On the conversion of CO_2 to value added products over a hybrid PdZn/H-ZSM-5 catalyst: excess Zn over Pd, a compromise or a penalty?

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Supporting information

N_2 adsorption

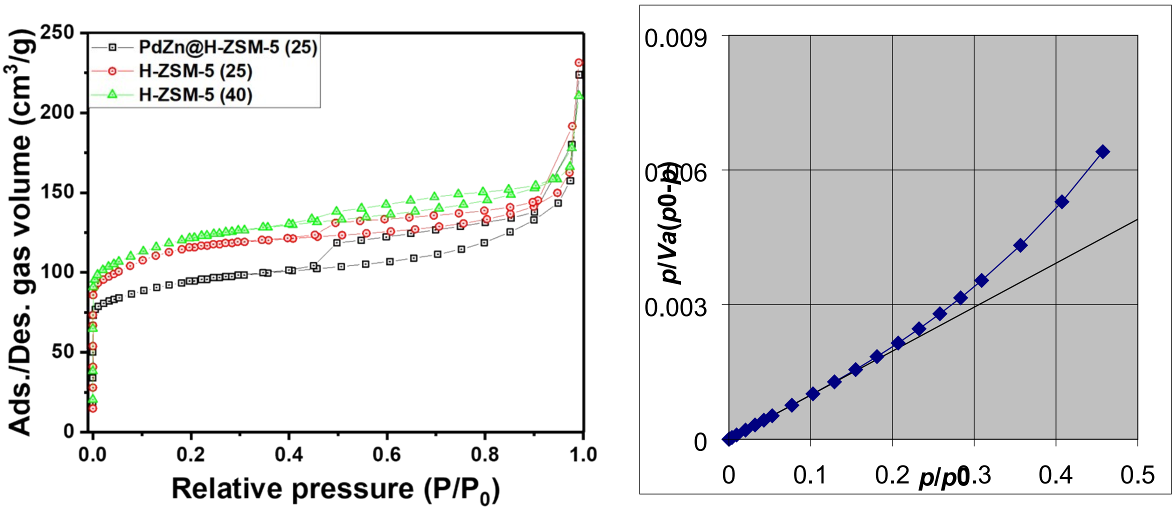

Fig. S 1 N_2 Adsorption and desorption of the PdZn@H-ZSM-5 and H-ZSM-5 (left) and $p/v(p_0-p)$ versus p/p_0 plot for estimating the BET surface area, where typical pressure ranged from 0 - 0.2 was used (right).

