

Supplementary material

Low-temperature aqueous-phase reforming of ethanol for CO-free H₂ production on bimetallic PdZn catalyst

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Measurement of active sites in the supported Pd and Pd-Zn catalysts

As explained in the manuscript, it is difficult to use chemisorption to count sites in Pd and PdZn due to variable adsorption stoichiometry for CO and absorption of H₂ in Pd. We therefore used reactivity for CO oxidation to count active sites. This involved two steps, first we measured the specific activity of metal powders of Pd and PdZn where number of surface atoms per gram were known from the BET surface area and bulk composition. The known TOF was then used to back out the number of active sites in the supported metal catalysts. The two steps involved are explained below.

Measurement of TOF for CO oxidation on the metal powders (Pd, PdZn_α, PdZn_β)

CO oxidation experiments were carried out on a Varian CP-4900 Micro-GC utilizing a TCD detector with 20 mg of each sample being used for each experiment. Each sample was reduced at 250 °C in situ for 2 h in 6% H₂/He followed by a cool down in 6% H₂/He to room temperature. The samples were then exposed to CO oxidation conditions which used 1.5 mL/min CO, 1 mL/min O₂, and 75 mL/min He (~2%CO). The temperature was then ramped to 300 °C with a ramp rate of 2 °C/min and sampling performed every 3 min.

Pure Pd powder from Aldrich and pure aerosol-derived PdZn metal powders were used as reference standards to determine the specific activity of Pd and PdZn. The Pd powder was reduced at 500 °C for 2 h under 6% H₂/He followed by a cool down in 6% H₂/He to room temperature. The sample was exposed to the same CO oxidation conditions as above and was ramped to 300 °C at 2 °C/min. The sample was repeatedly put through the CO oxidation showing the results were reproducible. The same experiment was carried out for the aerosol PdZn powder.

The equations below show how the TOF is calculated from our pure Pd and PdZn powders. The Turnover Frequency (TOF s⁻¹) was calculated knowing the amounts of CO₂ produced per second and the number of surface Pd sites calculated using the BET surface area of each powder.

