Supporting Information

An active and stable multifunctional catalyst with defective UiO-66 as support for Pd over the continuous catalytic conversion of acetone and hydrogen

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Potentiometric acid-base titrations were completed with a Metrohm Titrando 905 autotitrator equipped with Dosino 800 20 mL and 10 mL dosing units using a procedure previously reported.[1-4] Prior to each titration, calibrations were performed with 2.00 and 9.00 Metrohm buffer solutions. Sample preparation entailed using approximately 50 mg of sample (previously activated for 12 h at 150 °C under the condition of vacuum) that were crushed into a fine powder with a plastic spatula in a 100 mL beaker. Then approximately 50 mL of 0.01 M $NaNO_3$ solution was added and allowed to equilibrate for 18 h. Preceding each titration, a stir bar was added to the beaker and the pH was adjusted to a value of 3.00 with 0.1 M HCl. Following, the solution was titrated with a 0.1 M NaOH solution to a pH value of 10.5-11.0 with an injection volume of 0.025 mL at a rate of 0.020 mL min^{-1}. In order to better visualize the equivalence points, the first derivative of the titration curve (pH *vs.* Volume of 0.1 M NaOH added) was taken (dpH/dV *vs.* Volume of 0.1 M NaOH added). The first derivative plots were then subjected to Lorentzian function curve-fitting with Origin Pro V8.5 multiple peak fitting function.

Calculation of the number of defect sites via potentiometric acid-base titrations

Explanation of calculations: Owing to the fact that titrations are quantitative in nature and that defect sites inherently have titratable protons (under our conditions with a solution pH of 3), we are able to determine the number of defect sites in each sample. In order to determine the number of $Zr-OH_2$ and Zr-OH, we simply calculate the amount of NaOH titrant consumed for each species. With respect to the $Zr-OH_2$ species, we take the difference in the amount of NaOH titrant consumed between the second ($Zr-OH_2$) and first (μ_3-OH) equivalence points (each terminal water is deprotonated once, yielding an additional terminal hydroxyl group which we assume to be equivalent to the terminal hydroxyl group that was already present in the pair). In a similar fashion, the amount of Zr-OH species can be found by taking the difference in NaOH titrant consumed between the third (Zr-OH) and second ($Zr-OH_2$) equivalence points and removal yielding an additional terminal hydroxyl group. The relative amounts of defect sites from $Zr-OH_2$

and Zr-OH, with respect to each other, are then calculated and assigned the variables y and z, respectively. These values are then related to the molecular formula of UiO-66 that incorporates Zr-OH$_2$ and Zr-OH compensating missing linker defects, $Zr6O_4(OH)_4(bdc)_{6-x}[(OH_2)_y(OH)_z]_4$, where x is the number of missing linkers in an ideal $Zr_6O_4(OH)_4(bdc)_6$ cluster. Following, the number of missing linkers can be realized by comparing the experimental value of titrated protons from the calculated theoretical values with different numbers of missing linkers.

Table S1. Comparison of the catalytic performance of different catalysts.

Catalyst	Temp (℃)	H$_2$ Pressure (MPa)	Catalyst weight (g)	Volume of acetone (mL)	Reaction time (h)	Acetone conversion (%)	Selectivity to MIBK (%)
Pd/Ui-66(R=15:1)	120	0.75	0.02	5	2	54.44	92.86
Pd/Mg$_3$Al-MMO	120	2.8	0.35	10	5	38.5	82.8
Pd on the amorphous Zn–Cr (1:1)	180	0.75	2	2.5	2	38-40	70-78
Pt/ZSM-5@MS	180	1.4	0.2	2.5	1	39.7	92.4
Pd/SO$_3$H-Si-HS	160	1	0.2	2.5	2	43.1	90.7

Table S2. Catalytic performance of 0.5wt% Pd/UiO-66(R=15:1) at orthogonal experiments in the trickle bed reactor.

