

Enhanced stability of the Metal-Organic Framework MIL-101(Cr) by Embedding Pd nanoparticles for densification through compression

Supporting Information

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LABORATORY X-RAY POWDER DIFFRACTION

We have carried out laboratory X-ray powder diffraction on all samples, as depicted in Figure S1. In particular, the XRD pattern of pristine MIL-101 has been compared to the simulated one in Figure S2. Diffraction peaks from the pristine porous solid MIL-101 are preserved in the patterns of the Pd loaded composites proving the stability of the porous framework in our NPs synthetic conditions (reduction under H₂/Ar flow at 573 K). It is important to notice that no sharp and intense diffraction peak of the *fcc* Pd structure can be identified, despite the high metal loadings. Only a broad and weak contribution is noticed close to the expected Pd (111) main diffraction peak. The lack of sharp peaks and the broad shape of this feature can be explained by the very short coherence length of ultra-small NPs.[1] This also demonstrates the absence of undesired large NPs agglomerates on the outer surface of the grains, in line with TEM results.

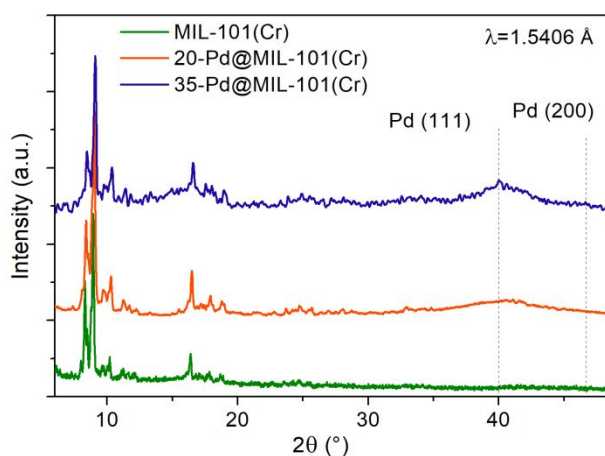


Figure S1. XRD patterns of pristine MIL-101(Cr) (green) and x-Pd@MIL-101(Cr) composites (orange and blue for x=20 and 35 wt.% Pd, respectively). Gray dashed lines indicate the position of the main *fcc* Pd peaks.

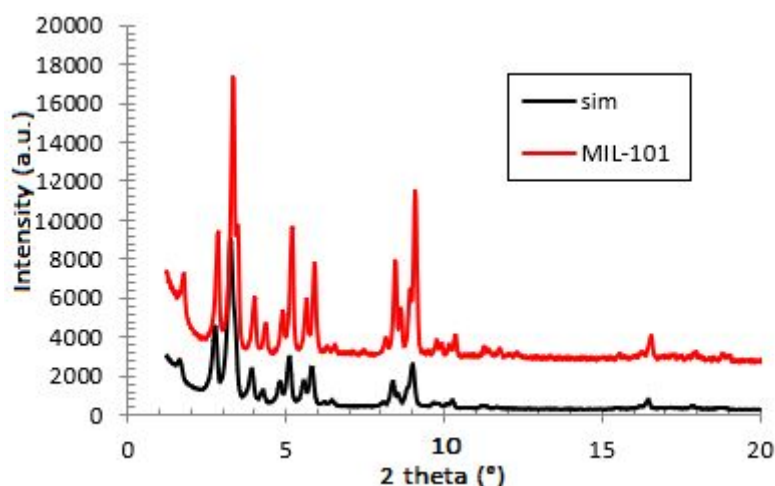


Figure S2. Experimental (red) and simulated (black) XRD patterns of pristine MIL-101

NITROGEN ADSORPTION/DESORPTION ISOTHERMS AT 77 K

The textural properties of samples were estimated from nitrogen adsorption/desorption isotherms at 77 K using a Sorptomatic 1990 (Thermo Electron Corporation) apparatus. Each sample was degassed at 220°C for 18 hours under dynamic vacuum before measurement. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area (S_{BET}) using the multiple-point method in the relative pressure range p/p_0 of 0.02-0.25. The specific pore volume was determined according to Gurvich's rule at p/p_0 of 0.95.