TEM imaging

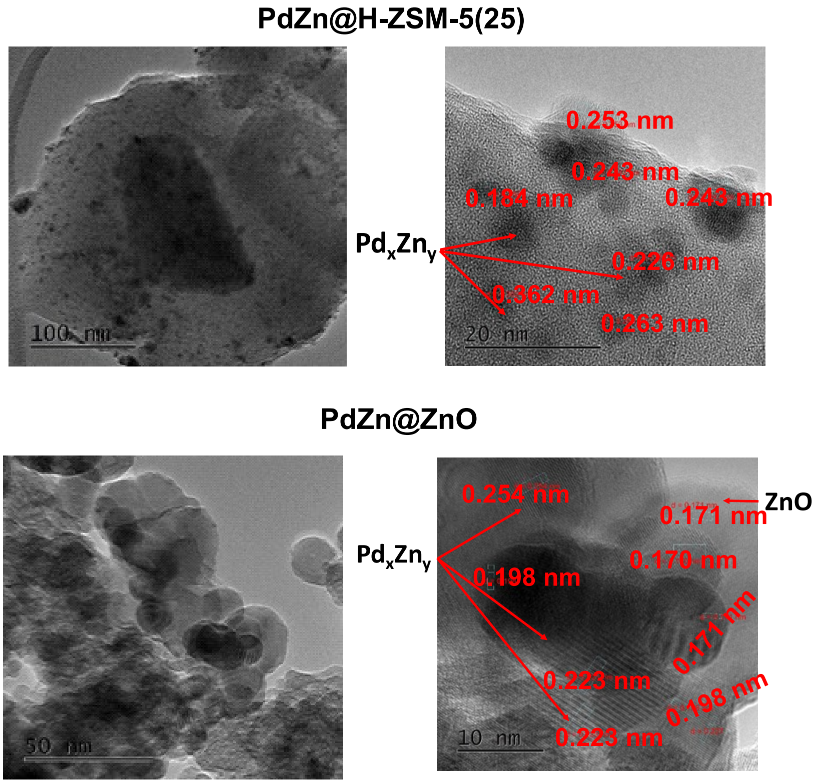

***Fig. S 2** (HR)TEM of the catalyst samples investigated. The PdZn@H-ZSM-5 sample was reduced in H_2 at 500 °C for 4 h, and the PdZn@ZnO sample was pretreated in H_2 at 400 °C for 1 h, prior to the investigation. The PdxZny phases were determined using the lattice spacing (d-values).*

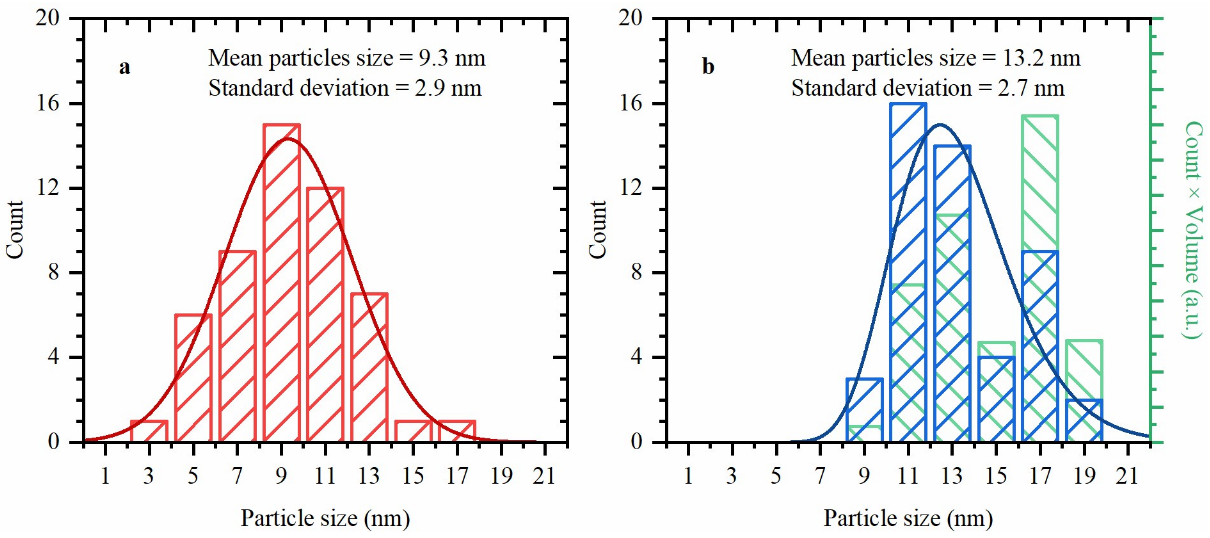

***Fig. S 3** Particle size distribution based on TEM imaging for PdZn@H-ZSM-5 (a) and PdZn@ZnO + H-ZSM-5 (b) samples. The green bars in panel (b) correspond to the data weighted by particle volume.*

