Supporting Information

Size-Tunable Synthesis of Palladium Nanoparticles Confined within Topologically Distinct Metal–Organic Frameworks for Catalytic Dehydrogenation of Methanol

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Table S1. Selected summary of catalytic performance for methanol dehydrogenation over Pd-based catalysts in this work and reported in literatures.

Catalyst	Prep. Method[a]	Pd loading (wt%)	Rxn temp. (°C)	H_2 production rate (mmol g-Pd^{-1} min^{-1})	H_2-TOF (h^{-1})	Ref.
Pd@UiO-66	SIM	5.2	225	137	874[d]	[1]
			200	72	459[d]	[1]
Pd@NU-902	SIM	2.6	225	102	651[d]	[1]
			200	46	291[d]	[1]
Pd@PCN-222	SIM	1.3	225	87	556[d]	[1]
			200	41	259[d]	[1]
Pd/ZrO_2	IMP	5.0	200	7[b]	43	[2]
Pd/ZrO_2	CP	10.0	200	10[b]	65	[2]
Pd/ZrO_2	CP	15.0	200	11[b]	68	[2]
Pd/Pr_2O_3	CP	15.0	200	16[b]	101	[2]
Pd/CeO_2	CP	15.0	200	15[b]	94	[2]
Pd/TiO_2	CP	15.0	200	5[b]	29	[2]
Pd/ZrO_2	DP	2.0	200	54[c]	346[c,d]	[3]
Pd/ZrO_2	IMP	2.0	200	21[c]	133[c,d]	[3]
Pd/CeO_2-Al_2O_3	SG	5.0	225	30[c]	192[c,d]	[4]
Pd/Al_2O_3	ALD	1.6	250	203	1300	[5]

[a] Abbreviations for preparation methods including solvothermal deposition in MOF (SIM), impregnation (IMP), coprecipitation (CP), deposition-precipitation (DP), sol-gel (SG), and atomic layer deposition (ALD). [b] calculated from the reported values of H_2-TOF and Pd loading. [c] calculated from reported methanol conversion assuming 100% H_2 selectivity. [d] normalized by total number of Pd atoms in catalysts.

[1] This work.

[2] Y. Usami, K. Kagawa, M. Kawazoe, Y. Matsumura, H. Sakurai and M. Haruta, *Appl. Catal. A-Gen.*, 1998, **171**, 123-130.

[3] Y. Matsumura, M. Okumura, Y. Usami, K. Kagawa, H. Yamashita, M. Anpo and M. Haruta, *Catal. Lett.*, 1997, **44**, 189-191.

[4] J. C. Brown and E. Gulari, *Catal. Commun.*, 2004, **5**, 431-436

[5] H. Feng, J. W. Elam, J. A. Libera, W. Setthapun and P. C. Stair, *Chem. Mater.*, 2010, **22**, 3133-3142.

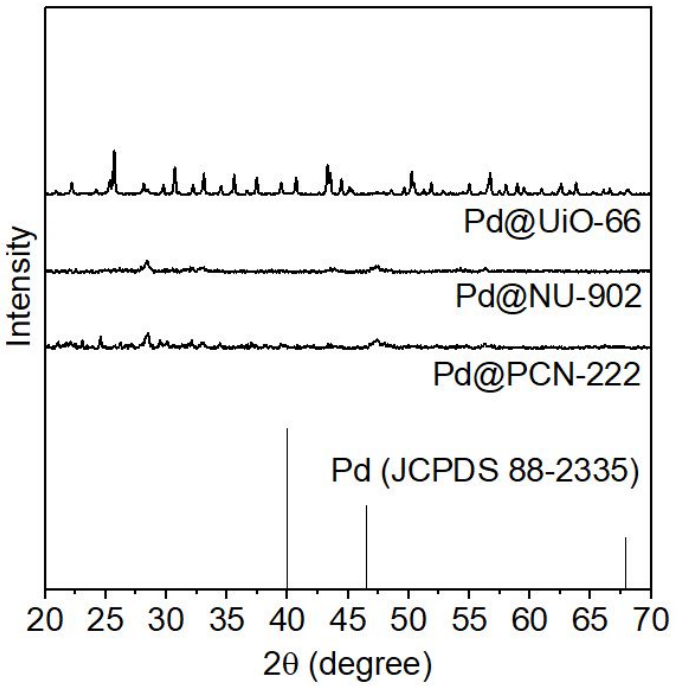

Figure S1. PXRD patterns of Pd@Zr-MOFs.

