[Electronic Supporting Information to accompany a manuscript submitted to *Catalysis Science & Technology*]

Comparative study of titanium-functionalized UiO-66: support effect on the oxidation of cyclohexene

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S1. Materials and methods

1,2-dihydroxyterephthalic acid was synthesized according to literature protocol.[S1] Unless otherwise stated, all reagents were used as received. Zirconium chloride was purchased from Strem Chemicals, Inc. (NewBuryport, MA). Terephthalic acid, titanium oxoacetylacetonate, titanium tetraisopropoxide, titanium tetrachloride tetrahydrofuran complex, hydrogen peroxide, cyclohexene, cyclohexene oxide, 2-cyclohexen-1-ol, 2-cyclohexene-one, chlorobenzene, and titanium and zirconium ICP standards were purchased from Sigma-Aldrich Co., LLC. (St. Louis, MO). Concentrated sulfuric acid and glacial acetic acid were purchased from VWR Scientific, LLC (Chicago, IL). Deuterated dimethylsulfoxide (DMSO-d_6, 99%), and deuterated sulfuric acid (D_2SO_4, 96−98% solution in D_2O) were purchased from Cambridge Isotope Laboratories, Inc. (Tewksbury, MA). Ultrapure deionized water (18.2 MΩ•cm resistivity) was obtained from a Millipore Milli-Q Biocel A10 instrument (Millipore Inc., Billerica, MA). Solvents were purchased from either Sigma-Aldrich Co., LLC. (St. Louis, MO) or Fisher Scientific, Inc. (Pittsburg, PA) and used as received. All the gases used for the adsorption and desorption measurements, as well as gases used in other instrumentations, were Ultra High Purity Grade 5 and were obtained from Airgas Specialty Gases (Chicago, IL).

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku X-ray Diffractometer Model ATX-G (Rigaku Americas, The Woodlands, TX) equipped with an 18 kW Cu rotating anode, an MLO monochromator, and a high-count-rate scintillation detector. Measurements were made over the range $2° < 2\theta < 40°$ in 0.05° step width with a 2°/min scanning speed.

N_2 adsorption and desorption isotherms were measured on either a Micromeritics Tristar II 3020 (Micromeritics Instrument Corporation, Norcross, GA) or an ASAP 2020 (Micromeritics Instrument Corporation, Norcross, GA) instrument at 77 K. Pore-size distributions were obtained using DFT calculations using a carbon slit-pore model with a N_2 kernel. Before each run, samples were activated at 150 °C for 24 h under high vacuum on a SmartVacPrep instrument (Micromeritics Instrument Corporation, Norcross, GA). Around 100 mg of sample was used in each measurement and BET surface area was calculated in the region $P/P_o = 0.005\text{-}0.05$.

Inductively coupled plasma optical-emission spectroscopy (ICP–OES) was conducted on a Varian Vista-MDX model ICP–OES spectrometer (Varian, Inc., Walnut Creek, CA) equipped with a CCD detector and an argon plasma to cover the 175–785 nm spectral range. Samples (2–4 mg) were digested in a small amount (1 mL) of a mixture of 3:1 v/v conc. H_2SO_4:H_2O_2 (30 wt % in H_2O) by heating in a Biotage SPX microwave reactor (Biotage, Uppsala, Sweden, software version 2.3, build 6250) at 180 °C until the solution became clear. The acidic solution was diluted to 25 mL with ultrapure deionized H_2O and analyzed for Ti (333.9141, 323.452, and 338.376 nm) and Zr (339.198, 343.823, and 349.619 nm) content as compared to standard solutions.

^1H and ^{13}C NMR spectra were recorded on a Bruker 500 FT-NMR spectrometer (Bruker Biospin Corp., Billerica, MA, 499.773 MHz for ^1H, 125.669 MHz for ^{13}C). ^1H and ^{13}C chemical shifts are reported in ppm from TMS with the residual solvent resonances as internal standards. MOF samples (~2–5 mg) were dissolved in conc. D_2SO_4 and then analyzed in conc. D_2SO_4, or diluted with enough DMSO-d_6 (1:10 v/v ratio of conc. D_2SO_4/DMSO-d_6) before analysis.

Centrifugation was carried out in an Eppendorf Centrifuge 5804 R, Model AG 22331 (Eppendorf AG, Hamburg, Germany) equipped with an F34-6-68 rotor. Unless otherwise stated, all centrifugations were carried out at 5200 rcf for 5 minutes.

Scanning electron microscopy (SEM) images were collected on a Hitachi SU8030 FE-SEM (Hitachi High Technologies America, Inc., Dallas, TX) microscope at Northwestern University's EPIC/NUANCE facility. Samples were activated and coated with Os to ~15 nm thickness in a Filgen Osmium Coater Model OPC-60A (Filgen, Nagoya, Japan) before imaging.

In-situ Diffuse Reflectance Infrared Fourier Transform (DRIFTS) measurements were made on a Nicolet 6700 FTIR spectrometer (Thermo Electron Scientific Instruments, LLC, Madison, WI) equipped with an MCT detector and a Harrick praying mantis accessory (Harrick Scientific Products, Inc., Pleasantville, NY). Samples were activated at 150 ºC under high vacuum for 24 h and used neat before each measurement. A sample of solid KBr was utilized as the background. Spectra were collected at 1 cm^{-1} resolution over 64 scans under an argon atmosphere. Samples were heated up to 350 ºC, dehydrated at 350 ºC for 5 minutes and then, in the rehydration step, water vapor diluted in Ar was introduced into the sample cell through a bubbler until the sample was cooled to ~150 ºC, at which point an argon atmosphere was used. The final spectra were recorded once the samples were cooled to room temperature.

Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 instrument (TA Instruments, New Castle, DE) in a flow of O_2 (20 % diluted in helium) at a heating rate of 20 ºC/min from room temperature to 600 ºC.

X-ray photoelectron spectroscopy (XPS) measurements were carried out at the KECK-II/NUANCE facility at NU on a Thermo Scientific ESCALAB 250 Xi instrument (Thermo Fisher Scientific, Inc., Al Kα radiation, hν = 1486.6 eV) equipped with an electron flood gun. XPS data was analyzed using Thermo Scientific Advantage Data System software and all spectra were referenced to the C1s peak (284.5 eV).

Metallation reactions by Atomic Layer Deposition (ALD) were carried out in a Savanah S100 system (Ultratech/Cambridge Nanotech, Waltham, MA) under N_2 gas.