FT-IR spectroscopy of adsorbed pyridine

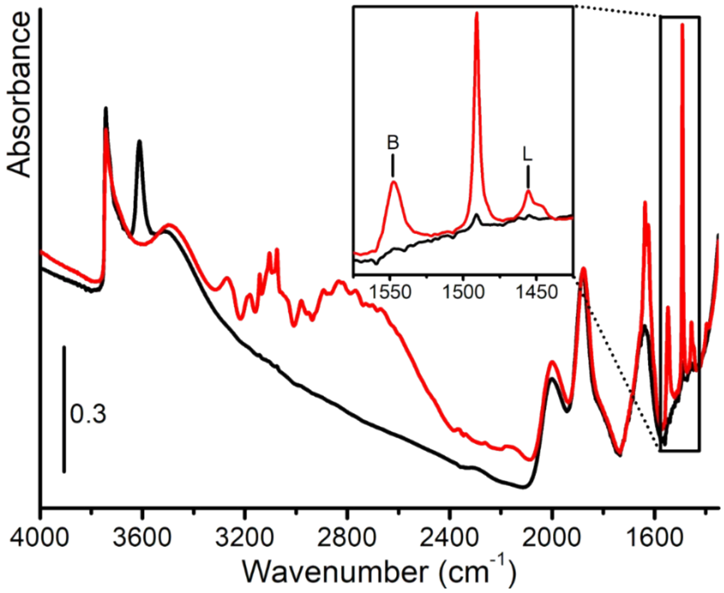

Fig. S 4 Typical FT-IR spectra of a ZSM-5 zeolite prior (black) and after (red) interaction with gaseous pyridine. Inset show the signal arising after interaction between pyridine and acid sites present in the zeolite, namely Brønsted type (labelled as B) and Lewis type (labelled as L).

Operando XAS and PXRD studies

In the beginning of the activation, XANES and EXAFS data (Figure S5 and Figure 5c of the main text) of PdZn@ZnO+H-ZSM-5 have some features of metallic Pd which disappear upon activation evidencing the formation of Pd-Zn alloy (Section 3.3. of the main text). Fourier analysis of EXAFS reveals that after activation there is a minor fraction of non-alloyed Pd particles which results in a shoulder at ca.2.8 Å (phase-uncorrected) in the FT-EXAFS data (Figure S6a). However, this feature completely disappears for the spent catalyst (Figure S6b), indicating that the alloying process proceeds under reaction conditions.

