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# Tuning adsorption energies and reaction pathways by alloying : PdZn versus Pd for CO<sub>2</sub> reduction to methanol

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## Abstract

The tunability offered by alloying different elements is useful to design catalysts with greater activity, selectivity, and stability than single metals. By comparing the Pd(111) and PdZn(111) model catalysts for CO<sub>2</sub> hydrogenation to methanol, we show that intermetallic alloying is a possible strategy to control the reaction pathway from the tuning of adsorbate binding energies. In comparison to Pd, the strong electron-donor character of PdZn weakens the adsorption of carbon-bound species and strengthens the binding of oxygen-bound species. As a consequence, the first step of CO<sub>2</sub> hydrogenation more likely leads to the formate intermediate on PdZn, while the carboxyl intermediate is preferentially formed on Pd. This results in the opening of a pathway from carbon dioxide to methanol on PdZn similar to that previously proposed on Cu. These findings rationalize the superiority of PdZn over Pd for CO<sub>2</sub> conversion into methanol, and suggest guidance for designing more efficient catalysts by promoting the proper reaction intermediates.

The reduction of CO<sub>2</sub> greenhouse gas emissions and the availability of a reliable, and secure carbon-neutral energy supply are vital in order to slow down the rate of climate change while replacing fossil sources.<sup>1</sup> Anthropogenic CO<sub>2</sub> conversion to methanol can help to face this double challenge.<sup>2,3</sup> Methanol is a safe, easily transportable and fastly biodegradable liquid fuel which can be used with today’s vehicle technology at minimal incremental costs.<sup>4</sup> Catalytic CO<sub>2</sub> hydrogenation to methanol (CO<sub>2</sub>+H<sub>2</sub>→H<sub>2</sub>O+H<sub>3</sub>COH), with hydrogen produced from water electrolysis, has proven to be a viable process at the pilot plant scale in several countries.<sup>5</sup> Because CO<sub>2</sub> is a very stable molecule, highly efficient catalysts are required to reduce it to methanol. For now, the Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst, initially developed for CO hydrogenation to methanol, is used in combination with harsh pressure conditions (> 50 bar).<sup>6</sup> In this context, the design of more efficient catalysts for decreasing the pressure as well as the temperature is an active field of research. Two main strategies are currently used to design new catalysts for CO<sub>2</sub> hydrogenation to methanol. First, the conception of copper-metal oxide interfaces such as Cu/ZnO, Cu/CeO<sub>2</sub>, and Cu/ZrO<sub>2</sub><sup>7-10</sup> has been reported to promote the formation of formate, thus increasing catalytic activity and selectivity<sup>11</sup> Another decisive approach is based on engineering the coordination environment of active metal atoms by alloying,<sup>12,13</sup> to control the reaction pathways that drive the chemical transformations. For instance, alloying Ni with Ga penalizes the rWGS (reverse Water Gas Shift) reaction on NiGa catalysts, thereby facilitating the production of methanol.<sup>14</sup>

Several Pd-based compounds are recognized as attractive catalysts for CO<sub>2</sub> reduction to methanol. Compared to Cu-based catalysts, they can be chemically stable, resistant to sintering,<sup>15-17</sup> and present superior activity toward methanol production at lower temperatures.<sup>18-20</sup> Current interest in this direction has been focused on several systems, such as Pd/ZnO,<sup>21,22</sup> Pd/Ga<sub>2</sub>O<sub>3</sub>,<sup>23,24</sup> Pd/In<sub>2</sub>O<sub>3</sub><sup>23,25</sup> or Pd/ZrO<sub>2</sub>.<sup>26</sup> The performances of Pd/ZnO are generally ascribed to the formation of the PdZn intermetallic compound at the oxide surface by reduction of the powder catalyst under H<sub>2</sub> at high temperature ( $T > 200^\circ\text{C}$ ).<sup>27-30</sup> The formation of heteroatomic bonds in PdZn, driven by electron transfer from Zn to Pd (Zn<sup>0.4+</sup>Pd<sup>0.4-</sup>),<sup>31</sup> changes the electronic environment of the active metal. Focusing on methanol steam reforming (MSR), which is the reverse reaction of methanol synthesis from CO<sub>2</sub> and H<sub>2</sub>, a clear correlation between electronic structure and CO<sub>2</sub> selectivity was recently obtained by comparing Cu with PdZn, PtZn, NiZn, and PdCd intermetallics on the basis of experiments and calculations.<sup>32</sup> The specific electronic structure of PdZn, characterized by a shift towards higher binding energies of the Pd *d*-band upon alloying, makes the density of states of the alloy resemble that of Cu.<sup>33</sup> This accounts for the similar catalytic performances of the two catalysts.<sup>32</sup> At the atomic scale, a correlation between adsorption energies and CO<sub>2</sub> se-