Gas chromatography was performed on an Agilent Technologies 6890N Network GC system (Agilent Technologies, Inc., Santa Clara, CA) equipped with an FID detector and an HP-5 capillary column (30 m × 320 µm × 0.25 µm film thickness). Analysis parameters were as followed: initial temperature = 35 °C, initial time = 5 minutes, ramp = 10 °C/min, final temperature = 200 °C, final time = 3 minutes. Elution times (min) = 3.9 (cyclohexene); 8.6 (cyclohexene oxide); 9.4 (2-cyclohexen-1-ol); 10.5 (2-cyclohexen-1-one); and 15.6 (naphthalene). Cyclohexene oxidation product concentration was calculated based on calibration curves using naphthalene as internal standard.

S2. Characterization data for UiO-66, HCl-treated UiO-66, Ti-UiO-66, UiO-66-Cat, UiO-66-Cat-Ti, and UiO-66-Ti$_{ex}$

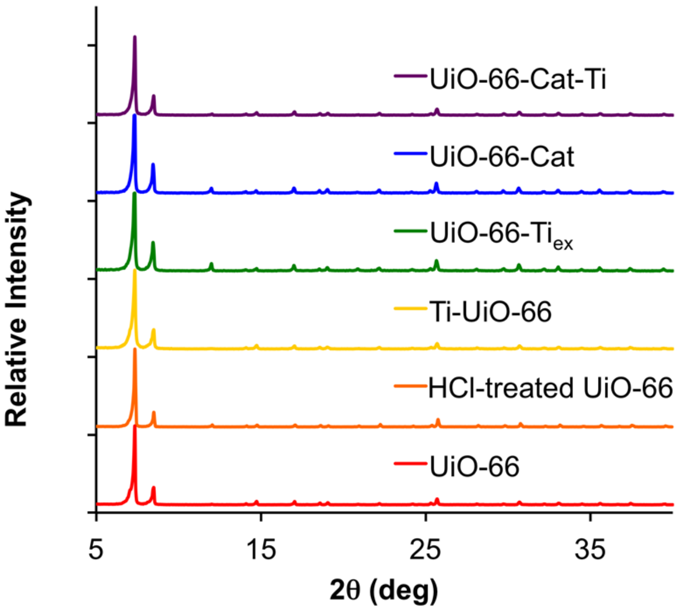

Fig. S1. PXRD patterns of UiO-66, HCl-treated UiO-66, Ti-UiO-66, UiO-66-Ti$_{ex}$, UiO-66-Cat, and UiO-66-Cat-Ti.

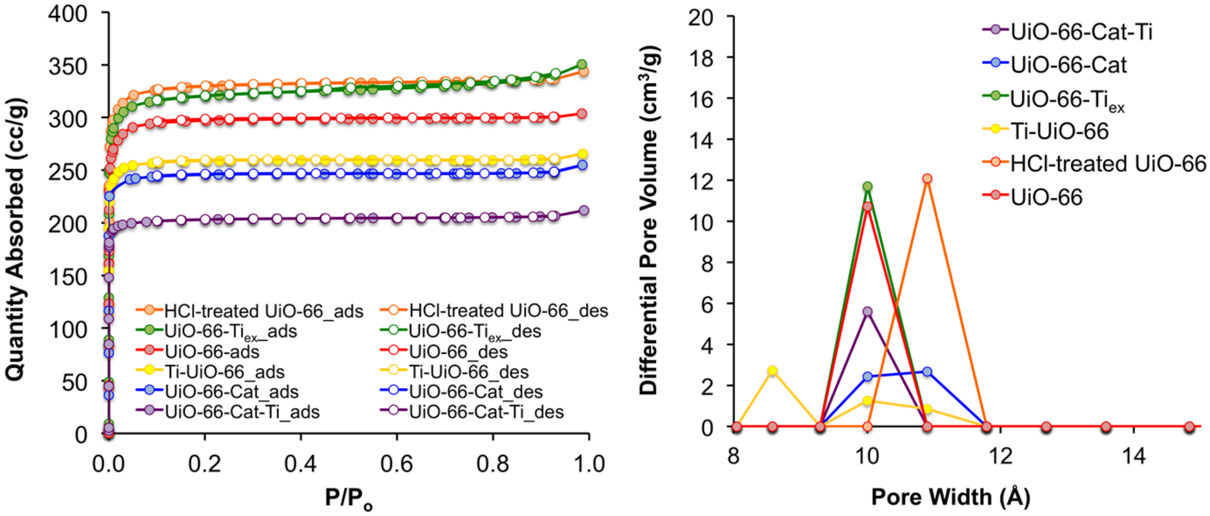

Fig. S2. Left: Representative N_2 isotherms for UiO-66, HCl-treated UiO-66, Ti-UiO-66, UiO-66-Ti$_{ex}$, UiO-66-Cat, and UiO-66-Cat-Ti collected at 77 K. Right: Pore-size distributions for UiO-66, HCl-treated UiO-66, Ti-UiO-66, UiO-66-Ti$_{ex}$, UiO-66-Cat, and UiO-66-Cat-Ti as obtained from DFT calculations (using a carbon slit-pore model with a N_2 DFT kernel).

