

# Alloying effects on the reactivity of Pd are ensemble dominated

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## ABSTRACT

In this paper the geometric (“ensemble”) and electronic (“ligand”) effects of alloying on surface reactivity and catalysis are considered. The effect of alloying on the behaviour of Pd, both in single crystal form, and as a nanoparticulate catalyst is discussed. The first case concerns Pd alloyed with Cu, and here the reactivity with formic acid and ethanol is modified by the presence of Cu. However, both Cu and Pd maintain their elemental integrity for the reactions, and it is shown that the main alloying effect is one of dilution of Pd atoms, rather than by global electronic factors such as d-band shifting and filling. Similarly, when Pd is alloyed with Au, then the adsorption characteristics (sticking probability and uptake) for CO, O<sub>2</sub>, ethene and acetaldehyde are dominated by changes in the surface arrangement of the two atoms. Au mainly acts as an adsorption blocker, but to different degrees depending upon the nature of the adsorbing molecule and its demand for particular ensemble sizes. Finally, nanoparticulate Pd is considered, and the effect of alloying on high pressure methanol synthesis from CO<sub>2</sub> and H<sub>2</sub> is outlined. Pd on its own is not very selective, instead it mainly produces CO and methane. However, by supporting on oxides such as ZnO, Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> and by reducing in hydrogen, the Pd forms alloys, which then results in high selectivity to methanol. Again, this is ascribed to the dilution of the Pd ensembles at the surface, which are the cause of methane production.

## 1. Introduction

There has been a long discussion regarding ‘ensemble’ vs ‘ligand’ effects in catalysis [1–10] which continues to this day [11–13]. These terms should be defined first. An ensemble generally means a group of atoms together in a surface or catalytic reaction, which are crucial for the performance. This group can be very small, maybe only two atoms, or much bigger. The ligand effect refers to the electronic changes due to the mixing of elements, which changes their respective electronic structure such that they no longer behave like the pure atoms. Often this is interpreted in terms of d-band changes when considering alloying between different transition metals (TMs) or between TMs and group 12 atoms for instance.

This paper reviews the effects of alloying on adsorption and catalysis by Pd, both on single crystal surfaces and on catalysts.

Why focus on Pd? There are two main reasons. Firstly, Pd is perhaps the most reactively mutable metal in the transition series, depending on what else it is also present on its surface. This is especially so if it is alloyed with other elements. This is because it has the most filled d-band, with decreasing filling on moving to the left in the transition

series. In group 12 of course (Cu, Ag, Au) the d-band is completely filled and shifted down in energy from the Fermi level, leaving much lower electron density at the Fermi level. Secondly Pd has interesting surface chemistry and catalysis and is widely used in big scale industrial and smaller scale pharmaceutical heterogeneous catalysis [14,15]. Thus, it is important to understand the surface chemistry associated with this reactivity.

Here the behaviour of the pure metal, in both bulk single crystal and nanoparticulate catalyst form is presented, especially focusing on the effect of alloying and in an attempt to differentiate between ligand (electronic) and ensemble (surface atom configuration) effects. It will be concluded that the latter are the most important in determining reactivity patterns.

## 2. Results and discussion

### 2.1. The behaviour of Pd alone – ethene, formic acid and ethanol

The reactivity of Pd single crystals with the three molecules above is considered here to compare with the effects of alloying given in the later

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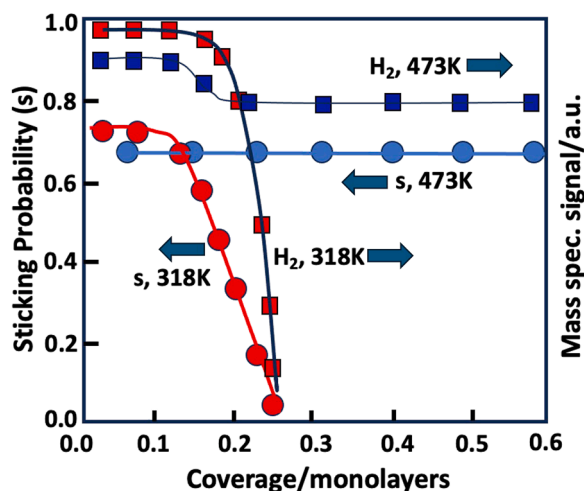


Fig. 1. The sticking probability of ethene and its dependence upon the amount adsorbed, measured using a thermal molecular beam [18]. Adapted with permission from J. Phys. Chem. B, 109 (2005), 2377–86. Copyright 2005 American Chemical Society.

sections.

### 2.1.1. Reactivity with ethene

The sticking of ethene on Pd(110) was determined using a thermal molecular beam and is shown in Fig. 1 below at two different crystal temperatures [16–20]. The reactivity is high, with just over 70 % of molecules adsorbing (initial sticking probability,  $s_0$  is 0.7) into a strongly held state at 318 K. At the same time hydrogen evolves from the surface due to the decomposition of ethene on the surface, but the reaction stops after the surface is covered by the carbonaceous intermediates left after decomposition. At that temperature that is mostly  $C_2H$  on Pd(110) [16,21,22]. If the reaction is carried out at 473 K  $s_0$  is very similar, but now carries on at the same rate with hydrogen evolution, apparently ad-infinitum. This is because the ethene decomposes to carbon on the surface and hydrogen in the gas phase. It might be expected that the carbon would poison the surface, but it does not because the carbon diffuses into the bulk of the crystal and the surface remains clean, hence the continued high reactivity [18,19]. A model for this behaviour is given in Fig. 2 [18]. In this figure there are temperature thresholds for reaction, namely molecular adsorption at low temperature, then partial dehydrogenation begins below room temperature, becoming complete by around 400 K, leaving carbon on the surface which can migrate below the surface at higher temperatures.