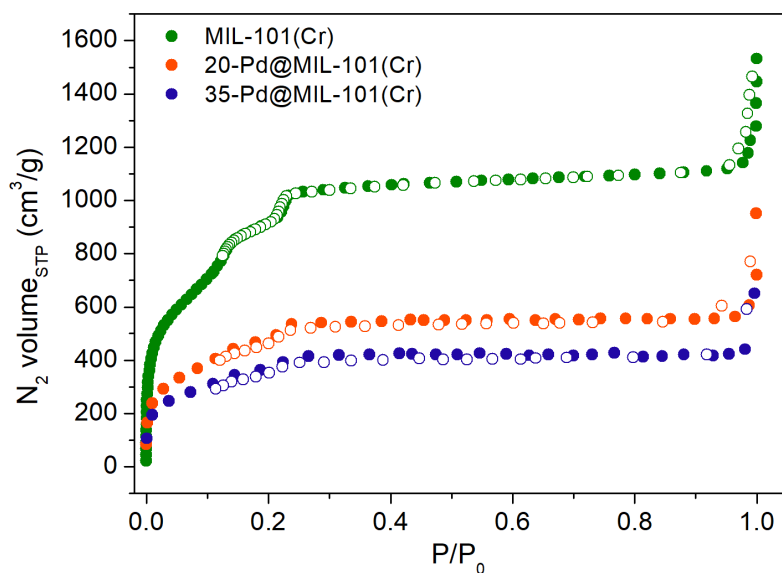


Figure S3. N_2 adsorption (filled points) and desorption (empty) curves of MIL-101(Cr) (green), 20-Pd@MIL-101(Cr) (orange) and 35-Pd@MIL-101(Cr) (blue) collected at STP conditions.

Table S1. BET surface area and pore volume values for each sample.

Sample	S_{BET} (m ² /g)	Pore volume (cm ³ /g)
MIL-101	3549	1.72
20-Pd@MIL-101	1839	0.86
35-Pd@MIL-101	1388	0.65

The pore size distribution was determined by applying the Dollimore-Heal model on the N₂ desorption isotherm data [2]. The calculated PSDs for all samples are shown below:

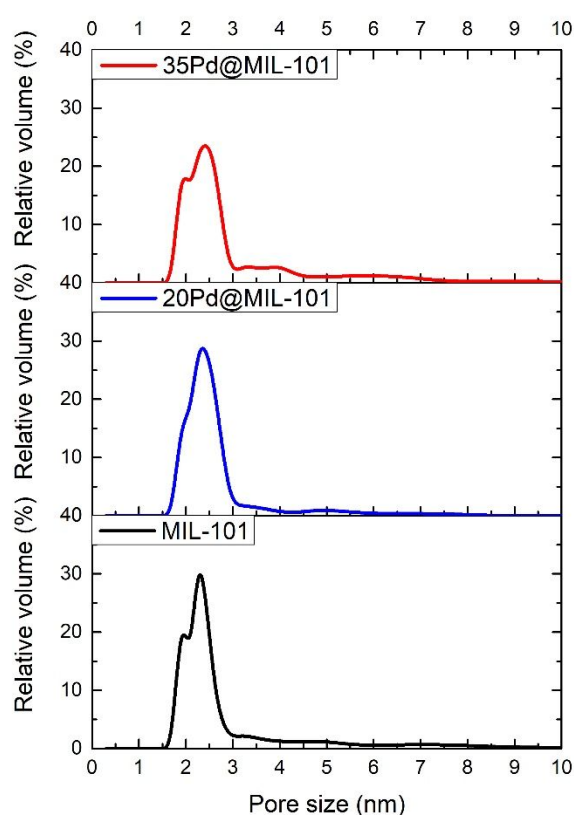


Figure S4. Pore size distribution expressed as relative pore volume (%) vs. pore size (nm) of the MIL-101(Cr), 20-Pd@MIL-101(Cr) and 35-Pd@MIL-101(Cr) samples.

Nanoparticle's insertion decreases the overall porous volume and seems to affect the mesopores mainly since the volume of the mesopores at around 2.5 nm significantly reduces by progressive doping with Pd. Micropores (< 2.0 nm) seem to be less affected by the presence of Pd nanoparticles.

THERMO GRAVIMETRIC ANALYSIS

To evaluate the thermal stability the pristine MIL-101 and the two Pd loaded composites thermo gravimetric analysis was performed by heating the samples to 600 °C with 10 °C/min under a flow of dry air. All the TGA curves present a first mass loss upon heating to around 100 °C which is explained by the desorption of adsorbed water molecules within the pores and corresponds to about 15-25% of the total weight. This initial water loss is then followed by a slightly sloping plateau where sample mass slowly decreases up to around 300°C and 400 °C for both Pd-containing samples and MIL-101, respectively. At these temperatures, a pronounced mass loss is noticed due to the oxidation of the organic linker and subsequent formation of CO_x volatile species. This reaction occurs at lower temperature in the presence of Pd nanoparticles which act as catalysts for the oxidation of organic linker. At higher temperature, the mass show negligible loss for all samples. The larger residual mass values for Pd-containing samples relative to pristine MIL-101 are due to the presence of Pd nanoparticles, that do not undergo decomposition.