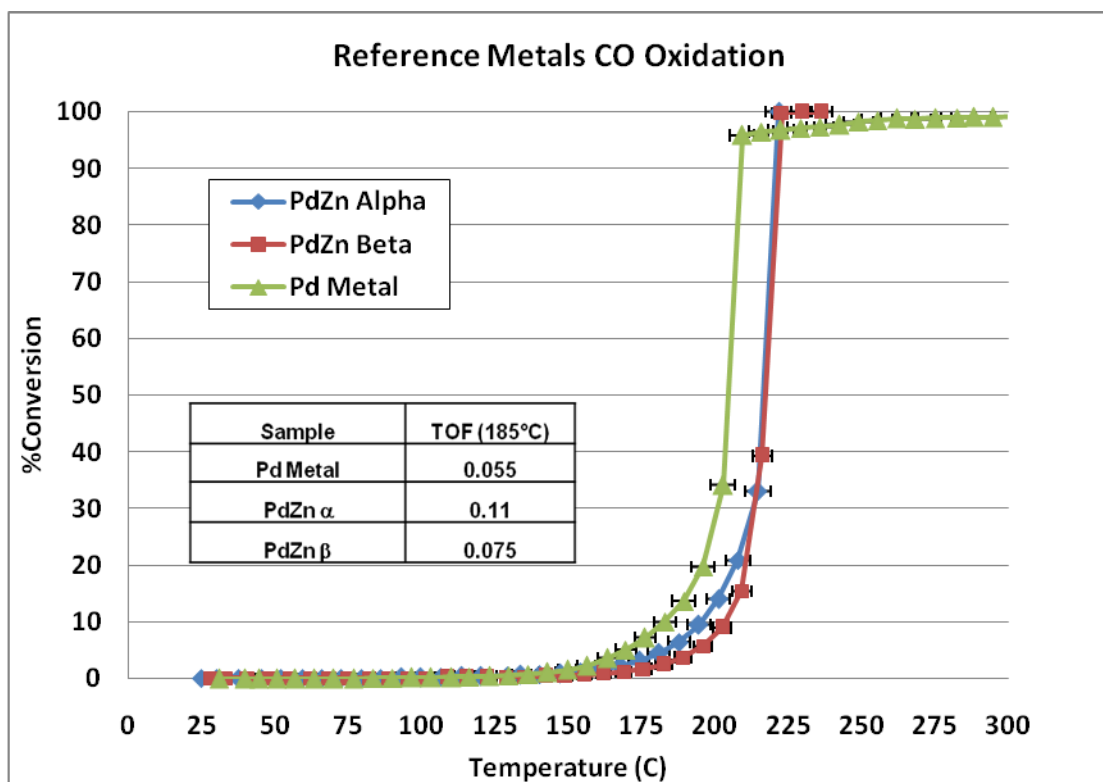


Figure S1. CO Oxidation light-off curves for the reference Pd, PdZn $_{\alpha}$, and PdZn $_{\beta}$ samples with TOF at 185°C.

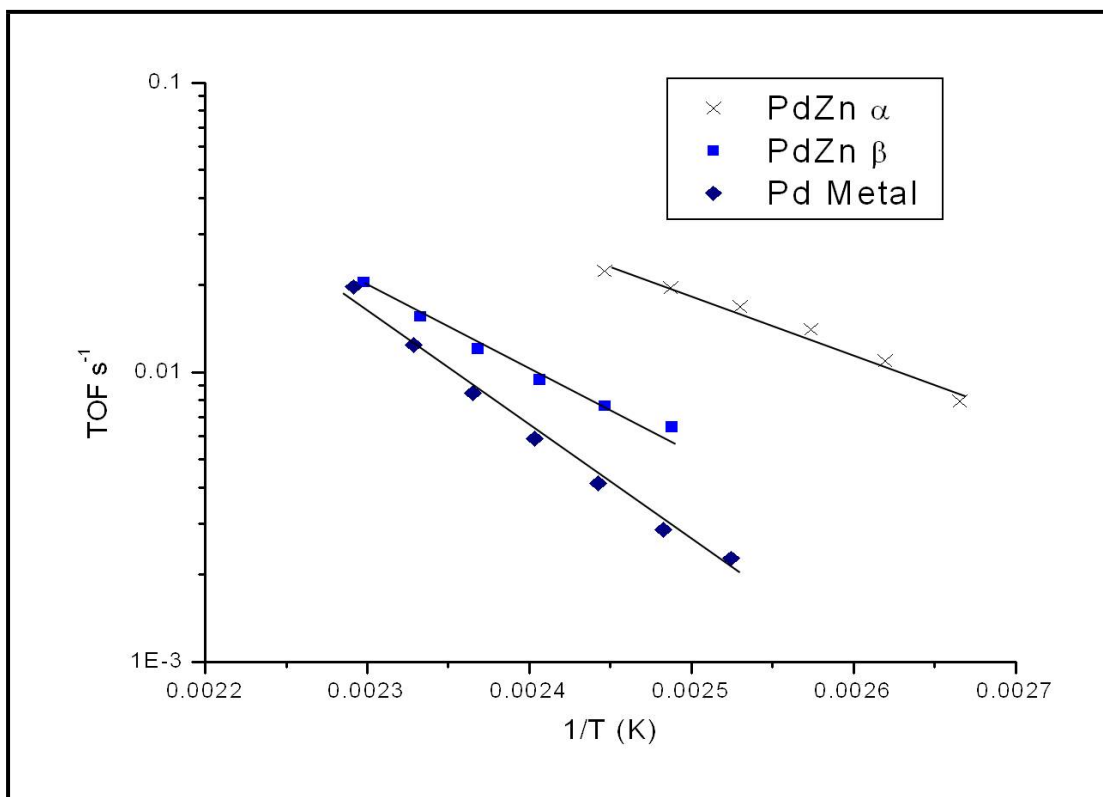


Figure S2. The TOF vs 1/T for the reference Pd, PdZn $_{\alpha}$, and PdZn $_{\beta}$ samples.