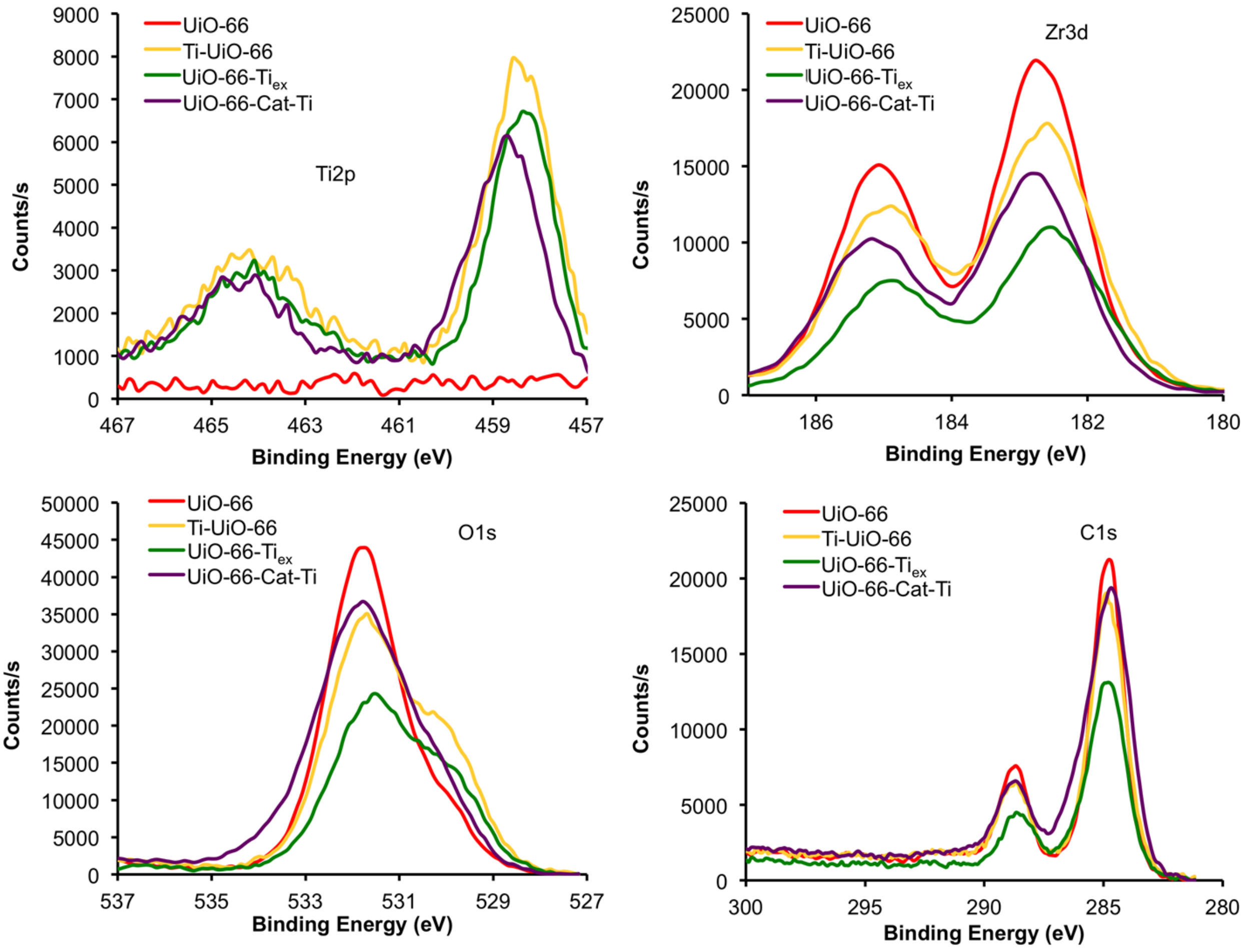

Fig. S3. C1s, O1s, Ti2p, and Zr3d X-ray photoelectron spectroscopy (XPS) spectra of UiO-66 (red), Ti-UiO-66 (golden yellow), UiO-66-Ti$_{ex}$ (green), and UiO-66-Cat-Ti (purple).

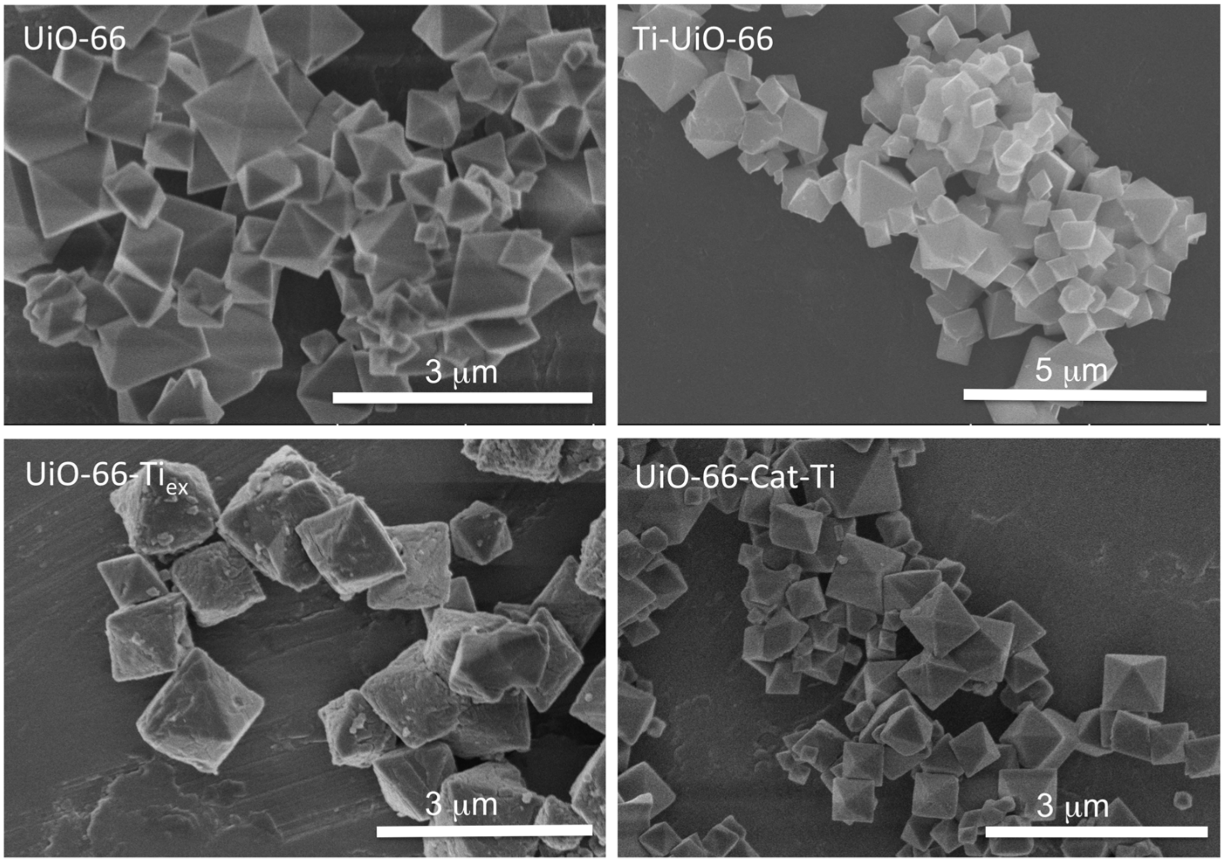

Fig. S4. SEM images of the parent UiO-66 MOF and the three Ti-functionalized UiO-66 MOFs.