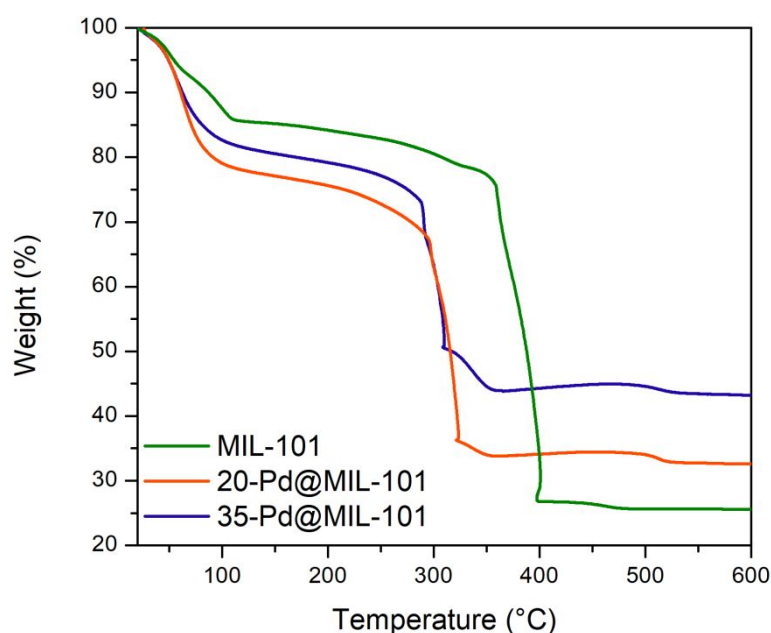


Figure S5. TGA curves of MIL-101 (green points), 20-Pd@MIL-101 (orange) and 35-Pd@MIL-101 (blue) under dry air with 10°C/min heating rate.

TRANSMISSION ELECTRON MICROSCOPY IMAGES

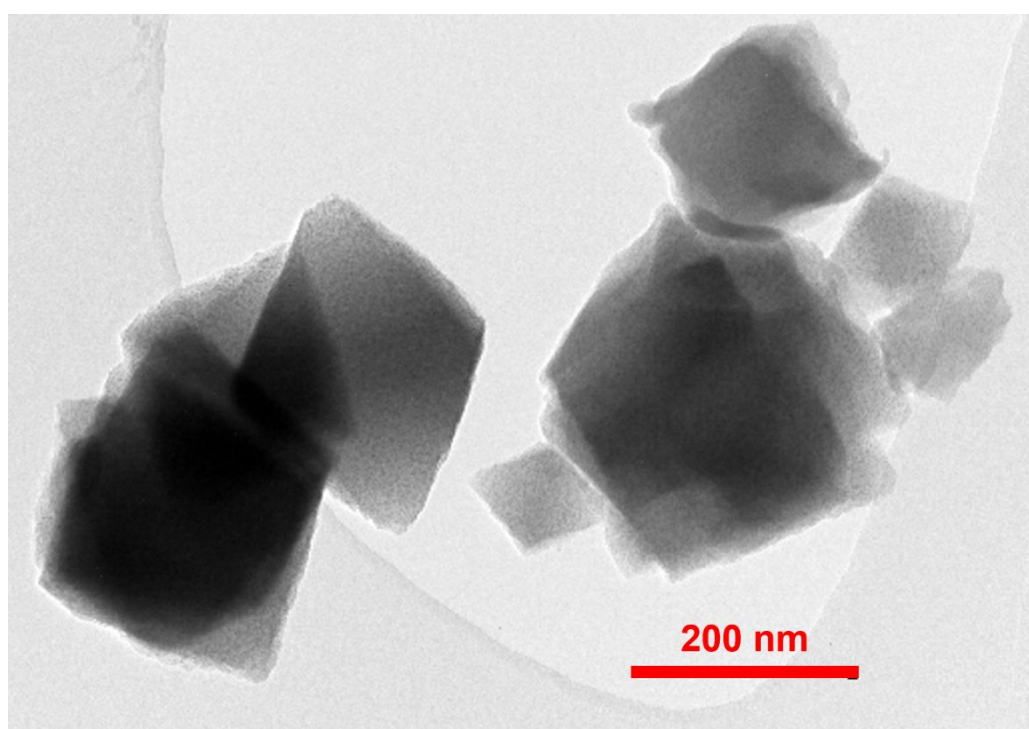


Figure S6. TEM image of 20-Pd@MIL-101(Cr).