$$\text{moles Pd}_{\text{surface sites}} = \frac{\text{catalyst mass(g)} \times \text{BET surface area(m}^2/\text{g)}}{\text{Area of Pd atom (m}^2/\text{atom)} \times \text{Avogadro \#(atoms/mol)}} \quad (\text{all known})$$

$$\text{moles CO converted sec}^{-1} = \frac{\text{known feed(sccm)} \times (1 \text{ mol} / 22,400\text{cc}) \times \text{fraction converted}}{60 \text{ (sec/min)}}$$

$$\text{TOF(s}^{-1}\text{)} = \frac{\text{moles CO converted sec}^{-1}}{\text{moles Pd}}$$

Estimation of number of sites in the supported catalysts

Using the TOF for the pure Pd and PdZn powders above, we were able to calculate the number of active Pd sites on the Pd/Carbon and PdZn/Carbon samples. We performed CO oxidation measurements of the supported catalysts using the same methods and procedures as for the reference catalysts.

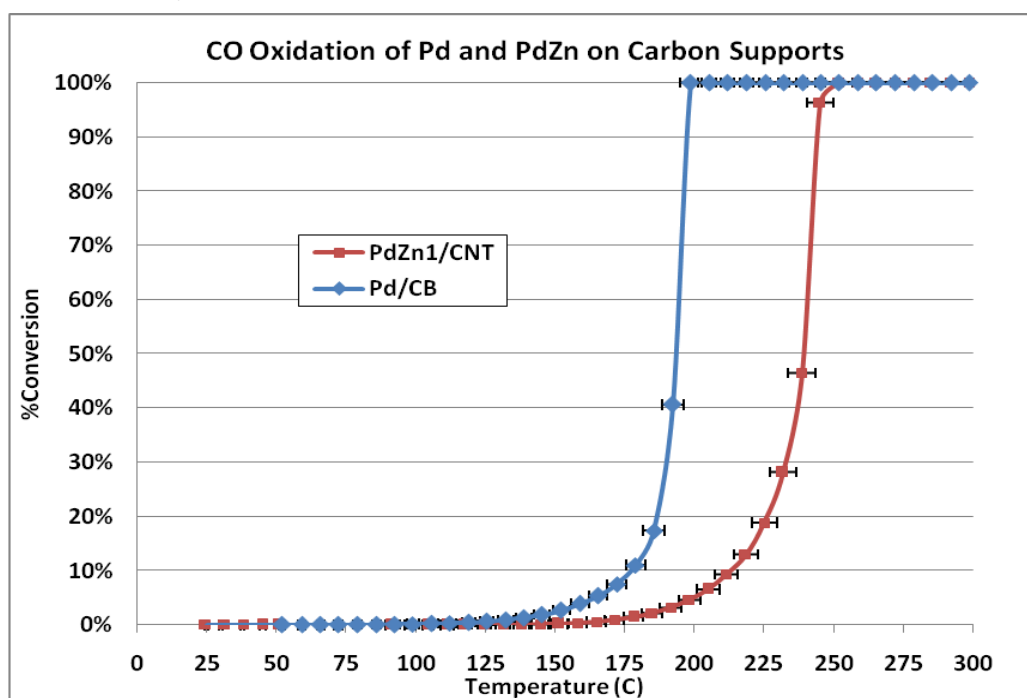


Figure S3. CO Oxidation light-off curves for PdZn and Pd carbon supported catalysts.

