cus site for 25% and 50% CO\* coverage. 75% CO\* coverage only allows single site adsorbates. Some CO<sub>2</sub>RR adsorbates like OCHO\* and H<sub>2</sub>COOH\* can attach to the catalyst surface through one or two active sites, due to the molecular geometry. Such bi-dentate adsorbates are allowed to remain so for 0-50% CO\* coverage. Lack of multiple neighboring vacant active sites forces them to be mono-dentate at 75% CO\* coverage.

A previous study has shown that binding free energy of O-atom coordinated CO<sub>2</sub>RR reaction intermediates scale with OH\* binding free energy on oxide catalysts surfaces<sup>20</sup>. Hence the strong spectator adsorbate interaction between CO\* and OH\* is expected to be valid for other O-atom coordinated CO<sub>2</sub>RR intermediates as well. Adsorbate binding energy diagrams at 0 V-RHE (Figure 4) for CO\* configurations dominant at 0%, 25% (bridge site), 50% (bridge + cus sites) at 75% coverage (bridge + 2\*cus sites) are used to obtain key conclusions here. Reaction intermediate free energy diagrams with two other CO\* coverage configurations are provided in the supporting information (50% coverage with all bridge sites occupied (Figure SI4) and 75% coverage with on cus site free (Figure SI5)). Binding energy of an adsorbate can change from both electronic interaction with spectators as well as modifications in adsorption geometry.

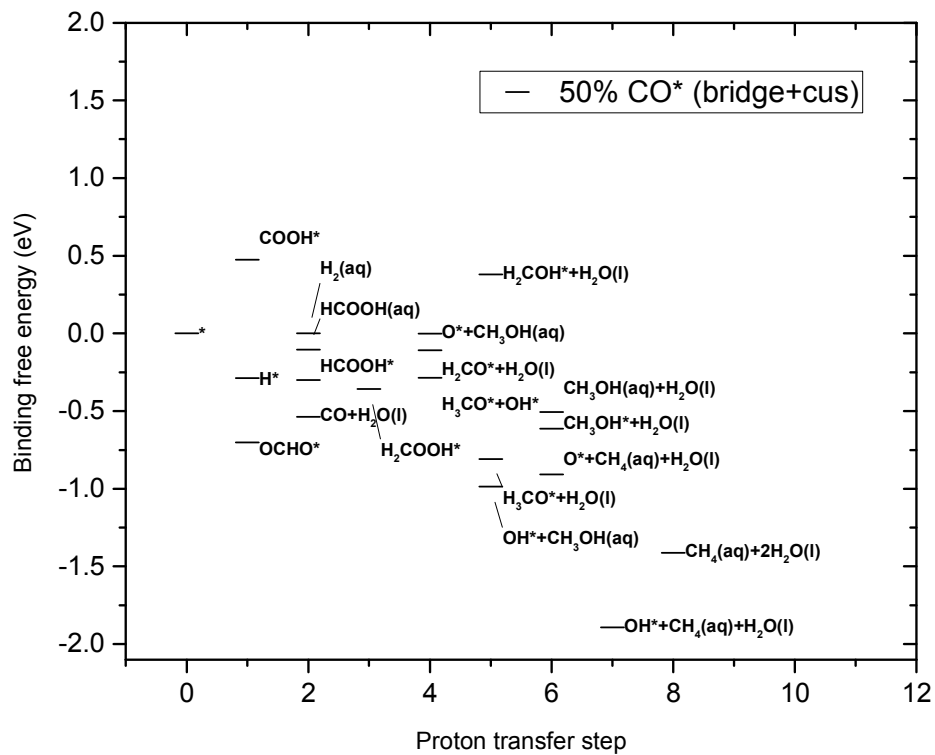


(a)

