Supporting Information

Copper Catalyzed Selective Methane Oxidation into Acetic Acid using O_2

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1. General Experiment. All the experiments were performed at ambient atmospheric conditions under air, except if any case was demonstrated. All the solvents were purchased from Finar and used without further purification. Tetrahydrofuran was dried with calcium hydride followed by distillation over Na/benzophenone. Methane oxidation reactions were performed using ultrapure deionized water as the solvent, which was obtained from Milli-Q-EQ 7000. All the reagents are commercially available and used directly as received. 4,4'-benzenedicarboxylic acid was purchased from Alfa Aesar; $AlCl_3.6H_2O$, sodium triethyl borohydride, aluminium oxide was purchased from Sigma Aldrich; and $CuCl_2.2H_2O$ was purchased from CDH Chemicals. All the characterization data of MIL-53-Cu after catalysis were recorded using the samples recovered after methane oxidation under the optimized reaction conditions. Thermogravimetric analysis (TGA) was performed on a PerkinElmer TGA7 system on well-grounded samples in a flowing nitrogen atmosphere with a heating rate of 10 °C/min with a range of 40-800 °C. Room temperature powder X-ray diffraction data were collected on a Bruker Advance diffractometer using Ni-filtered Cu Kα radiation (λ= 1.5406 Å). Data were collected with a step size of 0.05° and at a count time of 1s per step over the range $4°<2\theta<70°$. The experimental and simulated PXRD patterns are in good agreement indicating the monophasic nature of the bulk samples. For powder X-ray diffraction measurement of MOFs, a dry sample was mounted on a PXRD groove. The catalysis was carried out without any mechanical stirring, and the recovered MOF was dried before the measurement of PXRD to prevent any mechanical degradation and pore collapse of the MOF. ICP-OES data were obtained with an Agilent 5110 ICP-OES and analysed using Dichroic Spectral Combiner (DSC) for which samples were diluted in a 5% HNO_3. All the oxidation reactions were performed using high pressure autoclave reactor (100 mL; Amar Equipments, PP-100-6624-00). The vessel was pressurized directly from a methane gas tank using a gauge (0-3000 psi displayed, 0-200 bar). To analyse the chemical state of transition elements XPS were recorded on an X-ray photoelectron spectrometer, PHI 5000 VersaProbe III using Al-Kα (hν = 1486.6 eV) X-ray source. MOF samples were vacuum dried at room temperature, and then powder samples were measured at ultra-high vacuum environment. Surface area and pore volume were measured with a BELLSORP MAX II-high performance gas and vapor adsorption system with three microporous ports. For BET surface area measurement, MOF sample was first dried via freeze-drying method. For freeze-drying, MOF was first soaked with benzene. Then, the MOF slurry was frozen at -10 ℃ and dried slowly under vacuum at the same temperature. Then, samples were degassed under vacuum at 80 ℃ for 24 h before measurement. The morphology and chemical compositions were analysed with a Ziess Fe-SEM ultra plus55 operating at 20

kV. After vacuum drying, a very small amount of the powder samples of MOF (1-2 mg) were dispersed on the carbon tape for FE-SEM imaging. Infra-red (IR) spectra of samples were recorded with FT-IR Spectrometer (MS-632). The MOF samples were vacuum dried at 105 °C to remove the moisture, which was then taken inside the glovebox, and a KBr pellet of powder sample was made. The pellets were kept in inert conditions and IR was recorded under a nitrogen atmosphere. The EPR measurements were recorded by a Bruker A300-9.5/12/S/W in the X-band region. The data was recorded at room temperature by taking a small fraction of the reaction mixture to which 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was pre-added. Simulation of EPR spectra was performed with Bruker EPR Simfonia software. All control experiments were performed at a total pressure of 40 bar by applying a balance of N_2 if necessary.

2. Synthesis and characterization of MIL-53(Al) and MIL-53(Al)-Cu(OH).

2.1. Synthesis of MIL-53(Al).[1] MIL-53(Al) was synthesized via a solvothermal reaction of 1,4-benzenedicarboxylic acid and $AlCl_3.6H_2O$ in DMF. 1,4-Benzenedicarboxylic acid (0.050 g, 0.301 mmol) and $AlCl_3.6H_2O$ (0.048 g, 0.198 mmol) were dissolved in 3 mL DMF in a glass vial and the resultant mixture was stirred for 2 h. The solution was transferred to a hydrothermal bomb with a Teflon liner and kept it in a preheated oven at 120 °C for 48 h. After cooling to room temperature, the white solid was collected via centrifugation, which was washed several times with DMF. Finally, the resultant white crystalline solid of MIL-53(Al) was washed and stored in THF.

2.2. Synthesis of MIL-53(Al)-CuCl. *n*-BuLi (50 μL, 1.65 M in cyclohexane) was added to the slurry of MIL-53(Al) (0.015 g, 0.072 mmol) in 1 ml THF in a vial, and the mixture was stirred for 1.5 h at room temperature inside the glovebox. The solid was washed with THF several times to remove the excess *n*-BuLi. A THF solution of $CuCl_2$ (0.042 g, 0.312 mmol) was added to the brown solid of MIL-53(Al)-Li, and the mixture was stirred overnight at room temperature. The MIL-53(Al)-CuCl was obtained as crystalline green solid and washed with THF several times.

2.3. Synthesis of MIL-53(Al)-Cu(OH). Inside the glovebox, $NaEt_3BH$ (40 μL, 1 M in THF) was added dropwise to the vial containing slurry of MIL-53(Al)-CuCl (0.016 g) in 3 mL THF

and was kept at room temperature for 1 h. The resultant dark purple solid of MIL-53(Al)-CuH was separated via centrifugation and washed several times with THF to remove excess $NaEt_3BH$. MIL-53(Al)-CuH was taken out of the glovebox and was kept in water for 30 minutes to afford MIL-53(Al)-Cu(OH). The MIL-53(Al)-Cu(OH) has 24% copper loading with respect to μ_2-OH as analyzed by ICP-OES. This corresponds to the formula $AlO_{5.24}C_8H_5Cu_{0.24}$. TGA analysis showed that MIL-53(Al)-CuOH had 29% solvent weight.

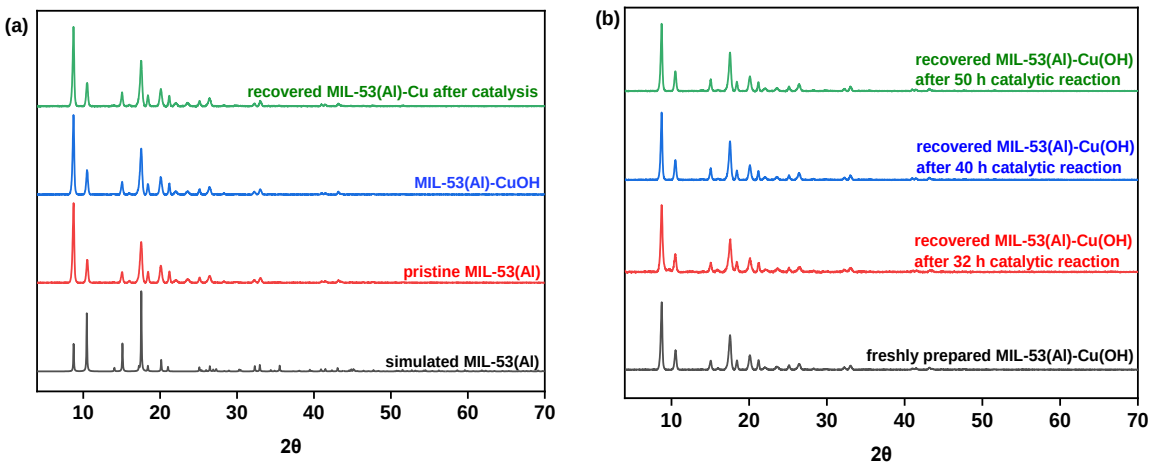


Figure S1. PXRD patterns of (a) simulated MIL-53(Al) MOF (black), pristine MIL-53(Al) (red), MIL-53(Al)-CuOH (blue), recovered MIL-53(Al)-Cu after methane oxidation for 32 h at 175 °C (run 1) (green), and 200 °C (magenta). (b) freshly prepared MIL-53(Al)-Cu(OH) (black), recovered MIL-53(Al)-Cu after 32 h of catalysis (red), 40 h of catalysis (blue), 50 h of catalysis (green); reaction conditions: 30 bar CH_4, 10 bar O_2, 175 °C and 7 mL water. The PXRD patterns indicate that the crystallinity and the framework of MIL-53(Al) MOF remained intact even after 50 h reaction.

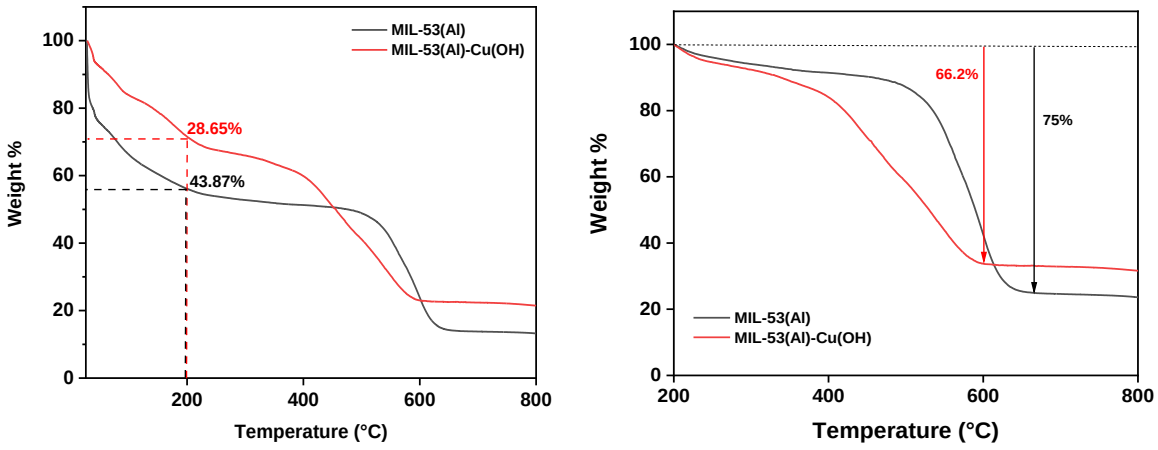


Figure S2. (a) TGA curve of freshly prepared MIL-53(Al) (black) and MIL-53(Al)-Cu(OH) (red). A solvent weight loss of 43.9% in MIL-53(Al) (black) and 28.7% in MIL-53(Al)-Cu(OH) (red) was observed from 40 °C to 200 °C. (b) TGA curve of freshly prepared MIL-53(Al) (black) and MIL-53(Al)-Cu(OH) (red) from 200-700 °C. The increased weight of MIL-53(Al)-Cu(OH) is due to the presence of Cu within the MOF.

Table S1. Determination of defect sites in MIL-53(Al) and MIL-53(Al)-Cu(OH) MOF by TGA analysis.

		% Solvent	% Linker	% Residue
MIL-53(Al)	Calculated	-	75.5	24.5
	TGA	44	42	14
	Corrected	-	75	25
MIL-53(Al)-Cu(OH) (24% Cu-loading)	Calculated	-	69.2	30.8
	TGA	29	47	24
	Corrected	-	66	34

Theoretical calculation:

(a) 1 mole of Al(OH)(BDC) = 0.5 moles Al_2O_3

208.1 g of Al(OH)(BDC) = 50.98 g Al_2O_3

% Residue = (50.98/208.1)*100 = 24.5%

% Linker = 100 – 24.5 = 75.5%

(b) 1 mole $Al(OH)_{0.71}(BDC)[OCu(OH)]_{0.24}$ = 0.5 moles Al_2O_3 and 0.24 moles CuO

227.19 g of $Al(OH)_{0.71}(BDC)[OCu(OH)]_{0.24}$ = 50.98 g Al_2O_3 and 19.09 g CuO

% Residue = [(50.98 + 19.09)/227.19]*100 = 30.8%

% Linker = 100 - 30.8 = 69.2%

The wt% ligand calculated theoretically matches closely with that of wt% ligand observed experimentally for MIL-53(Al) and MIL-53(Al)-Cu(OH) MOFs. This indicates the absence of any missing-linker defects within MIL-53(Al) and MIL-53(Al)-Cu(OH) MOFs.

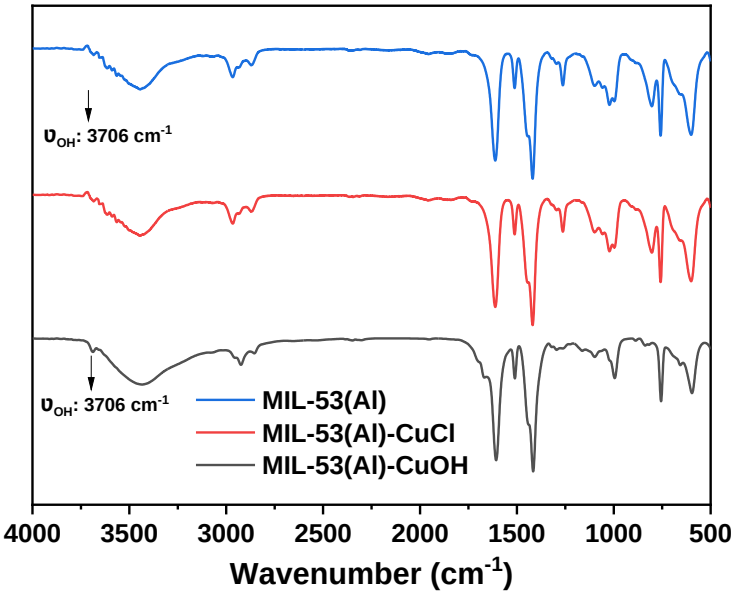


Figure S3. IR spectra of freshly prepared MIL-53(Al) (blue), MIL-53(Al)-CuCl (red), and MIL-53(Al)-CuOH (black). In the IR spectra, μ_2-OH stretching frequency peak of MIL-53(Al) at 3706 cm^{-1} disappeared upon metalation, however, a small peak of μ_2-OH reappeared for MIL-53(Al)-Cu(OH) due to protonation of unreacted μ_3-OLi with water. The peak intensity of μ_2-OH stretching frequency of MIL-53(Al)-CuOH at 3706 cm^{-1} was smaller compared to that of pristine MIL-53(Al) MOF due to the partial metalation of the μ_2-OH of the SBUs.