Reaction conditions				Acetone conversion (%)	Selectivity (%)						MIBK+MIBC yield (%)
temp (℃)	LHSV (h^{-1})	C$_3$H$_6$O/H$_2$ (mol/mol)	Pressure (MPa)		MIBK	MIBC	MO	DAA	IPA	Others	
100	0.12	1/1	1	24.91	82.54	3.17	0.02	5.69	6.93	1.65	21.35
100	0.15	1/2	2	23.45	84.02	1.61	0.03	6.83	6.28	1.23	20.08
100	0.18	1/3	3	20.72	88.14	1.26	0.32	7.97	0.610	1.70	18.52
100	0.24	1/4	4	23.78	83.39	1.31	0.31	7.6	6.42	0.97	20.14
110	0.12	1/2	3	35.33	86.99	4.25	0.14	2.45	4.59	1.58	32.25
110	0.15	1/1	4	40.04	89.11	3.36	1.30	2.77	3.30	0.16	37.02
110	0.18	1/4	1	36.02	88.08	3.41	1.29	2.09	4.97	0.16	32.95
110	0.24	1/3	2	34.75	90.42	2.83	0.28	3.15	1.90	1.42	32.40
120	0.12	1/3	4	39.62	89.66	3.94	1.49	1.56	0.87	2.48	37.08
120	0.15	1/4	3	42.28	92.23	3.91	0.14	1.04	1.29	1.39	40.65
120	0.18	1/3	2	51.37	89.95	6.30	0.15	1.32	0.64	1.64	49.44
120	0.24	1/2	1	44.99	90.13	5.05	0.17	1.12	1.53	2.00	42.82
130	0.12	1/4	2	60.29	86.13	8.36	0.08	0.49	1.58	3.36	56.97
130	0.15	1/3	1	58.51	83.10	10.68	0.06	0.28	0.8	5.08	54.87
130	0.18	1/2	4	60.79	84.95	8.64	0.06	0.62	0.63	5.10	56.89
130	0.24	1/1	3	57.19	83.84	5.86	3.41	0.85	2.73	3.31	51.30

The volume of catalytic is 6 mL and time on stream is 2 h. IPA is isopropanol. Others is mainly C$_9^+$.

Table S3. Calculation results of orthogonal test.

Experiment	Temp(℃)	LHSV(h^{-1})	C$_3$H$_6$O/H$_2$(mol/mol)	Pressure (MPa)	MIBK+MIBC yield (%)
1	1	1	1	1	82.5
2	1	2	2	2	85.6
3	1	3	3	3	88.1
4	1	4	4	4	84.4
5	2	1	2	3	87
6	2	2	1	4	89.1
7	2	3	4	1	88.1
8	2	4	3	2	90.4
9	3	1	3	4	89.7
10	3	2	4	3	92.2
11	3	3	1	2	89.95
12	3	4	2	1	90.13
13	4	1	4	2	86.13
14	4	2	3	1	83.1
15	4	3	2	4	85
16	4	4	1	3	83.8
K11	340.6	345.33	345.35	343.83	
K21	354.6	350	347.73	352.08	
K31	361.98	351.15	351.3	351.1	
K41	338.03	348.73	350.83	348.2	
K1L	85.15	86.3325	86.3375	85.9575	
K2L	88.65	87.5	86.9325	88.02	
K3L	90.495	87.7875	87.825	87.775	
K4L	84.5075	87.1825	87.7075	87.05	
R	5.9875	1.455	1.4875	2.0625	
Excellent level	120	0.18	1/2	2	

Table S4. Porosity property of various samples

samples	BET surface area (m^2/g)	V$_t$(cm^3/g)	V$_{meso}$(cm^3/g)
UiO-66	1677	0.88	0.08
UiO-66(R=15:1)	1068	1.03	0.66

V$_t$ stands for the total pore volume determined by using the adsorption branch of the N$_2$ isotherm at P/P$_0$=0.95. V$_{meso}$ stands for the mesopore volume obtained from the BJH adsorption cumulative volume.

Table S5. Calculation results of missing linker in UiO-66.