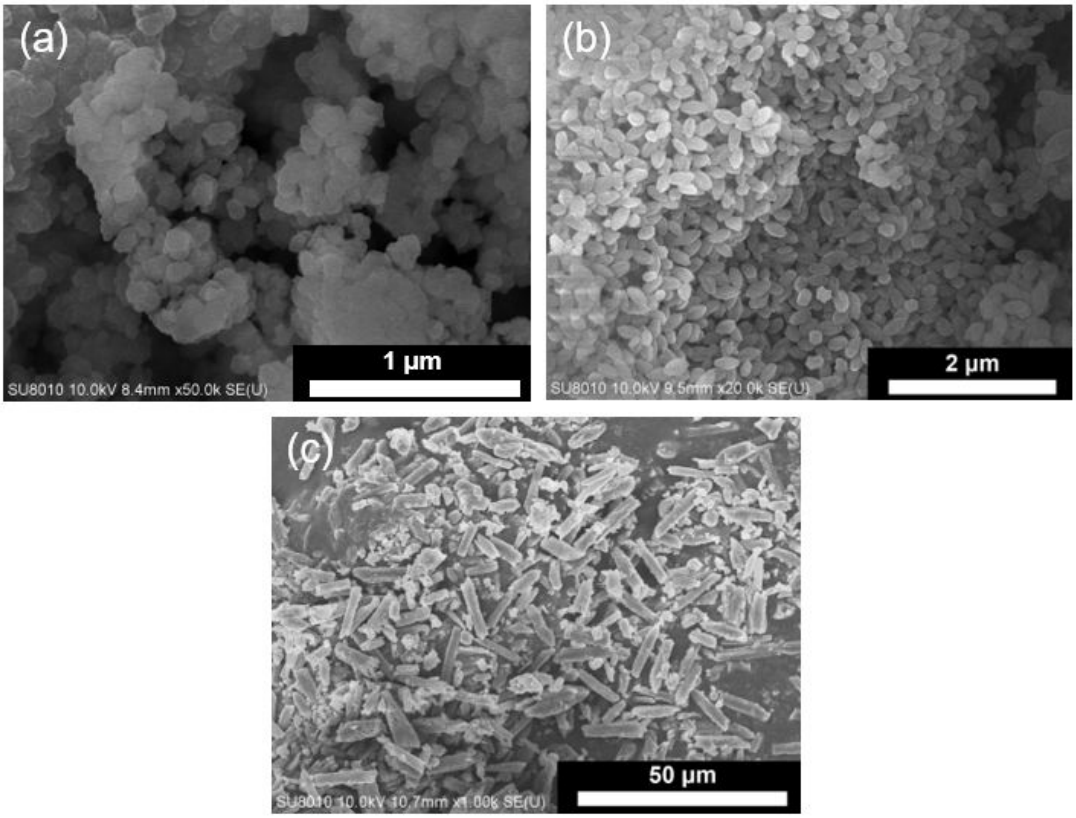

Figure S2. SEM images of (a) UiO-66, (b) NU-902, and (c) PCN-222.

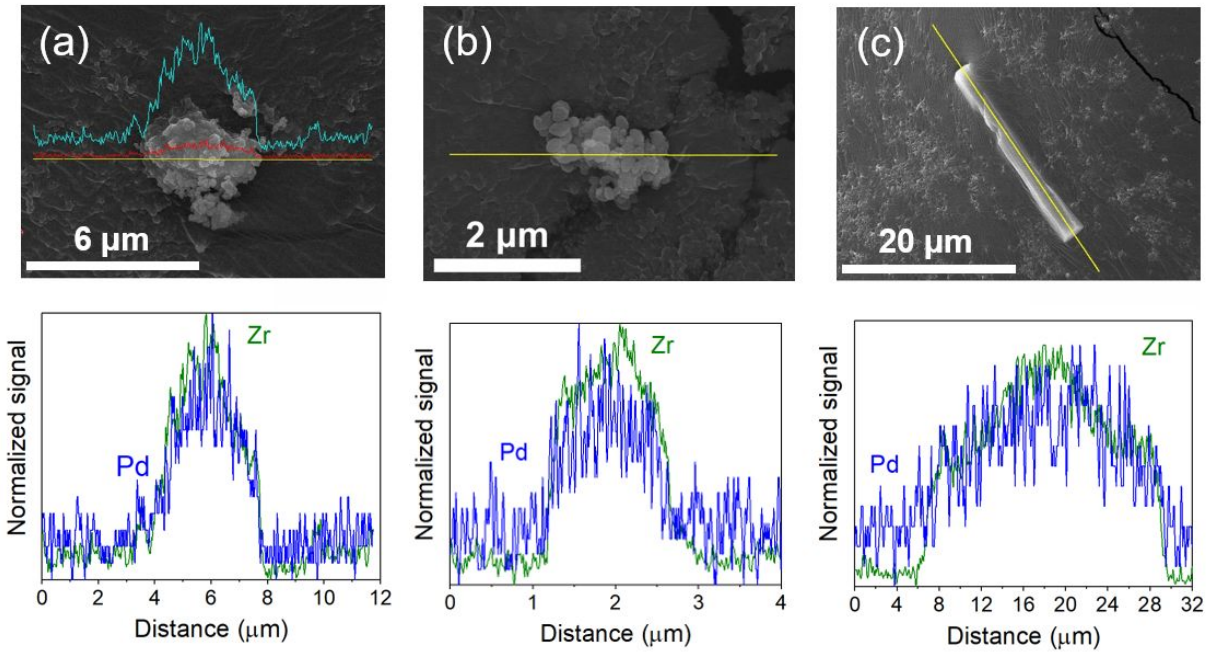

Figure S3. EDS line scans (yellow lines) and normalized EDS signals of (a) Pd@UiO-66, (b) Pd@NU-902, and (c) Pd@PCN-222.

