SUPPORTING INFORMATION

Structural and Catalytic Insights into Pd-UiO-67 Frameworks for CO_2 Hydrogenation to Methanol

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1. Synthesis of UiO-67

1.35 g of $ZrCl_4$ was placed into a 250 mL round-bottom flask. This was followed by the addition of 0.63 mL of distilled water and 22.43 mL of dimethylformamide (DMF), with the mixture being stirred at room temperature. The solution was then gradually heated to 80 °C, at which point 2.12 g of benzoic acid, acting as a modulator, was introduced. Stirring was continued until the benzoic acid was fully dissolved. Subsequently, 1.26 g of 1,1′-biphenyl-4,4′-dicarboxylic acid (BPDC) and 0.14 g of 2,2′-bipyridine-5,5′-dicarboxylic acid (BPYDC) were added to the solution. The resulting mixture was heated to 130 °C and held at this temperature overnight under reflux conditions, with continuous stirring. The product was then filtered, thoroughly washed with DMF and acetone, and finally dried at 80 °C in the air overnight.

2. Characterisation Procedures

1.1 MP-AES

Samples were digested in 500 µL of concentrated sulfuric acid (H_2SO_4) at 115 °C overnight. After digestion, 200 µL of 30 wt% hydrogen peroxide (H_2O_2) was added to the still warm solution (caution: this reaction is highly exothermic). The solution was then diluted to a total volume of 50 mL with distilled water. Before analysis, the solutions were filtered through a 0.22 µm syringe filter.

1.2 TDS

The apparatus consists of a sample holder mounted on a Cu block and surrounded by a heating spiral in an ultra-high vacuum chamber. The Cu block is also connected to a liquid helium cryostat,

allowing for cooling below 20 K.[1] A mixture of H_2 and D_2 isotopes was introduced to the samples, where the diatomic gas molecules underwent physisorption, enabling them to penetrate the framework and adsorb within. Following adsorption, the H–H and D–D bonds dissociate, allowing for recombination into diatomic molecules. Given the comparable thermodynamic stability of H_2 and D_2, the desorbed gas is expected to include HD molecules as well. The utilised gas mixture contained an equimolar ratio of H_2:D_2 (1:1). At dynamic equilibrium, the expected composition of the desorbed gas phase is a ratio of H_2:HD:D_2 of 1:2:1. However, due to quantum effects, deuterium diffuses more rapidly than hydrogen at low temperatures, leading to differences in the penetration rates of the isotopes through the framework.[2] Additionally, the rate of penetration is influenced by the exposure temperature, while the quantity of adsorbed isotopes depends on both the temperature and duration of exposure. It is possible to quantify the amount of desorbed gas by careful calibration of the instrument with $Pd_{95}Ce_5$ alloy.[3]

2. Characterisation of Fresh Catalysts

2.1. UiO-67

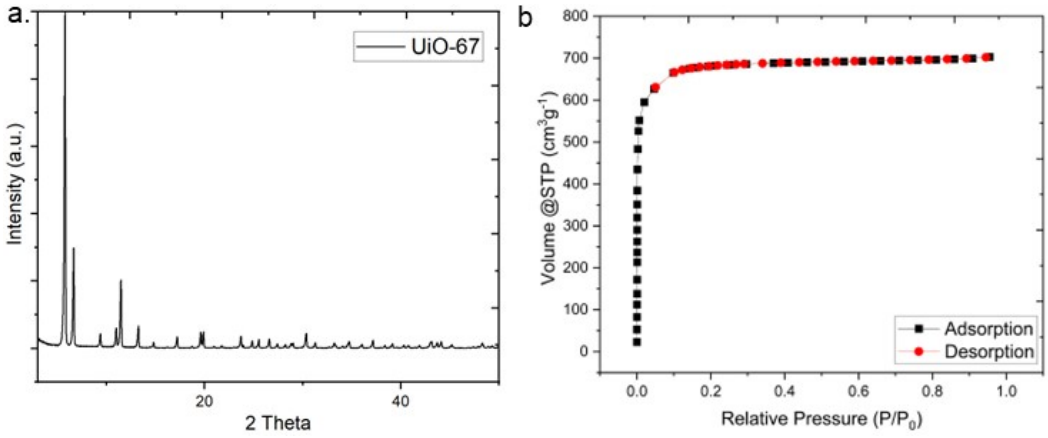

Figure S1. a XRD patterns and b. The nitrogen sorption isotherms for UiO-67.

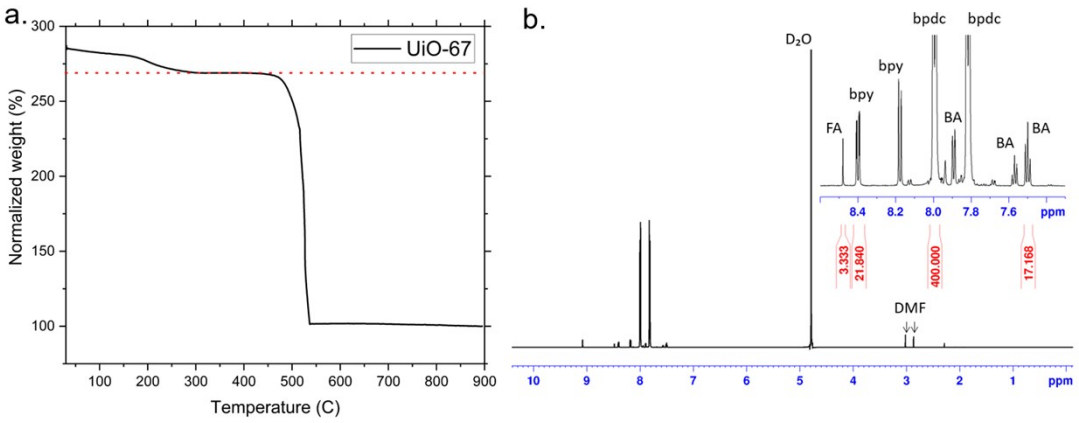

Figure S2. a. Thermogravimetric analysis of UiO-67. b. ^{1}H NMR spectrum (0.1 M NaOD in D_2O) of digested UiO-67