lectivity pointed the key role of formaldehyde, a weak adsorption of H<sub>2</sub>CO leading to a high theoretical selectivity.<sup>34</sup> Experimentally, the addition of Pd to ZnO was shown to slightly lower the thermodynamic stability of adsorbed formaldehyde, which correlates with increased selectivities to CO<sub>2</sub> and H<sub>2</sub>.<sup>35</sup> Meanwhile, the high activity was attributed to identical adsorption energies of methanol and water on PdZn/ZnO – as determined from micro-calorimetry and infrared spectroscopy, since methanol could competitively adsorb and react with water. However, no extensive mechanistic studies have been performed so far to relate the reaction paths of CO<sub>2</sub> hydrogenation to methanol on the PdZn catalysts, and thereby clearly reveal the role of alloying Pd with Zn.<sup>35</sup> Herein, using plane-wave density functional theory (DFT) calculations, we investigate how the addition of an ancillary metal (Zn) to a metallic catalyst (Pd) influences the mechanism of methanol synthesis through CO<sub>2</sub> hydrogenation. The theoretical study has been performed at P=0 and T=0. It is a mandatory first step towards the investigation and in-depth understanding of the alloying effect on the catalytic performances. We chose the Pd(111) and PdZn(111) surfaces, because this orientation is the most stable for both systems<sup>36-38</sup> and has been observed experimentally.<sup>39</sup> Adsorption ( $E_{ads}$ ) and reaction ( $\Delta E$ ) energies were systematically determined based on total energy calculations (section S1, Tabs S1-S5, Figs. S1-S5), while activation energies ( $E_{act}$ ) were ruled on by the climbing image nudged elastic band (CI-NEB) method (Fig. S6, Tab. S5).<sup>40-43</sup>

On both catalysts, carbon dioxide does not form stable chemical adsorption state (Fig. S2), similarly to what happens on other dense metallic surfaces,<sup>44</sup> where CO<sub>2</sub> is weakly physisorbed or unstable.<sup>45</sup> After the structural optimization, the molecule stands parallel and rather far from the surface (distance larger than 3 Å). No activation of CO<sub>2</sub> is identified at this stage: adsorption strengths are weak – but almost twice larger on PdZn than on Pd (Fig. S2) – and the C-O bond lengths computed for CO<sub>2</sub> physisorbed on Pd and PdZn are equal to the ones calculated for the gas phase (1.18 Å).

Considering all other species involved in CO<sub>2</sub> hydrogenation to methanol, alloying Pd with Zn leads to drastic modifications of the catalyst adsorption properties (Fig. 1). The adsorption energies of carbon-bound species – CO, HCO, H<sub>2</sub>CO, COOH, COH, HCOH, C(OH)<sub>2</sub>, H<sub>2</sub>COH – are strengthened on Pd, the largest changes being calculated for H<sub>2</sub>CO, COH, C(OH)<sub>2</sub>. In contrast, oxygen-bound species – H<sub>3</sub>COH, O, HO, H<sub>2</sub>O, H<sub>3</sub>CO, HCOOH, HCOO, H<sub>2</sub>COOH, H<sub>2</sub>COO – interact more strongly with PdZn(111), especially H<sub>2</sub>O. In regard to charge transfer, which is a key parameter for adsorption properties, this behavior can be attributed to the substantial electron-donating and weak electron-accepting ability of PdZn, resulting from its fully filled d-states.<sup>46</sup> In comparison, Pd presents an