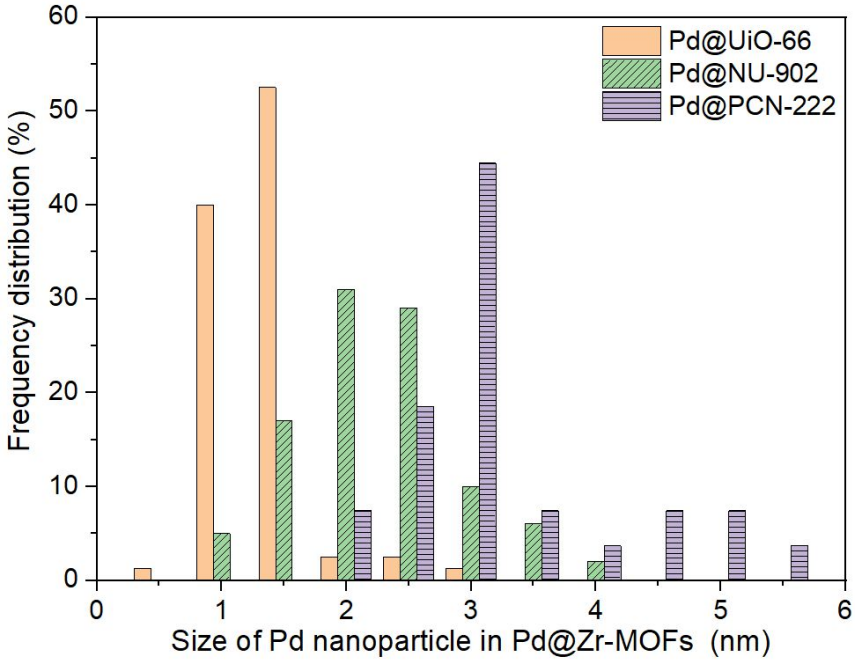

Figure S4. Size distribution of Pd nanoparticles in Pd@Zr-MOFs.

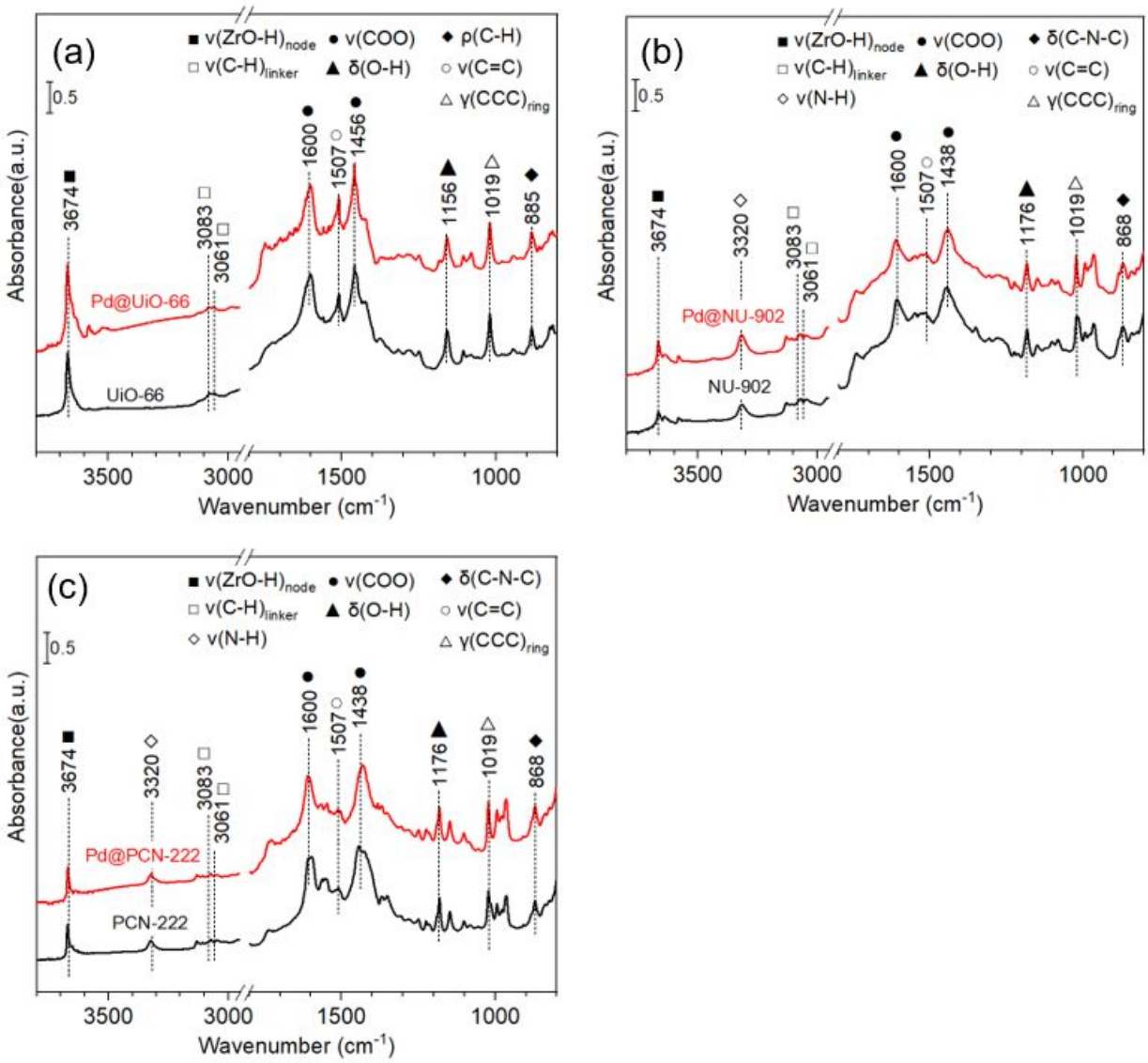

Figure S5. Infrared spectra of (a) UiO-66, (b) NU-902, and (c) PCN-222 before and after Pd incorporation by solvothermal deposition in MOFs (SIM) technique.