2.2. Pd incorporated UiO-67

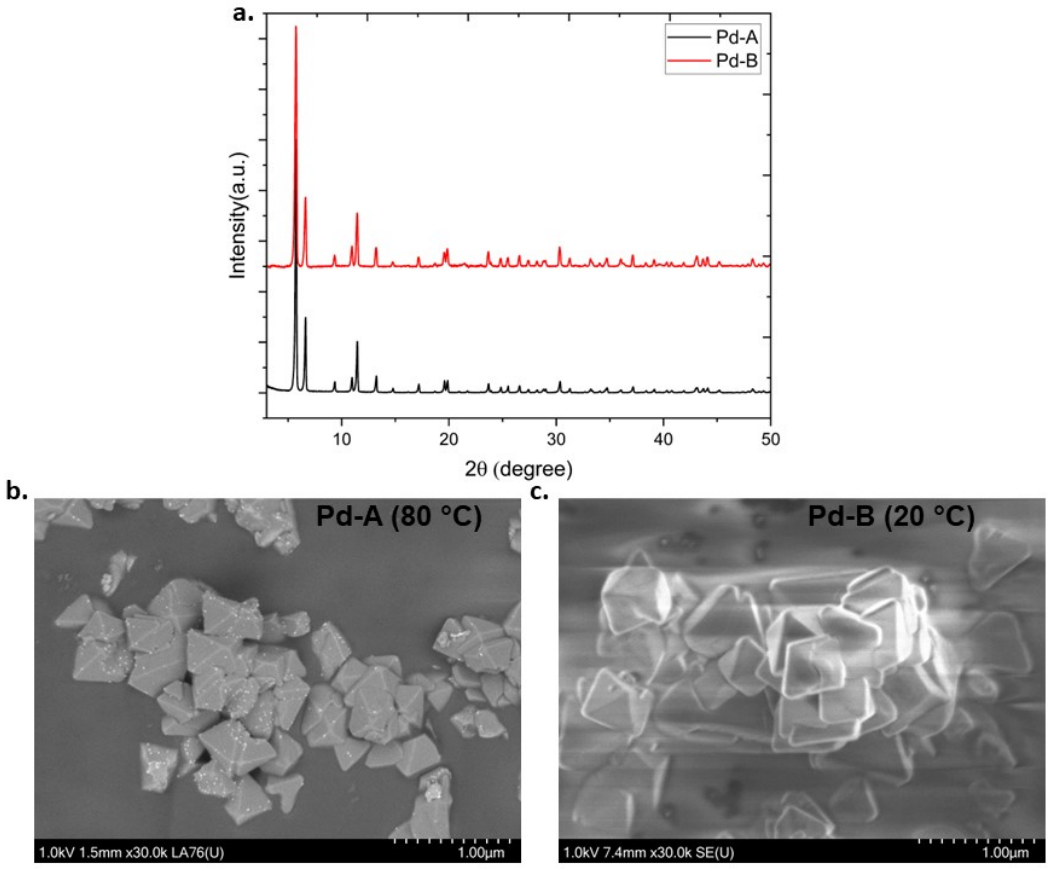

Figure S3.a XRD patterns for Pd-A and Pd-B samples. SEM images for **b.** Pd-A, **c.** Pd-B.

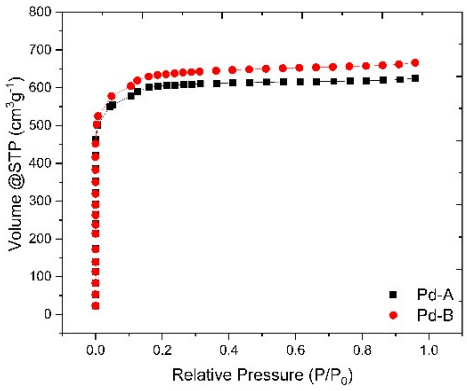

Figure S4. The nitrogen adsorption isotherms for pristine Pd-A and Pd-B samples.

3. Catalytic Testing Results and Characterisation of Spent Catalysts

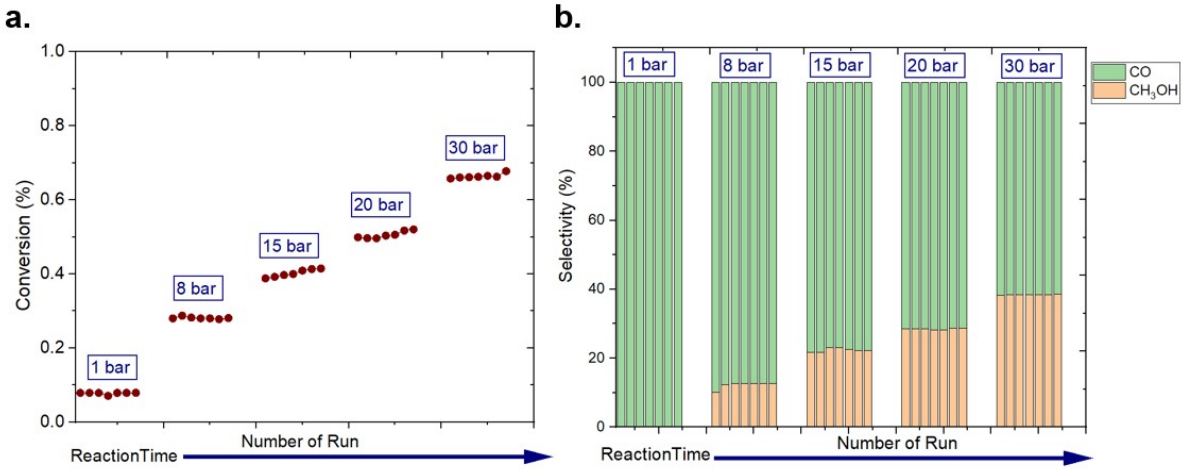

Figure S5. Time-resolved data for a. CO_2 conversion b. Product selectivity distribution for Pd-A catalysts under varying pressure and at 170 °C (CO_2/H_2/Ar = 1/6/2).