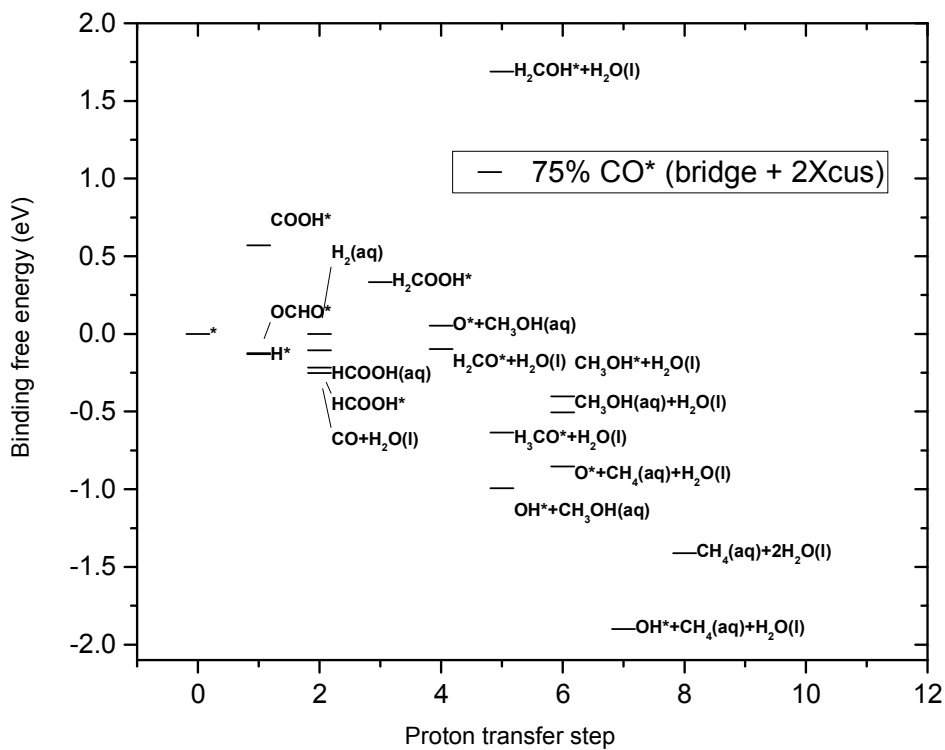


(b)





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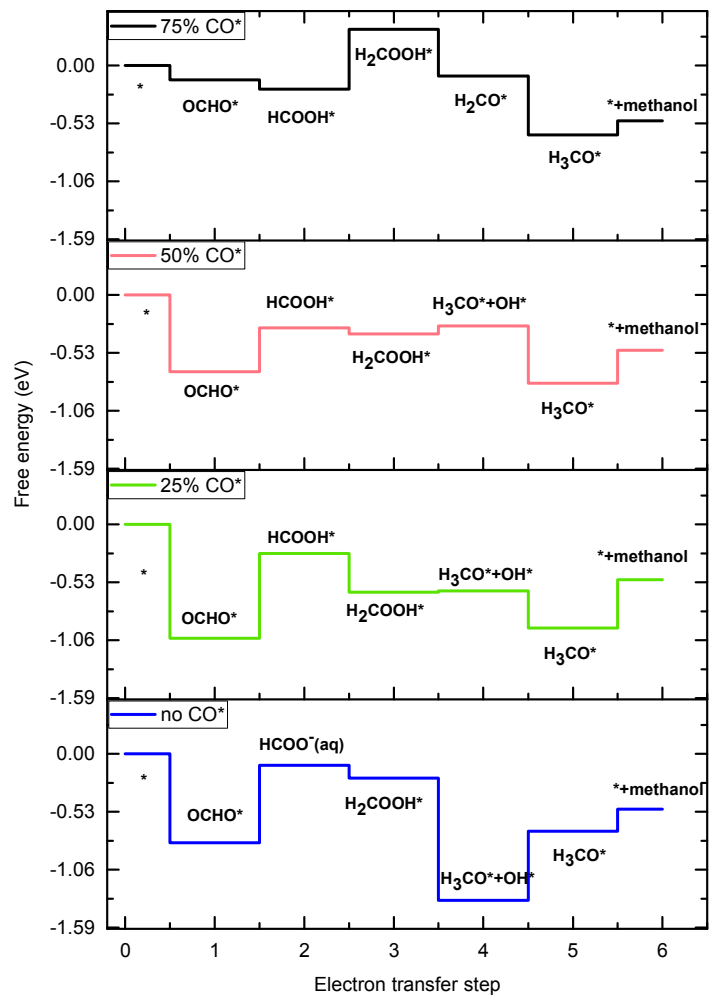
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3 *Figure 4: Free energy diagram of possible reaction intermediates for HER/CO<sub>2</sub>RR at*  
4 *four different coverages of CO\* spectators – (a) 0% (b) 25% utilizing bridge sites (c)*  
5 *50% utilizing half of bridge and cus sites (d) 75% utilizing all cus and half of bridge*  
6 *sites.. The sites occupied by spectator CO\* molecules are indicated. Adsorbate*  
7 *labels are on the right of the data point and adjusted in the y-direction to avoid*  
8 *superposition without changing the relative position between intermediates formed at*  
9 *the same electron transfer step.*  
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### 11 3.6. Impact of CO\* coverage on CO<sub>2</sub>RR