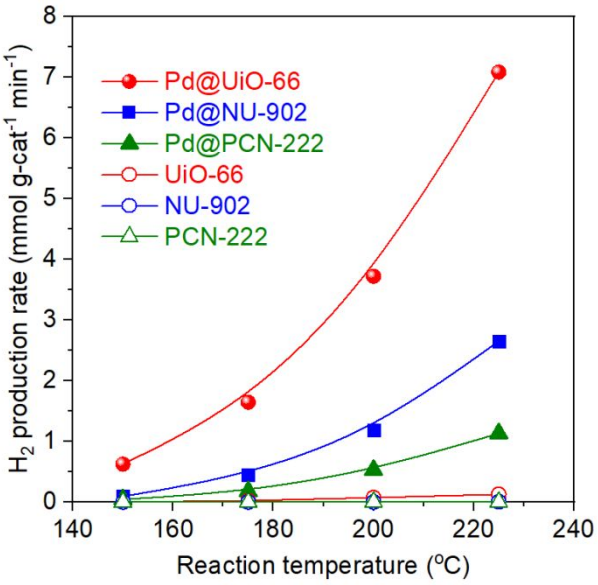

Figure S6. Catalytic methanol dehydrogenation over pristine Zr-MOFs and Pd@Zr-MOFs.

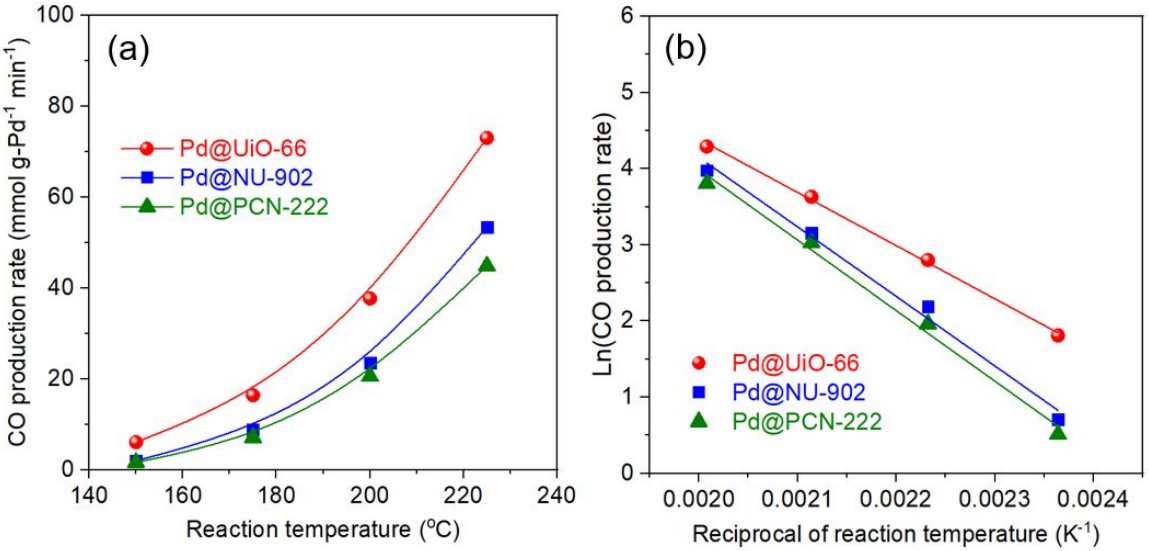

Figure S7. Catalytic methanol decarbonylation over Pd@Zr-MOFs. (a) CO production rate from methanol decomposition as a function of reaction temperature, and (b) Arrhenius plot for data in (a). The activation energies for Pd@UiO-66, Pd@NU-902, Pd@PCN-222 are 58, 76, and 77 kJ mol^{-1}.

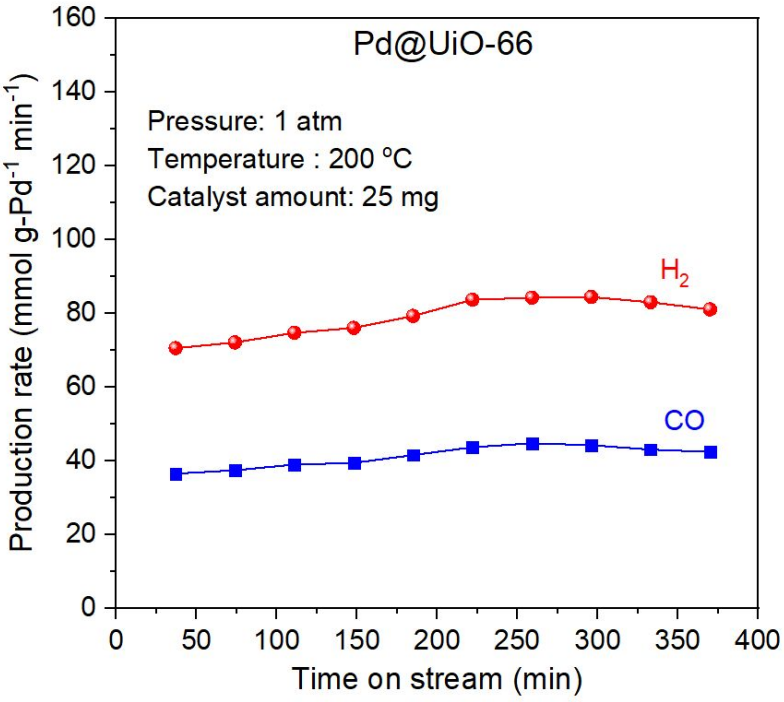

Figure S8. Time on stream of H_2 and CO production rates from methanol dehydrogenation over Pd@UiO-66 at 200 °C.