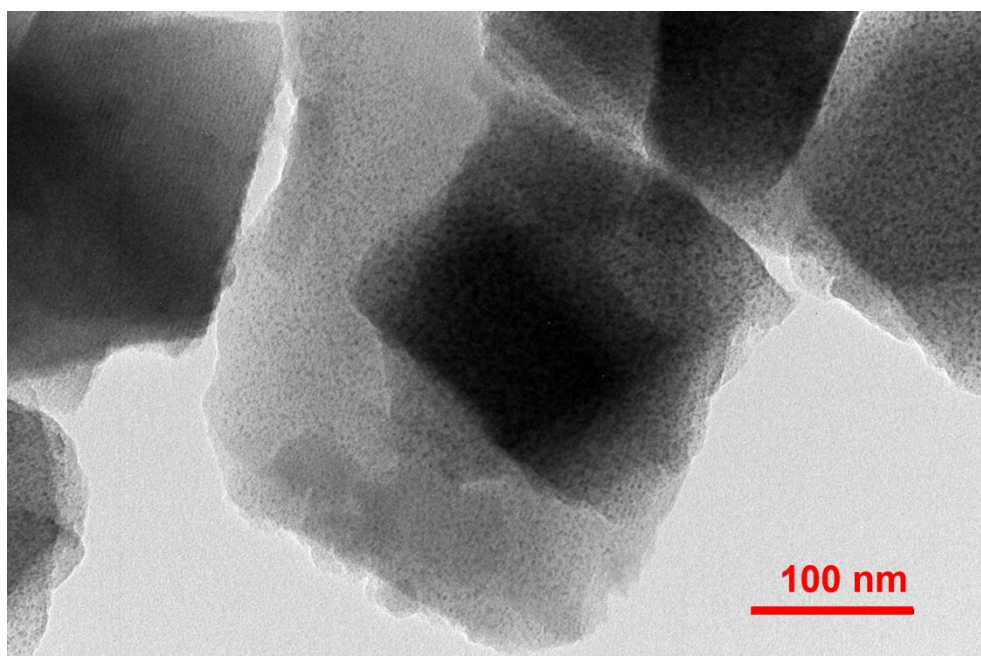


Figure S7. TEM image of 20-Pd@MIL-101(Cr)

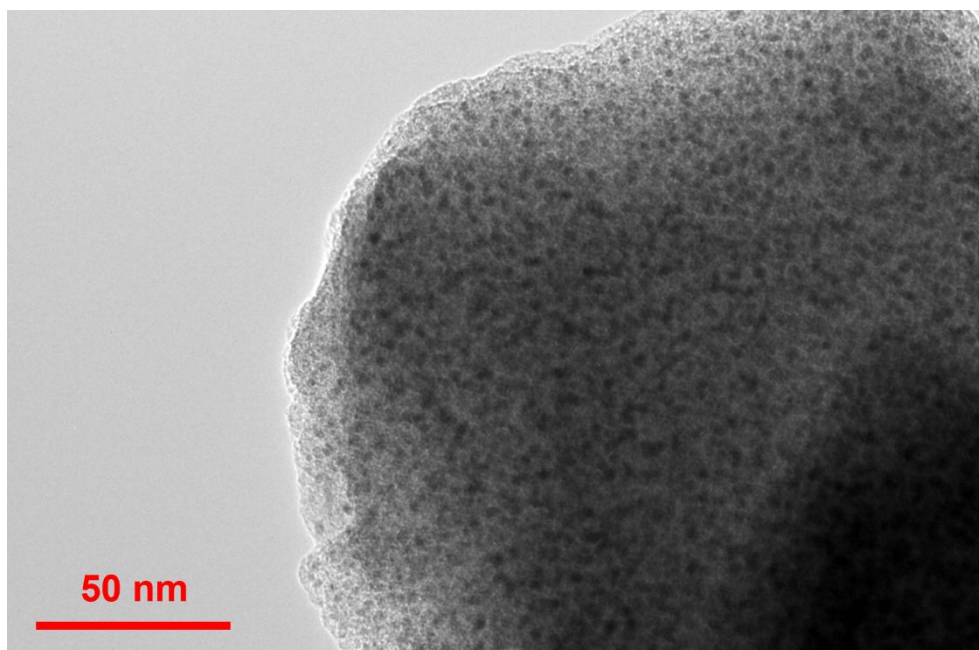


Figure S8. TEM image of 20-Pd@MIL-101(Cr).