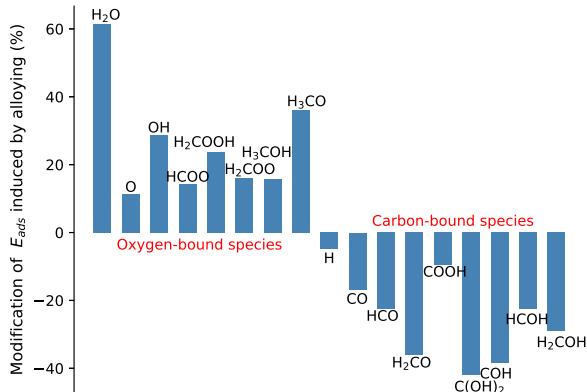


Figure 1: Modification of the catalyst adsorption properties due to alloying Pd with Zn. The relative changes are evaluated by  $(E_{ads}^{PdZn} - E_{ads}^{Pd})/E_{ads}^{Pd}$ , using data from Tabs S1-S4. A positive (resp. negative) value means that the adsorbate is more (resp. less) strongly adsorbed on PdZn than on Pd. The adsorption energies of the HCOOH intermediate are identical on PdZn and Pd.

electron-accepting and a weak electron-donating character, due to its partially filled d-states. Such an electronic effect also explains the larger modification of the water adsorption energy, induced by alloying, than of the methanol one, both adsorbed at top sites – top-Zn or top-Pd site on PdZn and Pd, respectively – since the oxygen electronegativity in methanol is weaker than in water ( $14.87 \text{ eV}\cdot\text{e}^{-1}$  and  $19.79 \text{ eV}\cdot\text{e}^{-1}$ , respectively).<sup>47</sup> Alloying can change the binding mode of the adsorbates as well. For example, H<sub>3</sub>CO binds to the surface through the oxygen atom, at a hollow site on Pd but at a bridge site on PdZn, thus maximizing O-Zn interactions on PdZn. A similar behavior can be observed for carbon-bound adsorbates, such as H, CO and COH, located in a hollow site on Pd and in a bridge Pd-Pd site on PdZn, which is likely to maximize the C-Pd interactions. The larger Pd-Pd distance at the PdZn(111) surface (4.41 Å) than at the Pd(111) surface (2.75 Å) may also contribute to the change of the binding mode, as observed for HCOH and *c*-COOH (*cis*-COOH), lying at top-Pd and bridge sites on PdZn and Pd, respectively.

So far, theoretical studies have identified three main reaction routes for methanol synthesis from CO<sub>2</sub><sup>48</sup> (Fig. 2, black arrows). The conventionally proposed pathways are the *formate pathways*, during which CO<sub>2</sub> is first hydrogenated to formate (HCOO), the latter being hydrogenated to H<sub>2</sub>CO through H<sub>2</sub>COO or HCOOH followed by H<sub>2</sub>COOH, and then methanol. This mechanism has been frequently invoked for Cu surfaces,<sup>49–52</sup> as well as for several Cu/oxide,<sup>53–57</sup> Cu/carbide,<sup>58</sup> Cu alloys,<sup>59–61</sup> and Pd/oxide<sup>62,63</sup> catalysts. Alternatively, the *CO pathway* is generally assumed to explain the formation of the CO byproduct, as observed for some Cu/oxide,<sup>7,10</sup> doped-Cu catalysts<sup>64</sup> or Cu-based alloys.<sup>65</sup> The formation of CO results from CO<sub>2</sub> hydrogenation via the COOH intermediate, and methanol is