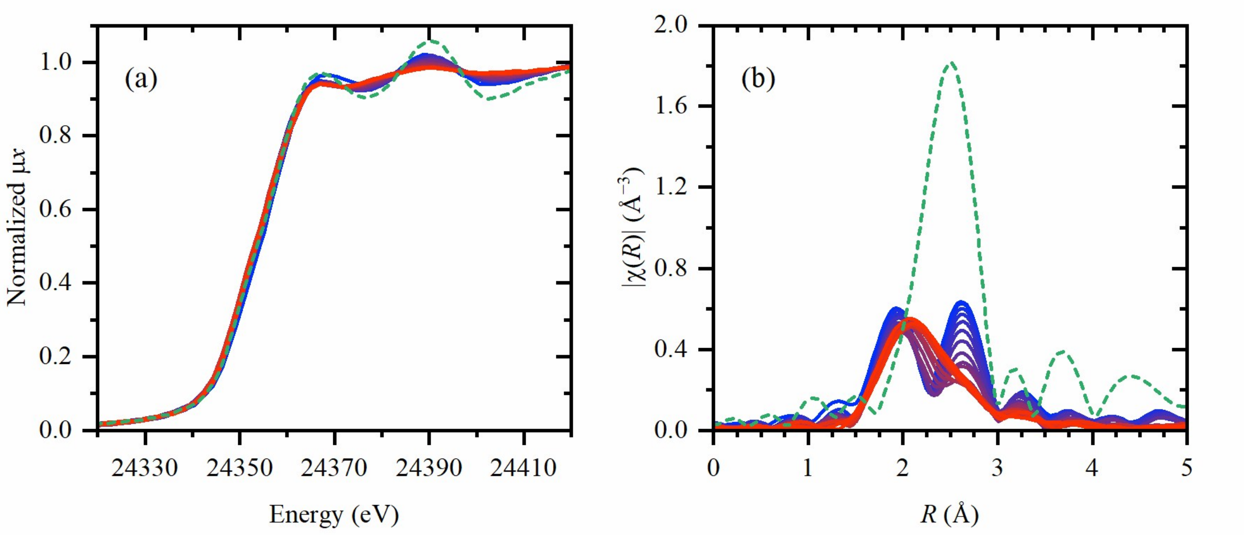

Fig. S 5 Two panels reproduce the XANES (a) and FT-EXAFS(b) data presented in Figure 5c of the main text, but without the first two points, at which PdII was present. Dotted green lines correspond to the ca. 3 nm Pd particles measured at room temperature at BM31 beamline of ESRF

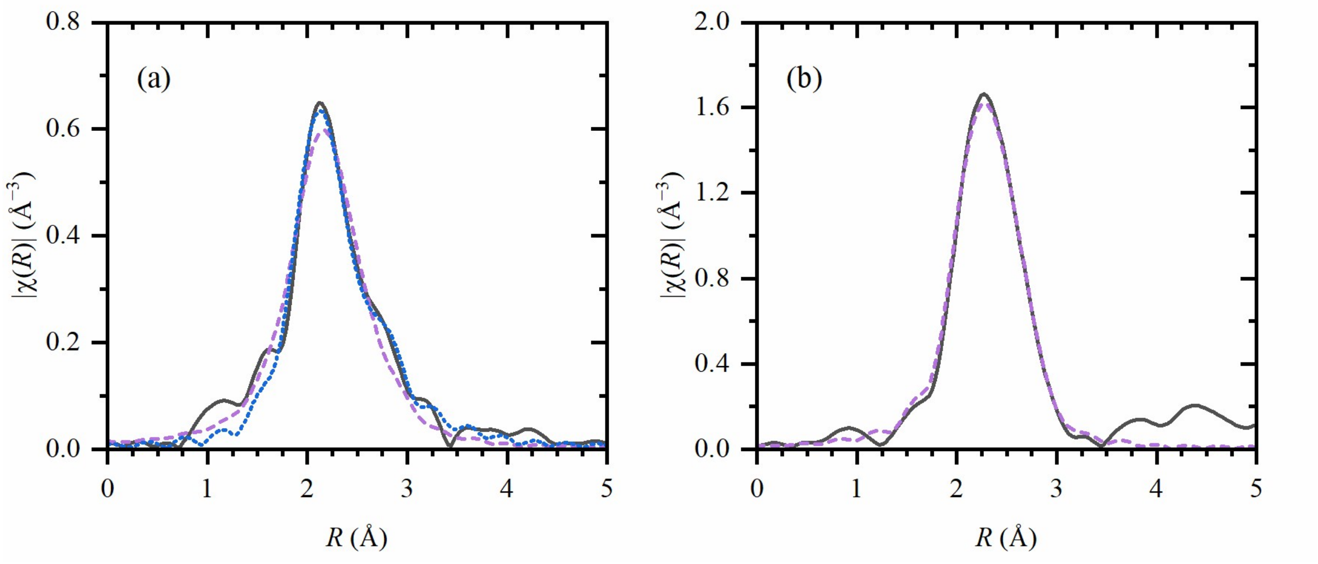

Fig. S 6 (a) Fit results for the activated sample using only tetragonal Pd-Zn phase (dashed purple line) and both Pd-Zn and pure Pd phases (dotted blue line). (b) Fit result for the spent sample using only tetragonal Pd-Zn phase (dashed purple line). Black lines represent experimental data.