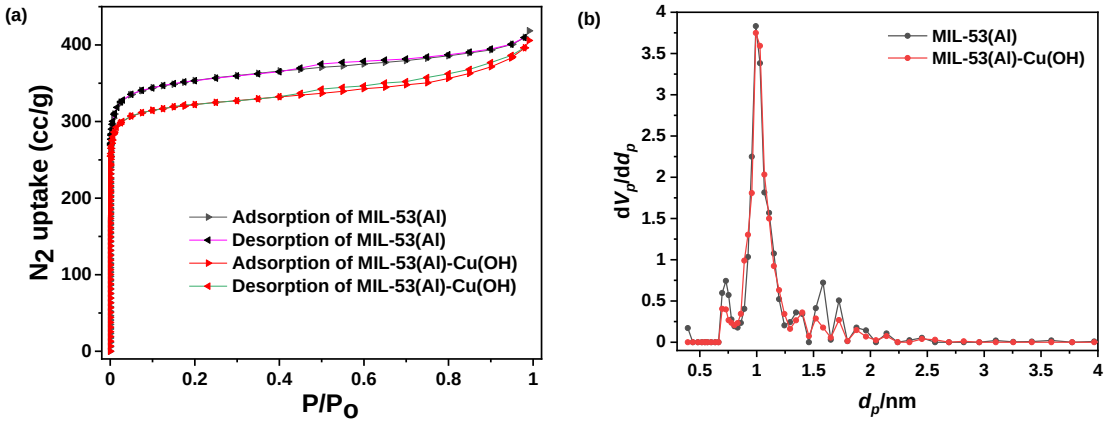


Figure S4. (a) N_2 sorption isotherms of MIL-53(Al) (black) and MIL-53(Al)-Cu(OH) (red) measured at 77 K. (b) NLDFT pore size distribution curve of MIL-53(Al) (black) and MIL-53(Al)-CuOH (red). BET surface for MIL-53(Al) and MIL-53(Al)-Cu(OH) are 1386 m^2/g and 1263 m^2/g and the average pore size for MIL-53(Al) and MIL-53(Al)-CuOH was determined to be 0.62 nm and 0.6 nm, respectively

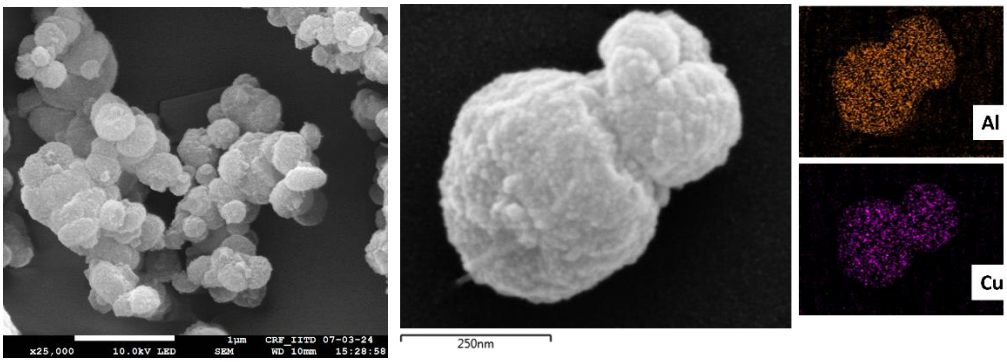


Figure S5. SEM image and EDX mapping for MIL-53(Al)-Cu(OH).The uniform distribution of Al and Cu suggests Al and Cu are homogeneously distributed throughout the MOF.

3. MIL-53(Al) catalysed oxidation of methane.

3.1. Standard procedure for MIL-53(Al) catalysed oxidation of methane to acetic acid using O_2.

$$CH_4 + O_2 \xrightarrow[H_2O,\ 175\ °C]{\text{MIL-53(Al)-Cu(OH)}} CH_3CO_2H$$

A 1 mL slurry of MIL-53(Al)-Cu(OH) (3.8 mg, 4.0 μmol Cu) in water was transferred to a glass liner containing 6 mL of water. Then the glass liner was fitted into a high-pressure reactor. The high-pressure reactor was sealed and then purged with methane two times. The reactor was pressurized with 30 bar methane followed by 10 bar oxygen and then heated at 175 °C for 32 h without any mechanical stirring. After the reaction, the reactor was cooled to room temperature, and the gas was analysed directly by GC-TCD. A 1 mL of the aqueous solution was transferred to a centrifuge tube, which was centrifuged for 1 min. Then, 1 mL of the clear solution was quickly transferred to a GC vial and 5 μL of ethylene glycol (internal standard) was added. The sample was then analysed by GC-FID/MS to identify the products and their yields in the liquid phase. 1 μL sample was injected in GC and standard calibration curves were used for the quantification of acetic acid. MIL-53(Al)-Cu(OH) (3.8 mg, 4.0 μmol Cu) under 30 bar of CH_4 and 10 bar of O_2 for 32 h, at 175 °C yielded 1.51 mmol of acetic acid (Entry 1, Table S2). The GC-MS analysis detected minor quantities of methanol (0.08 mmol) and ethanol (0.004 mmol), with no traces of formic acid or other oxygenated products.

3.2. Detection and quantification of liquid oxygenates.

GC-MS conditions: The column used was the Agilent DB-WAX column with 30 m length, 0.320 mm internal diameter, and 0.25 μm film. The chromatographic conditions were: flow rate of helium at 1 mL min^{-1}, injection volume: 1 μL, column oven temperature was initially 45.0 °C and then increased up to 230 °C with the rate of 5 °C per minute, and detector temperature was 250 °C.

GC-FID conditions: The column used was the Agilent DB-WAX column with 30 m length, 0.320 mm internal diameter, and 0.25 μm film. The chromatographic conditions were: flow rate of nitrogen at 1 mL min^{-1}, injection volume of 1 μL, column oven temperature at 40.0 °C for 4 minutes followed by 5 °C/min ramp to 70 °C and then followed by 35 °C/min ramp to 200 °C and finally a hold time of 5 minutes, and 19 min for total run time. The detector temperature was 250 °C. Products were quantified using a calibration plot of ethylene glycol as the internal standard.

3.3. Detection and quantification of methane and gaseous oxygenates.

GC-TCD conditions: The gas after catalysis was analysed by an Agilent GC (8890) equipped with a PoraPlot Q column in sequence with a molecular sieves column and a Thermal conductivity detector (TCD). The chromatographic conditions are as follows; Carrier gas: helium, Column: 45 °C, TCD: 250 °C, and Injection temperature: 100 °C. Retention time for CO_2, CH_4 and CO were 4 minutes, 9.3 minutes and 10.75 minutes, respectively.

The methane conversion was calculated by determining the mmol of methane before and after the catalysis using a GC-TCD response factor-based calculation. For this calculation, a high-pressure reactor containing a glass liner was filled with 7 mL mixture of water and MIL-53(Al)-Cu(OH) catalyst, and then purged it with methane two times. Then pressurized it with 30 bar methane followed by 10 bar oxygen. The gas was analysed with GC-TCD at room temperature (35 °C) before catalysis to quantify the amount of methane in the feed. The gas of the same high-pressure reactor was analysed after the reaction at room temperature (35 °C) to quantify the amount of unreacted methane after the catalysis and the other gaseous products. At the optimized reaction condition (entry 1, Table S2), the amount of methane was calculated as 34 mmol before catalysis and 30.8 mmol after catalysis. Therefore, the loss of methane during the reaction is 3.16 mmol and a methane conversion of ~9.3%.

Procedure for taking gas sample: First, the gas from the Parr reactor was filled in an evacuated tedlar bag via making an air-tight fitting connection of Parr reactor outlet with the bag using a hose pipe. Then 2.5 mL from the bag was taken in an air-tight syringe and injected into GC for analysis. Then, the mmol of methane, CO and CO_2 was calculated. Separately, 2.5 mL of a known sample of a standard gas containing a specific composition of CO, CO_2 and CH_4 was also injected, which was used to calculate the individual gas (x) response factor (R_f) following the given formula. The detailed calculation to quantify the initial methane amount in the feed is as follows:

Step 1:

$$\text{Rf (methane)} = \frac{\text{Fraction of methane (g)}}{\text{Area of peak of methane in chromatogram (GC−TCD)}}$$

$$\text{Fraction of methane} = \big(\text{Volume injected (mL)}\big) * \text{(Composition of methane in standard)}$$

$$\text{Fraction of methane} = 2.5\ \text{(mL)} * \frac{10^{-4}\text{g}}{\text{mL}}$$

Rf (methane) = $2.5*10^{-4}$g/62,000

Rf (methane) = $4.03*10^{-9}$ g

Step 2: The volume of CH_4 in the unknown sample taken from the high-pressure reactor was measured. The injected volume of the unknown sample was also the same as of standard 2.5 mL.

Amount of CH_4 in unknown sample: Rf (CH_4)*area of the peak of CH_4 in the chromatogram

Amount of CH_4 = $4.03*10^{-9}$ *1,78,000

Amount of CH_4 = $7.18*10^{-4}$ g

Step 3: Molar mass of CH_4 = 16.04 g/mol

Moles of CH_4 = $7.18*10^{-4}$/16.04 mol

Moles of CH_4 = 44.75 μmol

So, the initial moles of CH_4 in 2.5 mL of an unknown sample of gas was measured. This measurement is at atmospheric pressure and 308 K.

Subsequently, the initial amount of methane in the reactor before catalysis was calculated to be 34 mmol.

Using the similar method described above, the methane and other gaseous products were quantified after the catalysis.

Table S2. Optimization of catalytic conditions for MIL-53(Al)-Cu(OH) catalyzed oxidation of methane using O_2.[a]

Entry No.	Temperature (°C)	P[CH_4] (bar), Initial mmol of CH_4	P[O_2] (bar)	CH_3CO_2H (mmol)[b]	CH_3OH (mmol)[b]	C_2H_5OH (mmol)[b]	CO_2 (mmol)[c]
1	**175**	**30, 34**	**10**	**1.51**	**0.08**	**0.004**	**0.048**
2[d]	175	30, 34	10	0	0	0	0.04
3	175	30, 34	0	0	0	0	nd
4	100	30, 34	10	0.06	0.03	0	0.01
5	125	30, 34	10	0.42	0.09	0	0.019
6	150	30, 34	10	1.15	0.12	0.002	0.032
7	200	30, 34	10	0.72	0.06	0.001	0.84
8	175	30, 34	2	0.04	0.004	0	0.004
9	175	30, 34	4	0.21	0.007	0	0.008
10	175	30, 34	6	0.52	0.012	0	0.01
11	175	30, 34	8	0.87	0.038	0.001	0.02
12	175	10, 11	10	0.17	0.0089	0	0.01
13	175	20, 23	10	0.64	0.039	0	0.019
14	175	25, 29	10	0.97	0.056	0.003	0.024
15[e]	175	30; 34	10	0	0	0	0.001
16[f]	175	30; 34	10	0.18	0.01	0	0.002
17[g]	175	30; 34	10	0.38	0.018	0	0.016
18[h]	175	30; 34	10	0.72	0.29	0	0.04
19[i]	175	30; 34	10	1.68	0.12	0.005	0.17
20[j]	175	30; 34	10	1.61	0.18	0.01	0.244
22[k]	175	30; 34	10	0	0	0	0.45
23[l]	175	30; 34	10	0	0	0	nd
24[m]	175	30; 34	10	0	0	0	nd

[a] Standard conditions: 3.8 mg of MIL-53(Al)-Cu(OH) (4.0 μmol Cu), 7 mL H_2O, 32 h; N_2 balance was applied to optimize partial pressures of O_2 and CH_4 (entry 8-14) maintaining total reaction pressure at 40 bar; nd: not determined.
[b] Analysed by GC-FID using ethylene glycol as the internal standard.
[c] Analysed by GC-TCD.
[d] No catalyst was used.
[e] Reaction time was 1 h.
[f] Reaction time was 6 h.
[g] Reaction time was 12 h.
[h] Reaction time was 24 h.

[i] Reaction time was 40 h.
[j] Reaction time was 50 h.
[k] Toluene was used as the solvent.
[l] THF was used as the solvent.
[m] Heptane was used as the solvent.

Table S3. Control experiments for MIL-53(Al)-Cu(OH) catalyzed oxidation of methane to acetic acid.[a]

Entry No.	Temperature (°C)	P[CH_4] (bar), Initial mmol of CH_4	P[O_2] (bar)	CH_3CO_2H (mmol)[b]	CH_3OH (mmol)[b]	C_2H_5OH (mmol)[b]	CO/CO_2 (mmol)[c]
1	**175**	**30**	**10**	**1.51**	**0.08**	**0.004**	**0.048**
2[d]	175	30	10	0	0	0	0.08
3	175	30	0	0	0	0	0.02
4[e]	175	30	10	0	0	0	0.24
5[f]	175	30	10	1.51	0.078	0.003	0.061
6[g]	175	30	10	1.56	0.09	0.002	0.1
7[h]	175	30	10	0.03	0.01	0	0.04
8[i]	175	30	10	0.01	0.03	0	0.09
9[j]	175	30	0	0	0	0	nd
10[k]	175	30	10	1.61	0.07	-	0.052
11[l]	175	0	10	0	0	0	nd
12[m]	175	0	10	0.35	-	-	nd
13[n]	175	30	0	0.08	0	0	nd
14[o]	175	30	10	0.01	-	0	0.07
15[p]	175	30	10	0		0	0.22
16[q]	175	0	10	0.01	-	0.002	nd
17[r]	175	0	0	0.05	-	-	nd
18[s]	175	0	10	0.42	-	-	nd
19[t]	175	0	10	0.41	-	-	nd
20[u]	175	30	10	1.49	0.074	0.003	0.049
21[v]	175	30	10	1.61	0.02	NA	nd
22[w]	175	30	10	0.34	-	-	nd
23[x]	175	30	10	0.08	0.04	-	0.9
24	175	30	15	0.46	0.02	-	0.72

[a] Standard conditions: 3.8 mg of MIL-53(Al)-Cu(OH) (4.0 μmol Cu), 7 mL H_2O, 32 h; N_2 balance was applied to keep constant pressure of 40 bar if needed; nd: not determined; NA: not applicable.
[b] Analysed by GC-FID using ethylene glycol as the internal standard.
[c] Analysed by GC-TCD.
[d] MIL-53(Al) was used.
[e] MIL-53(Al)-CuCl was used.
[f] Na_2SO_3 was used as an $^{\bullet}OH$ scavenger.
[g] 7.6 mg of MIL-53(Al)-Cu(OH) (8.0 μmol Cu) was used as the catalyst.