Zr-OH$_2$		
EP2-EP1=	0.97	mL NaOH
	0.097	mmol defect sites from Zr-OH$_2$
Zr-OH		
EP3-EP2=	1.88	mL NaOH
	0.188	mmol defect sites from Zr-OH
	0.285	Total mmol defect sites from [(OH$_2$)(OH)]

Relative amount of defect sites from Zr-OH$_2$ =		34.1%
Relative amount of defect sites from Zr-OH =		65.9%

Missing Linker	Molecular Formula	MW	mmol defect sites in 0.0498 g sample
0	Zr$_6$O$_4$(OH)$_4$(C$_8$H$_4$O$_4$)$_6$	1664.06	0
1	Zr$_6$O$_4$(OH)$_4$(C$_8$H$_4$O$_4$)$_5$[(H$_2$O)$_{0.341}$(OH)$_{0.659}$]$_4$	1569.35	0.127
1.5	Zr$_6$O$_4$(OH)$_4$(C$_8$H$_4$O$_4$)$_{4.5}$[(H$_2$O)$_{0.341}$(OH)$_{0.659}$]$_6$	1521.99	1.96
2	Zr$_6$O$_4$(OH)$_4$(C$_8$H$_4$O$_4$)$_4$[(H$_2$O)$_{0.341}$(OH)$_{0.659}$]$_8$	1474.64	0.270
1.6	Zr$_6$O$_4$(OH)$_4$(C$_8$H$_4$O$_4$)$_{4.4}$[(H$_2$O)$_{0.341}$(OH)$_{0.659}$]$_{6.4}$	1512.52	0.211
1.58	Zr$_6$O$_4$(OH)$_4$(C$_8$H$_4$O$_4$)$_{4.42}$[(H$_2$O)$_{0.341}$(OH)$_{0.659}$]$_{6.32}$	1514.42	**0.208**
1.59	Zr$_6$O$_4$(OH)$_4$(C$_8$H$_4$O$_4$)$_{4.41}$[(H$_2$O)$_{0.341}$(OH)$_{0.659}$]$_{6.36}$	1513.47	0.209

Table S6. Calculation results of missing linker in UiO-66(R=15:1).

Zr-OH$_2$		
EP2-EP1=	0.58	mL NaOH
	0.058	mmol defect sites from Zr-OH$_2$
Zr-OH		
EP3-EP2=	2.91	mL NaOH
	0.291	mmol defect sites from Zr-OH
	0.349	Total mmol defect sites from [(OH$_2$)(OH)]

Relative amount of defect sites from Zr-OH$_2$ =		16.6%
Relative amount of defect sites from Zr-OH =		83.4%

Missing Linker	Molecular Formula	MW	mmol defect sites in 0.0498 g sample
0	Zr$_6$O$_4$(OH)$_4$(C$_8$H$_4$O$_4$)$_6$	1664.06	0
1	Zr$_6$O$_4$(OH)$_4$(C$_8$H$_4$O$_4$)$_5$[(H$_2$O)$_{0.166}$(OH)$_{0.834}$]$_4$	1568.64	0.127
1.5	Zr$_6$O$_4$(OH)$_4$(C$_8$H$_4$O$_4$)$_{4.5}$[(H$_2$O)$_{0.166}$(OH)$_{0.834}$]$_6$	1520.93	0.197
2	Zr$_6$O$_4$(OH)$_4$(C$_8$H$_4$O$_4$)$_4$[(H$_2$O)$_{0.166}$(OH)$_{0.834}$]$_8$	1473.22	0.271
1.8	Zr$_6$O$_4$(OH)$_4$(C$_8$H$_4$O$_4$)$_{4.2}$[(H$_2$O)$_{0.166}$(OH)$_{0.834}$]$_{7.2}$	1492.30	0.241
1.9	Zr$_6$O$_4$(OH)$_4$(C$_8$H$_4$O$_4$)$_{4.1}$[(H$_2$O)$_{0.166}$(OH)$_{0.834}$]$_{7.6}$	1482.76	0.256
1.88	Zr$_6$O$_4$(OH)$_4$(C$_8$H$_4$O$_4$)$_{4.12}$[(H$_2$O)$_{0.166}$(OH)$_{0.834}$]$_{7.52}$	1484.67	0.253
1.89	Zr$_6$O$_4$(OH)$_4$(C$_8$H$_4$O$_4$)$_{4.11}$[(H$_2$O)$_{0.166}$(OH)$_{0.834}$]$_{7.56}$	1483.72	**0.254**