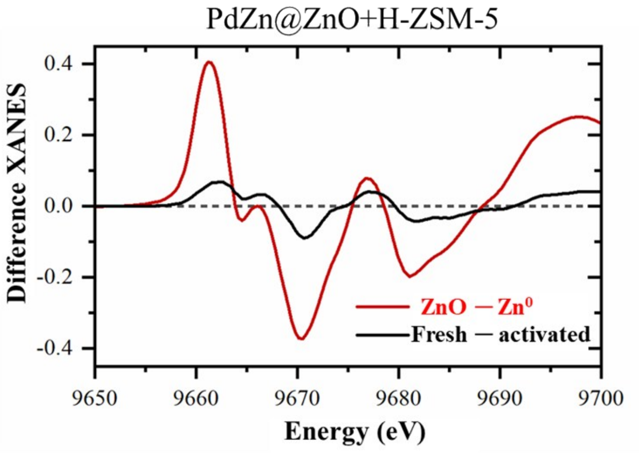

Fig. S 7 Comparison of Zn K-edge difference XANES spectra, obtained by calculating the difference between the XANES of Zn metal minus ZnO (red curve) and of PdZn@ZnO+H-ZSM-5 in its activated state (H2 at 400 °C) minus its initial state before the activation (He, 50 °C).

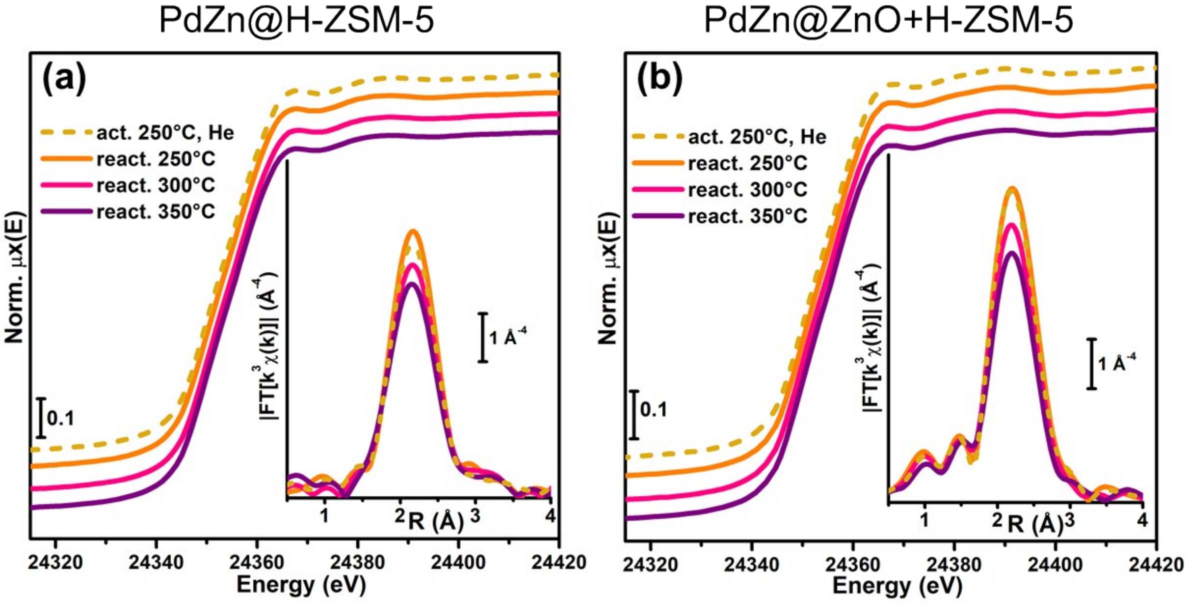

Fig. S 8 **Pd K-edge XANES (main panels) and FT-EXAFS spectra (insets, obtained transforming the $k^3\chi(k)$ EXAFS functions in the 3.2 – 11.0 Å^{-1} range) collected on (a) PdZn@H-ZSM-5 (25) and (b) PdZn@ZnO+H-ZSM-5 (40) under CO_2 hydrogenation conditions at 8 bar and at the different temperatures considered during laboratory catalytic tests. The final state of the catalysts after activation in H_2 at 400 °C, cooling down to 250 °C in H_2 and purge in He, is also reported for comparison as a dashed line. The XANES spectra are vertically traslated for the sake of clarity.**