[h] 6.0 mg of Al_2O_3 supported Cu(II) (4.0 μmol Cu).
[i] $Cu(OH)_2$ (1 mg, 10.24 μmol Cu) was used as the catalyst.
[j] 10 bar CO was used as the oxidant.
[k] 0.5 mmol ethanol was added to the reaction mixture.
[l] Nitrogen was used instead of methane.
[m] Oxidation of 1.5 mmol of ethanol using 10 bar O_2.
[n] CO_2 (10 bar) was used as an oxidant.
[o] CuO (1 mg, 12.6 μmol Cu) was used as a catalyst.
[p] Cu@MIL-53(Al) (4.0 μmol Cu) was used as the catalyst.
[q] Oxidation of 0.5 mmol of methanol.
[r] Oxidation of 1.5 mmol of methanol using 1 bar CO.
[s] Oxidation of 0.5 mmol of acetaldehyde, reaction time: 5 h.
[t] Oxidation of 0.5 mmol of acetaldehyde in the absence of catalyst, reaction time: 5 h.
[u] *t*-Butanol was used as an $^{\bullet}OH$ scavenger.
[v] MIL-53(Al)-Cu(OC_2H_5) (4.0 μmol Cu) was used as the catalyst.
[w] TEMPO was used as a radical scavenger.
[x] DUT-5(Al)-Cu(OH) (4.0 μmol Cu) was used as the catalyst.

Table S4. Summarized optimum conditions for MIL-53(Al)-Cu(OH) catalysed CH_4 oxidation using O_2.[a]

Entry No.	Temperature (°C)	P[CH_4] (bar)	P[O_2] (bar)	Time (h)	CH_4 conversion (%)	CH_3CO_2H (mmol)[b]	Selectivity (%)	$mmol_{product} \bullet mol_{Cu}^{-1} \bullet h^{-1}$
1	175	30	10	32	9.3	1.51	91.6	11,796
2	175	30	10	40	10.8	1.68	84.4	10,500

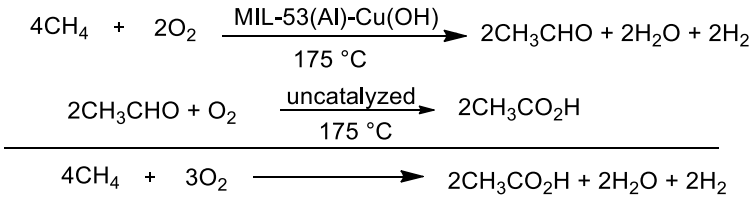
[a] 3.8 mg MIL-53(Al)-Cu(OH) (4.0 μmol Cu), 7 mL H_2O.
[b] Analysed by GC-FID using ethylene glycol as the internal standard.

Table S5. Carbon balance in MIL-53(Al)-Cu(OH) catalyzed oxidation of CH_4 using O_2.

Initial CH_4 (mmol)	Post-reaction CH_4 (mmol)	CH_4 consumed (mmol)	Oxygenates and other products (mmol)					Total Carbon yield (mmol)
			CH_3CO_2H (mmol)	CH_3OH (mmol)	CH_3CH_2OH (mmol)	CO_2 (mmol)	H_2 (mmol)	
34	30.8	3.2	1.51	0.08	0.004	0.048	1.4	3.16

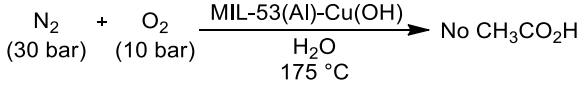
Under optimized reaction conditions (30 bar CH_4, 10 bar O_2, 175°C, 32 h), 1.51 mmol of acetic acid, 0.08 mmol of methanol, 0.004 mmol of ethanol, and 0.048 mmol of CO_2 were formed. The total carbon balance was confirmed, as 3.2 mmol of methane was consumed, yielding 3.16 mmol of carbon-containing products (carbon balance of 98.75%). Additionally, 1.4 mmol of H_2 was generated as a side product, further supporting our proposed mechanism.

Initially, methane reacts with O_2 to produce acetaldehyde, water, and hydrogen. The acetaldehyde is then converted into acetic acid in the presence of O_2.



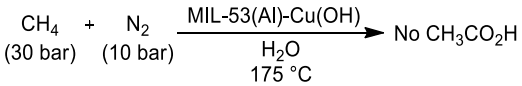
3.4. Control experiments for MIL-53(Al)-Cu(OH) catalyzed oxidation of methane.

Blank reaction with O_2 under N_2 without methane.



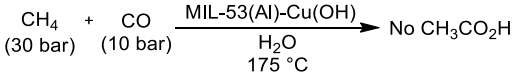
Reaction conditions: 3.8 mg of MIL-53(Al)-Cu(OH) (4.0 μmol Cu), 7 mL H_2O, 30 bar N_2, 10 bar O_2, 32 h. General procedure mentioned in Section 3.1. was followed replacing methane with nitrogen. No liquid products were detected (Entry 11, Table S3, suggesting CH_4 as the sole carbon source for CH_3CO_2H production in the MIL-53(Al)-Cu(OH) catalyzed methane oxidation.

Blank reaction without O_2 under N_2.



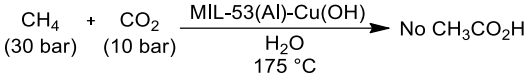
Reaction conditions: 3.8 mg of MIL-53(Al)-Cu(OH) (4.0 μmol Cu), 7 mL H_2O, 30 bar CH_4, 10 bar N_2, 32 h. General procedure mentioned in Section 3.1. was followed replacing oxygen with nitrogen. No liquid products were detected (Entry 3, Table S2, suggesting O_2 as the only oxidant for CH_3CO_2H production in the MIL-53(Al)-Cu(OH) catalyzed methane oxidation.

Reaction of methane in presence of CO using MIL-53(Al)-Cu(OH).



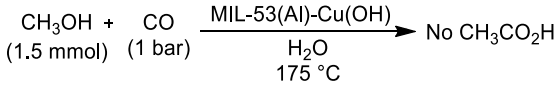
Reaction conditions: 3.8 mg of MIL-53(Al)-Cu(OH) (4.0 μmol Cu), 7 mL H_2O, 30 bar CH_4, 10 bar CO, 32 h. General procedure mentioned in Section 3.1. was followed replacing oxygen with carbon monoxide. In this reaction, no acetic acid (Entry 9, Table S3) was formed which rules out the formation of acetic acid via reaction of methane carbonylation with CO at 175 °C.

Reaction of methane in presence of CO_2 using MIL-53(Al)-Cu(OH).



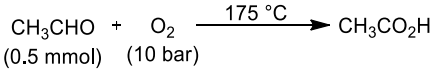
Reaction conditions: 3.8 mg of MIL-53(Al)-Cu(OH) (4.0 μmol Cu), 7 mL H_2O, 30 bar CH_4, 10 bar CO_2, 32 h. General procedure mentioned in Section 3.1. was followed replacing oxygen with carbon dioxide. In this reaction, negligible acetic acid (Entry 13, Table S3) was formed, which rules out the formation of acetic acid via methane carboxylation with CO_2 at 175 °C.

Reaction of methanol in presence of CO using MIL-53(Al)-Cu(OH).



Reaction conditions: 3.8 mg of MIL-53(Al)-Cu(OH) (4.0 μmol Cu), 7 mL H_2O, 1.5 mmol methanol, 1 bar CO, 32 h. General procedure mentioned in Section 3.1. was followed replacing oxygen with carbon monoxide and methane with methanol. In this reaction, no significant amount of acetic acid (Entry 18, Table S3) was formed. We thus conclude that MIL-53(Al)-Cu(OH) catalyzed methane oxidation does not occur via the reaction of insitu generated methanol and CO.

Reaction of acetaldehyde in presence of O_2 in the absence of MIL-53(Al)-Cu(OH).



Reaction conditions: 7 mL H_2O, 0.5 mmol acetaldehyde, 10 bar O_2, 32 h. General procedure mentioned in Section 3.1. was followed replacing methane with acetaldehyde and the reaction was done in the absence of the catalyst. In this reaction, 0.41 mmol of acetic acid (Entry 19, Table S3) was formed. We thus conclude that acetaldehyde formed gets oxidized to acetic acid without the aid of MOF catalyst.

3.5. Test for "heterogeneity of MIL-53(Al)-Cu(OH) in methane oxidation to acetic acid.

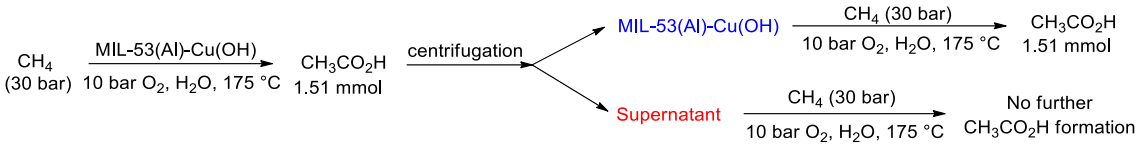
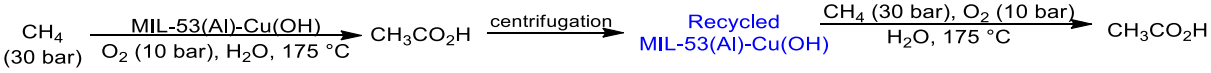


Figure S6. Heterogeneity test of MIL-53(Al)-Cu(OH) in the oxidation of methane.

General procedure mentioned in Section 3.1. was followed. After 32 h of reaction, the solid was centrifuged out of suspension. Two reactions were set up separately in two different high-pressure reactors with solid and supernatant. The extracted solid and supernatant were added into two separate glass liners. Then added 7 mL of water to the glass liner containing solid MOF. Then both the glass liners were fitted into two separate reactors. The reactors were sealed and purged them with methane. The reactors were pressurized with 30 bar methane and 10 bar oxygen and then heated at 175 °C for 32 h without any mechanical stirring. The reactor was cooled to room temperature, and gas was analysed directly with GC-TCD. The liquid phase of reactions was analysed with GC. No further acetic acid was produced in the reaction involving just the supernatant. While the other reaction containing the solid MOF yielded 1.51 mmol of acetic acid. This experiment excludes the potential of any leached Cu-species responsible for catalysis and confirms that solid MIL-53(Al)-Cu(OH) was the actual catalyst for the oxidation of methane.

3.6. Recycling of MIL-53(Al)-Cu(OH) for oxidation of methane.



The recycle and reuse experiment was conducted to check the stability of the MOF-catalyst. General procedure mentioned in Section 3.1. was followed, except the recovered MOF-catalyst was washed several times with water. It was added to the glass liner along with 7 mL H_2O. The glass liner was fitted into a high-pressure reactor which was then sealed and purged with CH_4 twice. The reactor was pressurized with 30 bar CH_4 followed by 10 bar O_2 and then heated at 175 °C. The procedure was repeated 6 times with very minimal % leaching of copper and aluminium (Table S6). The MOF retains its crystallinity and stability as can be seen by the

PXRD patterns of the recycling experiments (Figure S1). The MOF could be recycled and reused at least 5 times without drop of activity giving a cumulative TON of 2204 (Figure S7).

Table S6. mmol of acetic acid formed and the leaching of Cu in various runs of the recycling of MIL-53(Al)-Cu(OH) for the oxidation of methane.

No. of Run	Time	Productivity ($mmol_{CH3CO2H} \bullet mol_{Cu}^{-1} \bullet h^{-1}$)	% Leaching (Al, Cu)
Run-1	32	11,767	0.05, 0.06
Run-2	32	11,533	0.03, 0.04
Run-3	32	11,689	0.03, 0.026
Run-4	32	11,377	
Run-5	32	11,611	0.08, 0.05
Run-6	32	11,221	

3.7. Comparison of catalytical activity between MIL-53(Al)-Cu(OH) and other materials for oxidation of methane with oxygen.

Cu(II)/Al_2O_3 catalyzed oxidation of methane. Al_2O_3 was activated at 150 °C under vacuum for 24 h. Then inside the glove box, *n*-BuLi (130 μL, 1.65 M in cyclohexane) was added to activated alumina (30.0 mg) in 1 mL THF in a 5 mL glass vial and kept for stirring at room temperature for overnight. The solid was washed with the THF several times. The lithiated Al_2O_3 was treated with $CuCl_2$ (108 mg, 0.808 mmol) and stirred overnight. The excess of $CuCl_2$ was washed away with the multiple washing using THF. The metalated Al_2O_3 was dried, and the content of copper in Cu(II)/Al_2O_3 was determined to be 3.8 wt % via ICP-OES. $NaEt_3BH$ (36 μL, 1 M in toluene) was added dropwise into the vial containing Al_2O_3-CuCl (30.0 mg, 0.018 mmol Cu) as a slurry in 3 mL THF and the mixture was stirred gently at room temperature for 1 h. The light grey solid was washed with THF several times and then it was taken outside from the glovebox and added water to afford alumina-supported Cu(II) [Al_2O_3-Cu(II)], which was directly used for catalysis.