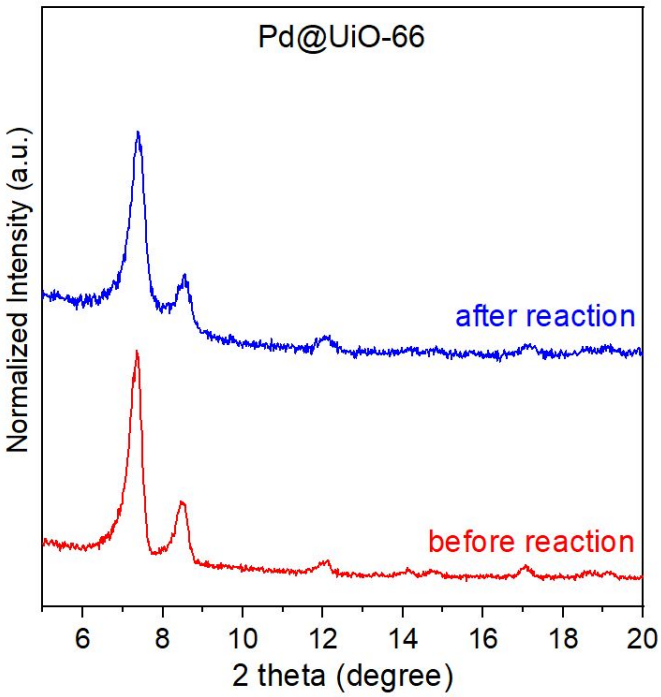

Figure S9. PXRD patterns of Pd@UiO-66 before and after catalytic reaction. Reaction condition: 25 mg of catalyst, methanol inlet flow (1 mL/h), methanol: N_2 = 1:4 (molar ratio), N_2 flow rate (40 mL/min), time on stream reaction at 200 °C for 6 hours.

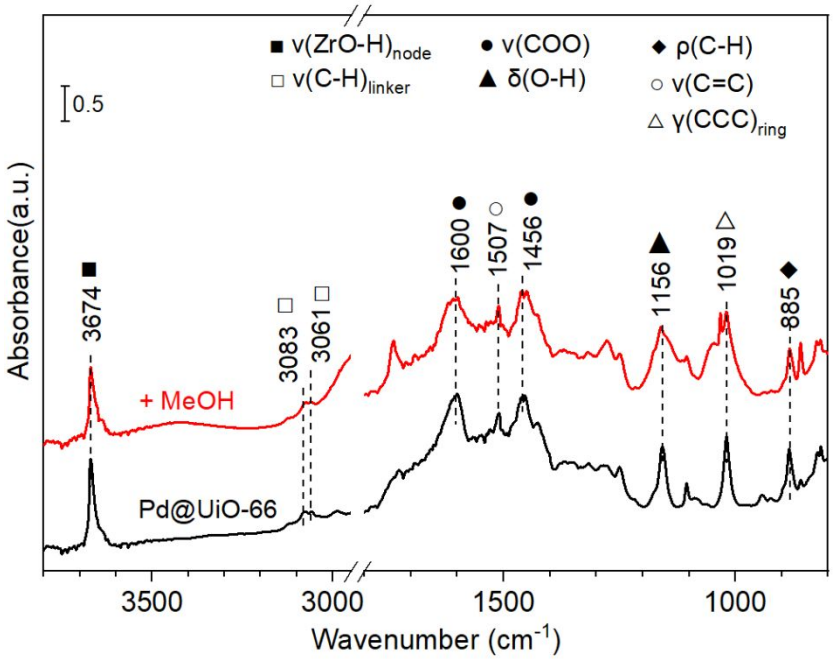

Figure S10. Infrared spectra of Pd@UiO-66 before and after exposing to methanol for 60 min at 200 °C.