produced from CO hydrogenation through HCO and H<sub>2</sub>CO. For Pd, our results point towards this mechanism as well (Fig. 2, blue arrows). The first hydrogenation step to *c*-COOH occurs with a rather large barrier (Figs 3, S6 and Tab. S5), while carbon monoxide forms from *c*-COOH rather easily ( $E_{act}^{Pd}(c\text{-COOH} \rightarrow \text{CO}) = 0.59 \text{ eV}$ ), compared to the one leading to HCOOH ( $E_{act}^{Pd}(c\text{-COOH} \rightarrow \text{HCOOH}) = 1.01 \text{ eV}$ ). This is in agreement with the substantial CO selectivity from CO<sub>2</sub> hydrogenation over Pd black, as experimentally measured.<sup>25</sup> Methanol is then obtained from CO, through HCO, H<sub>2</sub>CO, H<sub>2</sub>COH species (Figs. 3, S6 and Tab. S5), which have all been experimentally observed upon methanol decomposition on Pd.<sup>66</sup> However, several elementary steps present rather large activation energies: CO → HCO ( $E_{act}^{Pd} = 1.09 \text{ eV}$ ), HCO → H<sub>2</sub>CO ( $E_{act}^{Pd} = 0.97 \text{ eV}$ ), and H<sub>2</sub>CO → H<sub>2</sub>COH ( $E_{act}^{Pd} = 0.70 \text{ eV}$ ). This may explain why methanol is not produced from CO<sub>2</sub> or CO hydrogenation on Pd.<sup>25</sup> The *COOH pathway* is less frequently adopted in the literature.<sup>44,48,67</sup> A few examples include the catalysis by intermetallic compounds (Ga<sub>3</sub>Ni<sub>5</sub>,<sup>68</sup> PdCu<sub>3</sub>)<sup>69</sup> and oxidized copper, surface oxygen or water-derived species facilitating the formation of methanol.<sup>70</sup>

On PdZn, like on Pd, the spontaneous dissociate adsorption of H<sub>2</sub> can provide enough H coverage and promote subsequent reactions (Tab. S5). In addition, like on Pd, direct formation of CO from CO<sub>2</sub> is not likely on PdZn, since it proceeds through large barriers on both catalysts ( $E_{act} > 1.5 \text{ eV}$ , Tab. S5). The crucial step to determine the reaction pathway is the first elementary step of CO<sub>2</sub> hydrogenation, which consists in formate (HCOO) or carboxyl (COOH) formation. As shown in Fig. 1, alloying Pd with Zn results in a slight stabilization (relative change of the adsorption energy by -14%) of the formate species at the alloy surface and in a faint destabilization of the carboxyl species (+10%). Thus, the *formate pathways* are expected to be more favorable on PdZn. The previous picture is validated by NEB calculations, as explained in the following (Fig. 2, red arrows).

The formation of HCOO from CO<sub>2</sub> is found slightly exothermic (Tab. S5), with a smaller barrier on PdZn than on Cu(111) ( $E_{act}^{PdZn} = 0.58 \text{ eV}$ ;  $E_{act}^{Cu(111)} = 0.87 \text{ eV}$ )<sup>52</sup>. These findings are consistent with the presence of formate species on the PdZn surface, as experimentally observed<sup>21,71</sup> Alloying is thus demonstrated to change the picture, the formation of HCOO from CO<sub>2</sub> being endothermic on Pd, and occurring with a huge barrier ( $E_{act}^{Pd} = 2.23 \text{ eV}$ ). No activation of the CO<sub>2</sub> molecule is compulsory on PdZn, in contrast to what has been proposed by Zhang *et al.* on Pd, starting from activated CO<sub>2</sub>, adsorbed in a bidentate configuration ( $E_{ads}^{Pd} > 0$ ) to make the *formate pathway* achievable. Comparable trends have been calculated by alloying Pd with other metals, whether the considered active surface presents a similar surface structure ( $E_{act}^{PdIn(110)} = 0.05 \text{ eV}$ )<sup>72</sup> or not ( $E_{act}^{PdCu(111)} = 0.62 \text{ eV}$ ).<sup>73</sup> Once HCOO is