General procedure mentioned in Section 3.1 was followed, using Cu(II)/Al_2O_3 (6.7 mg, 4.0 μmol Cu) instead of MIL-53(Al)-Cu(OH). Reaction conditions: Cu(II)/Al_2O_3 (6.7 mg, 4.0 μmol Cu), 7 mL water, 30 bar CH_4, 10 bar O_2, 175 °C, 32 h. Results are summarized in entry

7, Table S3, the major product was CO and CO_2 with CH_3CO_2H productivity of 233.8 $mmol_{product}•mol_{Cu}^{-1}•h^{-1}$ in case of Cu(II)/Al_2O_3 while 11,767.45 $mmol_{product}•mol_{Cu}^{-1}•h^{-1}$using MIL-53(Al)-Cu(OH) (entry 1, Table S2). Al_2O_3-Cu(OH) is less active than MIL-53(Al)-Cu(OH).

CuO catalyzed methane oxidation. CuO nanoparticles were prepared according to the reported procedure.[2] $CuCl_2.2H_2O$ (1.70 g, 0.01 mole) was dissolved in 100 mL deionised water. 0.1 M NaOH solution was slowly added under vigorous stirring until the colour of the solution changed from blue to deep black and pH reached 14. Black precipitate of CuO nanoparticles was thus obtained and washed with water and ethanol.

General procedure mentioned in Section 3.1 was followed, using CuO (1 mg, 12.6 μmol Cu) instead of MIL-53(Al)-Cu(OH). Reaction conditions: CuO (1 mg, 12.6 μmol Cu), 7 mL water, 30 bar CH_4, 10 bar O_2, 175 °C, 32 h. Results are summarized in entry 7, Table S3. No acetic acid was observed (Entry 14, Table S3).

Cu@MIL-53(Al) catalyzed methane oxidation. In a 5 mL round bottom flask, $CuCl_2·2H_2O$ (50 mg, 0.18 mmol) was dissolved in ethyl acetate (2 mL), followed by the addition of the MIL-53(Al) (100 mg). The mixture was heated for 48 h at a temperature of 50 °C. After which the solid was collected after centrifugation and washed thoroughly and dried to give MIL-53(Al)-$CuCl_2$. $NaBH_4$ (10 mg) was added to 6 mL of deionized water in a round-bottom flask, after which 80 mg of MIL-53(Al)-$CuCl_2$ was added. The pH was controlled in the range of 6-8 throughout the addition of $NaBH_4$. The obtained mixture was stirred for 30 min, then was subject to filtration. The collected solid was washed thoroughly with deionized water to give black powder of Cu@MIL-53(Al).[3] The content of Cu in Cu@MIL-53(Al) is 4.2 wt%.

General procedure mentioned in Section 3.1 was followed, using 6.1 mg Cu@MIL-53(Al) (4.0 μmol of Cu) instead of MIL-53(Al)-Cu(OH). Reaction conditions: 6.1 mg Cu@MIL-53(Al) (4.0 μmol of Cu), 7 mL water, 30 bar CH_4, 10 bar O_2, 175 °C, 32 h. CO and CO_2 were observed as significant products (Entry 15, Table S3) with no acetic acid observed in the liquid phase.

MIL-53(Al)-Cu(OC_2H_5) catalyzed methane oxidation. MIL-53(Al)-CuH was synthesised as per the method mentioned in Section 2.3, and was taken out of the glovebox and was kept in ethanol for 30 minutes to afford MIL-53(Al)-Cu(OC_2H_5).

General procedure mentioned in Section 3.1 was followed, using MIL-53(Al)-Cu(OC_2H_5) (4.0 μmol of Cu) instead of MIL-53(Al)-Cu(OH). Reaction conditions: MIL-53(Al)-Cu(OC_2H_5) (4.0 μmol of Cu), 7 mL water, 30 bar CH_4, 10 bar O_2, 175 °C, 32 h. 1.61 mmol of acetic acid was observed (Entry 21, Table S3) in the liquid phase, confirming MIL-53(Al)-Cu(OC_2H_5) as one of the intermediate in the reaction pathway.

DUT-5(Al)-Cu(OH) catalyzed methane oxidation.

Synthesis of DUT-5(Al)-Cu(OH): DUT-5(Al) was synthesized via modifying the reported procedure.[4] A solution of 4,4'-bipenyldicarboxylic acid (0.100 g, 0.412 mmol) in 3 mL DMF was transferred to a vial containing a solution of aluminium chloride hexahydrate (0.064 g, 0.270 mmol) in 3 mL DMF and kept on stirring for 2 h. The solution was kept in a preheated oven at 120 °C in a Teflon lined hydrothermal autoclave for 48 h. After cooling to room temperature, the white solid was collected via centrifugation, which was washed with DMF several times. The PXRD pattern of DUT-5(Al) MOF matches well with the simulated PXRD of DUT-5(Al). The resulting solid was stored in THF at room temperature to give DUT-5(Al) as a white solid with 58% yield. *n*-BuLi (0.235 mL, 1.65 M in cyclohexane) was added to the slurry of DUT-5(Al) (0.050 g, 0.17 mmol) in 1.5 mL THF in a vial, and the mixture was stirred for 1.5 h at room temperature inside the glovebox. The light brown solid was washed with THF several times to remove the excess *n*-BuLi. A THF solution of $CuCl_2.2H_2O$ (0.06 g, 0.34 mmol) was added, and the mixture was stirred overnight at room temperature. The DUT-5(Al)-CuCl was centrifuged out of the suspension, and the resultant yellowish-green solid was washed with THF several times. Inside the glovebox, $NaEt_3BH$ (300 µL, 1 M in toluene) was added dropwise into a vial containing DUT-5(Al)-CuCl (0.080 g) as a slurry in 3 mL THF, and the mixture was kept at room temperature for 1 h. The resultant black solid of DUT-5(Al)-CuH was separated *via* centrifugation followed by washing with THF several times. DUT-5(Al)-CuH was taken outside of the glovebox and kept in water for 30 minutes to afford DUT-5(Al)-

Cu(OH). 25% iron-loading with respect to the μ_2-OH moiety was analyzed by ICP-OES, giving an empirical formula of $C_{14}H_9O_{5.25}AlCu_{0.25}$.

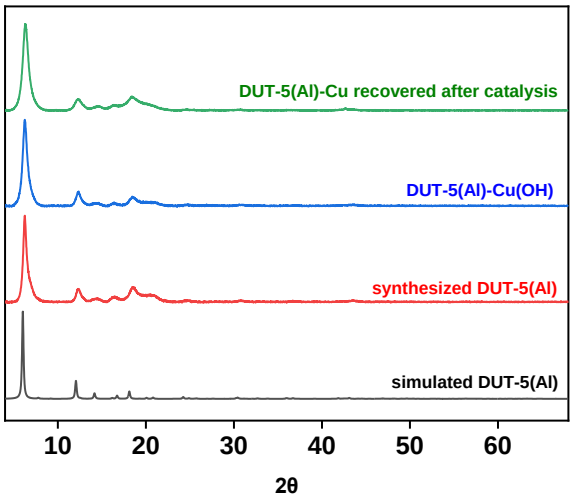


Figure S7. PXRD pattern of simulated DUT-5(Al) (black), synthesized DUT-5(Al) (red), DUT-5(Al)-Cu(OH) (blue), DUT-5(Al)-Cu MOF recovered after catalysis (green).

General procedure for methane oxidation to acetic acid mentioned in Section 3.1 was followed, using DUT-5(Al)-Cu(OH) (4.0 μmol of Cu) instead of MIL-53(Al)-Cu(OH). Reaction conditions: DUT-5(Al)-Cu(OH) (4.0 μmol of Cu), 7 mL water, 30 bar CH_4, 10 bar O_2, 175 °C, 32 h. 0.08 mmol of acetic acid along with 0.04 mmol of methanol was observed (Entry 21, Table S3) in the liquid phase, and 0.9 mmol of CO_2 in the gaseous phase. This reduction in selectivity can be attributed to increased diffusion of acetic acid into the larger pores of DUT-5(Al)-Cu(OH), where it undergoes further oxidation to CO_2. In contrast, MIL-53(Al) exhibits a unique diffusion profile that selectively facilitates the entry of methane (3.8 Å in diameter) to the catalytic sites while restricting the diffusion of larger products like acetic acid (5.9 Å in diameter). Thus, the mass transfer limitations and pore size play a critical role in controlling the reaction selectivity. By tuning the pore size, we can effectively control the diffusion of reactants and products, which is a key factor in maintaining high selectivity for acetic acid in methane oxidation reactions.

Radical scavenging experiment with MIL-53(Al)-Cu(OH) catalyst.

Radical scavenging experiment with Na_2SO_3. To investigate any role of •OH in MIL-53(Al)-Cu(OH) catalysed methane to acetic acid conversion, we had performed the catalysis in presence of a known •OH radical scavenger such as Na_2SO_3, and then catalytic activity and selectivity were compared to those of reactions done in absence of Na_2SO_3.

Reaction conditions: 3.8 mg of MIL-53(Al)-Cu(OH) (4.0 μmol Cu), 7 mL H_2O, 30 bar CH_4, 10 bar O_2, 32 h, Na_2SO_3 (250 mg, 1.98 mmol). General procedure mentioned in Section 3.1. was followed, and Na_2SO_3 (250 mg, 1.98 mmol) was added to study its effect on the catalytic reaction.

The yield of acetic acid as determined by GC using ethylene glycol as the internal standard was 1.48 mmol, which is similar to that obtained without scavenger under identical reaction conditions (Entry 5, Table S2). We conclude that the presence of the •OH radical scavenger (Na_2SO_3) does not affect the rate of the oxidation of methane to acetic acid catalysed by MIL-53(Al)-Cu(OH), which illustrates that •OH radicals do not participate in the mechanism.

Radical scavenging experiment with TEMPO To investigate any role of $•CH_3$ in MIL-53(Al)-Cu(OH) catalysed methane to acetic acid conversion, we had performed the catalysis in presence of a known $•CH_3$ and •OH radical scavenger such as TEMPO and then catalytic activity and selectivity were compared to those of reactions done in absence of •OH radical scavengers.

General procedure mentioned in Section 3.1. was followed, and TEMPO (249.8 mg, 1.6 mmol) was added to study its effect on the catalytic reaction. Reaction conditions: 3.8 mg of MIL-53(Al)-Cu(OH) (4.0 μmol Cu), 7 mL H_2O, 30 bar CH_4, 10 bar O_2, 32 h, TEMPO (249.8 mg, 1.6 mmol).

The yield of acetic acid as determined by GC using ethylene glycol as the internal standard was 0.34 mmol, which is significantly lower to that obtained without scavenger under identical reaction conditions (Entry 22, Table S3), which illustrates that $•CH_3$ radicals are involved in the reaction mechanism.

4. DFT Calculations. All quantum chemical calculations were done using the density functional theory (DFT) functional B3LYP/def2TZVP augmented with the D3 version of Grimme's empirical dispersion correction[5–7] as implemented in the Gaussian 16 software suite.[8–12] Electronic structure complexes were optimized at the unrestricted level. All calculations were performed in the solvated state and at 448.15 K. We used the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM) as the default SCRF method by using water as the solvent in this DFT calculation at 175 ºC. Each structure was first optimized, and then frequency calculation was performed to confirm its geometry, to obtain the thermochemical data, and to provide the thermal corrections to Gibbs free energy. MIL-53(Al)-Cu(OH) was calculated with zero, one, and two H_2O molecule coordinated to Cu. Internal energies were compared directly after accounting for the difference in the number of coordinated H_2O molecules. Optimized structures were visualized by GaussView 5.0 software.

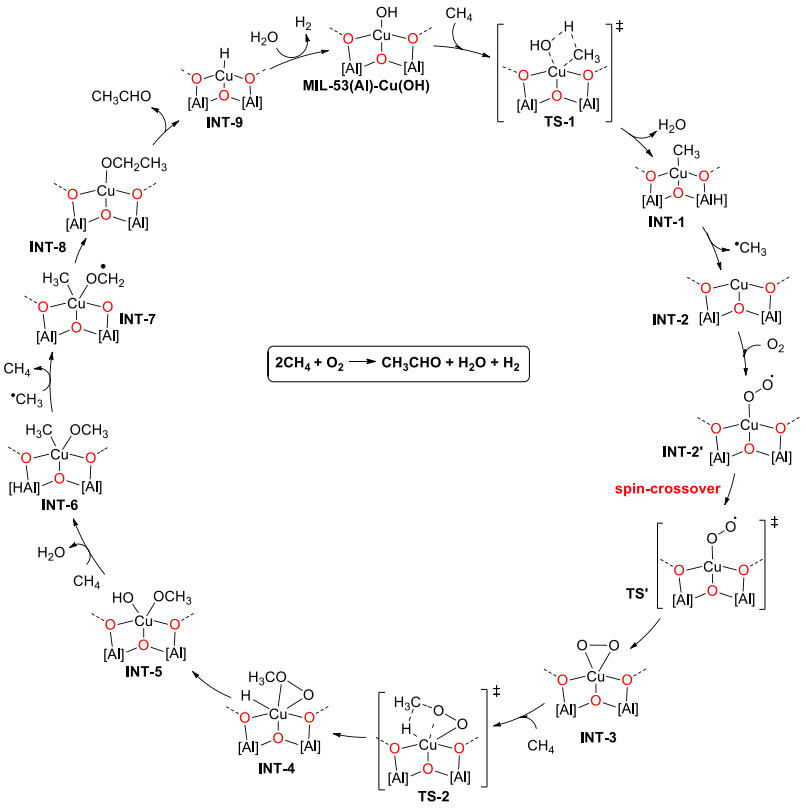


Figure S8. Proposed catalytic cycle of MIL-53(Al)-Cu(OH) catalyzed oxidation of methane to acetaldehyde.