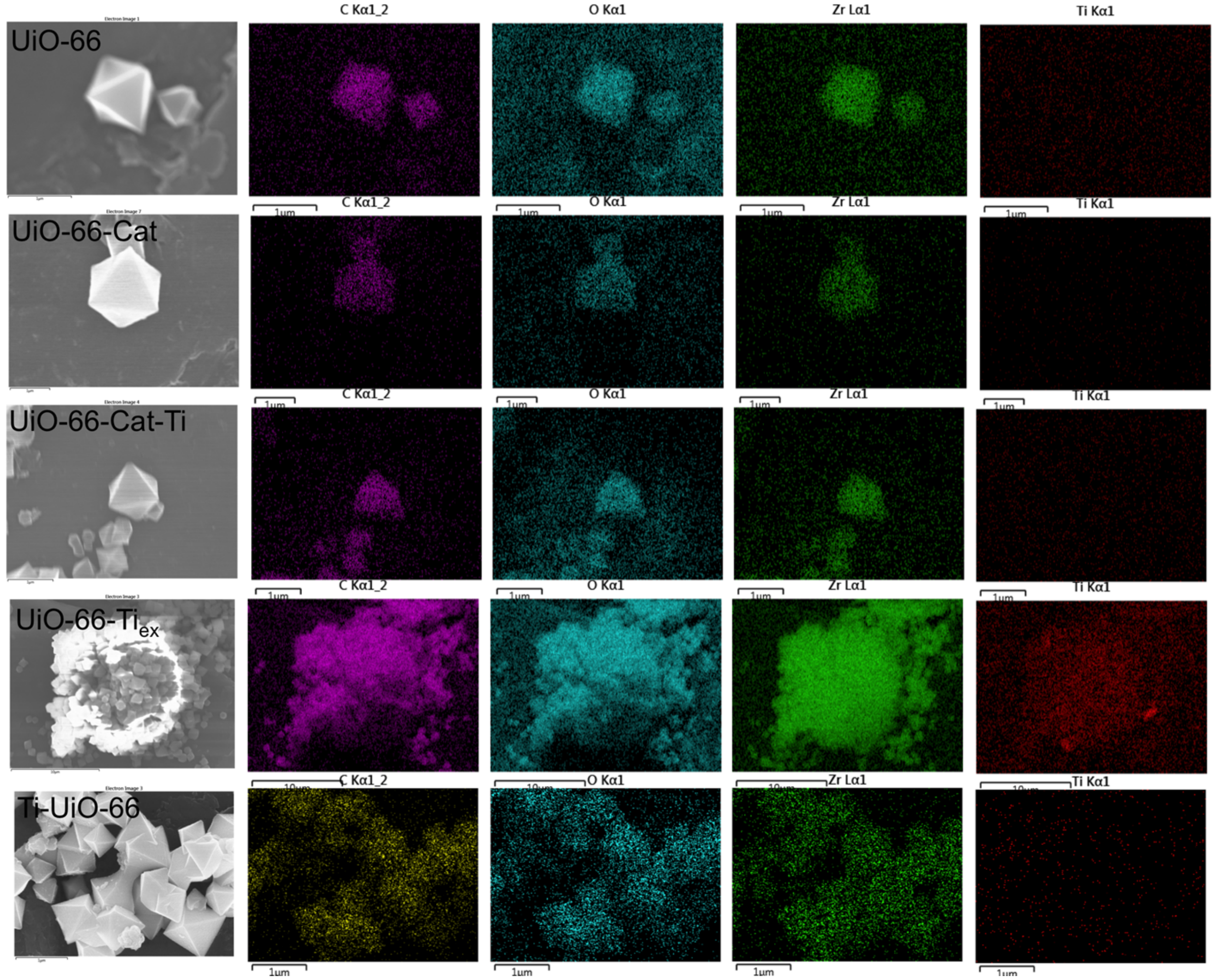

Fig. S5. Energy-dispersive X-ray (EDX) analysis of UiO-66, UiO-66-Cat, UiO-66-Cat-Ti, UiO-66-Ti$_{ex}$, and Ti-UiO-66. The presence of Ti^{IV} ions is clearly seen in UiO-66-Ti$_{ex}$, and is harder to detect for UiO-66-Cat-Ti and Ti-UiO-66 due to their much lower Ti^{IV} metal loadings.

Table S1. Ti-loading in different Ti-functionalized MOF samples based on ICP-OES analysis

Sample	Ti/Zr molar ratio
UiO-66-Ti$_{ex}$	0.28 ± 0.01 (=~22% Zr exchanged out with Ti)
Ti-UiO-66	0.04-0.08
UiO-66-Cat-Ti	0.02-0.04