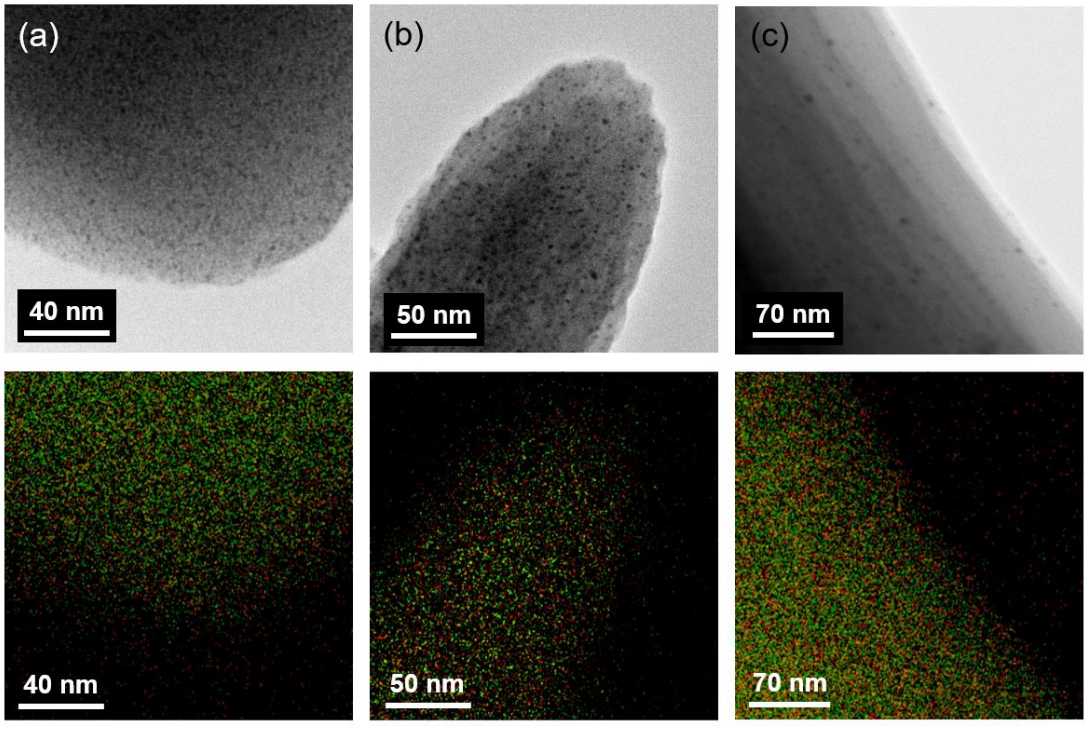

Figure S11. TEM images and elemental mapping (Red: Pd; Green: Zr) of (a) Pd@UiO-66, (b) Pd@NU-902, and (c) Pd@PCN-222 after catalytic reaction. Reaction condition: 25 mg of catalyst, methanol inlet flow (1 mL/h), methanol: N_2 = 1:4 (molar ratio), N_2 flow rate (40 mL/min), time on stream reaction at 200 °C for 6 hours.

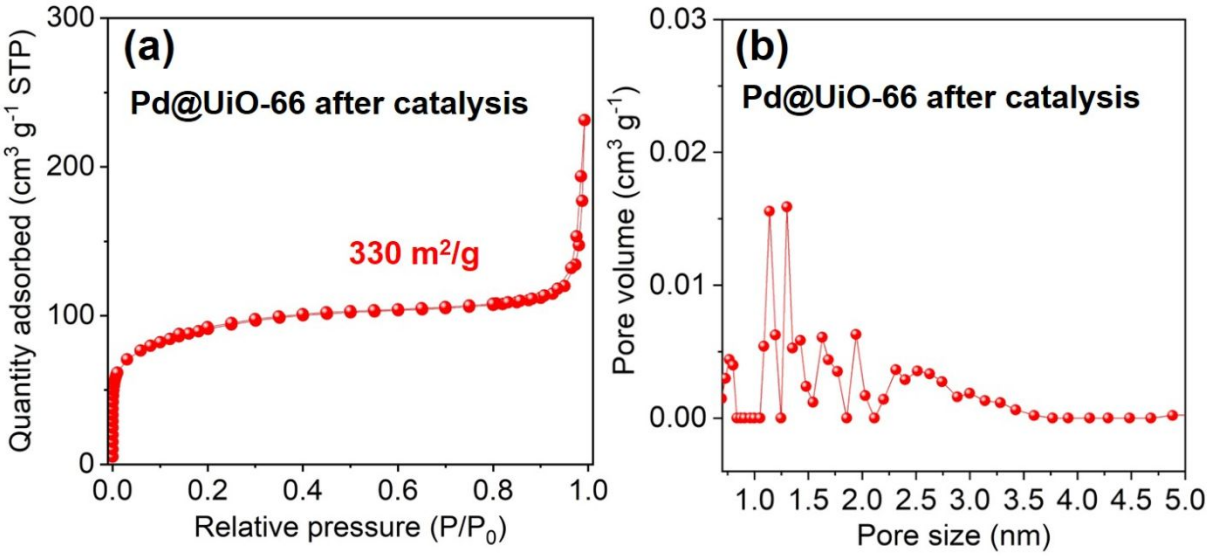

Figure S12. (a) Nitrogen adsorption-desorption isotherm and (b) DFT pore size distribution of Pd@UiO-66 after catalytic reaction. Reaction condition: 25 mg of catalyst, methanol inlet flow (1 mL/h), methanol: N_2 = 1:4 (molar ratio), N_2 flow rate (40 mL/min), time on stream reaction at 200 °C for 6 hours. The calculated BET surface area is also shown in (a).