14 The free energy diagram of reaction intermediates helps to identify which reaction  
15 intermediate is most favorable at a particular electron transfer step, and to determine  
16 the reaction mechanism. The H\*/OCHO\* binding free energy correlation helps us  
17 understand the HER/CO<sub>2</sub>RR selectivity; the HCOOH\* binding free energy w.r.t  
18 solvated formic acid in solution (Figure 3(b)) dictates whether formic acid is the major  
19 product or higher proton transfer products like methanol is dominant. If the catalyst  
20 surface fails to bind formic acid molecules to the active site, it will escape into  
21 solution in a solvated form, rendering further hydrogenation difficult. HCOOH\* being  
22 O-coordinated like OH\*, the trend in the binding free energy variation at different CO\*  
23 coverage are similar for these adsorbates (Figure 3 (b)). Adsorbate-adsorbate  
24 interaction effects inducing stronger OH\* binding can open up the possibility of  
25 methanol/methane as product as seen in the case of partial CO\* coverage.  
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30 If the formic acid molecule fails to bind at the catalyst site, H<sub>2</sub>COOH\* is expected to  
31 form by application of an additional electrochemical driving force (equivalent to the  
32 stability of deprotonated and solvated formic acid compared to surface bound  
33 HCOOH\*). However, the electrolyte needs to be saturated with formic acid to supply  
34 protonated formic acid molecules. Nevertheless, the accessibility requirement of  
35 solvated HCOO- and two protons close to the active site simultaneously suggests  
36 the kinetics will be extremely slow stopping further reduction. Absence of any CO\*  
37 coverage lead to release of formic acid in solution on hydrogenation of OCHO\*.  
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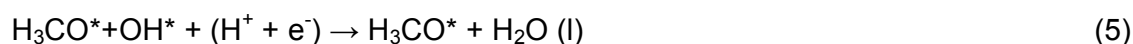
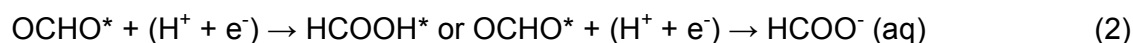


(a)

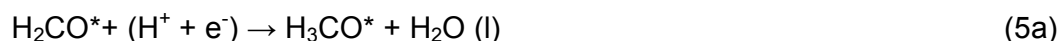
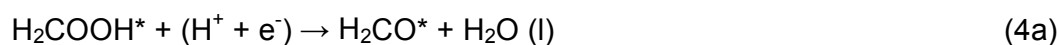