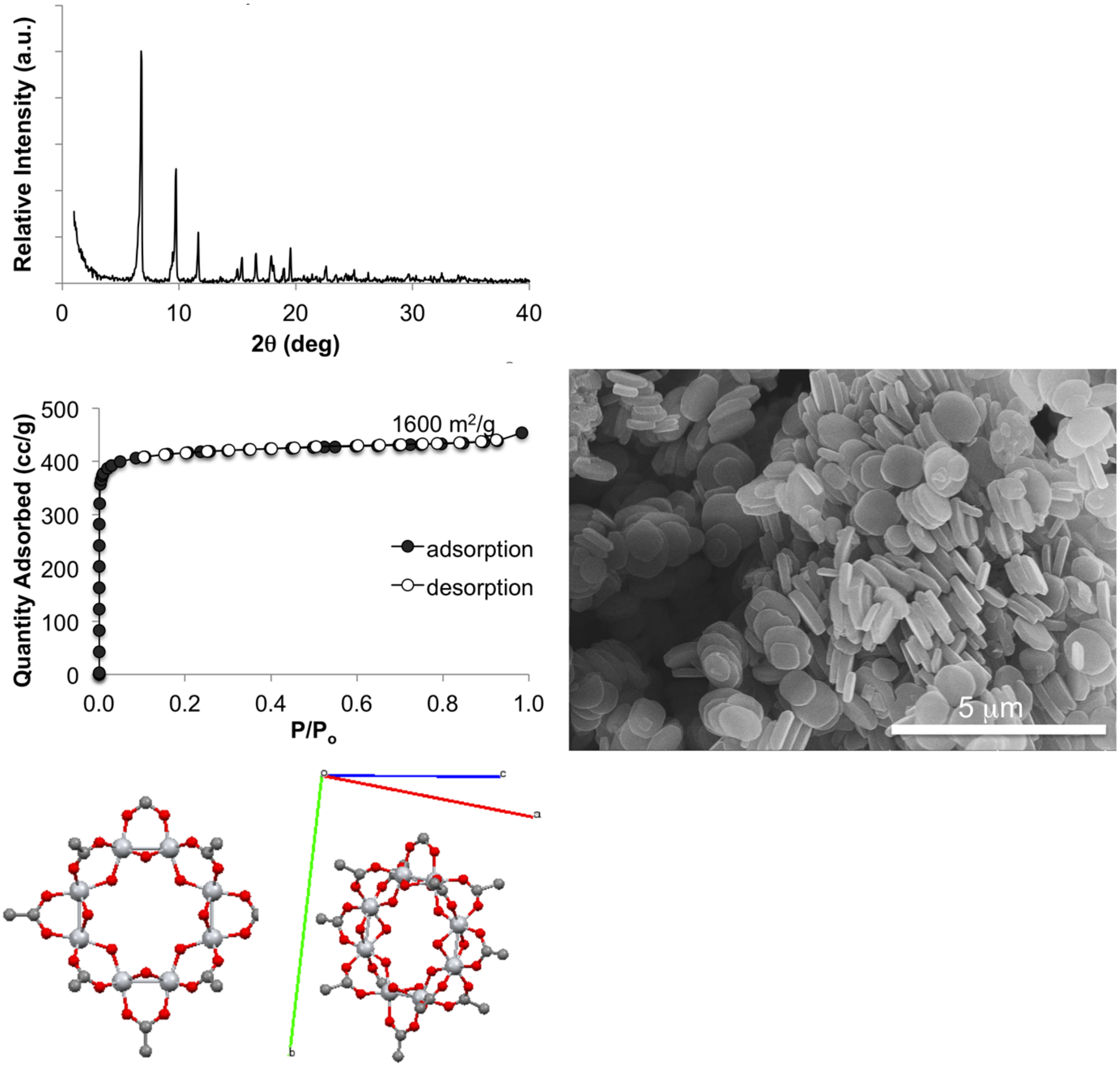

Fig. S6. Characterization data for MIL-125-NH_2: PXRD pattern (top-left panel), N_2 isotherms (top-right panel), and SEM image (bottom-left panel). A schematic drawing of the node crystal structure of MIL-125-NH_2 is shown in the bottom-right panel (Ti = light gray; C = gray; O = red).

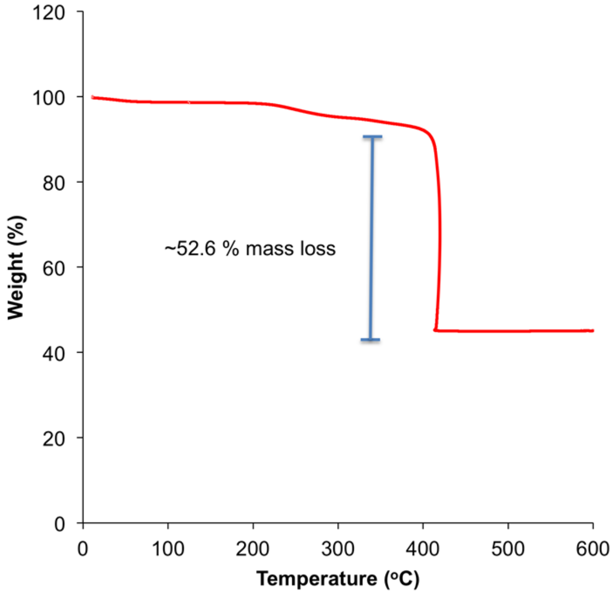

Fig. S7. TGA profile of UiO-66. The mass loss is calculated from the mass at 320 °C; presumably, ZrO_2 is formed at the final temperature.

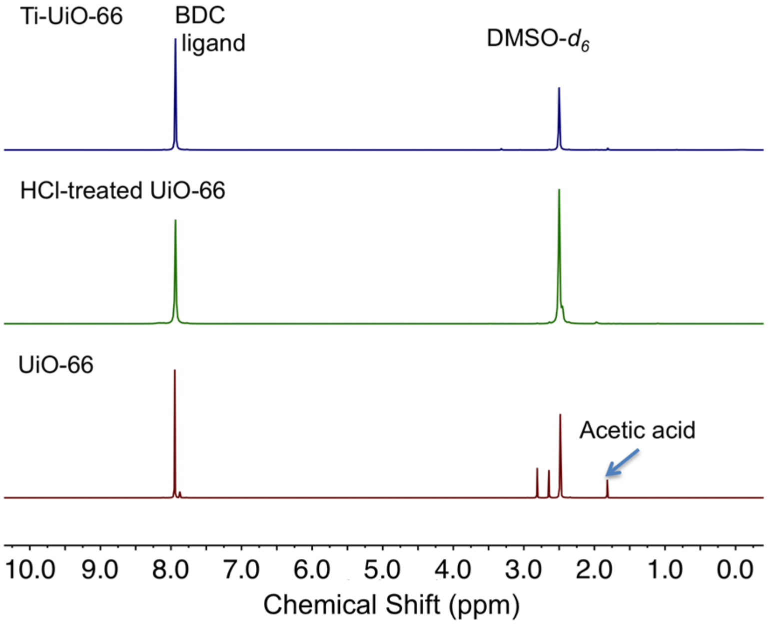

Fig. S8. ^1H NMR spectra of Ti-UiO-66, HCl-treated UiO-66, and UiO-66 in a mixture of D_2SO_4/DMSO-d_6 (1:9 v/v). As-synthesized UiO-66 shows some residual acetic acid (~4 mol % of the total ligand), while HCl-treated UiO-66 shows no acetic acid. In addition, there is only a small amount of acetic acid (< 1 mol % of the total ligand) observed in Ti-UiO-66.