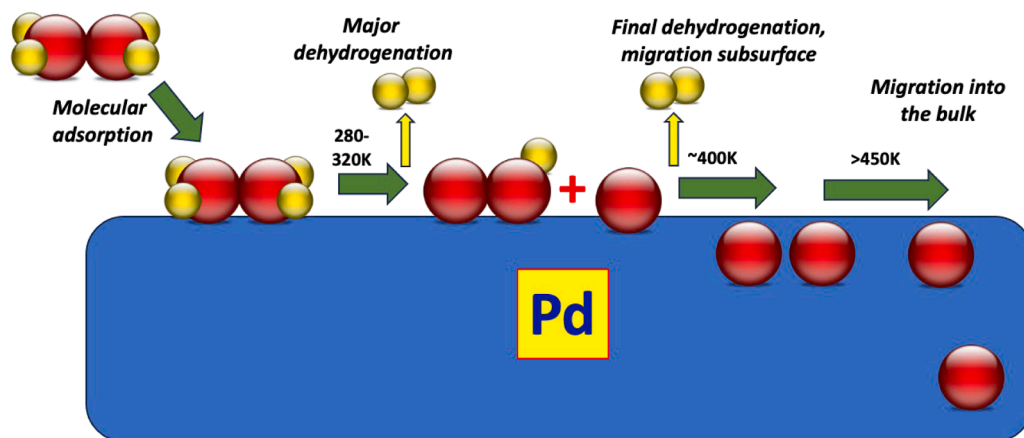


Fig. 2. A schematic model of the reactivity of ethene with Pd(110) and the effect of heating in decomposing it and depositing C on/in the material. Adapted with permission from J. Phys. Chem. B, 109(2005)2377–86 [18,20]. Copyright 2005 American Chemical Society.

### 2.1.2. Reactivity with ethanol

Another molecule which helps us understand reactivity of the alloys below is ethanol. TPD was used to study its reactivity and decomposition on the surface [23,24], Fig. 3. Here it can be seen that the main reaction is decarbonylation (reaction 1), that is, CO is extracted from the molecule and methane evolves at around 280 K. The dissociated methyl group is relatively stable to dehydrogenation under these conditions and so reacts with hydrogen atoms on the surface to produce the methane. However, some hydrogen also evolved which implies that there is also some dehydrogenation, which leaves carbon on the surface (reaction 2). CO is strongly adsorbed and is then left on the surface until it desorbs with a peak at around 500 K.



This behaviour can be compared it with the that of Cu for the reaction [25–27] (Fig. 3), since the effect of alloying Pd and Cu will be considered further below, in Section 2.1. Cu behaves very differently from Pd, enabling dehydrogenation of the molecule (reaction 3), producing acetaldehyde and hydrogen above ambient temperature, but unlike Pd, it cannot break the C–C bond.



### 2.1.3. Reactivity with formic acid

Formic acid is another molecule which helps with the understanding of the level of electronic effects on the reactivity. It is a bidentate adsorbate, that is, it anchors itself to the surface via the two oxygen atoms in the molecule, see Fig. 4. When adsorbed it makes a formate intermediate on the surface by loss of the acid hydrogen, and in TPD yields a coincident peak of  $CO_2$  and  $H_2$  at  $\sim 250$  K [28,29]. The effects of alloying with Cu will be described in the next section.

## 2.2. The effects of alloying Pd on its reactivity

### 2.2.1. PdCu

Alloying strongly affects the bulk electronic structure of the material. This was identified for PdCu by early valence band and Auger spectroscopy [30–32]. It was found that the d-band structure of Pd is strongly affected, with the d-band apparently filled and shifted down from the Fermi level and the material now looks more like Cu, that is, not like a transition metal. Thus, it might be expected it to behave chemically much more like Cu than Pd, at least if the d-band structure is a true indicator of reactivity. Below it will be argued that it is not.