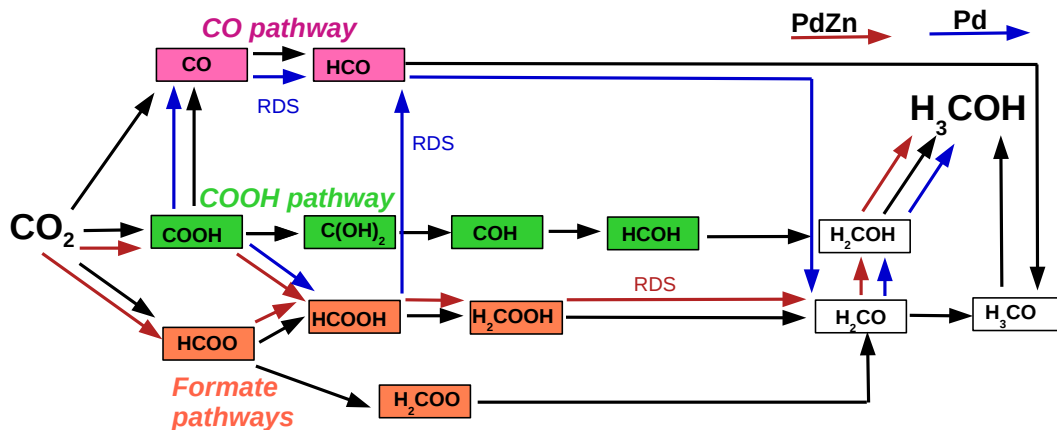


Figure 2: Main reaction routes frequently reported in literature, for methanol synthesis from  $\text{CO}_2$  hydrogenation (black arrows). The most energetically favorable pathways identified herein for Pd and PdZn are shown with blue and red arrows, respectively. The rate-determining steps on Pd and PdZn, identified from Tab. S5 and Fig. S6, are labeled “RDS”.

formed, several steps can be considered (Fig. S6, Tab. S5). Breaking the C-O bond to form  $\text{HCO}+\text{OH}$  is not likely ( $E_{act}^{\text{PdZn}} = 2.33$  eV). Similarly,  $\text{H}_2\text{COO}$  proceeds through a large barrier ( $E_{act}^{\text{PdZn}} = 1.56$  eV). In contrast, the hydrogenation of  $\text{HCOO}$  to formic acid ( $\text{HCOOH}$ ) is probable (Fig. 3), with an activation energy smaller than on Pd ( $E_{act}^{\text{Pd}} = 0.73$  eV;  $E_{act}^{\text{PdZn}} = 0.52$  eV) and Cu(111) ( $E_{act}^{\text{Cu(111)}} = 0.91$  eV<sup>52</sup>). The modification of the activation energy is found to strongly depend on the ancillary metal with which Pd is combined:  $E_{act}^{\text{PdIn(110)}} = 0.65$  eV<sup>72</sup> and  $E_{act}^{\text{PdCu(111)}} = 1.28$  eV.<sup>73</sup> The scenario on PdZn(111) differs from studies on Cu(111) in which  $\text{H}_2\text{COO}$  has been frequently invoked as the product of  $\text{HCOO}$  hydrogenation.<sup>52</sup> Formaldehyde, that is more stabilized on Pd than PdZn, likewise results from the C-O bond breaking in  $\text{H}_2\text{COOH}$ , which is more stabilized on PdZn than on Pd (Fig. 1). Thus, the reaction is not thermodynamically favored on PdZn ( $\Delta E^{\text{PdZn}} = 0.59$  eV, Tab. S5) and the barrier is the rate determining step ( $E_{act}^{\text{PdZn}} = 0.90$  eV, Fig. 3).

As shown before, alloying stabilizes the formate species at the PdZn surface, thus facilitating the *formate pathways*, and destabilizes the carboxyl species. However, the latter effect is small (10% increase in adsorption energy, in average). Is it enough to avoid the formation of the carboxyl species at the PdZn alloy surface? On PdZn,  $\text{CO}_2$  hydrogenation to  $\text{COOH}$  is found competitive with the formation of  $\text{HCOO}$  (Fig. 3). The reaction is endothermic for both the *cis* and *trans*  $\text{COOH}$  isomers (Tab. S5). The activation energies to form *t*- $\text{COOH}$  and  $\text{HCOO}$  are almost the same and moderate ( $E_{act}^{\text{PdZn}}(\text{CO}_2 \rightarrow \text{t-COOH}) = 0.61$  eV and  $E_{act}^{\text{PdZn}}(\text{CO}_2 \rightarrow \text{HCOO}) = 0.58$  eV). On PdZn, the *c*- $\text{COOH}$  configuration – less adsorbed on PdZn than Pd (Fig. 1) and resulting from isomerization ( $E_{act}^{\text{PdZn}}(\text{t-COOH} \rightarrow \text{c-COOH}) = 0.66$  eV) – provides an optimized geometry to spontaneously convert into formic acid, an intermediate more strongly adsorbed on PdZn than on Pd ( $E_{act}^{\text{PdZn}}(\text{c-COOH} \rightarrow \text{HCOOH}) = 0.03$  eV).