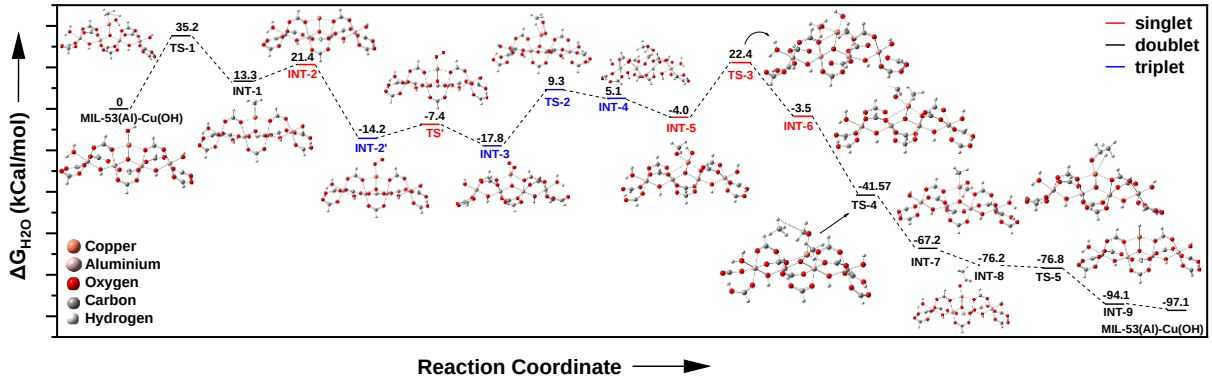
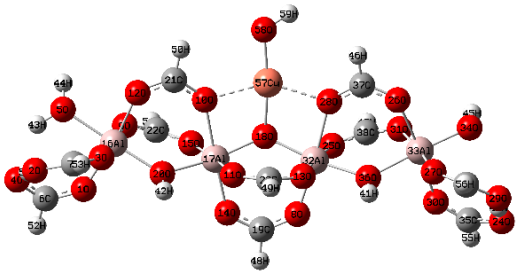
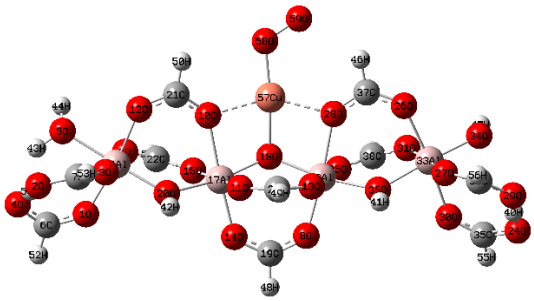


Figure S9. DFT-calculated free energy diagram of methane oxidation to acetaldehyde over MIL-53(Al)-Cu(OH) at 448 K.

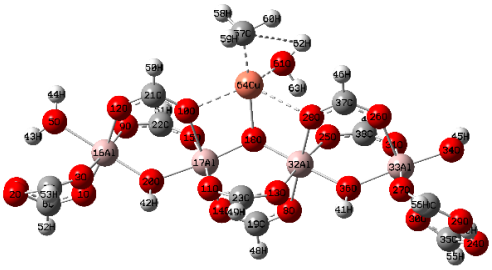
To explore the reaction mechanism and determine the turnover-limiting step (TLS), the entire catalytic cycle was examined through DFT calculations (Figure S9). The DFT-calculated energy profile reveals that methane C–H bond activation via σ-bond metathesis has an energy barrier of 35 kcal/mol. The formation of INT-1 (MIL-53(Al)-$Cu^{II}(CH_3)$) from MIL-53(Al)-Cu(OH) is endergonic by 13.3 kcal/mol. Subsequently, the homolytic cleavage of INT-1 to generate INT-2 (Cu^+ species) and a $^\bullet CH_3$ radical is slightly endergonic by 8.1 kcal/mol. INT-2 reacts with O_2 to form a Cu-OO• (triplet) species [INT-2'], an exergonic process by 35.6 kcal/mol. This is followed by a spin crossover to a Cu-OO• (singlet) species [TS'], with an associated barrier of 6.8 kcal/mol, leading to the formation of INT-3 (Cu^{III}-η²-peroxy). INT-3 undergoes σ-bond metathesis with CH_4 via TS-2, resulting in the formation of INT-4, with an energy barrier of 27.1 kcal/mol. INT-4 rearranges to form INT-5, an exergonic step by 4.2 kcal/mol. INT-5 undergoes a second σ-bond metathesis via TS-3 to generate INT-6, with a barrier of 26.4 kcal/mol. The $^\bullet CH_3$ radical abstracts a hydrogen atom from the methoxy group of INT-6 to form INT-7, a highly exergonic step by 63.7 kcal/mol. INT-7 then rearranges to form INT-8, an exergonic step by 9 kcal/mol. Finally, INT-8 undergoes β-hydride elimination via TS-4, which is exergonic by 17.9 kcal/mol, yielding acetaldehyde and MIL-53(Al)-CuH (INT-9). The hydrolysis of INT-9 regenerates MIL-53(Al)-Cu(OH), completing the catalytic cycle, an exergonic process by 3 kcal/mol. The energy profile showed that methane activation through σ-bond metathesis has the highest activation barrier and thus it is the turnover-limiting step.



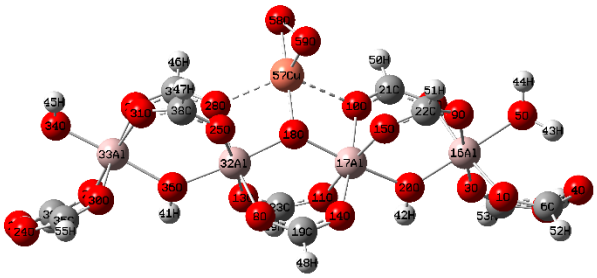
MIL-53(Al)-Cu(OH)



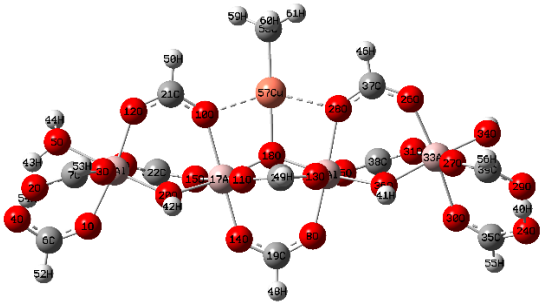
TS’



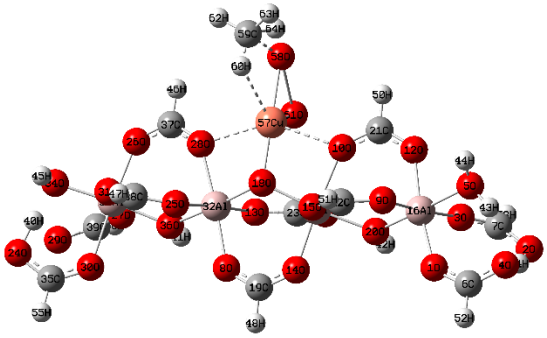
TS-1



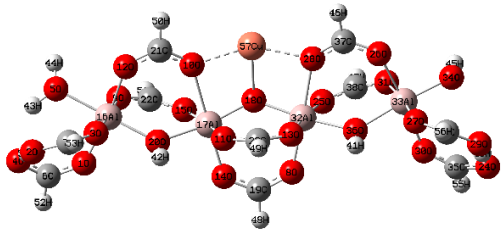
INT-3



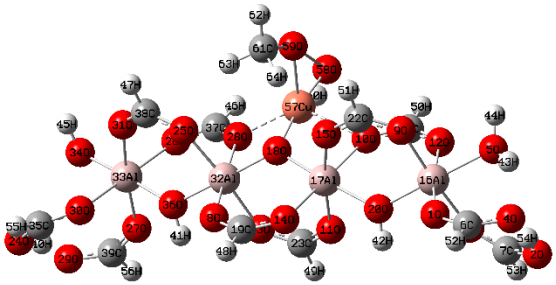
INT-1



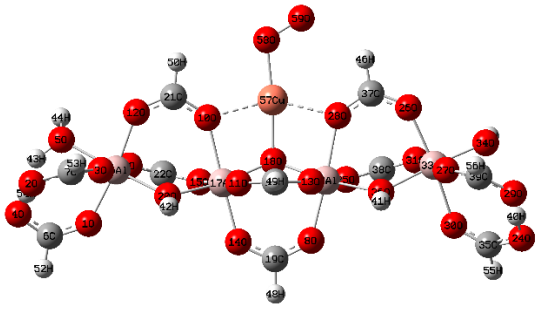
TS-2



INT-2



INT-4



INT-2’

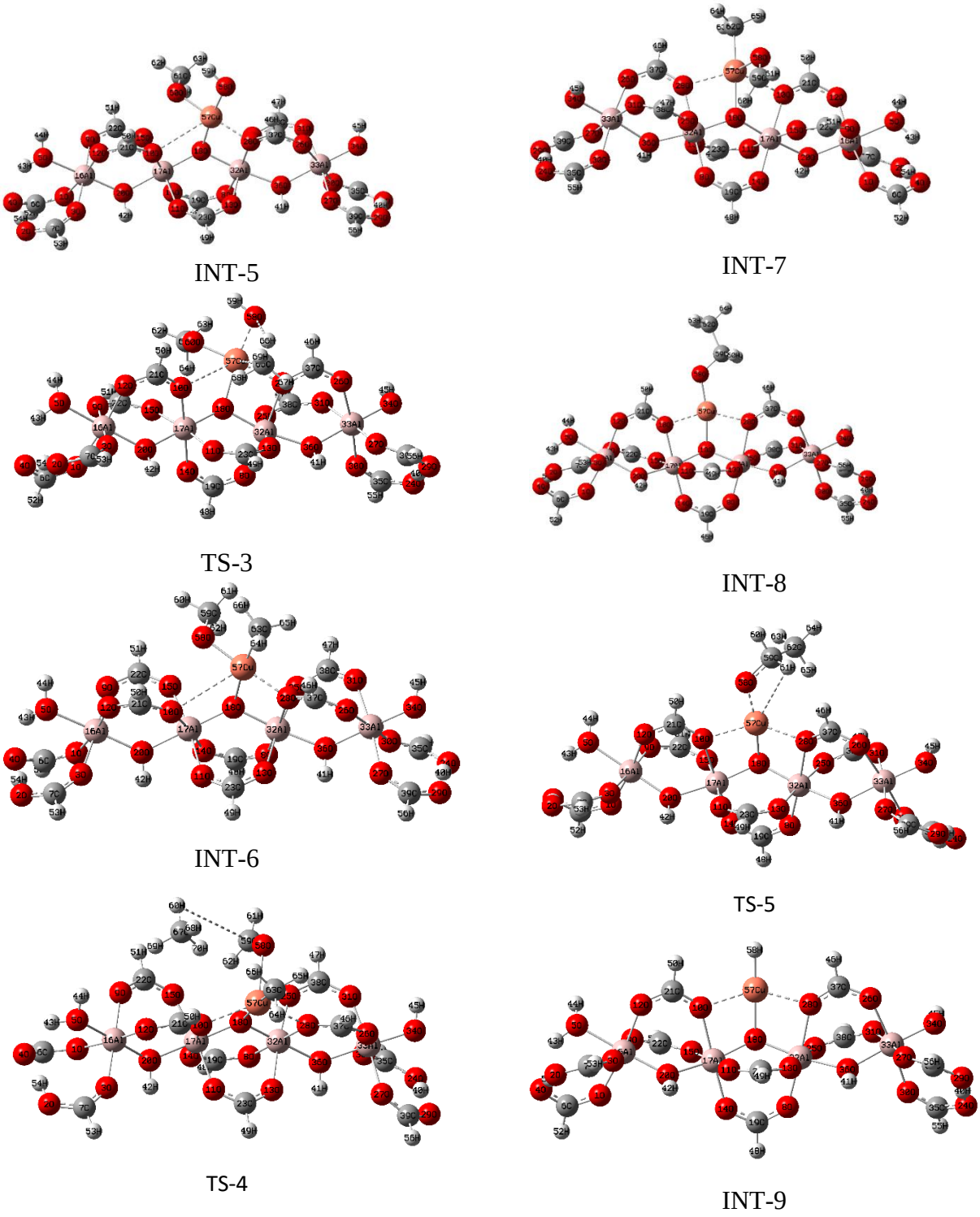


Figure S10. DFT-optimized structures of intermediates and transition states for MIL-53(Al)-Cu(OH) catalyzed oxidation of methane to acetaldehyde.

Cartesian coordiantes of the DFT-optimized structures.