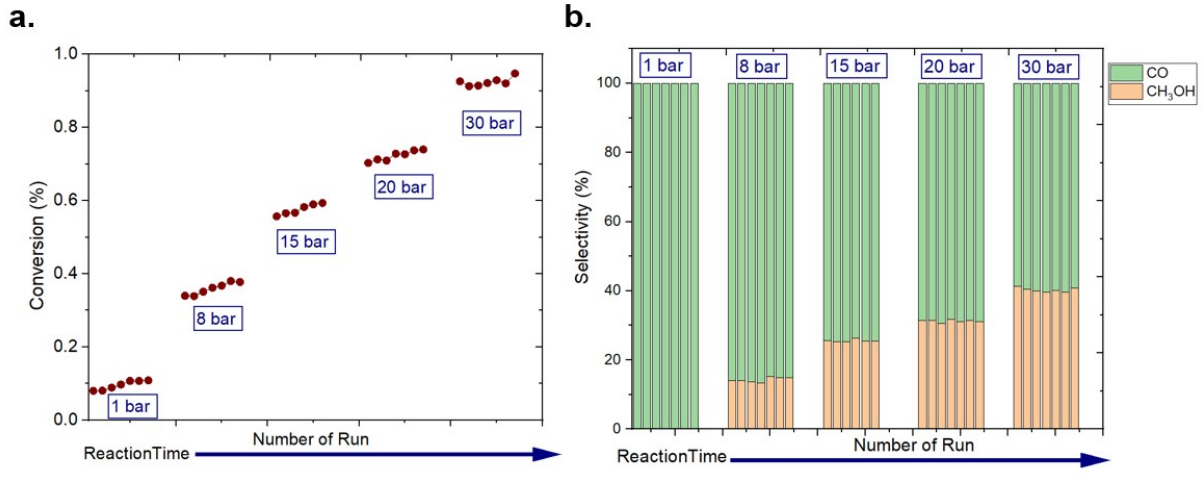

Figure S6. Time-resolved data for a. CO_2 conversion b. Product selectivity distribution for Pd-B catalysts under varying pressure and at 170 °C (CO_2/H_2/Ar = 1/6/2).

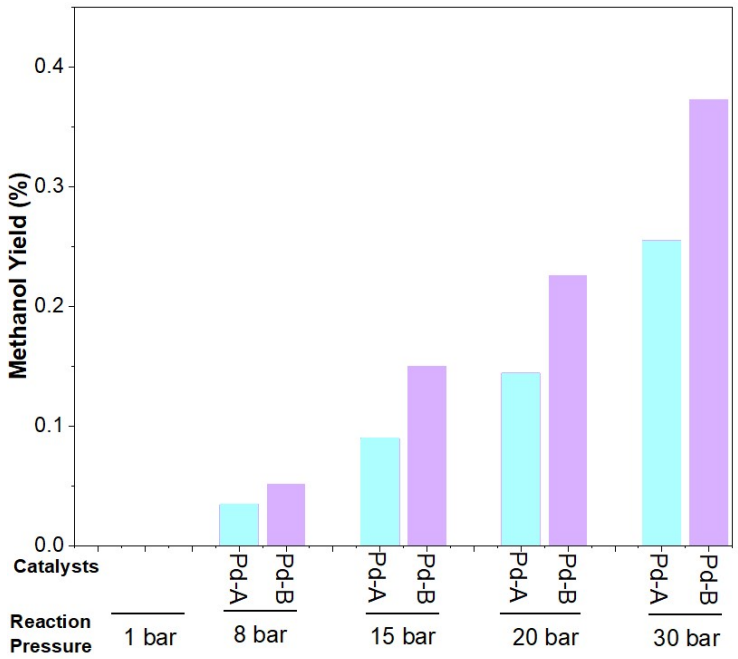

Figure S7. Methanol yield for Pd-A and Pd-B catalysts under varying pressure and at 170 °C ($CO_2/H_2/Ar$ = 1/6/2)

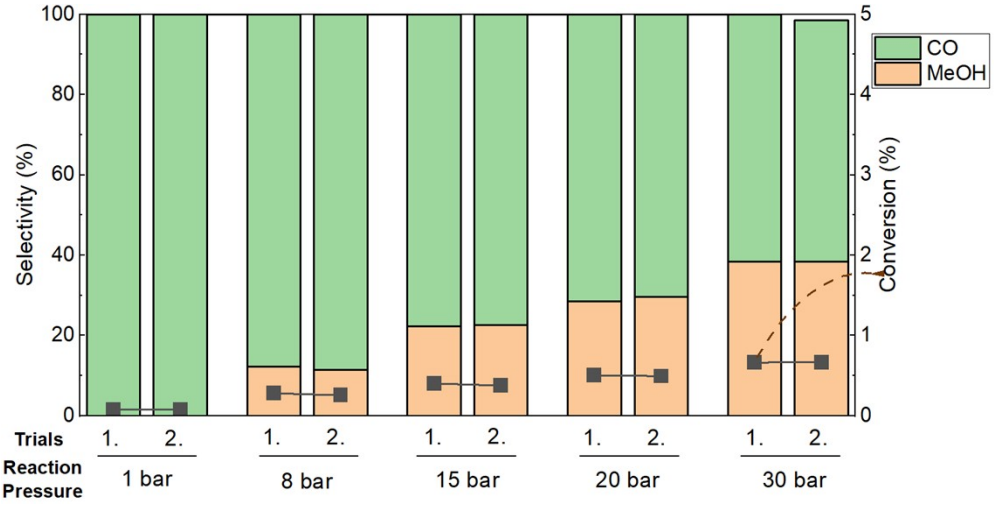

Figure S8. Product selectivity distribution (right axis) and CO_2 conversion (left axis) for Pd-A catalyst under varying pressure and at 170 °C ($CO_2/H_2/Ar$ = 1/6/2)