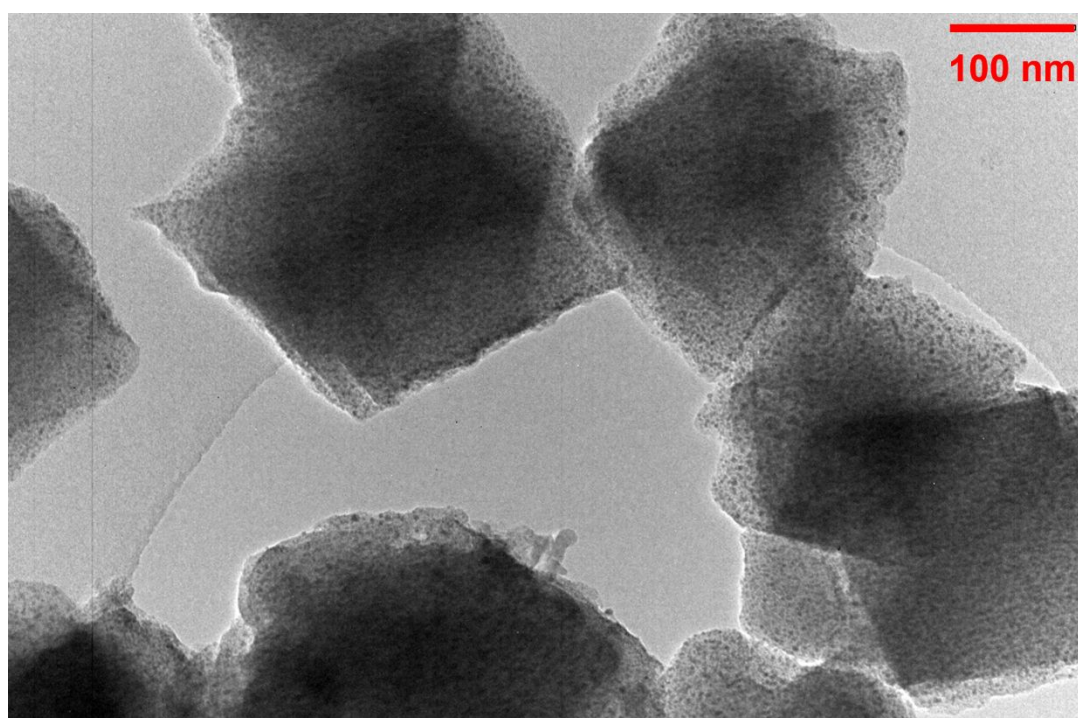


Figure S9. TEM image of 35-Pd@MIL-101(Cr).