From our reference catalyst PdZn_β shown in Figure S1, where the atomic ratio of Pd:Zn is 1:1, we know the TOF is 0.075s⁻¹ at a temperature of 185°C. We also know at a temperature of 185°C the PdZn₁/CNT has a conversion of 2.2% from the data in Figure S3. At that conversion the number of moles CO converted per second is known since the feed is also known. With this information the number of sites can be calculated using the equation below.

$$\text{Number of sites} = \frac{\text{moles CO converted sec}^{-1}}{\text{TOF measured from reference sample}} \times \text{Avogadro(atoms / mol)}$$

	TOF for Ref. Cat.	%Conversion	Mol. CO Converted/s	# of Sites	Total #of Pd atoms in supported Catalyst	Dispersion%
PdZn	0.075	2.2% for PdZn/CNT	2.50E-08	1.90E+17	5.60E+18	3.5
Pd	0.055	17.4% for Pd/CB	1.90E-07	2.20E+18	5.60E+18	37.5

The total number of Pd atoms available for the carbon supported catalyst is calculated using the wt% of Pd for the amount of used sample for the reaction. The dispersion, shown in the table above, can then be calculated since dispersion is the number of sites exposed (surface sites) that have been calculated in the equation above divided by the total number of atoms of the metal, in this case the Pd deposited on the carbon support. For the PdZn/CNT a dispersion of ~3.5% was calculated and using the same method, a dispersion of ~37.5% was calculated for a Pd/CB sample. Calculations were carried out similarly for the remaining Pd or PdZn carbon supported samples.

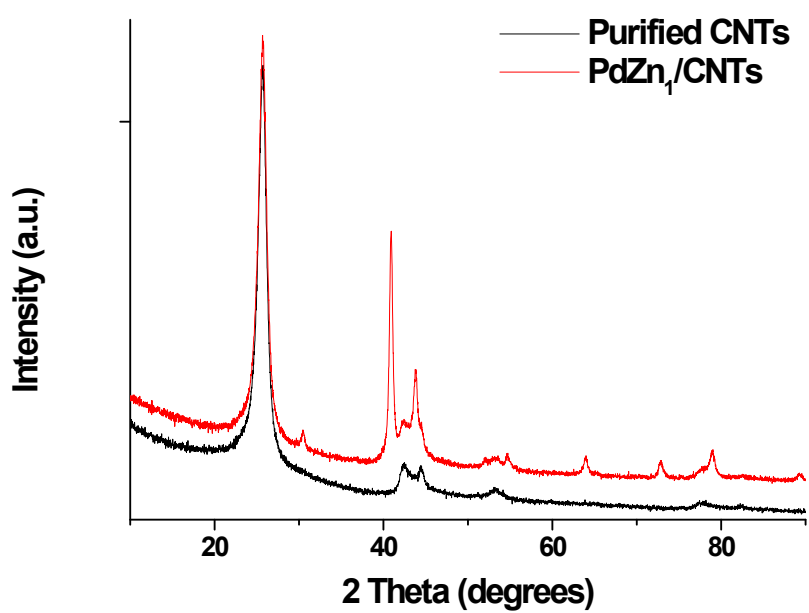


Figure S4. XRD patterns of CNTs and PdZn₁/CNT.