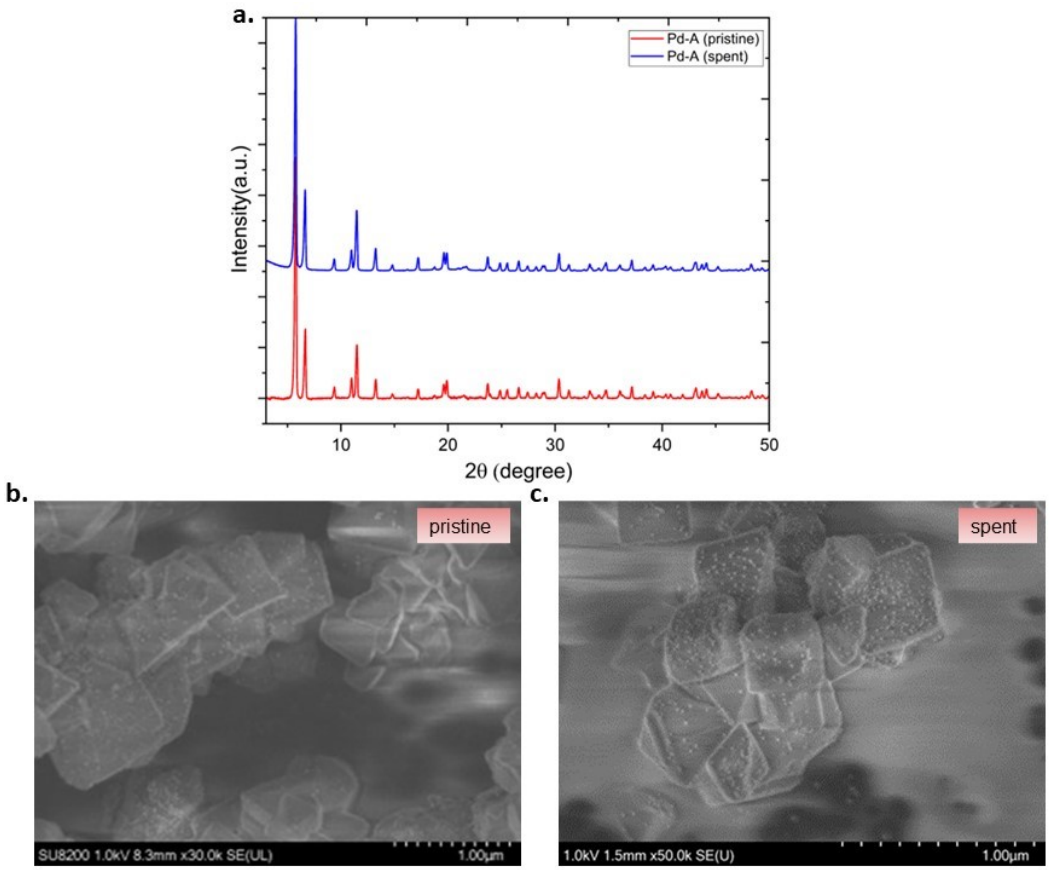

Figure S9.a XRD patterns for pristine and spent Pd-A sample. SEM images for **b.** Pd-A (pristine) **c.** Pd-A (spent).

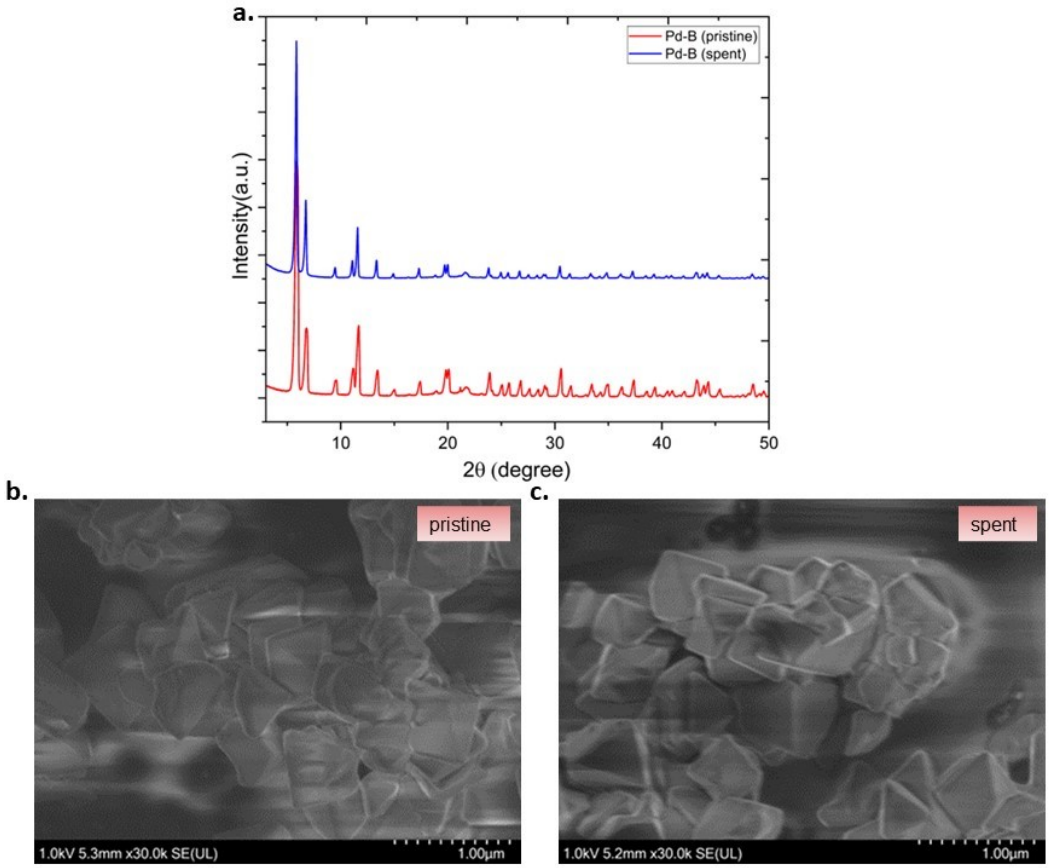

Figure S10.a XRD patterns for pristine and spent Pd-B sample. SEM images for **b.** Pd-B**, c.** Pd-B (spent).

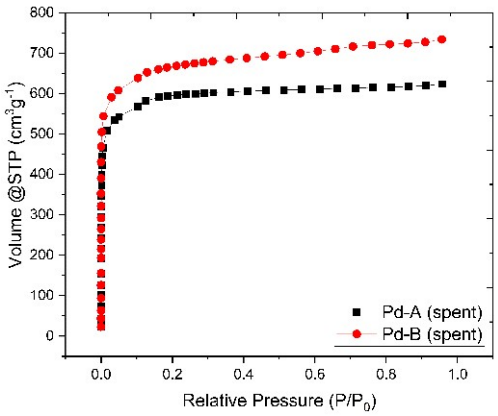

Figure S11. The nitrogen adsorption isotherms for spent Pd-A and Pd-B samples.