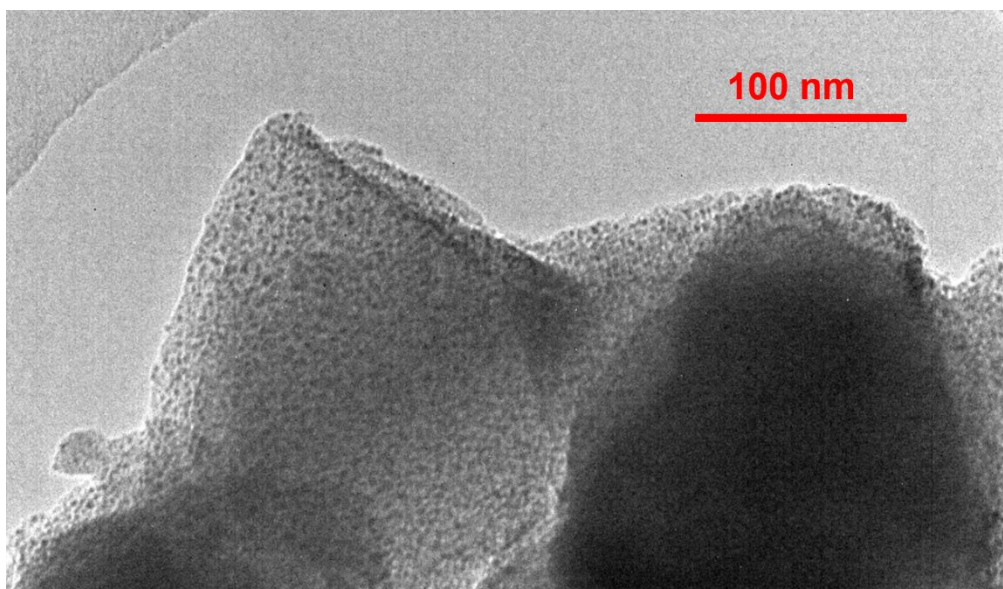


Figure S10. TEM image of 35-Pd@MIL-101(Cr).

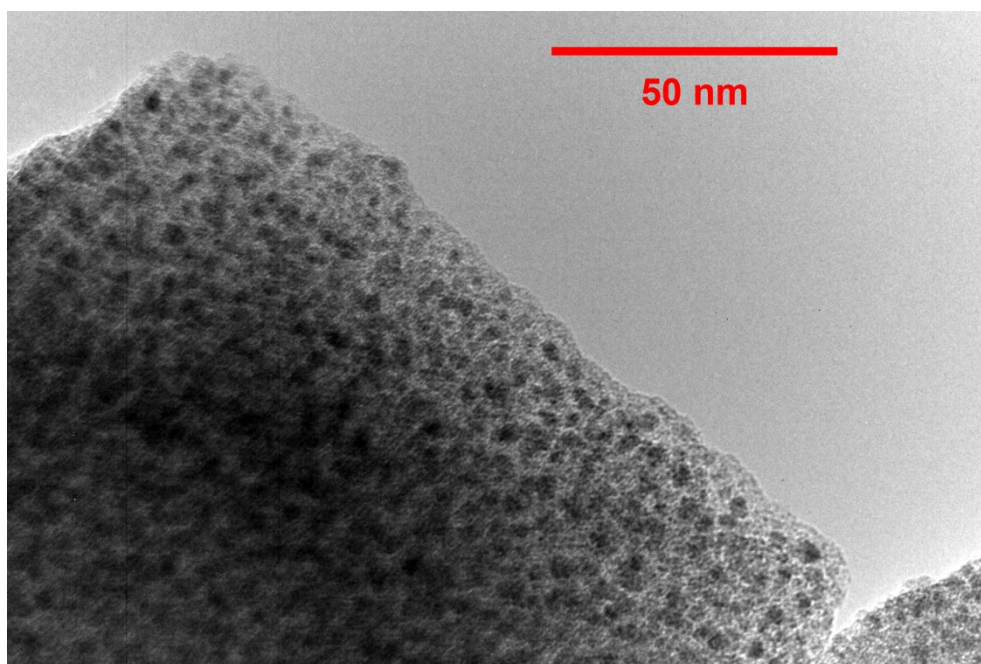


Figure S11. TEM image of 35-Pd@MIL-101(Cr).

DIAMOND ANVIL LOADING PROTOCOL

At variance with our previous work [3], grains of powder not exceeding the hole size were carefully placed in the cavity already filled with NaCl grains to avoid any possible precompression when closing the DAC. The DAC was sealed with screws inside the glovebox carefully checking the fringes on the gasket. This procedure ensures that the sample is not exposed to atmosphere when the DAC is brought outside the glovebox. Moreover, a larger number of XRD data between 0 and 0.1 GPa were collected.