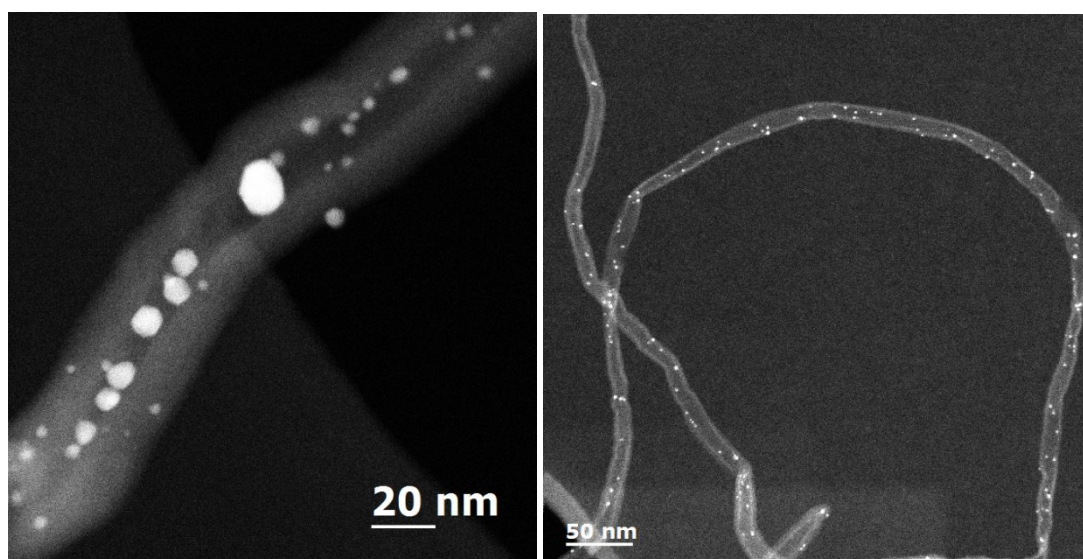


Figure S5. HAADF-STEM images of (a) PdZn₁/CNT and (b) PdZn₁/CNT-1 showing PdZn particles inside the CNT pore and the larger particles on the higher loaded catalyst on the left.

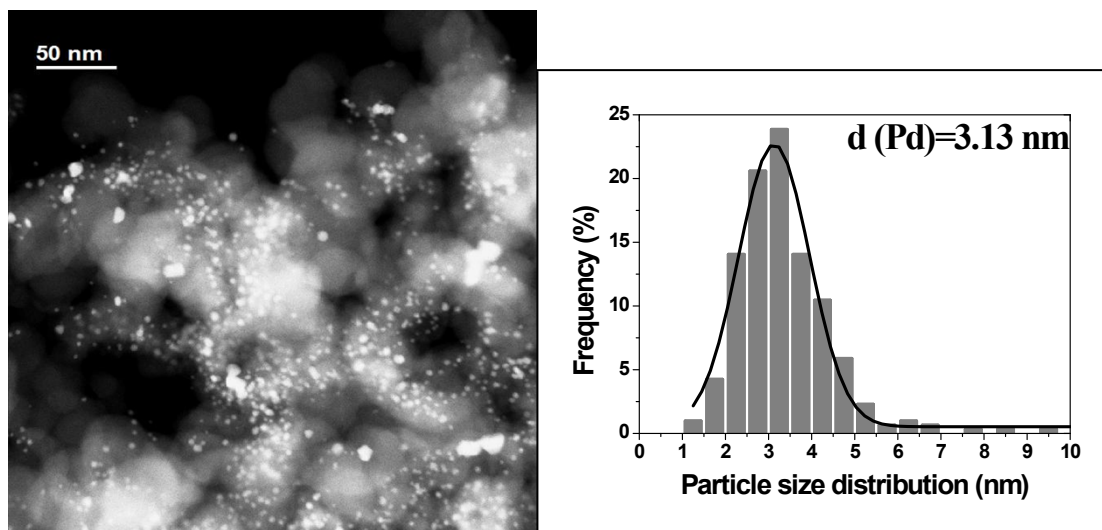


Figure S6. HAADF-STEM image of spent Pd/CB and particle size distribution after aqueous phase reforming of ethanol.

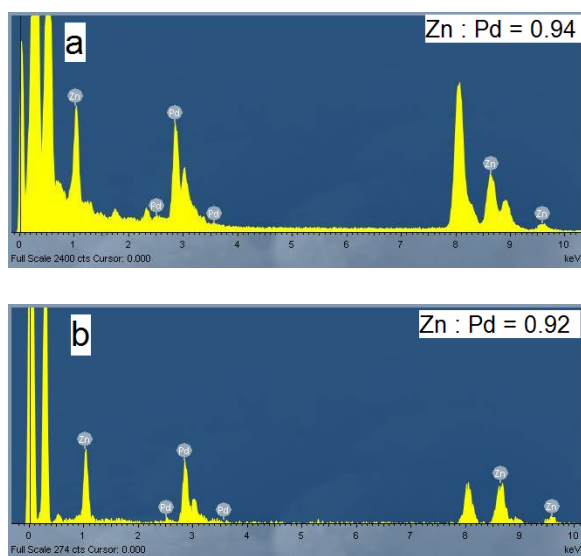


Figure S7. Energy dispersive spectroscopy of PdZn₁/CB catalyst (a) before and (b) after aqueous-phase reforming of ethanol.