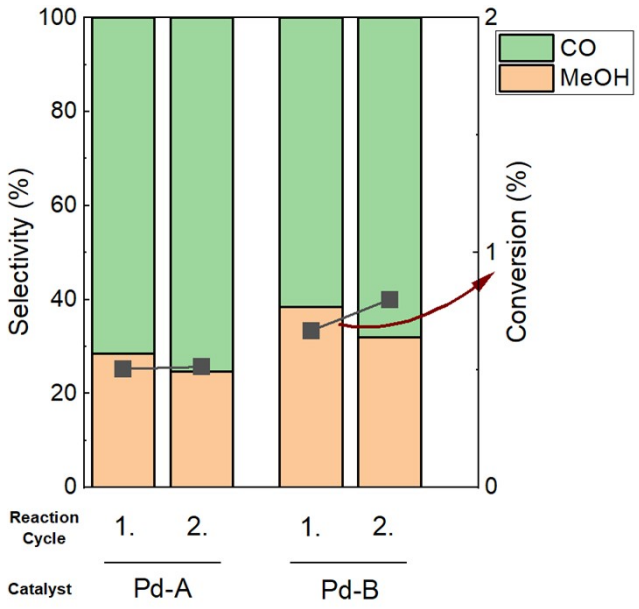

Figure S12. Product selectivity distribution (right axis) and CO_2 conversion (left axis) for Pd-A and Pd-B catalysts at 20 bar and 170 ° C ($CO_2/H_2/Ar$ = 1/6/2). After testing the material at 30 bars, the same catalyst was retested at 20 bars (second cycle).

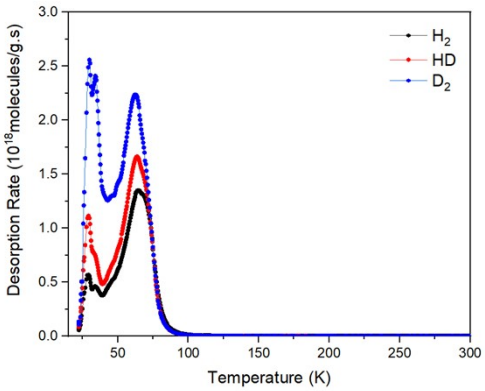

Figure S13. Thermal desorption spectra of UiO-67 after exposure to a 50 mbar 1:1 mixture of H_2/D_2 isotope mixture at RT for 30 minutes.

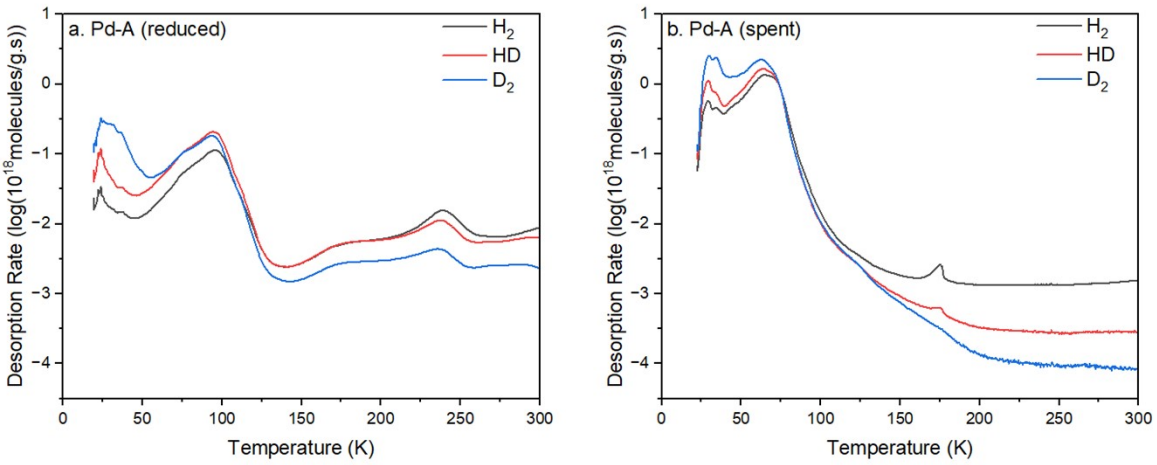

Figure S14. Thermal desorption spectra of **a.** Pd-A (reduced) and **b.** Pd-A (spent) samples after exposure to a 50 mbar 1:1 mixture of H_2/D_2 isotope mixture at RT for 30 minutes.

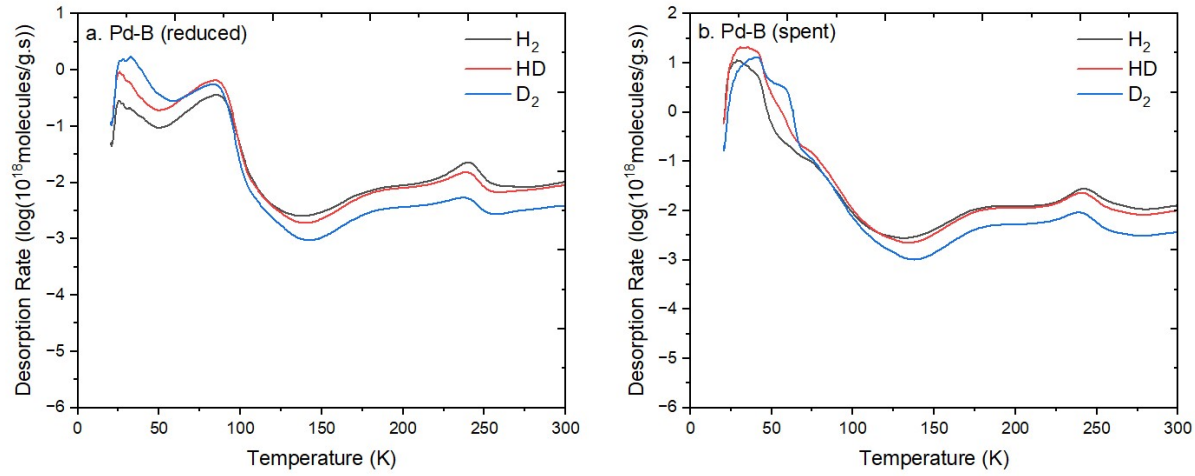

Figure S15. Thermal desorption spectra of **a.** Pd-B (reduced) and **b.** Pd-B (spent) samples after exposure to a 50 mbar 1:1 mixture of H_2/D_2 isotope mixture at RT for 30 minutes.