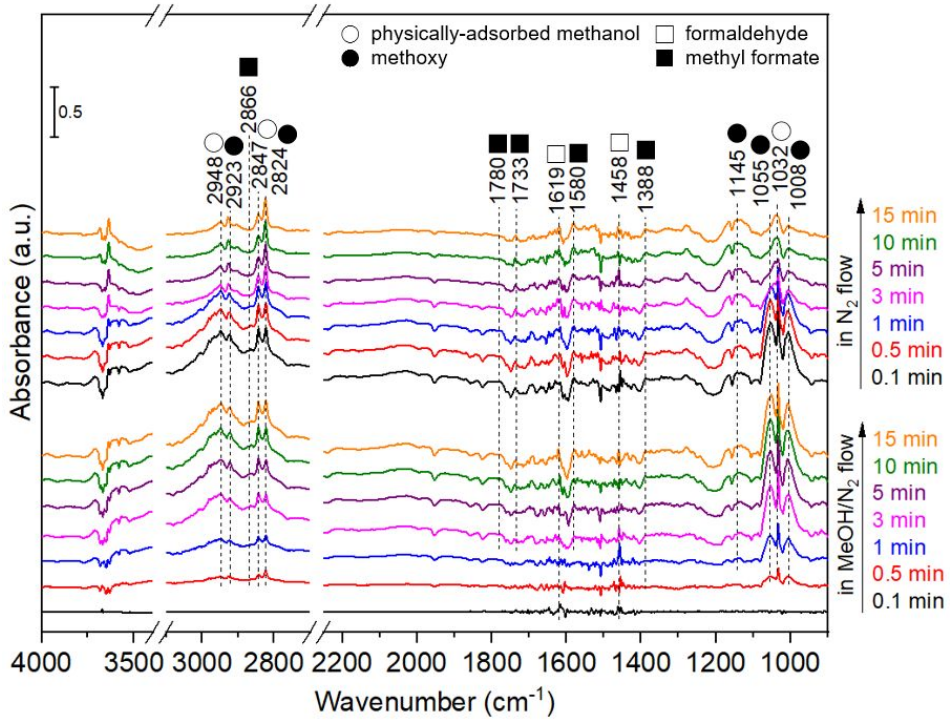

Figure S13. In-situ DRIFTS spectra of UiO-66 in the flow of methanol/N_2 followed by N_2 at 150 °C.

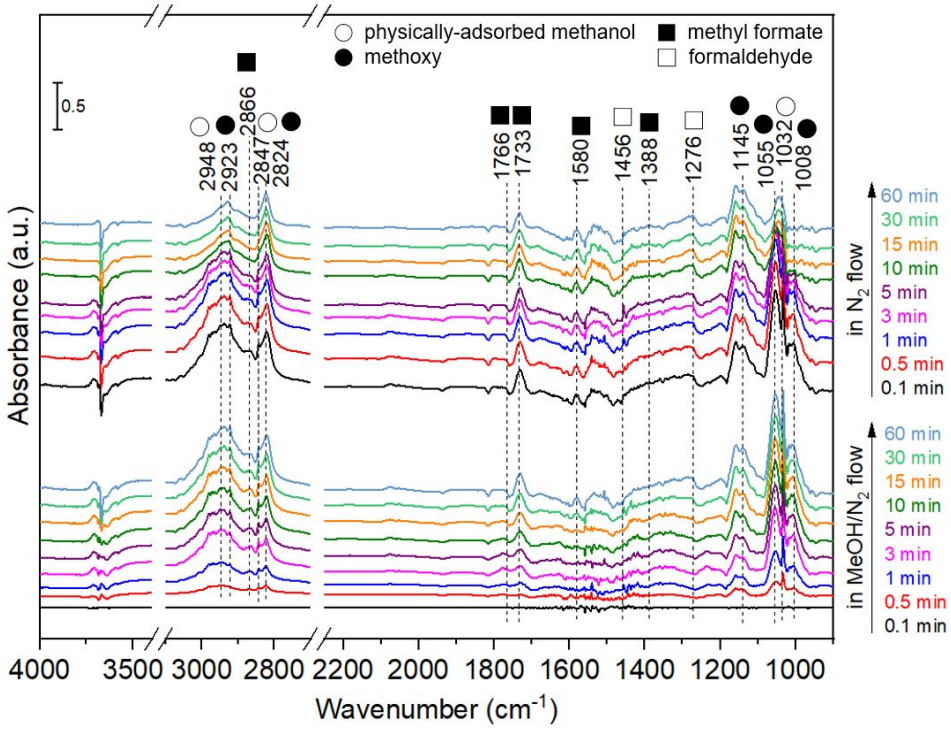

Figure S14. In-situ DRIFTS spectra of Pd@NU-902 in the flow of methanol/N_2 followed by N_2 at 150 °C.