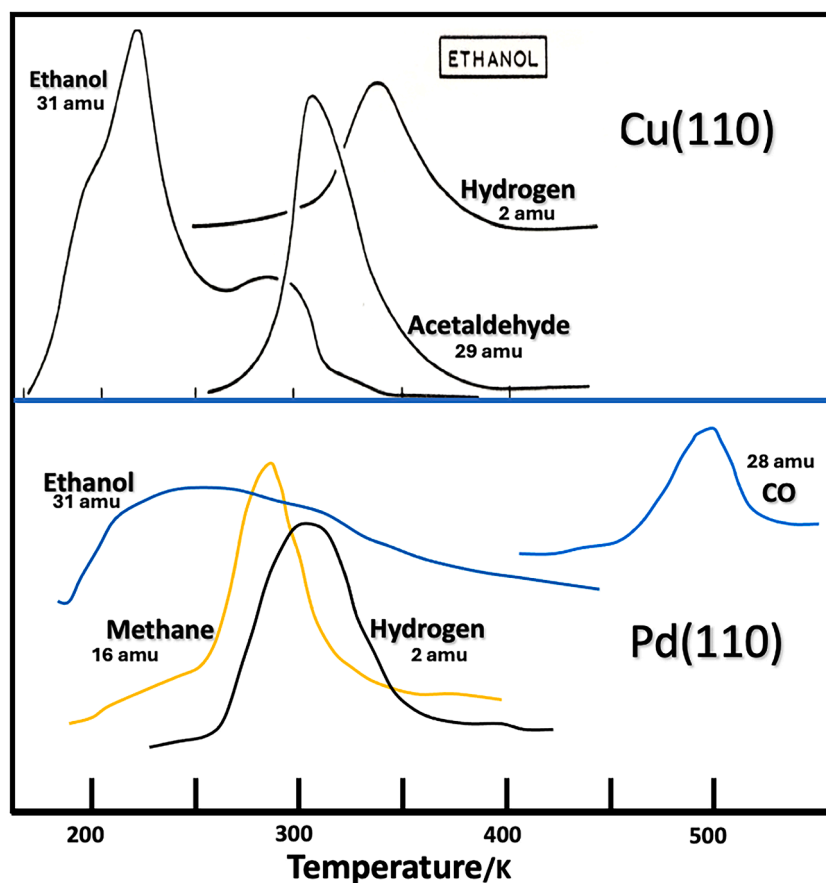


Fig. 3. TPD spectra comparing the behaviour of Cu and Pd for their reactivity with adsorbed ethanol. The ethanol was adsorbed from the gas phase onto a surface cooled to 180 K, the gas phase was then removed and heating begun [23-27]. Reprinted with permission from J. Phys. Chem. C 2022, 126, 15703–15709 [26]. Copyright 2022 American Chemical Society.

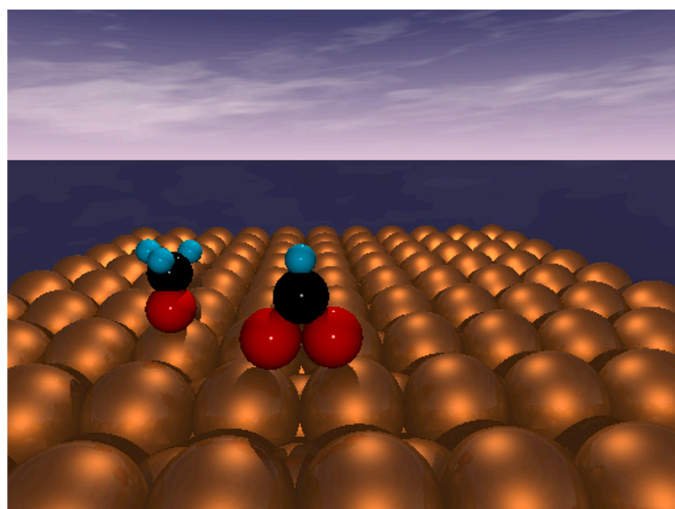


Fig. 4. Schematic model of monodentate (in this figure methoxy) and bidentate formate adsorption on a surface. Reprinted with permission from J. Phys. Chem. C 2022, 126, 15703–15709 Reprinted with permission from [26]. Copyright 2022 American Chemical Society.

A test of this is the behaviour with formic acid. Whether this is really a truly incisive test of the effects of alloying will be considered below. Formic acid decomposes by first deprotonation of the acid group to produce the formate intermediate as shown in Fig. 4, which has been shown to be a bidentate species [33-40]. In Fig. 5 it can be seen that

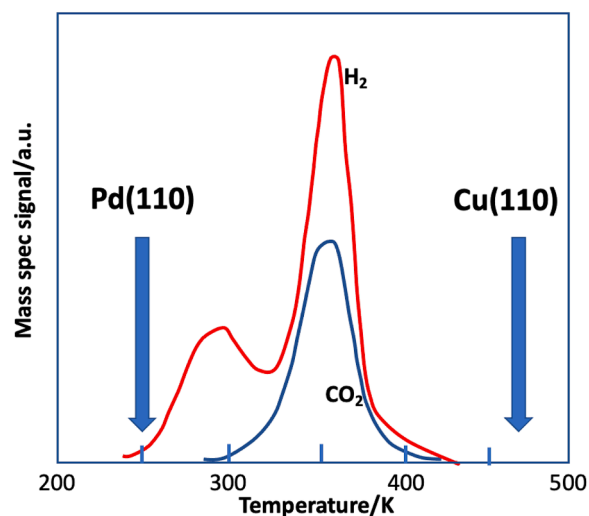


Fig. 5. TPD after formic acid adsorption on the CuPd(110) surface, and compared with the peak positions for pure Cu and Pd surfaces. Reprinted with permission from J. Phys. Chem. C 2022, 126, 15703–15709 [26]. Copyright 2022 American Chemical Society.