3. Experimental Protocol

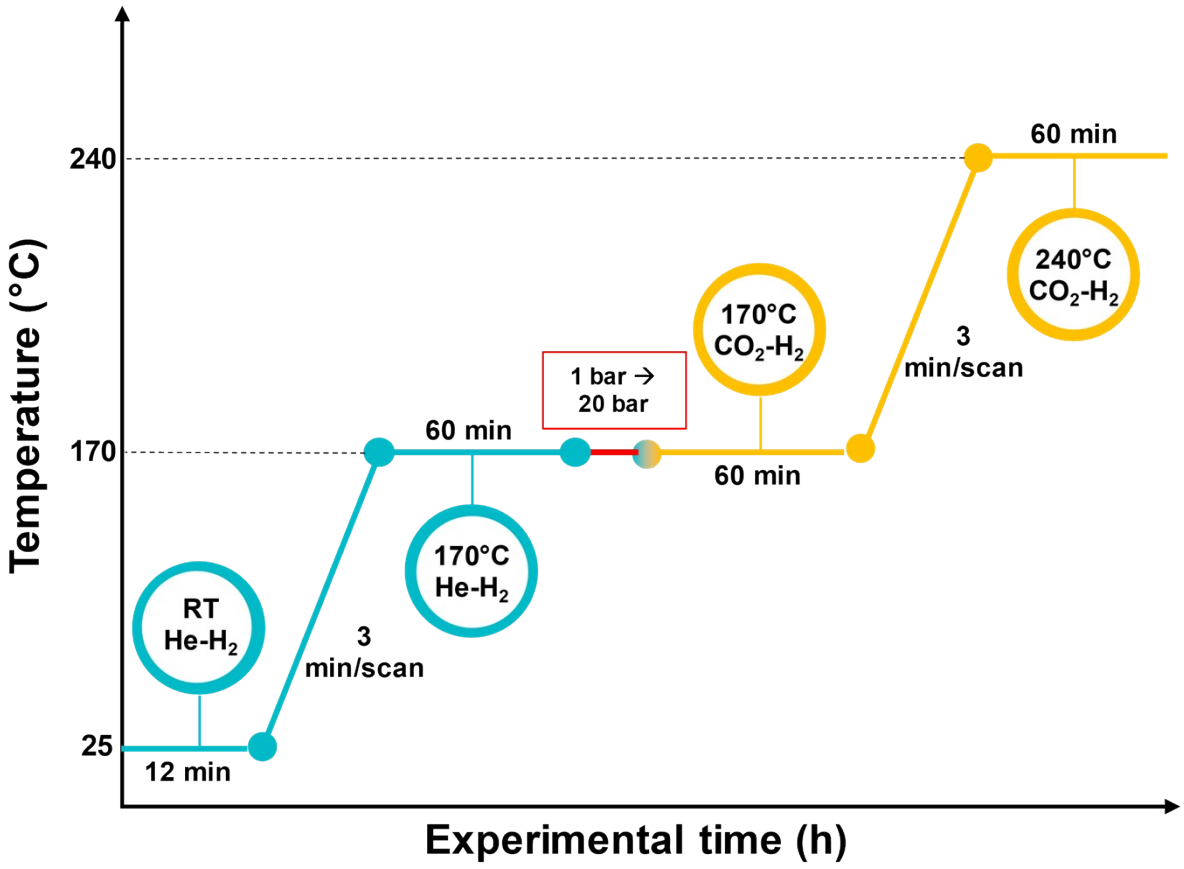

Figure S16: Experimental protocol for *in-situ* XAS over Pd-UiO-67 samples. The protocol involves activation in a He-H_2 atmosphere, ramping from RT to 170 °C at a rate of 10 °C min^{-1} and keeping these conditions for 1 h. Subsequently, CO_2:H_2 is introduced in a 1:6 ratio, followed by heating to 240 °C and holding at these conditions for 1 h.

4. *k*-space EXAFS spectra

4.1 Pd *K*-edge

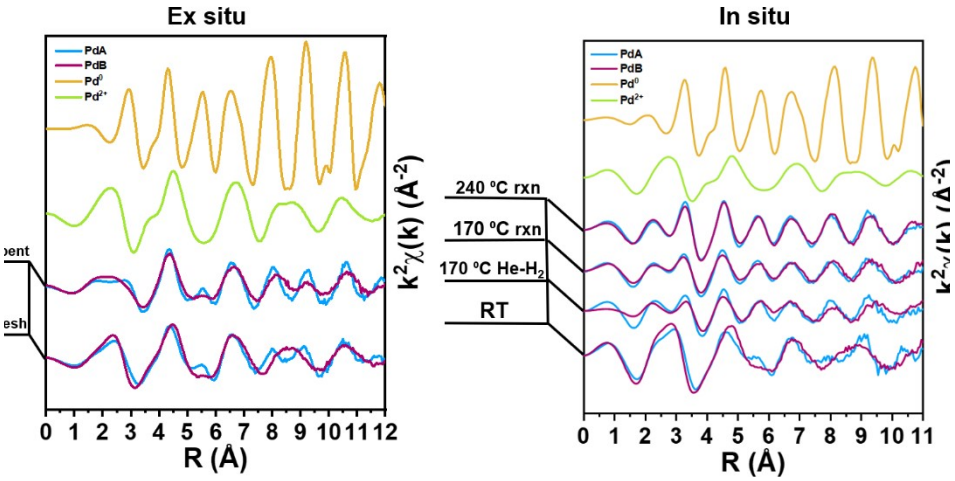

Figure S17: Pd *K*-edge *ex-situ* (left) and *in-situ* (right) *k*-space EXAFS spectra of Pd-A and Pd-B samples, compared with the spectra of relevant model compounds, including Pd acetate (Pd^{2+}) and Pd metal foil (Pd^{0}).