HCOOH\* from OCHO\* is downhill in energy for 75% coverage (Figure 3(b)). Binding free energy of HCOOH\* w.r.t. solvated formic acid in liquid water is ~0.1 eV, which is small enough for a large fraction of adsorbates to escape into solution instead of forming HCOOH\* (Figure 3(b)). Weakening of the OCHO\* adsorbate binding reduces the thermodynamic onset potential requirement to only -0.02 V-RHE. Therefore, at this CO\* coverage, we expect a high turnover of formic acid at very low over potential, in good agreement with Spataru et. al. who observed this at only ~-0.13 V-RHE<sup>11</sup> and pH 3.9.

Investigations of the most probable methanol formation pathways at different CO\* coverage using free energy diagrams enables us to identify the electron transfer steps requiring large reducing potentials to go forward. The preferred pathway has been established to be as following for CO\* coverage ≤50%.



The lack of more than one active site for 75% CO\* coverage forces the reaction pathway to go through H<sub>2</sub>CO\* instead of H<sub>3</sub>CO\*+OH\* adsorbates (Figure 5).



Formation of OCHO\* by CO<sub>2</sub> protonation is downhill at 0 V-RHE for all CO\* coverages. Reduction of the H<sub>2</sub>COOH\* intermediate (Figure 5 and Figure 4 (a)) is either downhill or slightly uphill (0.07 eV for 50% bridge+cus CO\* coverage). Formation of H<sub>3</sub>CO\* is downhill, except in absence of any CO\* coverage. In the absence of any spectators, H<sub>3</sub>CO\* and OH\* can both occupy bridge sites. Stronger OH\* binding energies require a large reducing potential for removal. Overall, OCHO\* activation for 0% CO\* coverage (0.71 eV), 25% CO\* coverage (0.78 eV), 50% CO\* coverage (0.4 eV) and H<sub>2</sub>COOH\* formation at 75% CO\* coverage (0.55 eV) are the thermodynamically most difficult steps (Figure 4 (a)). Thus application of a reducing potential same as the onset potential for these elementary steps automatically makes all other steps downhill as represented in Figure 4(b).