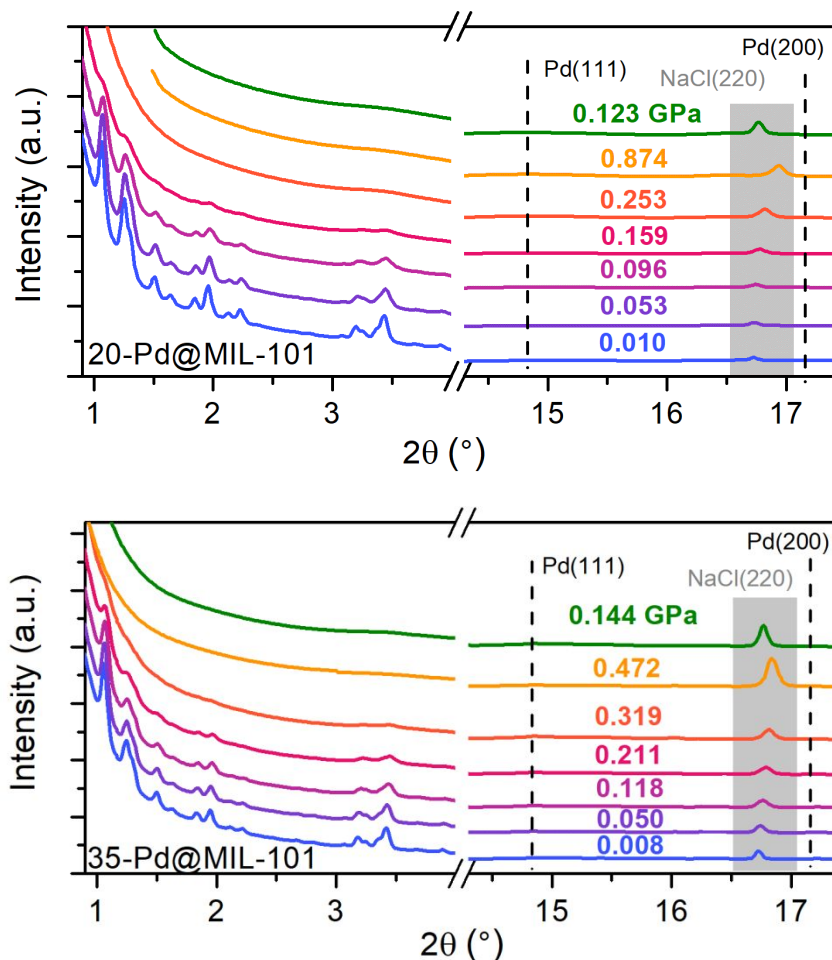


Figure S12. Selected powder XRD patterns ($\lambda = 0.5802 \text{ \AA}$) of 20-Pd@MIL-101 (upper panel) and 35-Pd@MIL-101 (down) under pressure with NaCl as PTM. Patterns are vertically stacked for sake of clarity. Patterns collected after the pressure release are shown in green. Black dashed lines indicate the position of *fcc* Pd peaks (not observed) while the gray areas show the NaCl (220) Bragg reflection.

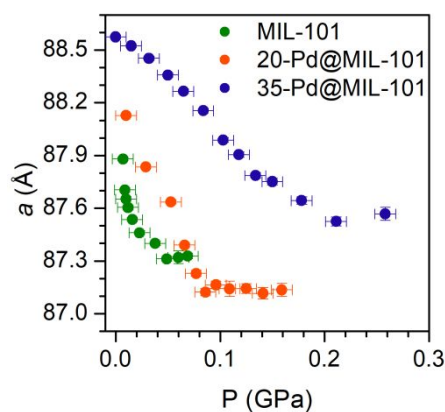


Figure S13. Pressure dependence of the lattice parameter a of pristine MIL-101 (green points), 20-Pd@MIL-101 (orange) and 35-Pd@MIL-101 (blue) up to 0.3 GPa.

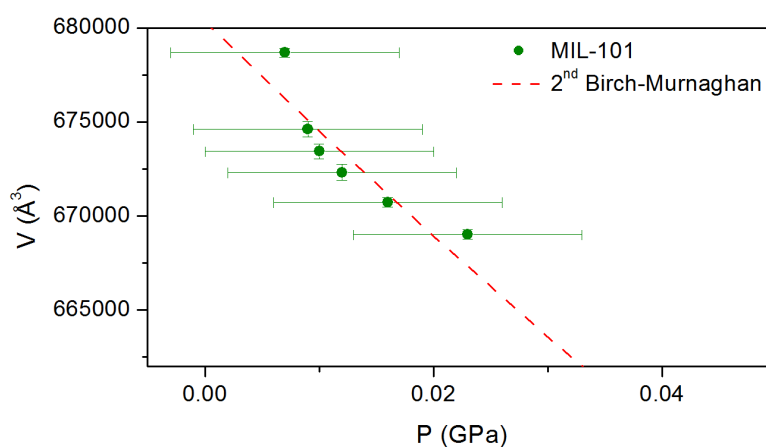


Figure S14. Unit cell volume of MIL-101 in the 0-0.08 GPa pressure range. Dashed line represents the second-order Birch-Murnaghan equation-of-state fit to the experimental points.