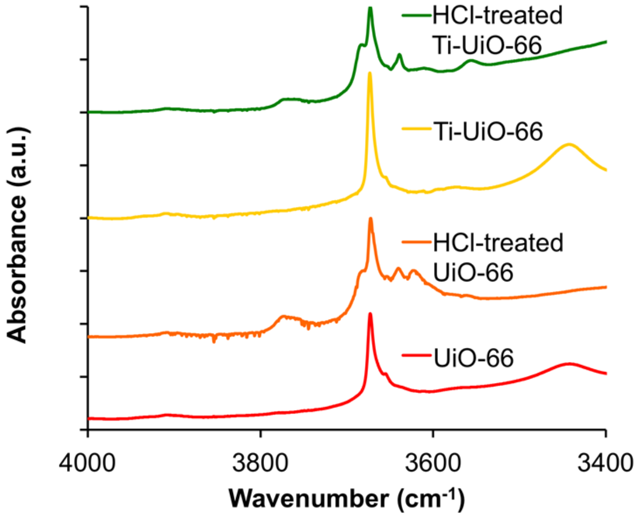

Fig. S9. *In-situ* DRIFTS spectra of UiO-66 (red), HCl-treated UiO-66 (orange), Ti-UiO-66 (yellow), and HCl-treated Ti-UiO-66 (green) over the 3400–4000 cm^{-1} range. Spectra were collected after cycling the samples from room temperature to 350 °C (for dehydration) and cooling back down to room temperature (rehydration step with water vapor from a bubbler). All samples show bridging –OH peak at ~3673 cm^{-1}. Additional –OH peaks could be observed for both HCl-treated UiO-66, suggesting successful removal of the capping modulator. The peak around 3773 cm^{-1} has been attributed to terminal –OH groups in the literature.[S2,3] The presence of the peak around 3773 cm^{-1} in HCl-treated Ti-UiO-66 suggests that some, but not all, of terminal –OH groups reacted with TiO(acac)$_2$ and agrees with observation that some of the Ti^{IV} ions were displaced during HCl treatment.

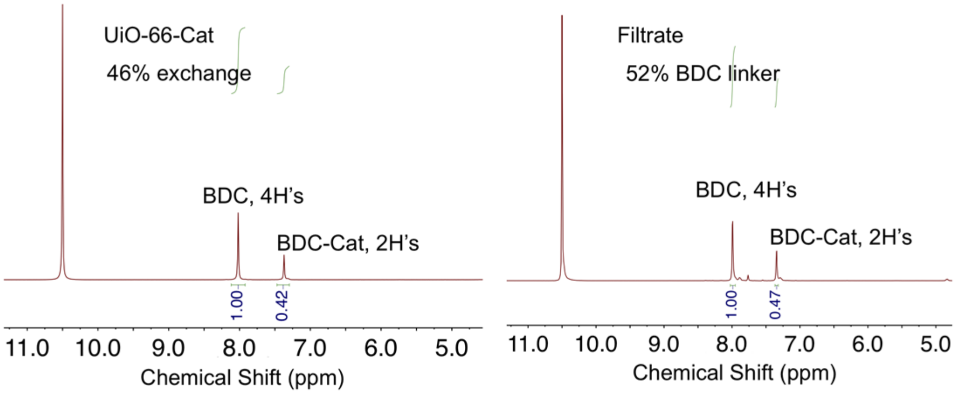

Fig. S10. ^{1}H NMR spectra of D_2SO_4-digested UiO-66-Cat in (left) and of the filtrate (right), showing that ~46 mol % of BDC ligand was exchanged for BDC-Cat ligand

S3. Catalytic data

Table S2. Yields, total turnover number (TON), and selectivity for the oxidation of cyclohexene at 50 °C using TiO_2 and different Ti-modified MOF catalysts

	Yields[a] (%)				Total TON (mol product/mol catalyst)			Selectivity (%)		
	epoxide	ol	one	total	epoxide	ol	one	epoxide	ol	one
TiO_2	4.2	0	0	4.2	42	0	0	100	0	0
Ti-UiO-66	0.7	2.0	6.6	9.3	7	20	66	8	22	70
UiO-66-Ti_{ex}	0.3	0.4	0.8	1.5	3	4	8	20	26	53
UiO-66-Cat-Ti	0	0.1	0.2	0.3	0	1	2		33	67
MIL-125-NH_2	0.1	0.1	0.3	0.5	1	1	3	20	20	60
UiO-66	0.3	0.3	0.8	1.4	3	3	8	21	21	58
Blank	3	0	0	3	30	0	0	100	0	0

[a] Based on cyclohexene. Epoxide = cyclohexene oxide; ol = 2-cyclohexen-1-ol; one = 2-cyclohexen-1-one.

Table S3. Filtration test of Ti-UiO-66 at 50 °C.

	Yields[a] (%)				Selectivity (%)		
	epoxide	ol	one	total	epoxide	ol	one
Reaction mixture at 4 h	0.2	0.1	0.3	0.6	33	17	50
Filtrate at 24 h	0.4	0.4	0.9	1.7	24	24	52
Ti-UiO-66 at 24 h	1.4	1.8	5.3	8.5	16	22	62

[a] Based on cyclohexene. Epoxide = cyclohexene oxide; ol = 2-cyclohexen-1-ol; one = 2-cyclohexen-1-one.

Table S4. Recyclability test of Ti-UiO-66 at 50 °C.

	Yields[a] (%)				Total TON (mol product/mol catalyst)			Selectivity (%)		
	epoxide	ol	one	total	epoxide	ol	one	epoxide	ol	one
Cycle 1	0.7	2.0	6.6	9.3	7	20	66	8	22	70
Cycle 2	0.4	0.9	2.5	3.8	4	9	25	11	24	66
Cycle 3	0.3	0.4	0.9	1.6	3	4	9	19	25	56

[a] Based on cyclohexene. Epoxide = cyclohexene oxide; ol = 2-cyclohexen-1-ol; one = 2-cyclohexen-1-one.

Table S5. Yields, total turnover number (TON), and selectivity for the oxidation of cyclohexene at 70 °C using TiO_2 and different Ti-modified MOF catalysts.

	Yields[a] (%)				TON (mol product/mol catalyst)			Selectivity (%)		
	Epoxide	ol	one	total	epoxide	ol	one	epoxide	ol	one
TiO_2	8.7	0.3	0.7	9.7	87	3	7	90	3	7
Ti-UiO-66	0.3 (1.5)	4.8	20.5	27.1	3 (15)	48	205	1(6)	18	76
UiO-66-Ti_{ex}	0.7	2.0	8.1	10.8	7	20	81	6	18	75
UiO-66-Cat-Ti	(1.0)	1.4	3.9	6.3	1.4	14	39	16 (diol)	22	62
MIL-125	0.6	2.3	10.0	12.9	6	23	100	5	18	78
UiO-66	0.3	3.4	9.0	12.7	3	34	90	2	27	71
Blank	10.6	0.5	0.6	11.7	106	5	6	91	4	5

[a] Based on cyclohexene. Epoxide = cyclohexene oxide; ol = 2-cyclohexen-1-ol; one = 2-cyclohexen-1-one. Number in parentheses = data for 1,2-cyclohexandiol

Table S6. Filtration test of Ti-UiO-66 at 70 °C.