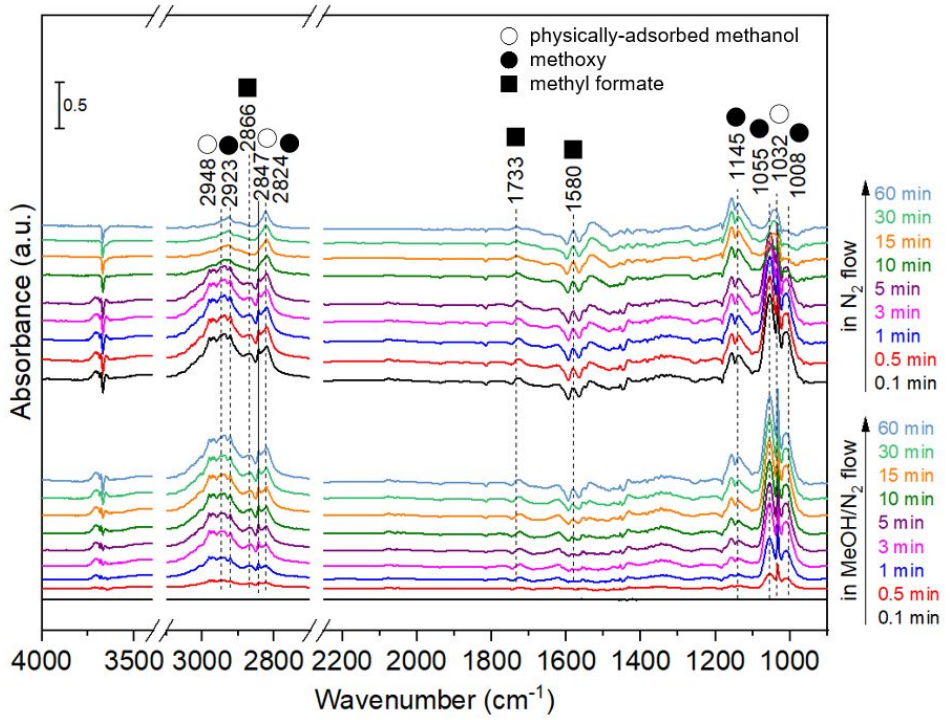

Figure S15. In-situ DRIFTS spectra of Pd@PCN-222 in the flow of methanol/N_2 followed by N_2 at 150 °C.

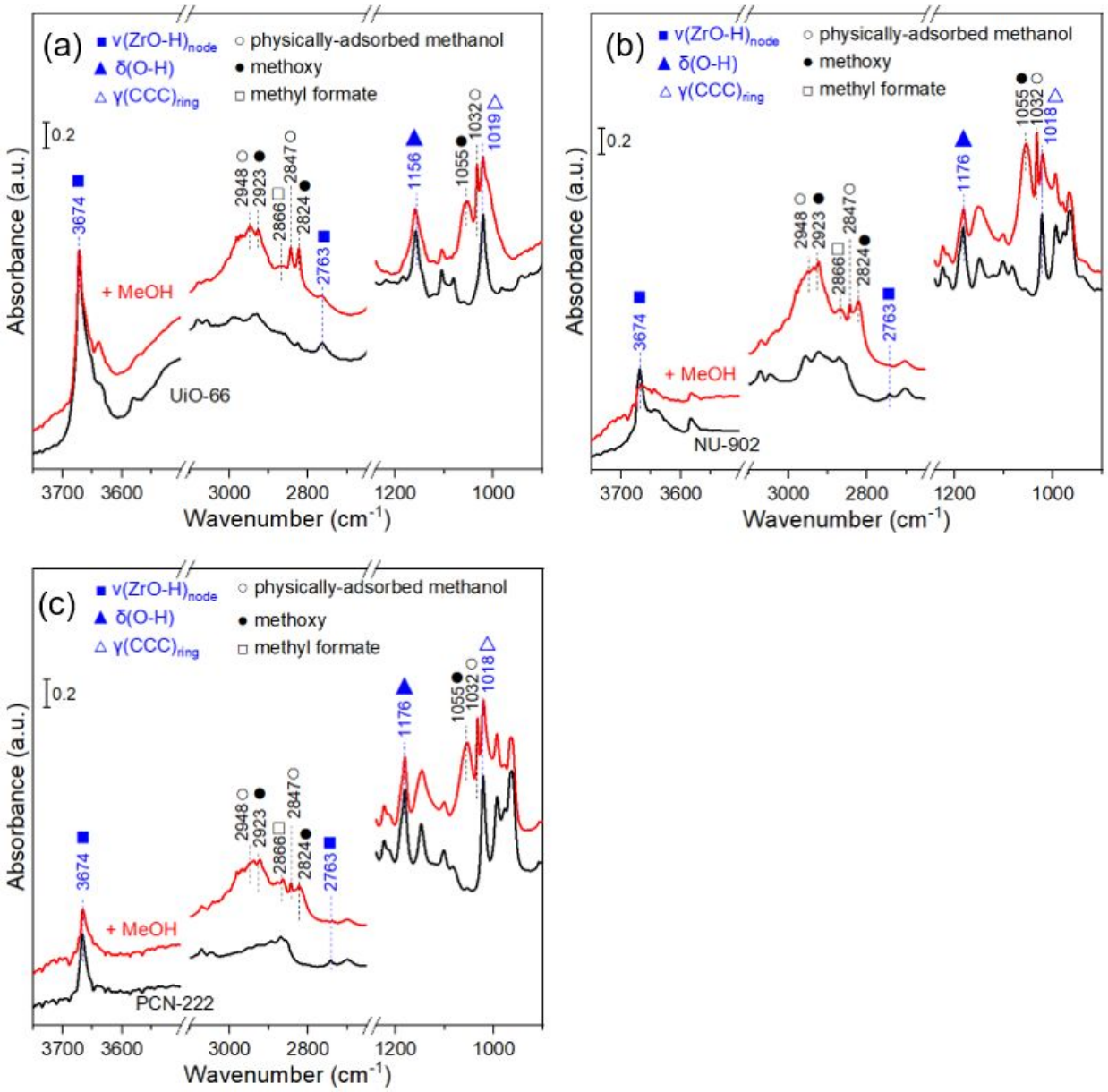

Figure S16. Infrared spectra of (a) UiO-66, (b) NU-902, and (c) PCN-222 before and after exposing to methanol at 150 °C for 15 min.