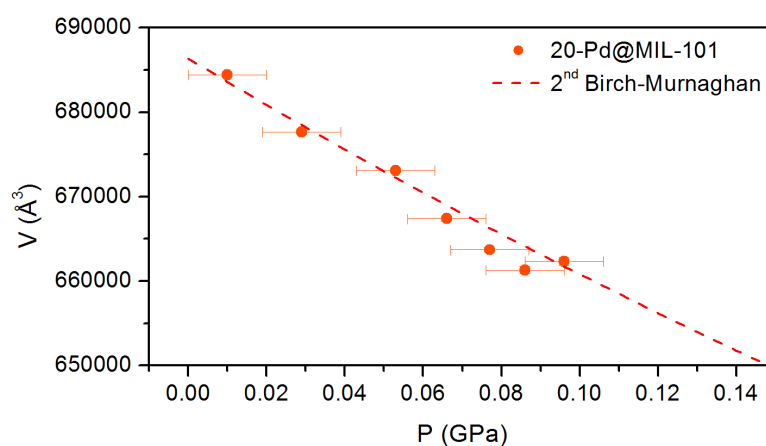


Figure S15. Unit cell volume of 20-Pd@MIL-101 in the 0-0.15 GPa pressure range. Dashed line represents the second-order Birch-Murnaghan equation-of-state fit to the experimental points.

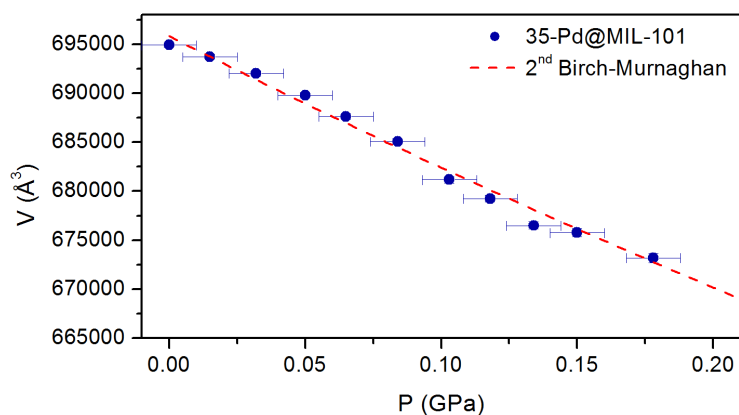


Figure S16. Unit cell volume of 35-Pd@MIL-101 in the 0-0.22 GPa pressure range. Dashed line represents the second-order Birch-Murnaghan equation-of-state fit to the experimental points.

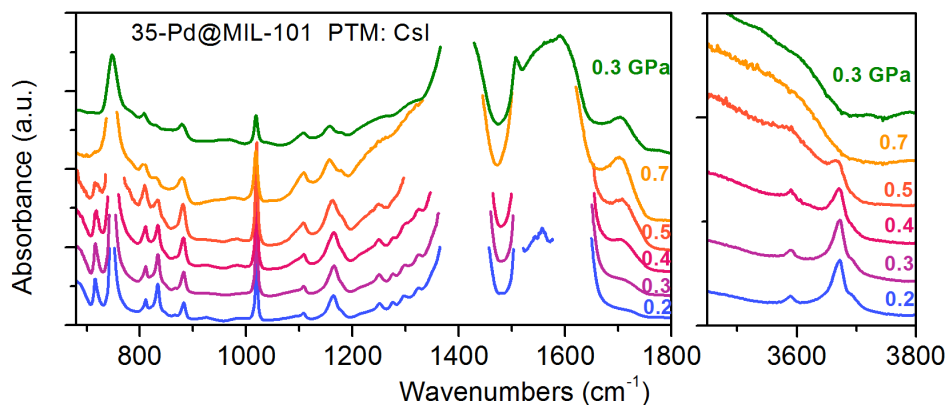


Figure S17. MIR spectra of 35-Pd@MIL-101 measured under pressure with CsI as PTM. Spectral regions where signal saturates are masked. The spectrum collected after the pressure release are shown in green.

References

- [1] S. Mourdikoudis, R. M. Pallares, e N. T. K. Thanh, «Characterization techniques for nanoparticles: comparison and complementarity upon studying nanoparticle properties», *Nanoscale*, vol. 10, n. 27, pagg. 12871–12934, 2018, doi: 10.1039/C8NR02278J.
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- [3] A. Celeste *et al.*, «Mesoporous Metal–Organic Framework MIL-101 at High Pressure», *J. Am. Chem. Soc.*, vol. 142, n. 35, pagg. 15012–15019, set. 2020, doi: 10.1021/jacs.0c05882.