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3 Similar to the OCHO\* adsorbate, H<sub>2</sub>COOH\* is also bi-dentate when two contiguous  
4 bridge and cus sites are available (Figure 2 (e),(h)); as is the case for CO\*  
5 coverages up to 50%. Forcing H<sub>2</sub>COOH\* to be mono-dentate at 75% CO\* coverage,  
6 makes it difficult (free energy increase of 0.6 eV more than 50% CO\* coverage) to  
7 reduce HCOOH\* forming H<sub>2</sub>COOH\* (Figure 5(a)). Consequently, this becomes the  
8 elementary proton transfer step, necessitating the most reducing potential. Due to  
9 interactions with spectating CO\*, the stability of different intermediates change  
10 differently causing reaction step height (free energy change) to vary as well. The  
11 relative ΔG shift of these proton transfer step from intermediate binding energy  
12 variation due to CO\* spectator interaction is provided in Figure SI6. Changing the  
13 CO\* coverage modifies the potential needed to drive the elementary steps forward,  
14 but OCHO\* activation remains the most difficult step for CO\* coverage 50% or lower  
15 (Figure 5(a)).  
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21 OH\* removal is not a limitation for CO<sub>2</sub>RR for any CO\* coverages, except 50%  
22 (Figure SI6), where OH\* removal needs a reducing potential 80 meV lower than  
23 OCHO\* protonation. For CO\* spectator coverage of 25% to 75%, methane and  
24 methanol evolution onset potential is close to OH\* removal potential (Figure 6). The  
25 magnitude of change in overall onset potential for methanol is not as abrupt as that  
26 observed for formic acid and hydrogen evolution (75% coverage). Observable  
27 methanol evolution at different CO\* coverages will therefore be dependent on kinetic  
28 barriers and competition from hydrogen and formic acid evolution. For methane  
29 evolution, the favored pathway is identical to methanol evolution until the 5<sup>th</sup>  
30 electron/proton transfer step, i.e. formation of H<sub>3</sub>CO\*, at all CO\* coverages. At the 6<sup>th</sup>  
31 step, methane is released by protonation on the carbon atom of the H<sub>3</sub>CO\*  
32 adsorbate, leaving an oxygen atom at the bridge site, which is eventually removed  
33 as water through two protonation steps. The thermodynamic limiting steps are  
34 identical to methanol evolution, except at 50% coverage, where the onset potential  
35 predicted of methane evolution from thermodynamic analysis is different from  
36 methanol (Figure 6). From H<sub>3</sub>CO\*, methane evolution will be preferred if C-O bond  
37 cleaving has a smaller barrier than detaching Ru-O bond.  
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43 Experimental evidence<sup>8,9</sup> points to methanol formation having a smaller barrier, as  
44 methanol has been observed to be produced in much larger quantities than  
45 methane<sup>9-11</sup>. Popic et. al. observed up to 30.5% product efficiency for methanol at ~  
46 -0.12 V-RHE, while no CO has been reported to be present. Conversely, Spataru et  
47 al. report excellent HCOOH/H<sub>2</sub> evolution with CO as minority product at similar  
48 potential on RuO<sub>2</sub> electrode. These experimental results directly correlate to our  
49 conclusion that, moderate CO\* coverage aid in methanol evolution and high CO\*  
50 coverage leads to HCOOH/H<sub>2</sub> at very low potential.  
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54 Our simulation model does not explicitly consider pH effects. The discrepancy  
55 between observed and predicted methanol onset potential can originate from  
56 variations in CO\* coverage, pH effects or other differences like composition and  
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surface structure. Preliminary work<sup>8</sup> by Bandi suggested strong dependence of methanol evolution efficiency on pH and observed a much better methanol efficiency in acidic solution than neutral electrolyte. The concentration of methanol in the solvent can also affect the reaction thermodynamics of methanol production. With higher concentration, free energy of methanol increases and release of methanol from  $\text{H}_3\text{CO}^*$  intermediate needs larger reducing potential.

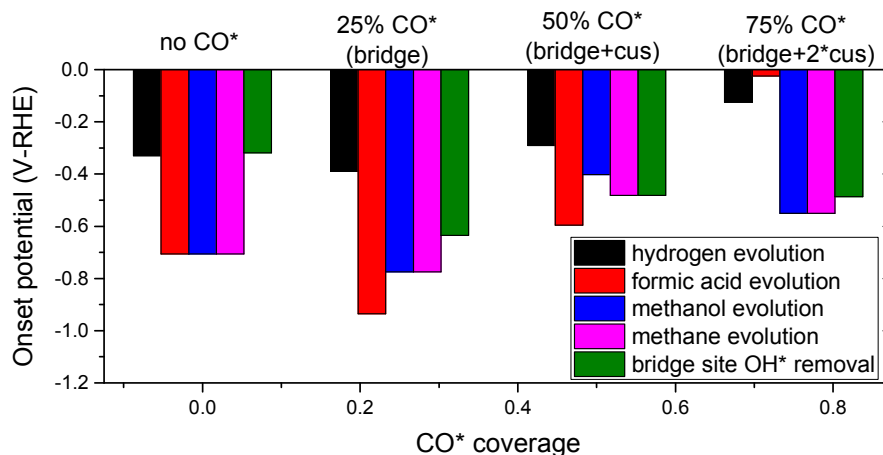


Figure 6: Onset potentials for hydrogen, formic acid, methanol, methane evolution at different  $\text{CO}^*$  spectator coverage.  $\text{OH}^*$  removal potential at bridge site included to provide information about possible  $\text{OH}^*$  blockage.