MIL-53(Al)-Cu(OH)

S.No.	Atoms	Coordinates (Angstroms) X	Y	Z
1	O	23.007351	12.375311	17.036534
2	O	20.565758	10.863509	19.156597
3	O	21.136450	13.042531	18.999734
4	O	21.799933	10.492970	16.876532
5	O	20.380511	12.700922	16.394554
6	C	22.878394	11.128020	16.828877
7	C	20.654206	12.073897	19.595291
8	O	26.009986	18.490461	18.681110
9	O	22.244916	14.510990	15.608678
10	O	21.359912	16.987642	17.685584
11	O	23.155932	16.730612	19.912611
12	O	20.290436	15.040724	17.443303
13	O	23.880670	18.802624	20.435702
14	O	25.278202	16.416406	18.157504
15	O	23.551670	16.287708	16.060288
16	Al	21.752589	13.780943	17.283833
17	Al	23.384502	16.637533	17.957673
18	O	23.402361	18.416715	17.777891
19	C	26.169313	17.269178	18.425628
20	O	22.967845	14.820628	18.219611
21	C	20.310711	16.286389	17.580486
22	C	23.024909	15.453973	15.288584
23	C	23.404546	17.672976	20.714805
24	O	27.932037	24.416017	20.924055
25	O	25.049844	20.497871	17.107854
26	O	22.984887	22.664556	19.493031
27	O	24.785965	22.755590	21.538106
28	O	22.660952	20.640933	18.594368
29	O	26.074185	24.283137	22.585896
30	O	27.034640	22.813347	19.612523
31	O	25.126640	22.673825	17.689886
32	Al	24.419452	19.594898	18.682669
33	Al	24.990800	22.825084	19.636795
34	O	24.936204	24.604483	19.554230
35	C	27.949173	23.567573	19.956075
36	O	25.141139	20.936536	19.746302
37	C	22.254542	21.766848	19.046093
38	C	25.230091	21.722604	16.876453
39	c	25.145887	23.459236	22.534847
40	H	27.069105	24.364040	21.513977
41	H	25.160096	20.674925	20.673187
42	H	23.040717	14.594298	19.153690
43	H	20.616470	11.766359	16.224040
44	H	19.847720	13.058320	15.674110
45	H	25.083562	24.937686	18.666235
46	H	21.169873	21.917334	19.014642
47	H	25.500334	21.984605	15.845595
48	H	27.200723	16.898056	18.442802
49	H	23.180235	17.481338	21.771677
50	H	19.360399	16.827279	17.606510
51	H	23.253575	15.548635	14.221657

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S.No.	Atoms	Coordinates (Angstroms) X	Y	Z
1	O	22.683704	12.948666	17.113356
2	O	20.802492	11.037637	19.400491
3	O	21.121815	13.268895	19.388866
4	O	21.697177	10.945216	16.966110
5	O	19.962285	13.006051	16.938075
6	C	22.666640	11.721292	16.804853
7	C	20.835506	12.206347	19.942729
8	O	25.394008	19.097663	18.524493
9	O	21.456223	15.039625	16.005770
10	O	20.745694	17.285971	18.434326
11	O	22.874781	17.104881	20.240046
12	O	19.854917	15.248551	18.177134
13	O	23.704251	19.134638	20.748651
14	O	24.661787	17.005176	18.115286
15	O	22.580381	16.951311	16.370707
16	Al	21.362371	14.180928	17.676761
17	Al	22.765243	17.153612	18.292848
18	O	22.695287	18.926074	18.203294
19	C	25.544625	17.900470	18.185596
20	O	22.604851	15.280228	18.453256
21	C	19.781369	16.478063	18.413747
22	C	22.032937	16.101912	15.638206
23	C	23.262849	17.996815	21.037068
24	O	27.945133	24.539426	21.019646
25	O	23.942070	21.162372	17.398984
26	O	22.881568	23.185784	19.933581
27	O	24.806585	23.050432	21.845966
28	O	22.173199	21.091998	19.518736
29	O	26.228900	24.494043	22.824064
30	O	26.873609	23.002888	19.768585
31	O	24.849450	23.136427	17.983358
32	Al	23.789741	20.075068	19.025906
33	Al	24.851579	23.178737	19.942755
34	O	24.956967	24.955400	19.953873
35	C	27.849349	23.698638	20.051724
36	O	24.860184	21.303203	19.925012
37	C	22.002247	22.307324	19.813161
38	C	24.435004	22.300502	17.155540
39	C	25.259860	23.714664	22.823359
40	H	27.120516	24.535195	21.676105
41	H	25.142624	20.954139	20.775691
42	H	22.918453	14.985303	19.314276
43	H	20.284638	12.133050	16.635101
44	H	19.354878	13.377065	16.285380
45	H	24.997696	25.339833	19.075659
46	H	20.961420	22.618584	19.970774
47	H	24.490638	22.582013	16.096269
48	H	26.564935	17.590535	17.926149
49	H	23.213214	17.747277	22.104886
50	H	18.787681	16.890369	18.615688
51	H	22.042533	16.292304	14.559169
52	H	23.589421	11.327482	16.360063
53	H	20.579811	12.199771	21.003494
54	H	21.097869	11.025777	18.427361
55	H	28.760285	23.623406	19.448854
56	H	24.731127	23.562537	23.777293
57	C	18.955275	20.016145	18.350119
58	H	18.375156	19.615429	17.513405
59	H	18.556250	19.610888	19.285514
60	H	18.855206	21.105330	18.361580
61	O	21.327651	20.676454	16.387703
62	H	20.912718	21.548001	16.380591
63	H	22.284050	20.827358	16.522566
64	Cu	20.835359	19.510230	18.163099

INT-1

S.No.	Atoms	Coordinates (Angstroms) X	Y	Z
1	O	23.087255	12.424929	17.076709
2	O	20.728249	10.789805	19.109902
3	O	21.192061	12.994030	19.024765
4	O	21.999311	10.480676	16.866968
5	O	20.445717	12.637790	16.429084
6	C	23.034881	11.183433	16.834260
7	C	20.751811	11.987887	19.583528
8	O	25.908182	18.499712	18.715912
9	O	22.217783	14.507369	15.659210
10	O	21.259195	16.953943	17.761528
11	O	23.027491	16.773212	19.936140
12	O	20.287036	14.957724	17.506487
13	O	23.771248	18.833245	20.458171
14	O	25.160682	16.436645	18.197087
15	O	23.429333	16.346925	16.103190
16	Al	21.781105	13.767651	17.332086
17	Al	23.279186	16.677875	17.999459

18	O	23.313863	18.443247	17.801872
19	C	26.057183	17.280540	18.459129
20	O	22.948634	14.843824	18.250366
21	C	20.254133	16.201034	17.651792
22	C	22.941548	15.490477	15.336273
23	C	23.260675	17.720894	20.730856
24	O	28.024666	24.307517	20.828854
25	O	24.936429	20.495064	17.137860
26	O	23.054566	22.698000	19.597232
27	O	24.905424	22.725100	21.573167
28	O	22.615925	20.698896	18.692983
29	O	26.230187	24.253414	22.557733
30	O	27.067405	22.697072	19.578183
31	O	25.098577	22.658797	17.730225
32	Al	24.327140	19.598785	18.716374
33	Al	25.041715	22.782537	19.671349
34	O	25.056218	24.560716	19.620930
35	C	28.002877	23.437925	19.882139
36	O	25.131573	20.903196	19.760455
37	C	22.279437	21.833792	19.158882
38	C	25.146027	21.712007	16.909585
39	C	25.290761	23.439599	22.544793
40	H	27.173152	24.291204	21.448541
41	H	25.182625	20.627593	20.681287
42	H	23.067656	14.602239	19.174929
43	H	20.750034	11.729425	16.229073
44	H	19.979278	13.004255	15.666955
45	H	25.117950	24.912767	18.730364
46	H	21.205149	22.049740	19.158227
47	H	25.390476	21.975309	15.872462
48	H	27.086625	16.902299	18.469727
49	H	22.986673	17.550931	21.780001
50	H	19.271029	16.680391	17.680795
51	H	23.153419	15.599665	14.267023
52	H	23.988978	10.706538	16.576218
53	H	20.330275	12.066204	20.586823
54	H	21.172222	10.695813	18.199788
55	H	28.940890	23.382071	19.320420
56	H	24.725498	23.301307	23.479498
57	Cu	21.498267	19.120572	17.812324
58	C	19.672576	19.802512	17.698759
59	H	19.102144	19.235399	16.957368
60	H	19.186470	19.698622	18.673828
61	H	19.673935	20.858602	17.415517

INT-2

S.No.	Atoms	Coordinates (Angstroms) X	Y	Z
1	O	23.039916	12.402129	17.068797
2	O	20.594906	10.849339	19.072432
3	O	21.137335	13.035490	18.994359
4	O	21.902761	10.485998	16.862631
5	O	20.415722	12.690787	16.390651
6	C	22.956189	11.160750	16.832192
7	C	20.649690	12.046170	19.544881
8	O	25.960295	18.474481	18.738984
9	O	22.255059	14.513200	15.646154
10	O	21.344129	16.969763	17.706403
11	O	23.059427	16.761734	19.918522
12	O	20.303721	15.013903	17.456407
13	O	23.798397	18.823655	20.437373
14	O	25.215342	16.408449	18.228146
15	O	23.531644	16.303624	16.106580
16	Al	21.772358	13.779719	17.309259
17	Al	23.343727	16.640038	17.991712
18	O	23.390220	18.415839	17.780923
19	C	26.110105	17.251127	18.500010
20	O	22.963826	14.821490	18.244553
21	C	20.308183	16.257773	17.583594
22	C	23.022519	15.464931	15.332594
23	C	23.284297	17.712770	20.711564
24	O	27.935045	24.407551	20.793519
25	O	25.014360	20.463406	17.138727
26	O	23.022955	22.641755	19.568256
27	O	24.867192	22.738717	21.543933
28	O	22.642389	20.654000	18.622463
29	O	26.131530	24.327392	22.511440
30	O	27.034825	22.747745	19.565360
31	O	25.082167	22.637673	17.707355
32	Al	24.395149	19.578455	18.710729
33	Al	25.017137	22.783651	19.645793
34	O	24.973426	24.558817	19.574630
35	C	27.946836	23.520585	19.863876
36	O	25.144262	20.903729	19.756686
37	C	22.269346	21.770415	19.116807
38	C	25.180047	21.685525	16.898177
39	C	25.221868	23.480905	22.507179
40	H	27.079292	24.378103	21.407375
41	H	25.174116	20.643327	20.683196
42	H	23.052935	14.579210	19.172552
43	H	20.688163	11.775005	16.183807
44	H	19.942591	13.073266	15.640693
45	H	25.020074	24.904667	18.680747
46	H	21.189078	21.951825	19.128471
47	H	25.430411	21.945510	15.861999
48	H	27.137022	16.869404	18.537322
49	H	22.998718	17.549077	21.758108
50	H	19.350053	16.784506	17.583774
51	H	23.256685	15.563484	14.267219
52	H	23.898974	10.658257	16.581456
53	H	20.209633	12.142061	20.538610
54	H	21.056962	10.737070	18.172393
55	H	28.890856	23.479554	19.311385
56	H	24.657040	23.335948	23.440914
57	Cu	21.612440	19.073428	17.776007

INT-2’

S.No.	Atoms	Coordinates (Angstroms) X	Y	Z
1	O	23.065145	12.415609	17.069404
2	O	20.662739	10.824426	19.091538
3	O	21.164300	13.020020	19.003730
4	O	21.956360	10.482290	16.868865
5	O	20.430923	12.660041	16.405888
6	C	22.999422	11.172999	16.833973
7	C	20.700067	12.023293	19.560883
8	O	25.933222	18.487056	18.727677
9	O	22.233990	14.505655	15.642932
10	O	21.279113	16.973240	17.720046
11	O	23.039244	16.772532	19.909894
12	O	20.293264	14.985122	17.469664
13	O	23.771319	18.836093	20.430661
14	O	25.194780	16.420624	18.205793
15	O	23.478605	16.320749	16.093822
16	Al	21.775949	13.773094	17.312757
17	Al	23.321839	16.658548	17.981981
18	O	23.367271	18.424902	17.767103
19	C	26.086937	17.266921	18.478473
20	O	22.950900	14.838578	18.238624
21	C	20.266036	16.227837	17.604401
22	C	22.978930	15.473255	15.323637
23	C	23.262094	17.723463	20.704046
24	O	27.971507	24.344895	20.850738
25	O	24.983175	20.477342	17.125135
26	O	23.049000	22.691151	19.510621
27	O	24.848837	22.743040	21.533478

28	O	22.622276	20.676364	18.636259
29	O	26.131883	24.297252	22.532397
30	O	27.058732	22.712429	19.595428
31	O	25.138480	22.646365	17.698619
32	Al	24.358412	19.591995	18.698501
33	Al	25.033143	22.787872	19.636440
34	O	25.037728	24.565102	19.571203
35	C	27.980861	23.463754	19.914724
36	O	25.130838	20.907714	19.744697
37	C	22.278737	21.824635	19.069708
38	C	25.199510	21.692026	16.888465
39	C	25.202587	23.472557	22.506369
40	H	27.103840	24.330329	21.446900
41	H	25.158916	20.644193	20.670208
42	H	23.042195	14.604406	19.168558
43	H	20.719779	11.747954	16.203205
44	H	19.956476	13.031909	15.651392
45	H	25.109190	24.910709	18.678836
46	H	21.206659	22.043503	19.028680
47	H	25.463778	21.943783	15.853506
48	H	27.115876	16.889043	18.506591
49	H	22.978542	17.556674	21.750821
50	H	19.286767	16.716093	17.618496
51	H	23.200514	15.577987	14.256107
52	H	23.948756	10.684565	16.580203
53	H	20.267655	12.113208	20.558518
54	H	21.117601	10.718867	18.187351
55	H	28.933700	23.407556	19.378690
56	H	24.616597	23.337380	23.428636
57	Cu	21.565705	19.082824	17.764676
58	O	19.765433	19.602629	17.587805
59	O	19.578871	20.872636	17.538256

TS’

