

Supporting Information

Pd-doped HKUST-1 MOFs for enhanced hydrogen storage: effect of hydrogen spillover

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Table S1. The physical and chemical properties of samples.

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Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$) ^a	V_{micro} ($\text{cm}^3 \text{g}^{-1}$) ^a	Average Pore Size (\AA) ^a	Cu/Pd content (%) ^b
HKUST-1	1456.22	0.50	8.58	-
Pd@HKUST-1- DS	1033.88	0.35	8.04	26.3/2.15
Pd/HKUST-1-IM	612.84	0.26	-	28.7/2.22

^a The N_2 physical adsorption-desorption at 77 K;

^b The value was determined by inductively coupled plasma optical emission spectrometry (ICP-OES);

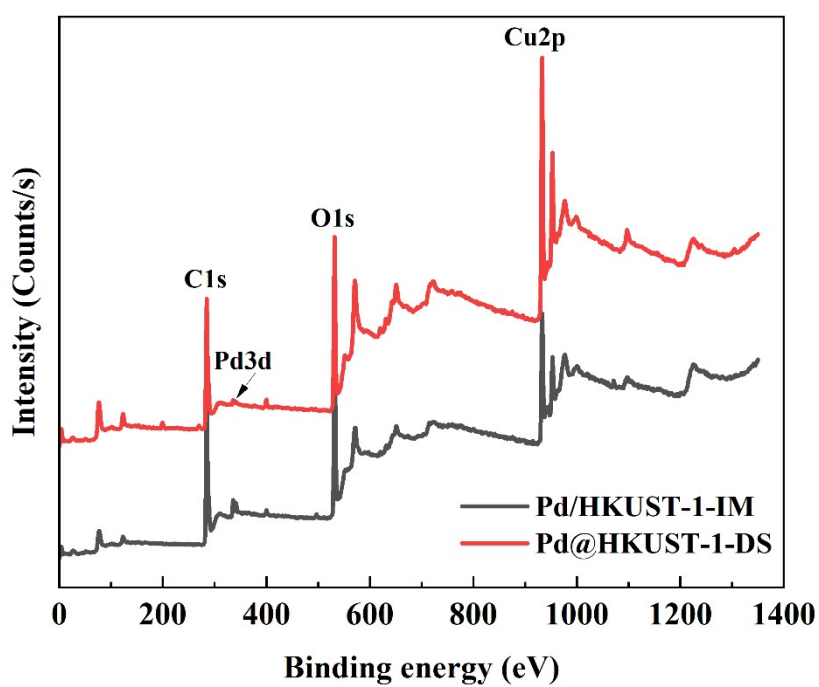


Fig. S1 XPS full spectra of Pd@HKUST-1-DS and Pd/HKUST-1-IM.

Table S2. Binding energies of Pd 3d peaks and Cu 2p peaks of samples.

Peak	Pd 3d _{3/2} / eV	Pd 3d _{5/2} / eV	Cu 2p _{1/2} / eV	Cu 2p _{3/2} / eV
	Pd ⁰ /Pd ²⁺	Pd ⁰ /Pd ²⁺		
Pd nanocubes ^[1]	339.4/342.2	334.2/335.9	-	-
HKUST-1	-	-	953.3	933.4
Pd/HKUST-1-IM	340.8/342.3	335.3/337.0	952.8	932.9
Pd@HKUST-1- DS	340.9/342.4	335.4/337.1	952.6	932.7

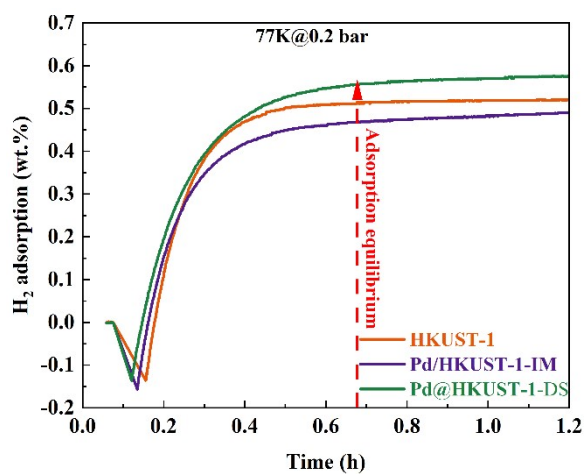


Fig. S2. Hydrogen adsorption kinetic of HKUST-1, Pd@HKUST-1-DS and Pd/HKUST-1IM at 77 K and 0.2 bar H₂

Table S3. Comparison of hydrogen adsorption capacities of catalyst-decorated MOFs in the present work and previously reported spillover data and the comparison between measured and expected hydrogen adsorption in spillover materials in the recent literature and this Work.

Samples	Specific surface area (m ² /g)	Temperature (K)	Pressure (bar)	H ₂ uptake (wt.%)
ZIF-8 ^[2]	1297	298	10	0.078
ZIF-8/GO ^[2]	1247	298	10	0.073
Pt@ZIF/GO ^[2]	619	298	10	0.17
MIL-100(Al) ^[3]	1200	298	40	0.19
Pd/MIL-100(Al) ^[3]	380	298	40	0.35
IRMOF-8 ^[4]	1430	298	100	0.44
Pt/IRMOF ^[4]	1175	298	100	0.85
Cu-BTC ^[5]	1641	298	20	0.17
PtC/Cu-BTC ^[5]	1350	298	20	0.61
MIL-100 ^[6]	1797	298	31	0.25
Pt/AC-MIL-100 ^[6]	1552	298	31	0.41
UIO ^[7]	1386	303	31	0.18
aUIO-Ac ^[7]	1166	303	30	0.06
Pt/aUiO-Ac ^[7]	932	303	34	0.38
aUiO-Cl ^[7]	1070	303	31	0.08
Pt/aUiO-Cl ^[7]	893	303	33	0.71
OMHCS ^[8]	543	313	35	0.25
Pd@OMHCS-R ^[8]	359.9	313	35	0.51
Pd@OMHCS-I ^[8]	283.3	313	35	0.34
ACF ^[9]	1996	298	20	0.18
Pd-ACF ^[9]	1990	298	20	0.26
MIL-100(Fe)/GO-M ^[10]	1801	298	50	2.02
HKUST-1	1456.22	298	180	0.61
Pd@HKUST-1-DS	1033.88	298	30/180	0.15/1.63
Pd@HKUST-1-IM	612.84	298	30/180	0.12/1.14