4.2 Zr K-edge

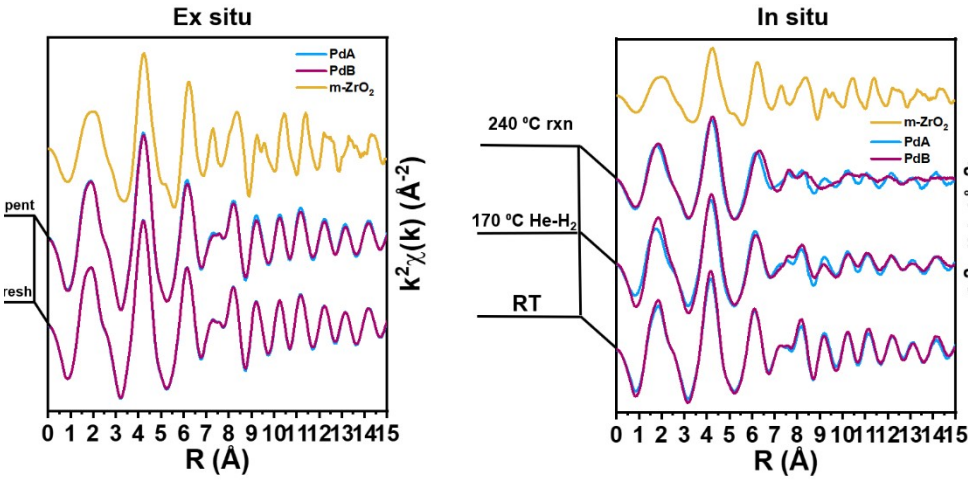

Figure S18. Zr *K*-edge *ex-situ* (left) and *in-situ* (right) *k*-space EXAFS spectra of Pd-A and Pd-B samples, compared with the spectra of relevant model compounds, including zirconia in its monoclinic polymorph (*m*-ZrO_2).

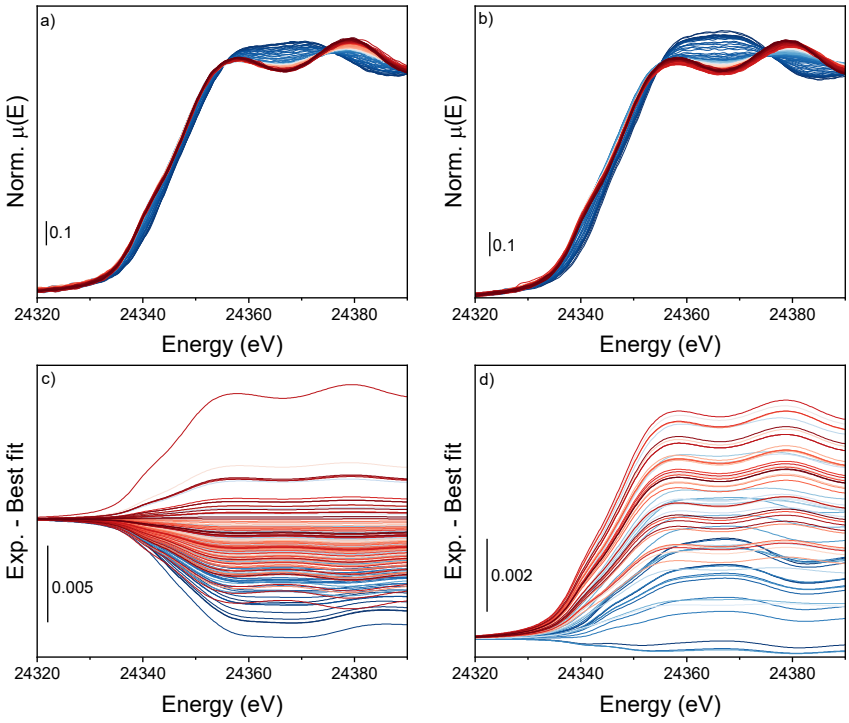

Figure S19. Pd *K*-edge *in-situ* XANES spectra of **a.** Pd-A and **b.** Pd-B catalysts collected during experimental protocol reported in Figure S8**.** The protocol time evolution follows the lines from blue to red colour. Residuals from MCR-ALS routine calculated as the difference from experimental and best fit spectra of **c.** Pd-A and **d.** Pd-B.

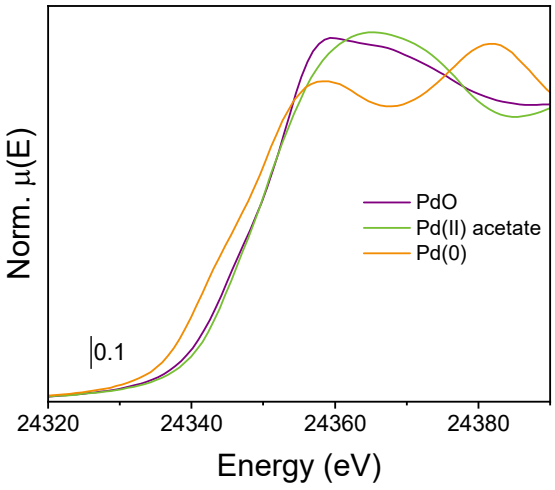

Figure S20. *Ex-situ* Pd *K*-edge XANES spectra of reference PdO (purple line), Pd (II) acetate (green line) and Pd metal (orange line).