Table S7. Results of the mass percent (P), Pd dispersion (D), and Pd particle average size (d) of

three catalysts.

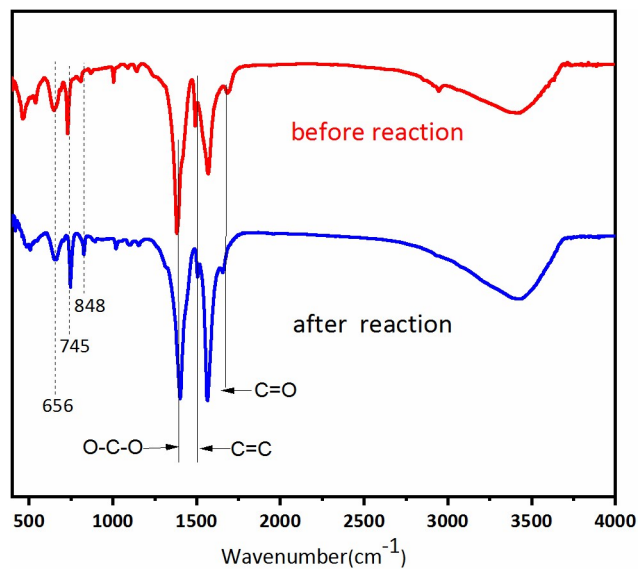| Catalyst	P (wt %)	D (%)	d (nm)
Pd/UiO-66 before reaction	0.481	36.8	3.05
Pd/UiO-66(R=15:1) before reaction	0.486	47.3	2.20
Pd/UiO-66(R=15:1) after reaction	0.442	39.8	2.73

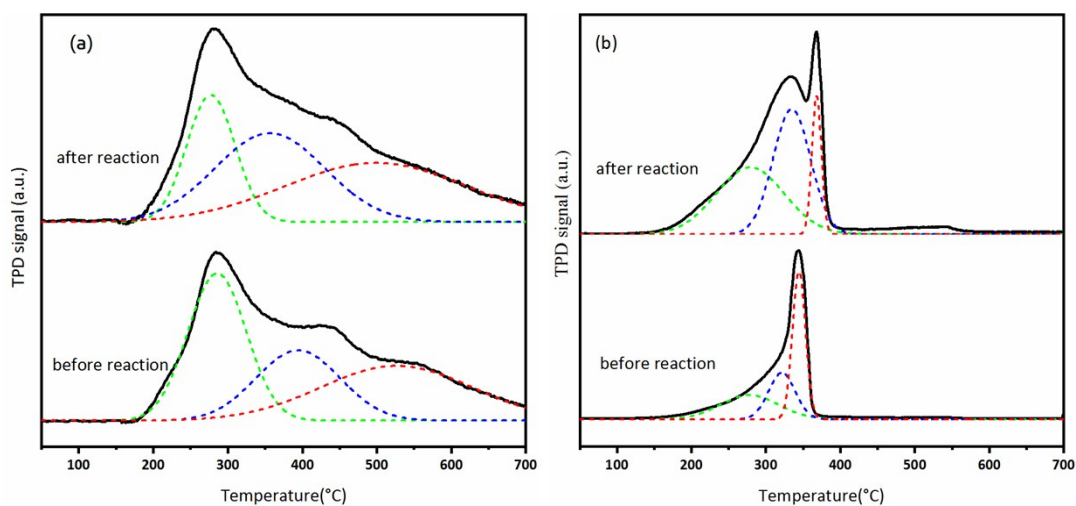**Figure S1**. FT-IR spectra of Pd/UiO-66(R=15:1) before and after 1000h reaction.