Carbon and hydrogen balance calculation for the most active catalyst PdZn₁/CNT

According to the product distribution in Table 2, using as basis 1 mole of total products, the number of carbon and hydrogen atoms can be calculated for the effluent stream. We include also the H₂ produced. The material flows are also included on our proposed mechanistic model shown on the next page.

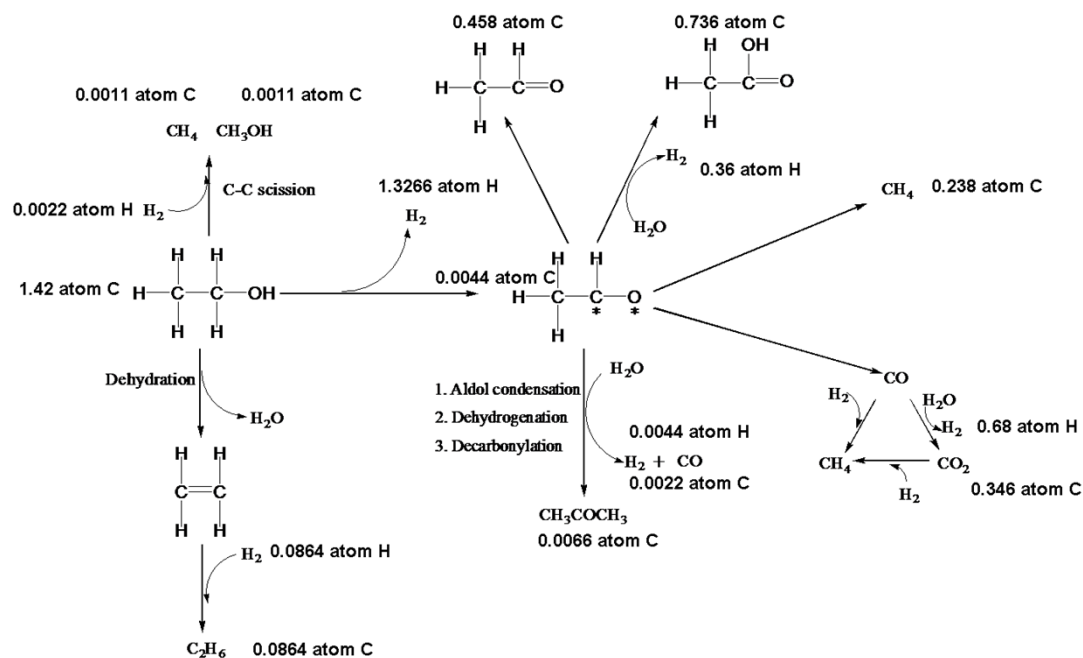


Figure S8. The overall C and H balance for PdZn₁/CNT catalyst. Using the mole fractions in the effluent, Table 1 (C species only) we calculate the number of carbon atoms in each product stream and include the corresponding H₂ flows as appropriate. This allows us to calculate the net production of H₂ per mole of ethanol.

$$\text{C atoms} = 0.238 + 0.346 + 0.736 + 0.0066 + 0.0864 + 0.0044 + 0.0011 + 0.0011 + 0.022 = 1.4218$$

$$\text{H atoms} = -0.0022 - 0.0864 + 1.3266 + 0.736 + 0.68 = 2.654$$

Then: H/C = 2.654 / 1.42 = 1.88, which is consistent with 1.9 in Table 2.

The varying H₂ selectivity per mole of ethanol converted (and resulting CH₄/CO₂ ratio) can be explained by the hydrogenation of CO or CO₂ to form CH₄, which consumes H atoms.