	Yields[a] (%)				Selectivity (%)		
	epoxide	ol	one	total	epoxide	ol	one
Reaction mixture at 4 h	0.6	1.5	3.9	6.0	10	25	65
Filtrate at 24 h	2.3	5.4	10.7	18.4	13	29	58
Ti-UiO-66 at 24 h	0.3	5.8	24.7	30.8	1	19	80

[a]Based on cyclohexene. Epoxide = cyclohexene oxide; ol = 2-cyclohexen-1-ol; one = 2-cyclohexen-1-one.

Table S7. Recyclability test of Ti-UiO-66 at 70 °C.

	Yields[a] (%)				Total TON (mol product/mol catalyst)			Selectivity (%)		
	epoxide	ol	one	total	epoxide	ol	one	epoxide	ol	one
Cycle 1	0.3(1.5)	4.8	20.5	27.1	3(15)	48	205	1(5)	18	76
Cycle 2	0.3 (1.0)	4.5	17.2	23	3 (10)	45	172	1(4)	20	75
Cycle 3	0.4 (1.2)	4.0	15.3	20.9	4 (12)	40	153	2(6)	19	73

[a]Based on cyclohexene. Epoxide = cyclohexene oxide; ol = 2-cyclohexen-1-ol; one = 2-cyclohexen-1-one. Number in parentheses = data for 1,2-cyclohexandiol

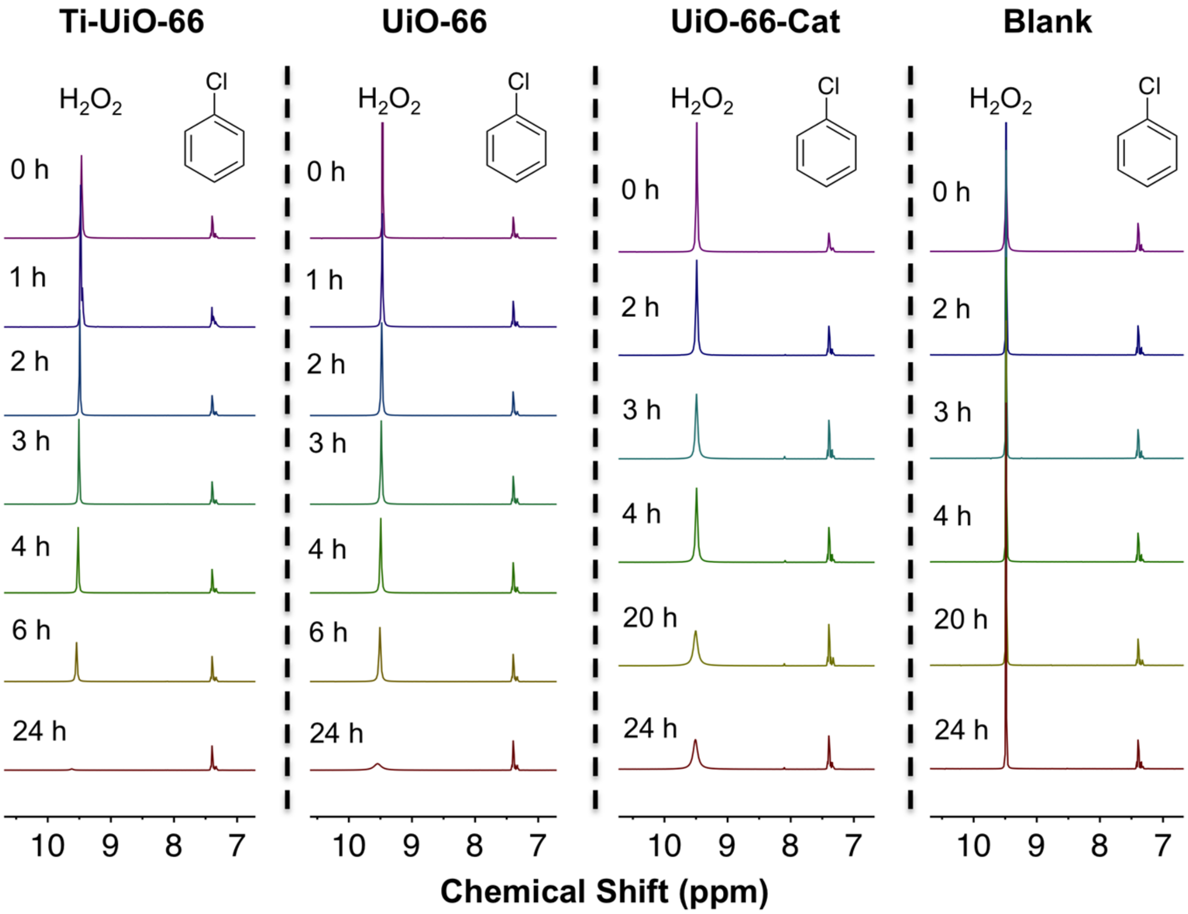

Fig. S11. ^1H NMR spectra of CD_3CN solutions of aqueous H_2O_2 in the presence of: (left-to-right) Ti-UiO-66, UiO-66-Cat, UiO-66, and “no catalyst” (i.e., blank) after being heated at 50 °C. Data were obtained at various time points between 0 and 24 h.