alloying has a big effect on the stability of the molecule compared with the two individual metals. It decomposes at around 470 K on pure Cu single crystal surfaces [33,35,39]. Pd also produces the formate, but the surface is much more reactive, with a peak of CO<sub>2</sub> and H<sub>2</sub> evolution below ambient temperature at ~250K [28,29]. When formic acid

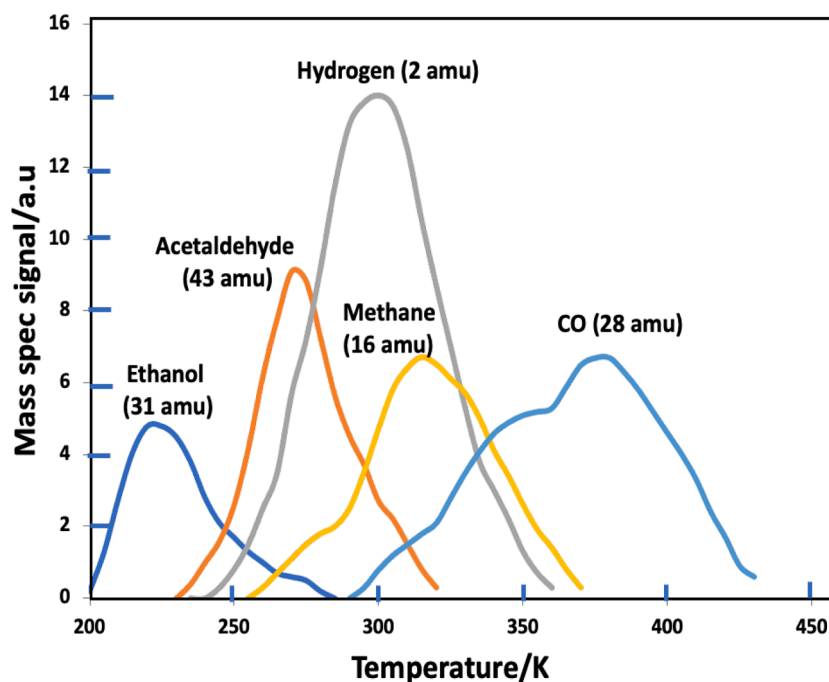


Fig. 6. The TPD products evolved after adsorption of ethanol on CuPd(110) at 190K [26]. Reprinted with permission from J. Phys. Chem. C 2022, 126, 15703–15709 [26]. Copyright 2022 American Chemical Society.

adsorption is carried out on a carefully prepared 1:1 alloy surface [41-44] then, as might be expected, the peak for formate decomposition is almost exactly between these two, at a temperature of 350 K. This could indicate a very strong electronic (ligand) effect, or it could simply be because the bidentate formate is binding between two different atoms (an ensemble effect).

It requires a different approach to determine which of these factors is most important, and for this a very specific *monodentate* adsorbate is used, namely ethanol. The reason for this approach is that, firstly, this molecule might be considered to be a more localised probe of reactivity and will bind to only a single atom on the surface, and secondly the behaviour is very different on Cu and Pd. On Cu it undergoes partial dehydrogenation to acetaldehyde as shown above in Fig. 3 [25,26], whereas on Pd it undergoes both total dehydrogenation and decarbonylation [23-25], as given in reaction 1 and 2 above.

However, for a CuPd alloy crystal [26], Fig. 6, both types of reaction occur, indicating that the individual nature of the two atoms in the alloy is little changed. This is probably because each atom bonds in a monodentate fashion to Cu and Pd. However, there is a shift in the peak positions – in the direction that might be expected. That is, acetaldehyde is shifted lower in temperature (by  $\sim 40$  K) compared with the pure Cu surface, indicating an increased reactivity, as might be expected if the Cu-bound ethoxy intermediate were adjacent to the more reactive Pd. The converse applies to the decarbonylation reaction typical of Pd, it is shifted to higher peak temperature (by  $\sim 30$  K), due to its presence next to the less reactive Cu. But could this be an electronic (ligand) effect of alloying? It is possible, but it could also be possible for the reason outlined above, that is, the mere adjacency of two different atoms of very differing reactivity.

So, is it possible to get a handle on the extent of electronic effects in this case? It can because the reaction of formic acid with an alloy dilute in Pd makes an interesting case. Here instead of the Pd being in the top layer it forms an ordered immediately subsurface layer in a  $(2 \times 1)$  structure, see Fig. 7. In this structure every surface Cu atom is bonded to a Pd below it, and the bulk electronic structure is changed in the way described above [30-32,46] (Fig. 5). However, unlike in Fig. 5, there is a much smaller shift in the formate decomposition temperature [45-47],