		Coordinates (Angstroms)		
S.No.	Atoms	X	Y	Z
1	O	23.064937	12.415582	17.069379
2	O	20.663092	10.824609	19.091926
3	O	21.164258	13.020263	19.003866
4	O	21.955875	10.482492	16.868402
5	O	20.430761	12.659974	16.406063
6	C	22.999070	11.173018	16.833785
7	C	20.700290	12.023500	19.561185
8	O	25.933504	18.487012	18.727415
9	O	22.233875	14.505647	15.642998
10	O	21.279160	16.973182	17.719917
11	O	23.039373	16.772551	19.909799
12	O	20.293103	14.985147	17.469705
13	O	23.771681	18.836031	20.430591
14	O	25.194850	16.420655	18.205551
15	O	23.478579	16.320714	16.093709
16	Al	21.775803	13.773151	17.312788
17	Al	23.321888	16.658578	17.981855
18	O	23.367457	18.424907	17.767030
19	C	26.087096	17.266860	18.478153
20	O	22.950914	14.838621	18.238531
21	C	20.266019	16.227887	17.604453
22	C	22.978898	15.473150	15.323607
23	C	23.262466	17.723391	20.703982
24	O	27.971555	24.344259	20.851614
25	O	24.983407	20.477322	17.125044
26	O	23.049111	22.691159	19.510350
27	O	24.848661	22.743144	21.533230
28	O	22.622410	20.676304	18.636171
29	O	26.130898	24.297620	22.532774
30	O	27.058814	22.712618	19.595161
31	O	25.138762	22.646349	17.698492
32	Al	24.358720	19.591929	18.698365
33	Al	25.033159	22.787932	19.636280
34	O	25.037768	24.565148	19.571152
35	C	27.980922	23.463718	19.915052
36	O	25.131069	20.907714	19.744529
37	C	22.278856	21.824579	19.069517
38	C	25.199689	21.692014	16.888339
39	C	25.201756	23.472733	22.506280
40	H	27.104012	24.329456	21.447963
41	H	25.159236	20.644182	20.670034
42	H	23.042353	14.604308	19.168413
43	H	20.719663	11.747868	16.203515
44	H	19.956337	13.031702	15.651484
45	H	25.109108	24.910905	18.678835
46	H	21.206790	22.043474	19.028376
47	H	25.463868	21.943759	15.853355
48	H	27.116012	16.888915	18.506155
49	H	22.979233	17.556493	21.750828
50	H	19.286752	16.716154	17.618717
51	H	23.200545	15.577723	14.256075
52	H	23.948344	10.684473	16.579998
53	H	20.268007	12.113431	20.558874
54	H	21.117824	10.719102	18.187680
55	H	28.933762	23.407915	19.378979
56	H	24.615291	23.337548	23.428229
57	Cu	21.565805	19.082871	17.764651
58	O	19.765048	19.602633	17.588371
59	O	19.578611	20.872790	17.538517

INT-3

		Coordinates (Angstroms)		
S.No.	Atoms	X	Y	Z
1	O	23.007351	12.375311	17.036534
2	O	20.565758	10.863509	19.156597
3	O	21.136450	13.042531	18.999734
4	O	21.799933	10.492970	16.876532
5	O	20.380511	12.700922	16.394554
6	C	22.878394	11.128020	16.828877
7	C	20.654206	12.073897	19.595291
8	O	26.009986	18.490461	18.681110
9	O	22.244916	14.510990	15.608678
10	O	21.359912	16.987642	17.685584
11	O	23.155932	16.730612	19.912611
12	O	20.290436	15.040724	17.443303
13	O	23.880670	18.802624	20.435702
14	O	25.278202	16.416406	18.157504
15	O	23.551670	16.287708	16.060288
16	Al	21.752589	13.780943	17.283833
17	Al	23.384502	16.637533	17.957673
18	O	23.402361	18.416715	17.777891
19	C	26.169313	17.269178	18.425628
20	O	22.967845	14.820628	18.219611
21	C	20.310711	16.286389	17.580486
22	C	23.024909	15.453973	15.288584
23	C	23.404546	17.672976	20.714805
24	O	27.932037	24.416017	20.924055
25	O	25.049844	20.497871	17.107854
26	O	22.984887	22.664556	19.493031
27	O	24.785965	22.755590	21.538106
28	O	22.660952	20.640933	18.594368
29	O	26.074185	24.283137	22.585896
30	O	27.034640	22.813347	19.612523
31	O	25.126640	22.673825	17.689886
32	Al	24.419452	19.594898	18.682669
33	Al	24.990800	22.825084	19.636795
34	O	24.936204	24.604483	19.554230
35	C	27.949173	23.567573	19.956075
36	O	25.141139	20.936536	19.746302
37	C	22.254542	21.766848	19.046093

38	C	25.230091	21.722604	16.876453
39	C	25.145887	23.459236	22.534847
40	H	27.069105	24.364040	21.513977
41	H	25.160096	20.674925	20.673187
42	H	23.040717	14.594298	19.153690
43	H	20.616470	11.766359	16.224040
44	H	19.847720	13.058320	15.674110
45	H	25.083562	24.937686	18.666235
46	H	21.169873	21.917334	19.014642
47	H	25.500334	21.984605	15.845595
48	H	27.200723	16.898056	18.442802
49	H	23.180235	17.481338	21.771677
50	H	19.360399	16.827279	17.606510
51	H	23.253575	15.548635	14.221657
52	H	23.803711	10.588551	16.589897
53	H	20.251312	12.199192	20.601260
54	H	20.984549	10.735234	18.246087
55	H	28.901310	23.545030	19.416245
56	H	24.559504	23.295002	23.452510
57	Cu	21.617433	19.043682	17.875396
58	O	20.283805	19.292515	18.801035
59	O	20.790674	19.663560	16.598874
60	H	19.795938	19.976465	17.398739
61	O	20.496665	19.125380	20.139066
62	H	19.081334	21.193188	17.828751
63	H	18.421825	19.448262	17.304944
64	H	17.938830	20.389655	18.360535

TS-2

S.No.	Atoms	Coordinates (Angstroms) X	Y	Z
1	O	22.460309	12.597699	17.566406
2	O	19.968907	11.009199	19.791186
3	O	20.526150	13.189529	19.538079
4	O	21.432176	10.627830	17.259523
5	O	19.814316	12.800523	16.920352
6	C	22.446946	11.357064	17.309839
7	C	20.061262	12.237290	20.168502
8	O	25.252080	18.675547	19.254274
9	O	21.597667	14.684372	16.168553
10	O	20.629709	17.100213	18.231637
11	O	22.395767	16.936581	20.449498
12	O	19.635120	15.119143	17.975385
13	O	23.125931	19.001014	20.977255
14	O	24.515028	16.614063	18.726790
15	O	22.831198	16.502475	16.636367
16	Al	21.133563	13.923860	17.825062
17	Al	22.642832	16.820280	18.515877
18	O	22.657205	18.617264	18.330208
19	C	25.407423	17.457476	19.000577
20	O	22.290155	14.999663	18.768145
21	C	19.612879	16.360169	18.114086
22	C	22.335809	15.658798	15.858256
23	C	22.633318	17.879851	21.249394
24	O	27.396722	24.448469	21.421761
25	O	24.327803	20.653805	17.681111
26	O	22.404060	22.902471	20.070661
27	O	24.206683	22.937267	22.083883
28	O	21.996079	20.893960	19.181772
29	O	25.536736	24.450307	23.082328
30	O	26.426549	22.874773	20.137546
31	O	24.494896	22.821686	18.253987
32	Al	23.696517	19.790653	19.253296
33	Al	24.399955	22.977581	20.192999
34	O	24.418728	24.750267	20.116803
35	C	27.371861	23.593120	20.461405
36	O	24.473511	21.094254	20.304256
37	C	21.640743	22.033799	19.632410
38	C	24.546184	21.868804	17.442947
39	C	24.592925	23.644056	23.062357
40	H	26.539550	24.432802	22.026526
41	H	24.493043	20.832871	21.230869
42	H	22.363531	14.768308	19.700614

INT-4

S.No.	Atoms	Coordinates (Angstroms) X	Y	Z
1	O	22.912907	12.423347	16.826359
2	O	20.471314	10.911545	18.946422
3	O	21.042006	13.090567	18.789559
4	O	21.705489	10.541007	16.666357
5	O	20.286068	12.748958	16.184379
6	C	22.783950	11.176057	16.618702
7	C	20.559762	12.121933	19.385116
8	O	25.915542	18.538497	18.470935
9	O	22.150472	14.559026	15.398503
10	O	21.265468	17.035678	17.475409
11	O	23.061489	16.778648	19.702435
12	O	20.195992	15.088760	17.233127
13	O	23.786227	18.850660	20.225527
14	O	25.183758	16.464442	17.947329
15	O	23.457227	16.335745	15.850113
16	Al	21.658146	13.828979	17.073658
17	Al	23.290058	16.685569	17.747498
18	O	23.307917	18.464752	17.567716
19	C	26.074869	17.317214	18.215452
20	O	22.873401	14.868664	18.009436
21	C	20.216267	16.334425	17.370311
22	C	22.930465	15.502010	15.078408
23	C	23.310102	17.721012	20.504630
24	O	27.837593	24.464053	20.713880
25	O	24.955400	20.545907	16.897679
26	O	22.890443	22.712592	19.282856
27	O	24.691521	22.803626	21.327931
28	O	22.566508	20.688969	18.384193
29	O	25.979741	24.331173	22.375721
30	O	26.940196	22.861383	19.402348
31	O	25.032197	22.721861	17.479710
32	Al	24.325008	19.642934	18.472494
33	Al	24.896356	22.873120	19.426619
34	O	24.841760	24.652519	19.344055
35	C	27.854729	23.615609	19.745900
36	O	25.046695	20.984573	19.536127
37	C	22.160098	21.814884	18.835918
38	C	25.135647	21.770640	16.666278
39	C	25.051443	23.507272	22.324672
40	H	26.974661	24.412076	21.303801
41	H	25.065652	20.722961	20.463012
42	H	22.946273	14.642335	18.943515

43	H	20.522026	11.814395	16.013865
44	H	19.753277	13.106356	15.463935
45	H	24.989119	24.985722	18.456060
46	H	21.075429	21.965371	18.804467
47	H	25.405891	22.032641	15.635420
48	H	27.106279	16.946092	18.232626
49	H	23.085791	17.529374	21.561502
50	H	19.265955	16.875315	17.396334
51	H	23.159132	15.596671	14.011481
52	H	23.709267	10.636587	16.379722
53	H	20.156869	12.247229	20.391084
54	H	20.890105	10.783270	18.035912
55	H	28.806867	23.593066	19.206070
56	H	24.465060	23.343038	23.242334
57	Cu	21.522989	19.091719	17.665221
58	O	20.019054	19.553393	17.896226
59	O	21.342904	19.286521	16.046820
60	H	21.732905	19.510413	15.198663
61	C	21.151019	18.905942	19.560142
62	H	20.215307	19.372542	19.787360
63	H	21.102754	17.867618	19.814023
64	H	21.929836	19.375201	20.124180

43	H	20.805766	11.733077	16.235678
44	H	20.002329	12.992800	15.684957
45	H	25.131165	24.959019	18.935955
46	H	21.264910	22.175735	19.049282
47	H	25.461434	22.064155	16.039555
48	H	26.988105	16.911991	18.332103
49	H	23.070623	17.539295	21.831360
50	H	19.226787	16.573599	17.983839
51	H	22.982615	15.765995	14.269241
52	H	24.066953	10.774950	16.567579
53	H	20.410078	12.052054	20.596373
54	H	21.257772	10.707984	18.197613
55	H	28.985521	23.413000	19.559772
56	H	24.703437	23.282893	23.646632
57	Cu	21.855175	19.720078	17.361403
58	O	20.574299	20.950732	17.067732
59	H	20.043934	20.614177	16.333156
60	O	21.294219	18.799925	15.909141
61	C	22.101890	19.097774	14.797296
62	H	21.728353	18.476090	13.973175
63	H	22.021986	20.147338	14.490232
64	H	23.149582	18.837173	14.969420

INT-5

S.No.	Atoms	Coordinates (Angstroms) X	Y	Z
1	O	23.131809	12.474023	17.071917
2	O	20.820032	10.789909	19.110798
3	O	21.243924	13.003432	19.033291
4	O	22.081888	10.509405	16.854985
5	O	20.479879	12.632342	16.442917
6	C	23.103437	11.233075	16.825681
7	C	20.826140	11.987764	19.589565
8	O	25.863969	18.503877	18.785417
9	O	22.214084	14.522266	15.636638
10	O	21.187797	16.940276	18.105030
11	O	23.107007	16.816539	19.964810
12	O	20.309355	14.959886	17.504920
13	O	23.756135	18.891894	20.524079
14	O	25.042706	16.545468	18.043785
15	O	23.168485	16.498121	16.119560
16	Al	21.801207	13.799280	17.327746
17	Al	23.117711	16.776487	18.016644
18	O	23.264987	18.584394	17.832348
19	C	25.969649	17.314968	18.382943
20	O	22.956943	14.897351	18.226342
21	C	20.237689	16.166388	17.868209
22	C	22.794652	15.602354	15.336312
23	C	23.307276	17.747391	20.780670
24	O	28.048046	24.313985	21.069979
25	O	24.990912	20.563136	17.274880
26	O	23.075542	22.737746	19.747306
27	O	24.925008	22.723848	21.739053
28	O	22.685953	20.778642	18.765572
29	O	26.224354	24.246652	22.763915
30	O	27.104607	22.734331	19.770767
31	O	25.146142	22.715286	17.906038
32	Al	24.362015	19.649657	18.839959
33	Al	25.102070	22.814787	19.848892
34	O	25.084166	24.589838	19.820432
35	C	28.039216	23.464704	20.107004
36	O	25.169942	20.932853	19.902366
37	C	22.319419	21.934283	19.200526
38	C	25.204727	21.784173	17.068683
39	C	25.287632	23.431200	22.725757
40	H	27.185713	24.293218	21.677472
41	H	25.205201	20.645338	20.820763
42	H	23.200534	14.611840	19.111892