## 4. Conclusions

In summary, without  $\text{CO}^*$  coverage,  $\text{RuO}_2(110)$  is expected to start producing hydrogen via the cus sites (-0.33 V-RHE) with hydroxylated bridge sites. Repulsive interactions with  $\text{CO}^*$  spectators destabilize  $\text{H}^*$ . If the availability of  $\text{CO}_2$  in the reaction layer and the kinetic barriers for  $\text{CO}_2$  activation are not limiting,  $\text{OCHO}^*$  is preferred over  $\text{H}^*$  as the 1<sup>st</sup> proton transfer product, as seen from a purely thermodynamic perspective. Transient formation of  $\text{CO}^*$  from  $\text{CO}_2\text{RR}$  leads to 25% to 75%  $\text{CO}^*$  coverage. A large reducing potential is required to protonate stable bi-dentate  $\text{OCHO}^*$  and break one Ru-O bond at 0-50%  $\text{CO}^*$  coverage. At 25%  $\text{CO}^*$  coverage, methanol is expected to be the main  $\text{CO}_2\text{RR}$  product, with an onset potential of -0.78 V-RHE because  $\text{HCOOH}^*$  is surface bound. 50%  $\text{CO}^*$  coverage is predicted to provide the best activity towards methanol formation. At this  $\text{CO}^*$  coverage, the HER cannot start above -0.56 V-RHE due to bridge site hydroxylation (Table 2) while methanol formation (onset of -0.4 V-RHE) is active at the  $\text{OH}^*$  removal potential (-0.48 V-RHE). At a sufficient reducing potential, the  $\text{CO}_2\text{RR}$  pathway to methanol is expected to show significant activity in conjunction with little hydrogen evolution for 25%-50%  $\text{CO}^*$  coverage. The 75%  $\text{CO}^*$  covered surface, on the contrary, have close to ideal onset potential for formic acid production, due to weakly bound mono-dentate  $\text{OCHO}^*$ . Once  $\text{OH}^*$  is removed from the active site, both hydrogen and formic acid is expected to form. Suppression of HER at 50% or

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3 lower CO\* coverage by formation of OCHO\* at the active sites is critically dependent  
4 on fast reaction kinetics for OCHO\* formation. Good activity and selectivity obtained  
5 for CO<sub>2</sub>RR on RuO<sub>2</sub> catalysts are highly dependent on the CO\* coverage in the  
6 reaction environment. At high CO\* coverages (75%), excellent availability of CO<sub>2</sub> is  
7 critical for formic acid evolution. If, however, CO<sub>2</sub> molecules are not readily available,  
8 hydrogen is expected to be the only observable product.  
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11 Binding energy alteration of both H\* and CO<sub>2</sub>RR intermediates emerging from  
12 adsorbate interaction with CO\* lets us observe switching of CO<sub>2</sub>RR/HER activity and  
13 CO<sub>2</sub>RR product selectivity at the optimal CO\* coverage. 25%-50% CO\* coverage is  
14 most conducive for methanol formation and higher CO\* coverage for formic acid  
15 evolution.  
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18 RuO<sub>2</sub> based electrocatalysts have been shown experimentally to hold great promise  
19 for direct conversion of CO<sub>2</sub> to methanol and formic acid. Based on this theoretical  
20 exploration, we show that CO\* spectators hold the key to good CO<sub>2</sub>RR activity and  
21 selectivity.  
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## 24 **Supporting Information**

25 Additional visualizations of and explanation for CO\* coverage configurations,  
26 adsorbate free energy diagrams, thermodynamic data for adsorbates and molecules,  
27 figure for methanol evolution elementary reaction step onset dependency on CO\*  
28 coverage, free energy of CO\* coverage configurations, visualization for all possible  
29 CO\* spectator models as well as atomic position data and visualization all catalyst  
30 surface simulations are provided.  
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41 work.  
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## TOC Graphic