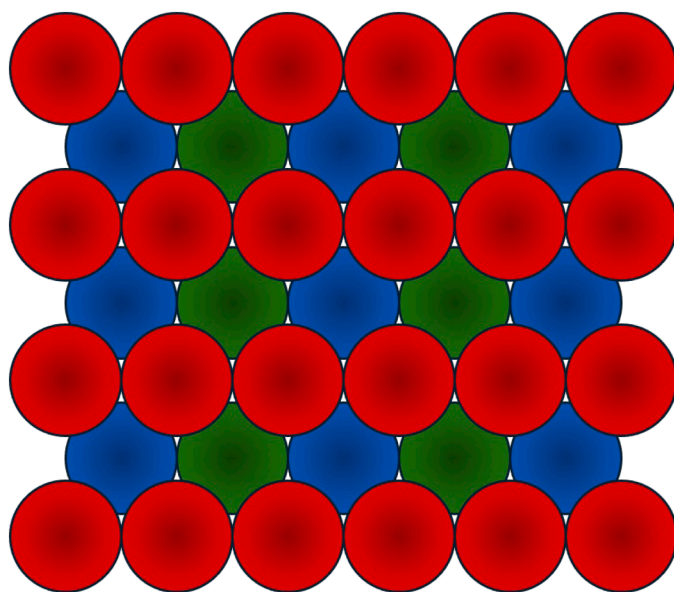


Fig. 7. Model of the  $(2 \times 1)$  structure of the 85:15 CuPd(110) surface. Top surface layer Cu atoms, red; underlayer Cu atoms are green and underlayer Pd atoms are blue.

reducing by between zero and 25 K, depending on which paper is examined for the formate TPD peak temperature [33-35,37,39], even though every Cu atom is bonded to a Pd atom. This is a relatively small effect, and maybe a result of the changed electronic structure. This is a much smaller effect than when Pd is in the top layer, where temperature shift is  $\sim 120$  K (Fig. 5), and so it is likely to be due to binding in the transition state during decomposition to a Cu atom. Thus, the electronic effect, if any, appears to be small, while the geometric, ensemble effect has a big effect on formate stability.

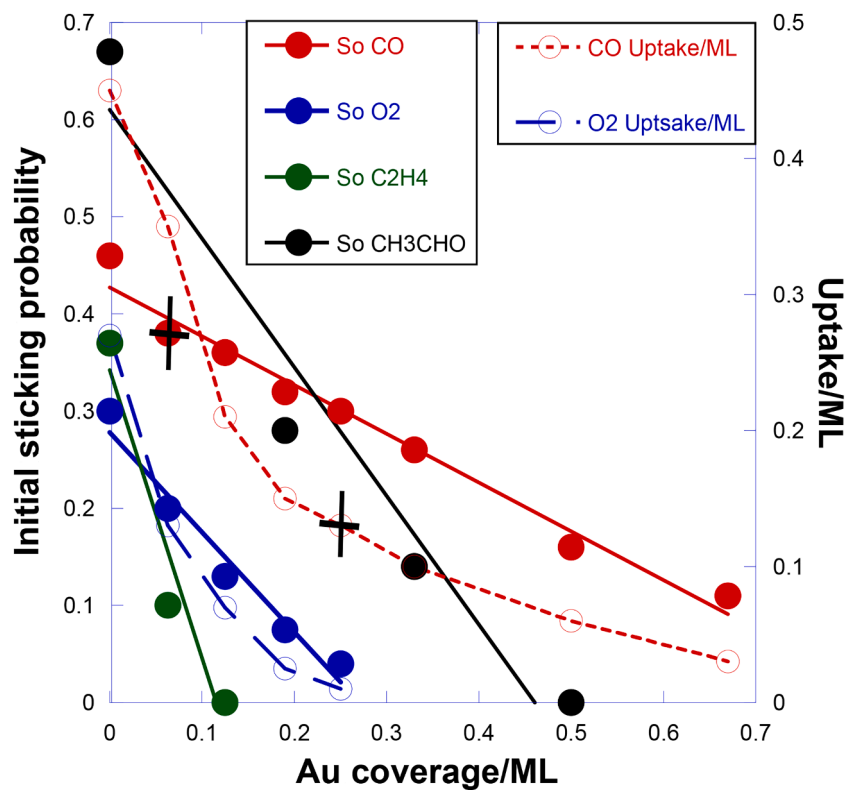


Fig. 8. The initial sticking probability and uptake dependence upon coverage of the surface by Au. Uptake was only measured for CO and oxygen. Adapted from reference 48.