The latter can then react according to the *formate mechanism* detailed before. Such a step has not been invoked so frequently in literature for  $\text{CO}_2$  reduction to methanol, the corresponding barriers being usually much larger ( $E_{act}^{\text{Ga}_3\text{Ni}_5(221)} = 0.93$  eV,<sup>68</sup>  $E_{act}^{\text{Cu(111)}} = 0.64$  eV,<sup>74</sup>  $E_{act}^{\text{Pd(111)}} = 0.75$  eV<sup>75</sup>). The previous scenario, as a hybrid pathway between the formate and  $\text{COOH}$  ones (Fig. 3), is more likely than the one following the complete *COOH mechanism*. Indeed, the hydrogenation of  $\text{COOH}$  to  $\text{C(OH)}_2$  is endothermic and occurs with rather large barriers ( $\Delta E^{\text{PdZn}} = 1.01$  eV,  $E_{act}^{\text{PdZn}} = 1.02$  eV).

As demonstrated in the previous sections, formaldehyde is a key intermediate in the  $\text{CO}_2$  hydrogenation to methanol. This carbon-bound species is more strongly adsorbed on Pd than on PdZn (Fig. 1, Tab. S2), in agreement with other theoretical calculations.<sup>76</sup> This tendency is however reverse to the experimental findings, suggesting that formaldehyde is more strongly bound on PdZn.<sup>77,78</sup> This may arise from the structural complexity of actual catalyst surfaces, as well as the influence of reaction conditions. The addition of Zn changes the most favorable adsorption site from  $\eta_{\text{Pd}}^1(\text{C})\eta_{\text{Pd}}^1(\text{O})$  on Pd (Fig. S5) to  $\eta_{\text{Pd}}^1(\text{C})\eta_{\text{PdZn}_2}^3(\text{O})$  on PdZn (Fig. S4), in agreement with the results of Smith *et al.*<sup>79</sup> The experimental observations by Jerero and Vohs, who reported that  $\text{H}_2\text{CO}$  binds to Pd-Zn dimers, with the carbon end of the molecule bound to Pd and the oxygen end bound to Zn,<sup>77</sup> slightly differ from our findings. Starting from formaldehyde, the methanol formation can proceed through  $\text{H}_3\text{CO}$  or  $\text{H}_2\text{COH}$  (Fig. 3). The barriers are smaller through  $\text{H}_2\text{COH}$  than through  $\text{H}_3\text{CO}$  (Tab. S5), which is attributed to the specific configuration of adsorbed  $\text{H}_2\text{COH}$ , with the C-O bond almost parallel to the surface (Figs. S4-S5). Alloying Pd with Zn again facilitates the transformation from  $\text{H}_2\text{CO}$  to methanol, the barriers being smaller on PdZn than