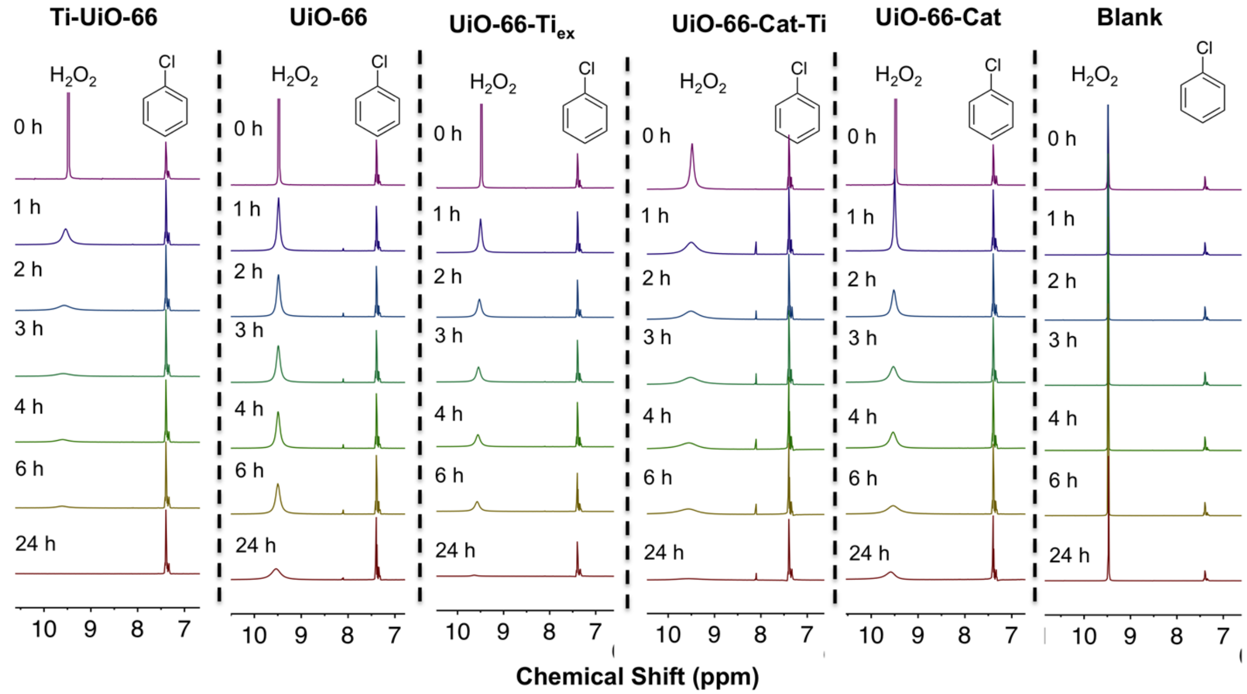

Fig. S12. ^{1}H NMR spectra of CD_3CN solutions of aqueous H_2O_2 in the presence of: (left-to-right) Ti-UiO-66, UiO-66, UiO-66-Ti$_{ex}$, UiO-66-Cat-Ti, UiO-66-Cat, and "no catalyst" (i.e., blank) after being heated at 70 °C. Data were obtained at various time points between 0 and 24 h.

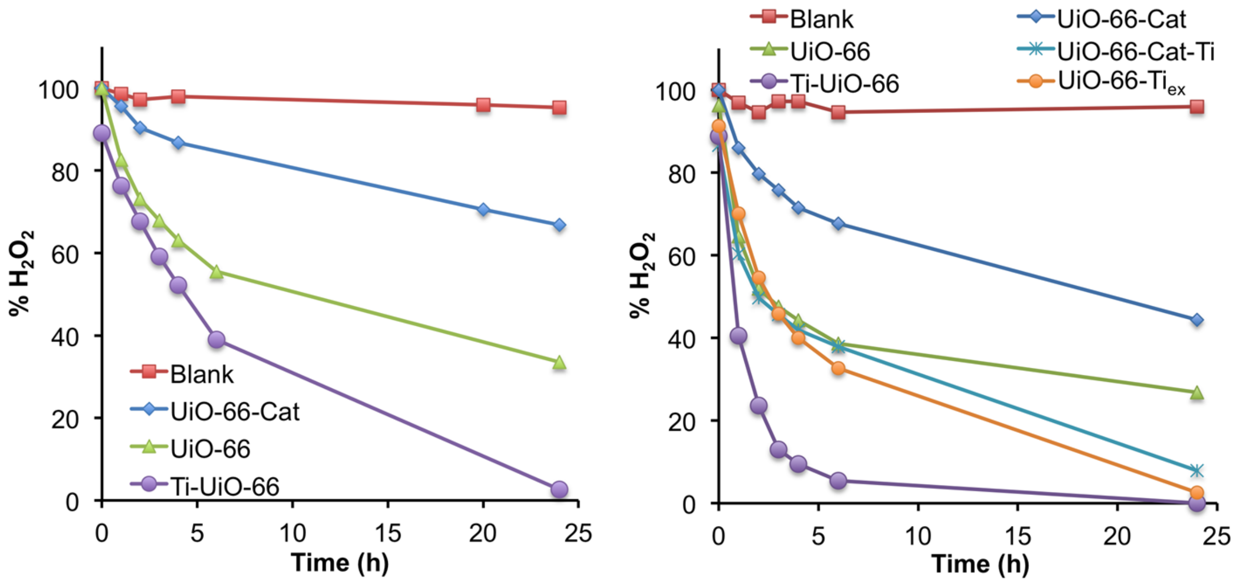

Fig. S13. H_2O_2 conversion profile in the presence of the different MOF samples at 50 °C (left) and 70 °C (right).

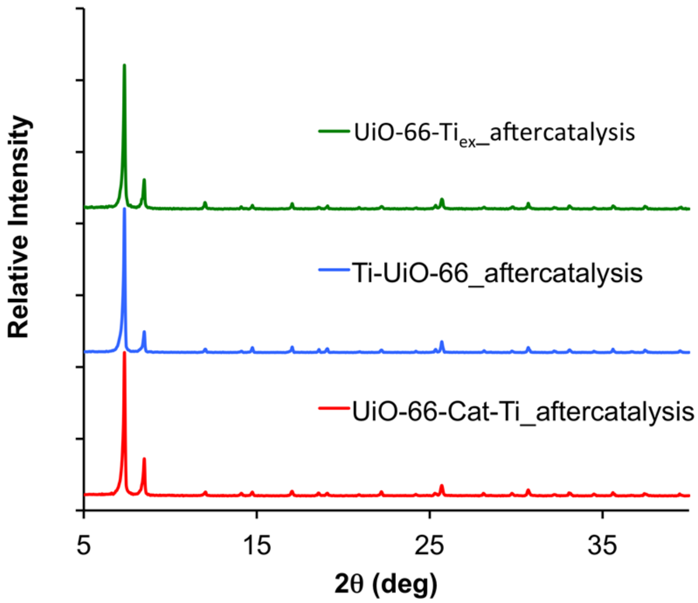

Fig. S14. PXRD patterns of Ti-functionalized UiO-66 MOFs after catalysis at 70 °C.

S4. Author contribution audits

Except when noted below, H.G.T.N. carried out all the experiments. L.M. carried out the XPS measurements. Z.J.B. developed the linker-exchange conditions for the synthesis of UiO-66-Cat. A.W.P. helped with the ALD metallation experiments. C.O.A. carried out the TGA measurement and SEM-EDS imaging. O.K.F., J.T.H., and S.T.N. supervised the project. H.G.T.N. wrote the initial drafts of the paper. H.G.T.N and S.T.N. finalized the manuscript with inputs from all co-authors.

S5. References

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