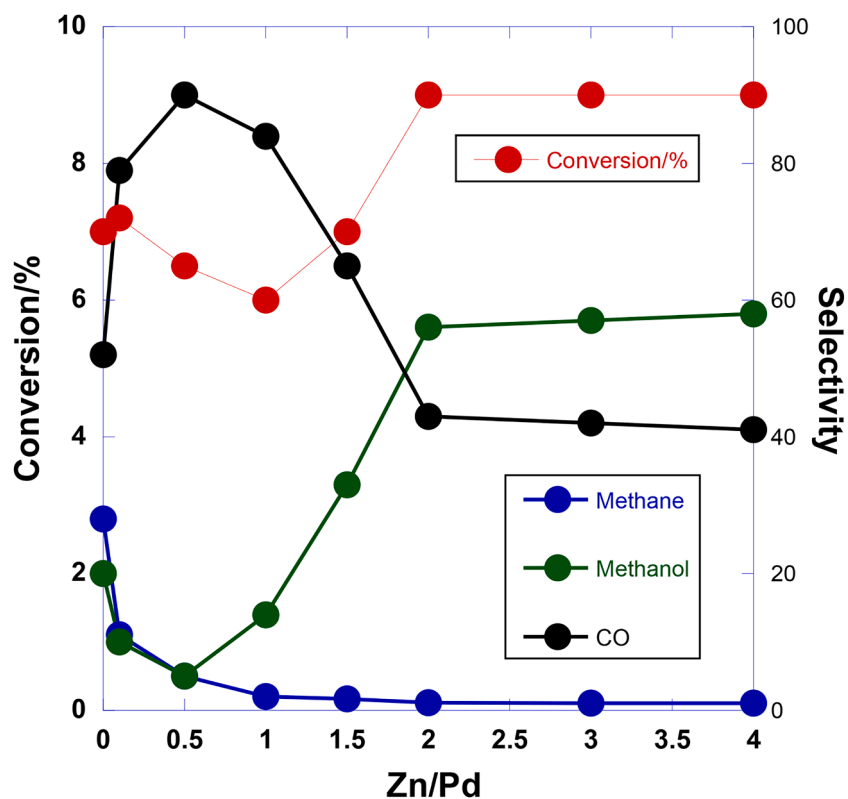


Fig. 9. The effect of adding Zn in the preparation of Pd/TiO<sub>2</sub> catalysts for the reaction between CO<sub>2</sub> and H<sub>2</sub>. Conditions: 20 bar total pressure, 503 K, flow rate 30 ml/min, H<sub>2</sub>:CO<sub>2</sub> ratio = 2.5 (plus 24 % inerts in the flow), 0.5 g of catalyst [53,54].



### 2.2.2. AuPd

Now turning to a different system – alloying Pd with Au. The effects on reactivity of the surface in terms of adsorption of a range of molecules, namely O<sub>2</sub>, CO, C<sub>2</sub>H<sub>4</sub> and CH<sub>3</sub>CHO [48,49] is shown in Fig. 8. These results are for the Pd(111) surface with different amounts of Au deposited by metal vapour deposition (MVD). The initial sticking coefficient (the probability of a molecule being trapped into a long-lived state) for each molecule on the clean surface is high. But they are different, with the highest being for acetaldehyde at 0.7, whereas the lowest is for oxygen at 0.3. However, the effect of gold coverage is dramatic with a continuous decrease for all these molecules with increasing Au coverage on the surface. The initial sticking can be fitted, within experimental uncertainty, as linear with increasing Au, but a notable distinction is the point at which blockage of adsorption is completed, this being approximately in the order C<sub>2</sub>H<sub>4</sub> (by ~0.1 ML Au coverage), O<sub>2</sub> (by ~0.25), CH<sub>3</sub>CHO (~0.5) and CO (~1.0). It might be imagined that ethene requires a number of sites on the surface to dissociate at this temperature (373 K), probably initially from a flat-lying molecular state. This requires a large ensemble of sites on the surface, hence why it is blocked at such a low coverage of Au.

O<sub>2</sub> needs at least two sites to dissociate, while CO is capable of terminal adsorption (though it does prefer bridge sites, at least at low coverage). Perhaps acetaldehyde is the odd one out, since it would be thought that it would need at least as many sites as ethene. However, as can be seen in Fig. 3, methane and hydrogen desorb fast at this temperature, leaving just CO on the surface, and presumably plenty of free sites, at least at the beginning of reaction. By 0.5 monolayer of Au, the adsorption of acetaldehyde is blocked, presumably because no dual sites remain.

The molecule uptake dependence on coverage by Au was determined, but was only carried out for CO and O<sub>2</sub> [48]. For the oxygen, the saturation uptake was severely curtailed from the uptake of about 0.4 monolayers on the clean surface down to zero at approximately 0.25 monolayers of Au. For CO, the effect is most marked at low Au coverage where there is a steep drop in uptake from 0.4 monolayers with no Au but is halved by 0.2 monolayers of Au deposition. The loss of adsorption then slows down and continues even up to 0.67 monolayers of Au when the uptake has dropped to 0.03. This almost certainly represents blocking of the bridge-bound CO species at low Au coverage, leaving adsorption onto on-top only sites at high coverage, which then begin to be blocked at high Au coverages. This is similar to the findings of others [50-52], who generally find a weakening of adsorbate binding in the presence of Au, due to dilution of Pd ensembles.

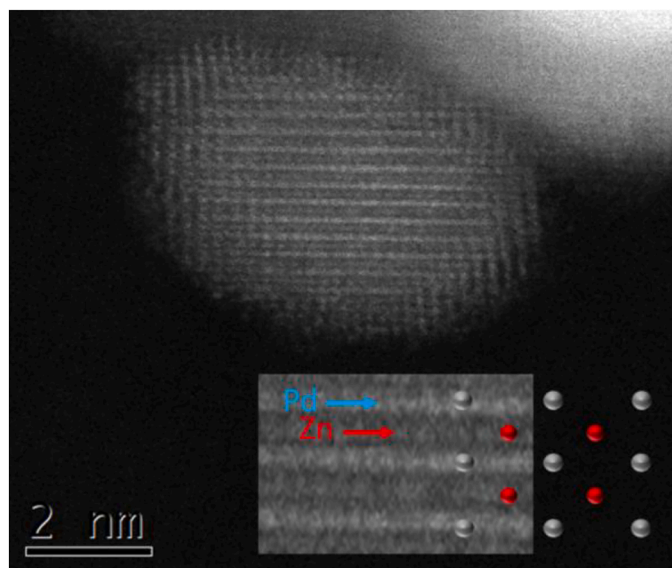
### 2.3. Pd alloying on catalysts

The effect of alloying Pd with Zn, In, Ga on the activity of Pd catalysts for methanol synthesis has been examined at high temperatures and pressures.