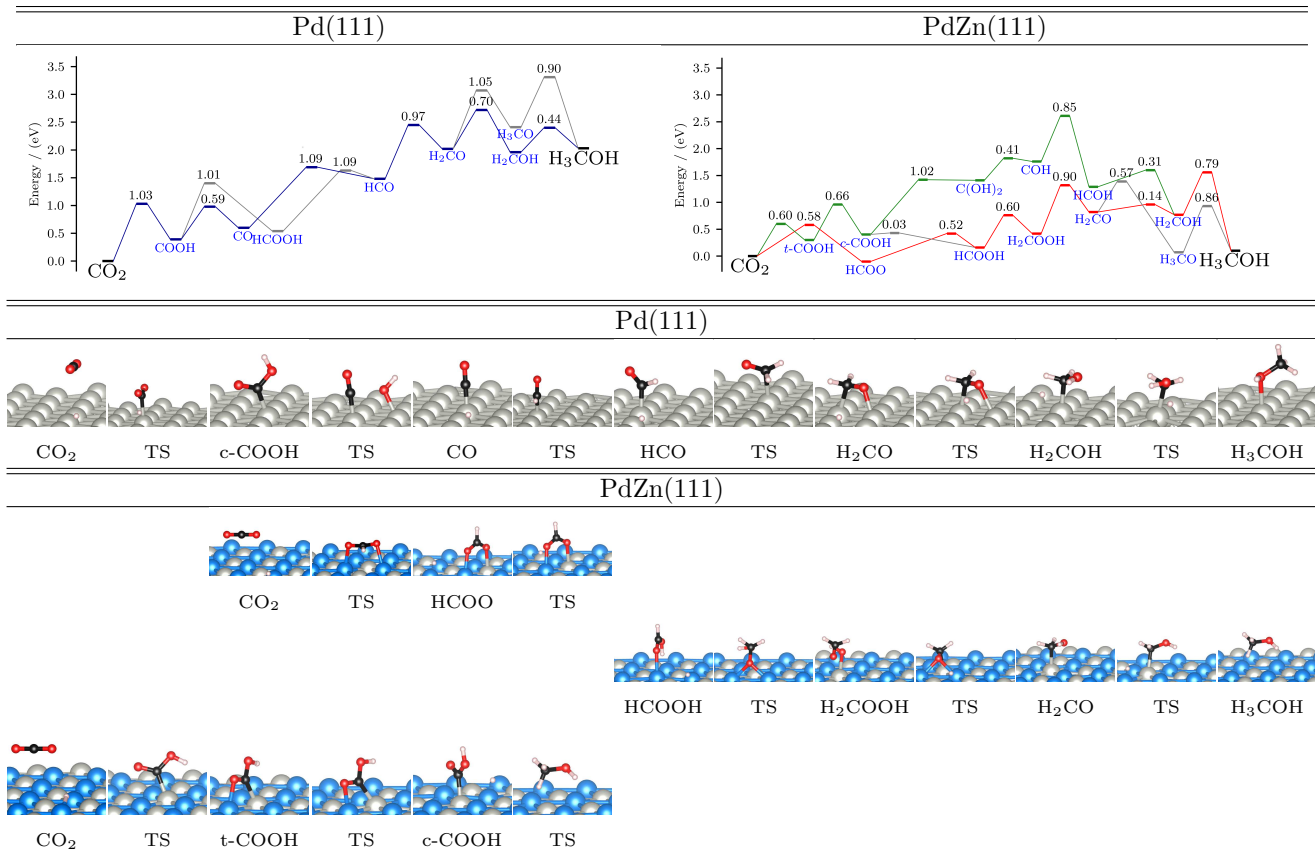


Figure 3: Top : Energy landscape for CO<sub>2</sub> hydrogenation to methanol on Pd and PdZn. The values indicated on the graph represent the activation energy barriers in eV. *Formate*, *COOH* and *CO* pathways are depicted in red, green and blue, respectively. Alternative paths are shown in gray. Bottom : Adsorbates and transition states (TS) structures. c-COOH and t-COOH stands for *cis*-COOH and *trans*-COOH, respectively.

on Pd (Fig. S6, Tab. S5). This last sequence is quite different to what is generally proposed in the literature, i.e. the hydrogenation of H<sub>2</sub>CO to H<sub>3</sub>CO and methanol, as found by Zhang et al. on Pd(111),<sup>80</sup> Wu and Yang on PdIn(110),<sup>72</sup> and Nie *et al.* on PdCu(111).<sup>73</sup>