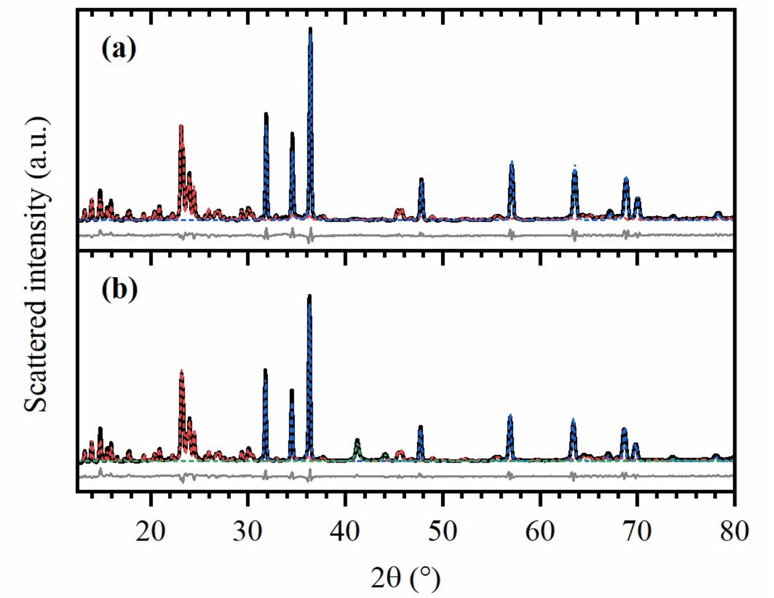

Fig. S 9 Experimental (λ = 0.51067 Å) PXRD patterns (solid black lines) of PdZn@ZnO+H-ZSM-5 in the initial state (a) and after activation (b). Dashed red, blue and green lines correspond to ZSM-5, ZnO, and, respectively, PdZn contributions, obtained from Rietveld refinement. The difference patterns are shown by grey line.

Catalytic testing at 8 bar

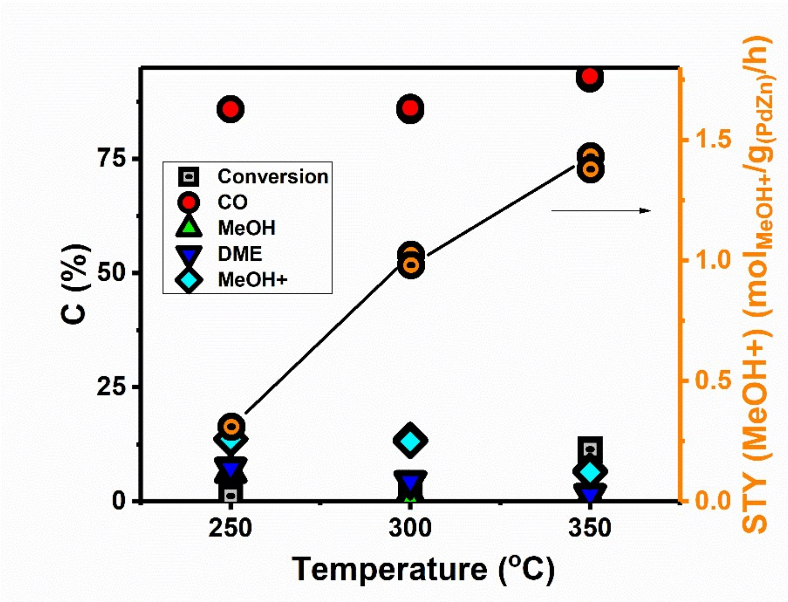

Fig. S 10 A plot of conversion, selectivity and Space Time Yield (STY) versus temperature over PdZn@ZnO+H-ZSM-5, Pre-treatment: in H_2 at 400 ℃, testing at 8 bar with H_2/CO_2=3, and WHSV= 6000 ml/g h