Pd itself is not a good material for methanol synthesis from synthesis gas (in this case CO<sub>2</sub> and H<sub>2</sub>). A series of catalysts were made for Pd supported on TiO<sub>2</sub>, with varying amounts of Zn added [53,54]. These catalysts were made by CVI (chemical vapour impregnation). As can be seen in Fig. 9, for Pd alone the main products from such a reaction are CO (the reverse water gas shift reaction, reaction 4 below) and methane (methanation reaction 5 below) with some methanol, reaction 6.



However, when Zn is added to the material, then dramatic effects on the chemistry can be observed. At even very low levels of Zn (Zn:Pd 1:10) there is already a significant reduction in methane production, by approximately a factor of 2. This effect increases with more Zn, until the



**Fig. 10.** Lattice imaging of the structure of the PdZn particles in sample 1, 5 % Pd/ZnO1, after reduction, using HAADF STEM, together with a model showing the [0–10] projection of the top layer [55]. Reprinted with permission from ACS Catal., 12 (2022), 5371–9. Copyright 2022 American Chemical Society.

methane production is very low at a ratio of 1:1. The CO increases up to a ratio of 0.5, at the expense of both methane and methanol. However, as the ratio increases further, and especially above a 1:1 ratio, so the methanol increases dramatically, at the expense of CO. By 2:1 ratio the selectivity to methanol is very high at 60 %, with most of the rest being CO. What is happening here is that, at ratios <1:1, the Zn present in the catalyst is being utilised to make the PdZn alloy, as can be seen by HRTEM in Fig. 10 [55]. This alloy is the 1:1 β-PdZn alloy. This then knocks out CO dissociation on the Pd surface, which is required for methane production. Since such a big effect on methane is already seen at a ratio of Zn:Pd of 0.1 it is likely that Zn is segregated to the surface of the Pd nanoparticles which are present. These are, on average ~ 4 nm in diameter [55]. The reason that selectivity to methanol increases when the ratio increases above 1:1 and is very high when it reaches 2:1 is that ZnO is a crucial factor in the synthesis, probably adsorbing the CO<sub>2</sub> in a favourable configuration. Up to a 1:1 ratio, the most favourable situation for Zn is in the Pd alloy, and when this value is exceeded the Zn forms as ZnO on top of the support TiO<sub>2</sub>. It is also important to note that it is used in commercial catalysts and is crucial for efficient methanol synthesis.

A little like the data above for Cu and Au it can be argued in this case that the dilution of ensembles of Pd is necessary for stopping the dissociation of CO on the metal surface and this occurs by dilution with Zn. Jeroro, Vohs et al. also consider this to be mainly an ensemble effect on CuPd, but consider electronic effects to be important too on PdZn, since, at very low coverages of Zn on Pd(111) the CO desorption peak temperature is already decreased on Pd sites [56,57]. Such effects on the catalysis can also be obtained using other reducible oxides, such as Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> [58,59], as shown in Fig. 11 below. In all of these cases the alloy formation is driven by a very large energy of mixing with the Pd to form the alloy. PdZn is favoured for the Zn system and is usually the only ordered alloy seen in XRD [60-65]. This is because it is clear from Fig. 12 that it has the most favourable enthalpy of mixing compared with the other possible ordered alloy structures. Even though this is not so clear for Ga and In (several alloys seem to be similar in energy of mixing, Fig. 12), Pd<sub>2</sub>Ga and PdIn are favoured [58,59,66,67]