In summary, alloying Pd with Zn strongly alters the preferred binding configuration of several intermediates, such as CO, H<sub>2</sub>CO and H<sub>3</sub>CO. This deeply modifies the kinetically preferred pathway to methanol. The latter more likely proceeds through the *formate* mechanism, thus avoiding the formation of CO, in agreement with the experimental observations.<sup>21,25</sup> Such a reaction path is very similar to the one calculated on Cu(111)<sup>52</sup> – CO<sub>2</sub> → HCOO → HCOOH → H<sub>2</sub>COOH → H<sub>2</sub>CO → H<sub>2</sub>COH → H<sub>3</sub>COH. On both PdZn and Cu, the steps with the highest barriers are the C-O bond breaking to formaldehyde and H addition to H<sub>2</sub>COH (Fig. 3, Tab. S5). Overall, barriers are lower on PdZn than on Pd, in agreement with the superior methanol yields measured for catalysts containing the PdZn intermetallic phase.<sup>25,81</sup> The insights gained by studying the reaction networks on PdZn versus Pd shed light on its intrinsic catalytic properties at T=0 and P=0. Further work will include other effects such as the influence of the support and the reaction conditions on the catalytic properties. The extension of our study to other ancillary metals

combined with Pd may stimulate the discovery of novel alloy catalysts for CO<sub>2</sub> hydrogenation to alcohols.

## Computational methods

All calculations were performed based on the Density Functional Theory (DFT) using the Vienna *ab initio* simulation package (VASP).<sup>82–84</sup> The interaction between the valence electrons and the ionic core was described using the spin polarized projector-augmented wave (PAW) method<sup>85,86</sup> within the generalized gradient approximation of Perdew, Burke and Ernzerhof (GGA-PBE),<sup>87</sup> considering the valences for the atoms to be 4d<sup>9</sup>5s<sup>1</sup> (Pd), 4d<sup>10</sup>p<sup>2</sup> (Zn), 2s<sup>2</sup>2p<sup>4</sup> (O) 2s<sup>2</sup>2p<sup>2</sup> (C) and 1s<sup>1</sup> (H). To compensate for a poor description of van der Waals interactions by GGA functionals, the D3 correction method by Grimme was employed.<sup>88</sup> Structures were relaxed until the forces dropped below 0.01 eV/Å. Reaction energies ( $\Delta E$ ) were determined, as well as energy barriers ( $E_{act}$ ), based on the climbing image nudged elastic band (CI-NEB) method.<sup>40–43</sup> Seven intermediate images were produced by linear interpolations between relaxed images. The optimization was stopped when the change in the total (free) energy was smaller than 10<sup>-4</sup> eV. Vibrational analysis (for saddle

point verification), limited to the surface species and keeping the rest of the system fixed, was carried out by calculating Hessian matrix with finite difference approach with a step size of 0.015 Å.

One-electron Kohn-Sham orbitals were expanded with a kinetic energy cutoff of 450 eV. The reciprocal space integration was approximated with a Monkhorst-Pack k-point grid of  $9 \times 9 \times 9$ ,  $2 \times 4 \times 1$  and  $3 \times 3 \times 1$  for the bulk crystals, PdZn(111) and Pd(111) catalytic surfaces, respectively. This setup leads to lattice parameters for the PdZn (P4/mmm space group,  $a = 4.12$  Å,  $c = 3.42$  Å), in good agreement with other theoretical values ( $a = 4.14$  Å,  $c = 3.38$  Å;<sup>89</sup>  $a = 4.15$  Å,  $c = 3.39$  Å<sup>39</sup>), as well as with experimental ones (interpolated values for 50 at. % Zn,  $a = 4.11$  Å and  $c = 3.35$  Å<sup>39,90</sup>). All calculations have been performed using a bulk truncated model, since the strength of Pd-Zn bonds was demonstrated to prevent any surface segregation in the self-supported 1:1 alloy film.<sup>39</sup>

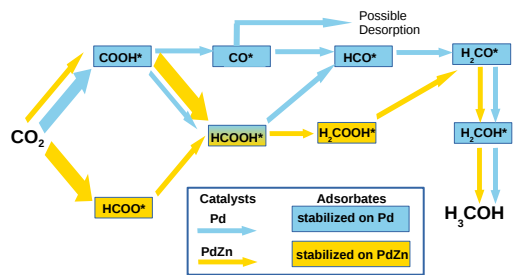
## Associated content

Summary of adsorption properties of Pd(111) and PdZn(111) towards all intermediates involved in the CO<sub>2</sub> reduction to methanol (adsorption energies and configurations); Scheme of all considered reaction paths; Table containing the corresponding reaction and activation energies.

## Acknowledgment

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**The authors declare no competing financial interest**





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