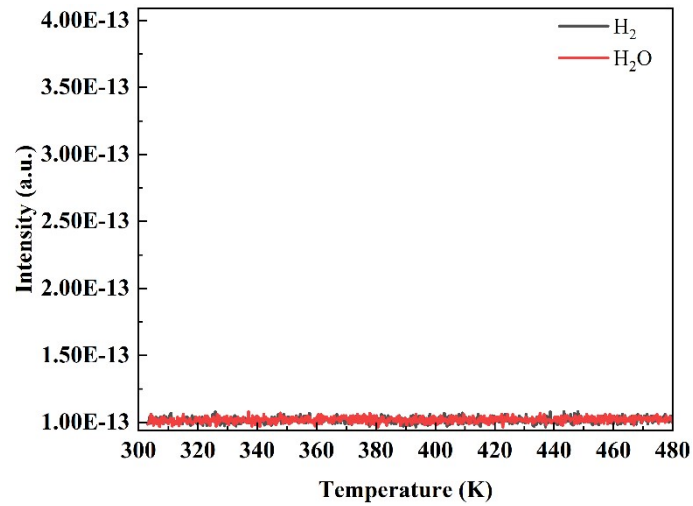


Fig. S3. Thermal desorption spectra of un-loading Pd@HKUST-1-DS at 298 K. The sample was evacuated for 5 min before heating at a rate of 5 K/min.

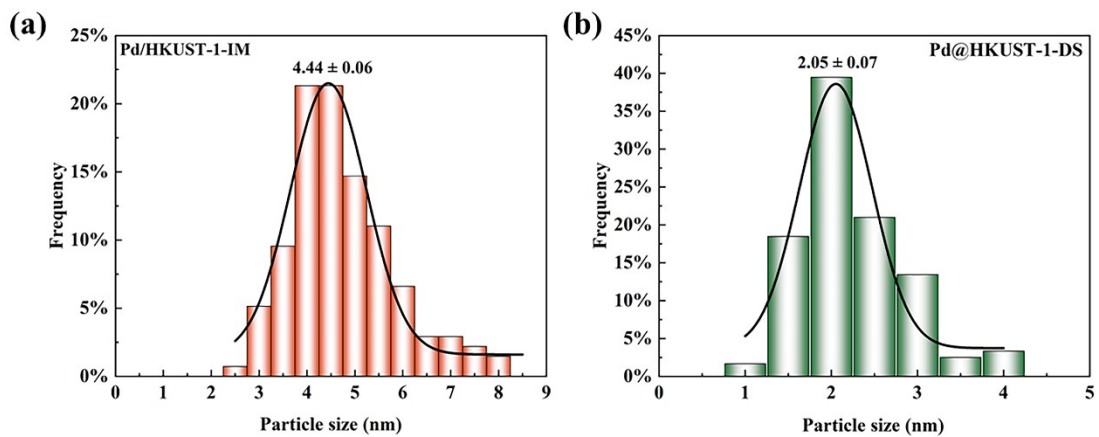


Fig. S4 Pd particle size distributions of Pd/HKUST-1-IM and Pd@HKUST-1-DS.

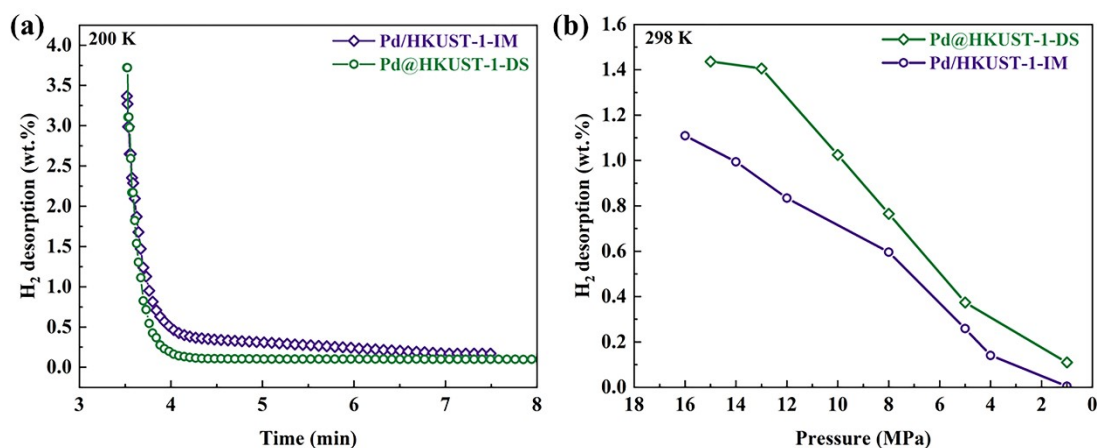


Fig. S5 Hydrogen adsorption isotherms of Pd@HKUST-1 and Pd/HKUST-1: (a) 200 K; (b) 298 K.

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