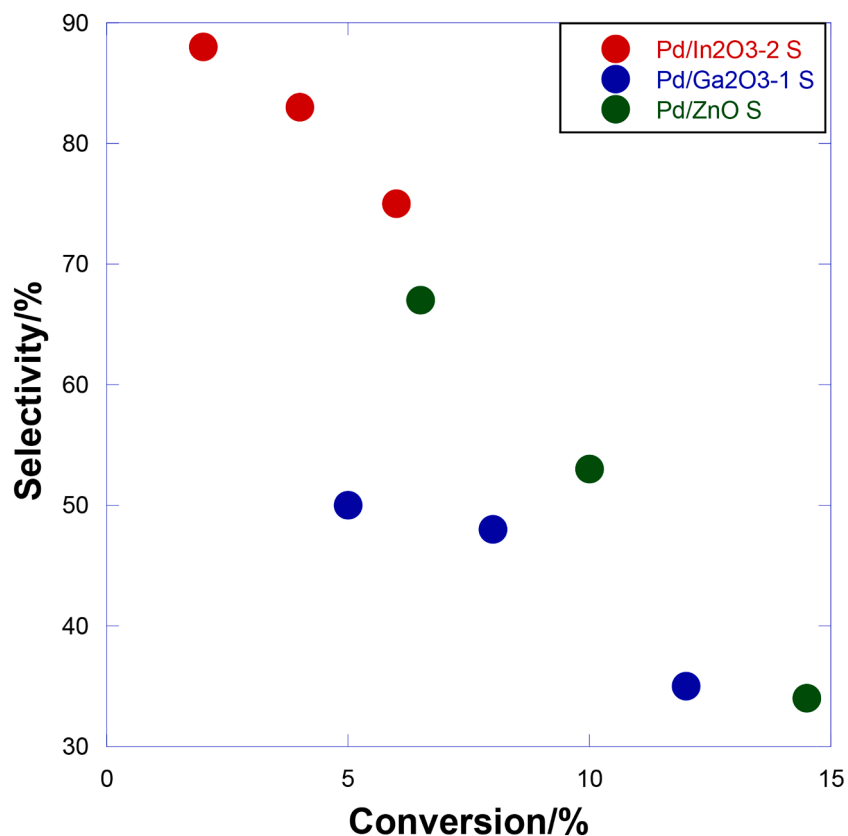


Fig. 11. Selectivity versus conversion data for Pd on three supports, which are all effective for methanol synthesis, once the Pd has alloyed with the cationic component after reduction.

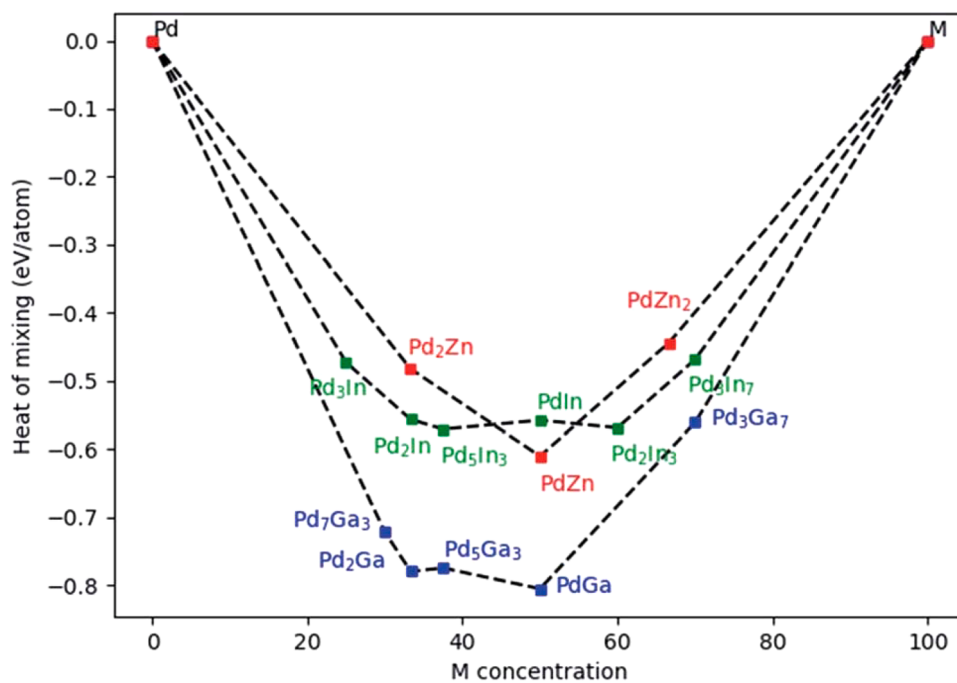


Fig. 12. The heat of mixing of Pd with Zn, Ga and In [58]. Reproduced from Faraday Discuss., 242 (2023), 193 with permission from the Royal Society of Chemistry.

### 3. Conclusions

The reactivity of Pd is modified by alloying, and although the d-band structure is strongly affected by such alloying, with d-band filling, the

surface chemistry is still dominated by elemental characteristics. Some specific examples have been given, and this is especially demonstrated by the reactivity of ethanol with the CuPd surface. Cu and Pd behave very differently, the former showing partial dehydrogenation to

acetaldehyde, whereas Pd dehydrogenates the molecules and split the C–C bond to produce methane during reaction. The alloy still shows both elemental reaction characteristics, producing both methane and acetaldehyde. It seems that, for the molecules and alloy systems reported here, the reactivity is dominated not by electronic ('ligand') factors, but by the geometric ('ensemble') arrangement of atoms at the surface. To quote Thomas and Thomas [68] "the concept of ensembles has gained considerable prominence because without it, it seems impossible to interpret the catalytic behaviour of alloys"

### Data availability

Information on the data underpinning the results presented here, including how to access them, can be found at the Cardiff University website at <https://orca.cardiff.ac.uk/id/eprint/54930/> and at <http://s://orca.cardiff.ac.uk/id/eprint/56027/>, and at [doi.org/10.1016/j.apcata.2024.119735](https://doi.org/10.1016/j.apcata.2024.119735) and <https://doi.org/10.1021/acs.jpcc.2c04881> and by contacting the author.

### Author statement

This review article was conceived and written in its entirety solely by the author.

### CRediT authorship contribution statement

**Michael Bowker:** Writing – original draft, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

### Declaration of competing interest

The author declares no competing interests

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