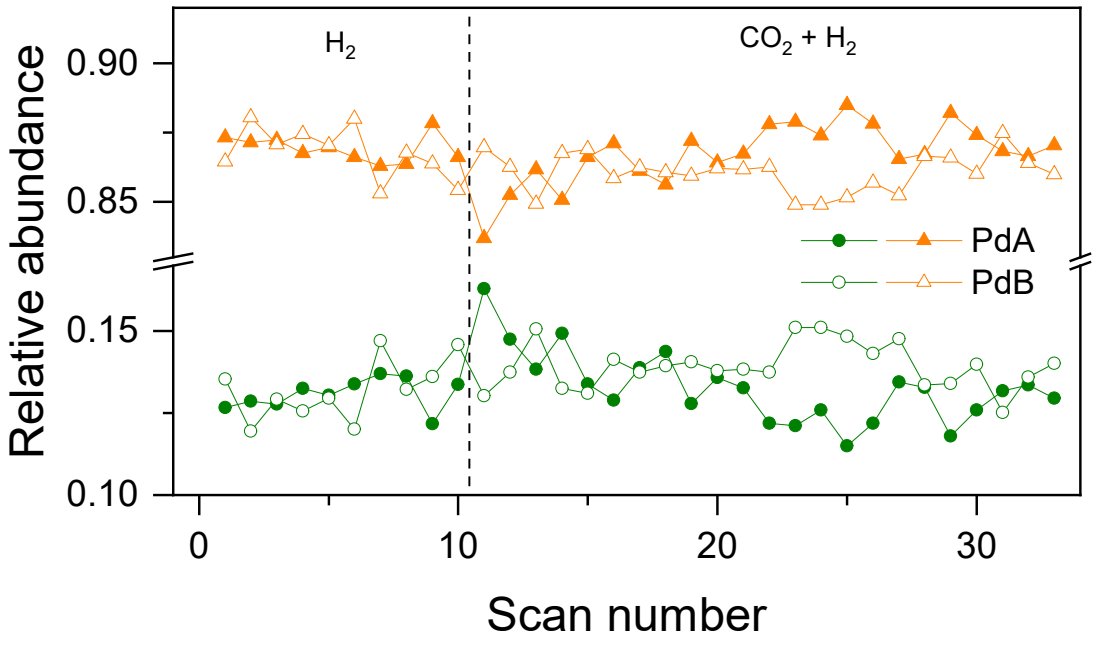

Figure S21. Detail of Pd^0 (orange symbols) and Pd^{2+} (green symbols) concentration evolution at 170 ºC during the change of gas atmosphere from H_2 to CO_2:H_2 mixture.

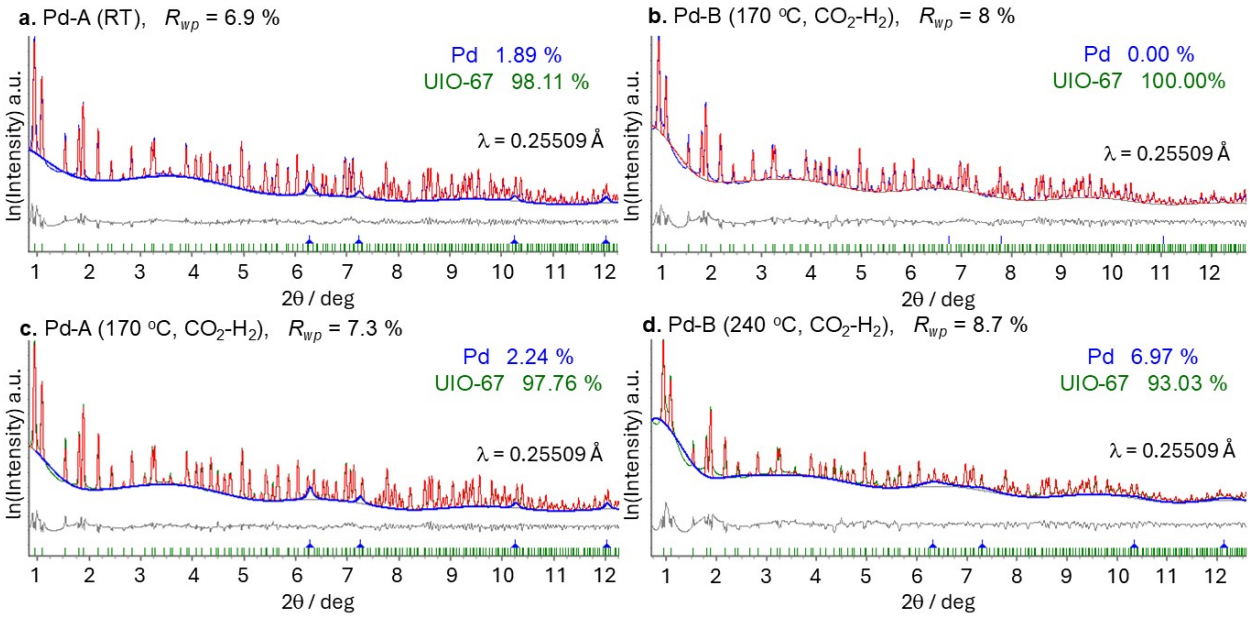

Figure S22. Two-phase Rietveld refinement of operando PXRD data of selected points. **a.** Pd-A catalyst at room temperature, **b.** Pd-B catalyst at 170 ºC under reaction environment**, c.** Pd-A catalyst at 170 ºC under reaction environment, **d.** Pd-B at 240 ºC under reaction environment. The Napierian logarithm of the intensity is plotted for clarity. I(obs) is shown as blue or green lines (a,

b, or c, d, respectively). Indexing lines corresponding to both phases are represented as blue for palladium metal and green for UiO-67. Weight percentages of each phase are given in the top right corner of each figure. The contribution of the palladium-metal phase is highlighted as a blue thick line, while the grey thin line represents the background. Fits are also reported in each figure.

REFERENCES

1. Panella, B.; Hirscher, M.; Ludescher, B. Low-temperature thermal-desorption mass spectroscopy applied to investigate the hydrogen adsorption on porous materials. *Microporous and Mesoporous Mater.* **2007**, *103* (1), 230-234. DOI:10.1016/j.micromeso.2007.02.001.

2. Kumar, A.V.A.; Jobic, H.; Bhatia, S.K.; Quantum Effects on Adsorption and Diffusion of Hydrogen and Deuterium in Microporous Materials. *J. Phys. Chem. B, **2006**, 110 (33),* 16666–16671. DOI.org/10.1021/jp063034n

3. von Zeppelin, F.; Haluška, M.; Hirscher, M. Thermal desorption spectroscopy as a quantitative tool to determine the hydrogen content in solids. *Thermochim. Acta* **2003**, *404* (1), 251-258. DOI: 10.1016/S0040-6031(03)00183-7.