Figure S2. NH$_3$-TPD (a) and CO$_2$-TPD (b) profiles of Pd/UiO-66(R=15:1) before and after 1000h reaction.
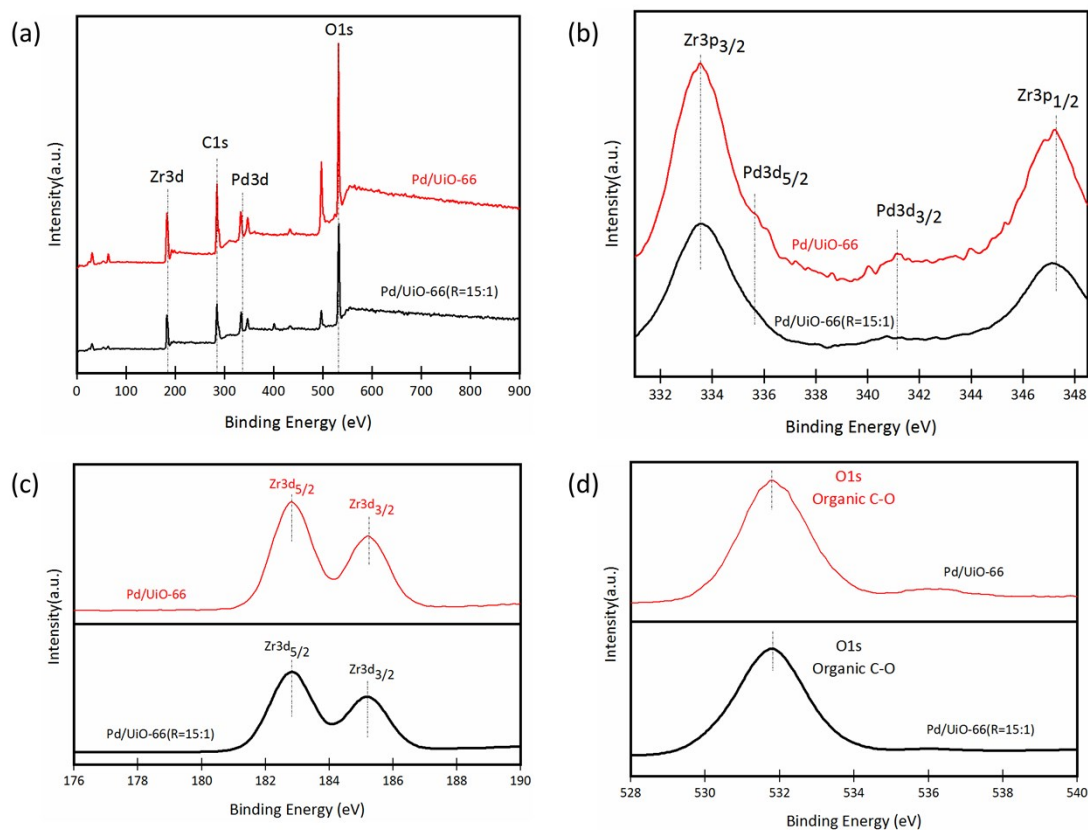
Figure S3. The XPS elemental surveys of Pd/UiO-66 and Pd/UiO-66(R=15:1) (a), the XPS spectra of Pd/UiO-66 and Pd/UiO-66(R=15:1) in the Zr 3p and Pd 3d regions (b), the XPS spectra of Pd/UiO-66 and Pd/UiO-66(R=15:1) in the Zr 3d region (c) and the XPS spectra of Pd/UiO-66 and Pd/UiO-66(R=15:1) in O 1s region (d).

References

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(4) D. Jiang, G. Fang, Y. Tong, X. Wu, Y. Wang, D. Hong, W. Leng, Z. Liang, P. Tu, L. Liu, K. Xu, J. Ni and X. Li, *ACS. Catal.,* 2018, **8**, 11973-11978.