TS-3

S.No.	Atoms	Coordinates (Angstroms) X	Y	Z
1	O	23.225460	12.475400	17.001341
2	O	20.979989	10.718724	19.058803
3	O	21.360674	12.940657	19.000039
4	O	22.206814	10.495279	16.775816
5	O	20.561311	12.591231	16.417133
6	C	23.215262	11.237127	16.741059
7	C	20.971840	11.911120	19.551470
8	O	25.920176	18.484317	18.742078
9	O	22.243755	14.525372	15.608832
10	O	21.237373	16.892898	18.080100
11	O	23.158613	16.800859	19.938196
12	O	20.363445	14.900330	17.517788
13	O	23.831018	18.868581	20.501223
14	O	25.087817	16.532603	17.999150
15	O	23.202009	16.500378	16.088948
16	Al	21.873790	13.771611	17.296871
17	Al	23.163830	16.761725	17.989243
18	O	23.297114	18.574061	17.824940
19	C	26.020037	17.297209	18.334589
20	O	23.023193	14.879067	18.190293
21	C	20.289328	16.107500	17.877889
22	C	22.815611	15.609498	15.306087
23	C	23.368625	17.728961	20.755086
24	O	28.179170	24.255390	21.003111
25	O	25.041131	20.537835	17.242258
26	O	23.176259	22.733060	19.742091
27	O	25.048263	22.700676	21.711071
28	O	22.763441	20.783004	18.752431
29	O	26.376812	24.209081	22.719606
30	O	27.203205	22.685329	19.716300
31	O	25.221611	22.687731	17.874619
32	Al	24.420310	19.631486	18.815322
33	Al	25.203241	22.788188	19.818708
34	O	25.204882	24.563409	19.788766
35	C	28.149544	23.405955	20.040796
36	O	25.249131	20.906333	19.872022
37	C	22.409328	21.937987	19.198207
38	C	25.262512	21.757370	17.035272
39	C	25.430647	23.403996	22.693077
40	H	27.324236	24.244424	21.621757
41	H	25.294238	20.616863	20.789312
42	H	23.302330	14.582916	19.061530

43	H	20.902791	11.699802	16.199457
44	H	20.073154	12.949444	15.664878
45	H	25.244563	24.931318	18.903406
46	H	21.355371	22.187432	19.059464
47	H	25.509374	22.036814	16.003580
48	H	27.036717	16.891054	18.274628
49	H	23.127191	17.522786	21.804876
50	H	19.278544	16.504697	18.025180
51	H	22.982713	15.781849	14.236922
52	H	24.182872	10.798862	16.464461
53	H	20.572159	11.955847	20.565952
54	H	21.403179	10.656589	18.137656
55	H	29.088505	23.343876	19.482105
56	H	24.856117	23.262423	23.621054
57	Cu	21.892673	19.726011	17.374288
58	O	20.632712	20.980273	17.087426
59	H	20.069570	20.637574	16.380702
60	O	21.287967	18.801806	15.943036
61	C	22.060422	19.098767	14.805996
62	H	21.658968	18.478923	13.993751
63	H	21.973225	20.148675	14.502389
64	H	23.112505	18.835338	14.943934
65	C	20.204632	19.378619	20.332024
66	H	19.891729	20.107287	19.584789
67	H	20.929072	19.834524	21.005401
68	H	20.663255	18.531323	19.825175
69	H	19.338468	19.039728	20.899398

INT-6

S.No.	Atoms	Coordinates (Angstroms) X	Y	Z
1	O	23.172870	12.505830	17.090497
2	O	20.831568	10.782720	19.066541
3	O	21.247098	12.998935	19.026161
4	O	22.149545	10.530825	16.837080
5	O	20.528239	12.646374	16.421251
6	C	23.162452	11.267333	16.832567
7	C	20.822776	11.975180	19.560719
8	O	25.874969	18.497428	18.870032
9	O	22.258032	14.554883	15.653715
10	O	21.189064	16.940430	18.128909
11	O	23.088671	16.820492	20.031860
12	O	20.322804	14.963427	17.497451
13	O	23.708832	18.913608	20.573860
14	O	25.069478	16.520857	18.148108
15	O	23.210063	16.526840	16.159032
16	Al	21.827969	13.823754	17.334518
17	Al	23.138890	16.802062	18.070130
18	O	23.276218	18.572985	17.897499
19	C	25.987716	17.302745	18.485826
20	O	22.960451	14.915563	18.262864
21	C	20.245941	16.169202	17.871522
22	C	22.840793	15.639337	15.367116
23	C	23.262977	17.768160	20.835148
24	O	28.112398	24.243280	21.032511
25	O	24.994851	20.545693	17.297919
26	O	23.100218	22.745507	19.790295
27	O	24.967038	22.722397	21.754844
28	O	22.629033	20.837544	18.729908
29	O	26.309458	24.228385	22.751892
30	O	27.114029	22.678907	19.755823
31	O	25.140264	22.703284	17.914242
32	Al	24.342243	19.626827	18.859411
33	Al	25.106946	22.798502	19.856859
34	O	25.132347	24.575902	19.828269
35	C	28.069950	23.387053	20.074158
36	O	25.135860	20.921785	19.919923
37	C	22.310574	21.966662	19.249204
38	C	25.202919	21.764651	17.083846
39	C	25.358029	23.429370	22.730928
40	H	27.262223	24.245020	21.652088
41	H	25.155722	20.635350	20.839038
42	H	23.190140	14.628276	19.151414
43	H	20.867991	11.754026	16.206922
44	H	20.062337	13.013301	15.659191
45	H	25.179195	24.938851	18.941071
46	H	21.254463	22.244249	19.198750
47	H	25.461401	22.039850	16.053397
48	H	27.009168	16.902969	18.452774
49	H	23.004381	17.574126	21.884343
50	H	19.231056	16.570804	17.976140
51	H	23.033685	15.810457	14.301720
52	H	24.135754	10.822201	16.588025
53	H	20.386581	12.023656	20.559988
54	H	21.288446	10.715071	18.162423
55	H	29.009504	23.307601	19.518581
56	H	24.784562	23.297613	23.661243
57	Cu	21.799020	19.733999	17.325906
58	O	21.190197	18.803028	15.897557
59	C	21.910799	19.115133	14.730766
60	H	21.623170	18.380211	13.968552
61	H	21.669294	20.113336	14.342479
62	H	22.994970	19.039477	14.871811
63	C	20.425231	21.036385	16.881510
64	H	19.903070	21.178182	17.827349
65	H	20.983200	21.918221	16.568133
66	H	19.777884	20.647634	16.105524

TS-4

S.No.	Atoms	Coordinates (Angstroms) X	Y	Z
1	O	23.109064	12.478888	17.046703
2	O	20.570367	10.860388	18.867948
3	O	21.073304	13.057615	18.846891
4	O	22.035012	10.537485	16.753513
5	O	20.525217	12.709778	16.201155
6	C	23.071225	11.237922	16.798630
7	C	20.567999	12.054093	19.352888
8	O	25.849870	18.499118	18.907267
9	O	22.371623	14.563482	15.568189
10	O	21.272960	17.015808	17.610626
11	O	22.847721	16.843274	19.898795
12	O	20.306884	15.027998	17.258777
13	O	23.578285	18.895294	20.470021
14	O	25.103818	16.451353	18.330103
15	O	23.537276	16.407811	16.102306
16	Al	21.798114	13.831347	17.204856
17	Al	23.243939	16.739423	17.992623
18	O	23.352695	18.497172	17.777691
19	C	25.994162	17.278631	18.657806
20	O	22.896236	14.898683	18.210678
21	C	20.278473	16.273272	17.410425
22	C	23.112131	15.550173	15.300556
23	C	23.021935	17.796294	20.702047
24	O	28.035309	24.167640	21.252239
25	O	25.067266	20.513617	17.245317
26	O	23.153124	22.806104	19.515471
27	O	24.783065	22.738572	21.682132
28	O	22.669570	20.800232	18.635879
29	O	26.069884	24.217093	22.786767
30	O	27.136326	22.583143	19.927314
31	O	25.378813	22.650775	17.876113
32	Al	24.290784	19.639579	18.780879
33	Al	25.109908	22.779801	19.802467
34	O	25.236721	24.554929	19.759125
35	C	28.069877	23.283623	20.318486

36	O	25.092267	20.902226	19.887776
37	C	22.372784	21.966949	19.028645
38	C	25.405522	21.708283	17.051440
39	C	25.100697	23.445613	22.683172
40	H	27.124051	24.199933	21.777174
41	H	25.073593	20.616410	20.806386
42	H	22.958581	14.648416	19.138192
43	H	20.833042	11.804058	16.001190
44	H	20.086152	13.088607	15.429050
45	H	25.399873	24.899060	18.878320
46	H	21.320179	22.254152	18.916339
47	H	25.755481	21.953286	16.040195
48	H	27.013447	16.880880	18.740652
49	H	22.646371	17.642722	21.722148
50	H	19.300108	16.760558	17.355170
51	H	23.400255	15.663478	14.249802
52	H	24.040742	10.759312	16.610211
53	H	20.057283	12.131022	20.314121
54	H	21.098511	10.765384	18.002791
55	H	29.057891	23.174956	19.859307
56	H	24.438310	23.342388	23.556872
57	Cu	21.590006	19.252729	17.402515
58	O	22.364640	20.062519	15.389653
59	C	23.440357	19.651778	15.004898
60	H	20.773148	17.428861	13.195352
61	H	23.941345	20.128747	14.148936
62	H	23.928515	18.805699	15.496688
63	C	19.759778	19.919471	17.237472
64	H	19.219052	19.751690	18.174274
65	H	19.771612	20.990326	17.016346
66	H	19.245801	19.393998	16.427686
67	C	20.374073	17.288154	14.199095
68	H	19.376189	17.720513	14.259853
69	H	20.323383	16.223243	14.422448
70	H	21.021833	17.785110	14.917951

INT-7

S.No.	Atoms	Coordinates (Angstroms) X	Y	Z
1	O	23.111269	12.517630	17.113181
2	O	20.669086	10.870576	19.046235
3	O	21.142471	13.073997	18.991046
4	O	22.064917	10.552667	16.882959
5	O	20.489513	12.689603	16.374458
6	C	23.088159	11.273345	16.880715
7	C	20.669938	12.068154	19.522768
8	O	25.849207	18.572633	18.753393
9	O	22.269449	14.570119	15.641526
10	O	21.184862	17.022898	17.837866
11	O	22.962056	16.857537	19.976736
12	O	20.276513	15.016938	17.418059
13	O	23.735654	18.899076	20.530576
14	O	25.067239	16.535046	18.190348
15	O	23.309612	16.506050	16.114546
16	Al	21.781435	13.847735	17.311246
17	Al	23.172698	16.801006	18.035345
18	O	23.246332	18.566039	17.864290
19	C	25.978071	17.360143	18.456544
20	O	22.903115	14.945332	18.252030
21	C	20.214703	16.253680	17.633294
22	C	22.914689	15.610883	15.337438
23	C	23.208580	17.789784	20.784564
24	O	28.154197	24.277309	20.878224
25	O	24.874171	20.599481	17.215887
26	O	23.121990	22.800170	19.773414
27	O	25.030202	22.746028	21.700126
28	O	22.619181	20.828122	18.837256
29	o	26.417492	24.231027	22.665480
30	O	27.128085	22.700031	19.639678
31	O	25.105625	22.745815	17.846360
32	Al	24.275292	19.686149	18.800985
33	Al	25.103225	22.831699	19.794163
34	O	25.166284	24.610617	19.772587
35	C	28.086137	23.419757	19.922356
36	O	25.150639	20.951755	19.845595
37	C	22.321847	21.960971	19.323881
38	C	25.103401	21.815843	17.005423
39	C	25.462013	23.435606	22.669898
40	H	27.322941	24.268314	21.524638
41	H	25.236858	20.652634	20.756115
42	H	23.063668	14.680182	19.163163
43	H	20.808794	11.789232	16.168554
44	H	20.016623	13.054410	15.615656
45	H	25.202889	24.974697	18.885475
46	H	21.253977	22.209063	19.335360
47	H	25.318174	22.095573	15.965780
48	H	27.003891	16.971256	18.432845
49	H	22.933721	17.607354	21.831734
50	H	19.216563	16.704301	17.636755
51	H	23.142424	15.739709	14.273340
52	H	24.058955	10.810966	16.660645
53	H	20.195272	12.145076	20.502343
54	H	21.166059	10.776383	18.163140
55	H	29.005054	23.354162	19.330709
56	H	24.925712	23.291907	23.620871
57	Cu	21.465800	19.359379	17.699039
58	O	21.635207	19.301396	15.420911
59	C	22.749812	19.171125	14.956902
60	H	23.631912	19.169810	15.603885
61	H	22.885409	19.050804	13.871428
62	C	19.653103	20.092342	17.767706
63	H	19.306706	20.135459	18.805057
64	H	19.644417	21.102384	17.347457
65	H	18.974601	19.460325	17.187446

INT-8

S.No.	Atoms	Coordinates (Angstroms) X	Y	Z
1	O	23.033923	12.437204	17.080433
2	O	20.562217	10.899712	19.065253
3	O	21.121806	13.081770	18.992992
4	O	21.893009	10.523340	16.872672
5	O	20.415094	12.733410	16.385115
6	C	22.948242	11.195416	16.847029
7	C	20.620832	12.096232	19.538189
8	O	25.973025	18.490653	18.750095
9	O	22.266716	14.546898	15.646535
10	O	21.356723	17.008463	17.706696
11	O	23.053551	16.804205	19.922300
12	O	20.305663	15.059142	17.442996
13	O	23.802464	18.862533	20.441485
14	O	25.212505	16.430922	18.238123
15	O	23.538662	16.340300	16.109516
16	Al	21.770343	13.821200	17.309617
17	Al	23.342247	16.680647	17.995691
18	O	23.406146	18.455997	17.783523
19	C	26.113483	17.266351	18.511120
20	O	22.960664	14.859703	18.248413
21	C	20.318760	16.303857	17.572607
22	C	23.035052	15.498843	15.335215
23	C	23.278818	17.755733	20.714265
24	O	28.061732	24.328015	20.854622
25	O	25.045583	20.488199	17.144619
26	O	23.117715	22.698751	19.552416
27	O	24.934772	22.752266	21.554125
28	O	22.669973	20.710596	18.629022

29	O	26.233305	24.297489	22.546402
30	O	27.124611	22.710791	19.597601
31	O	25.191862	22.657453	17.717925
32	Al	24.414262	19.607560	18.715827
33	Al	25.106280	22.797471	19.656057
34	O	25.109073	24.574004	19.591956
35	C	28.056605	23.451112	19.915225
36	O	25.186430	20.916804	19.764231
37	C	22.337017	21.846416	19.107735
38	C	25.255113	21.703998	16.906974
39	C	25.297856	23.479516	22.525200
40	H	27.197613	24.320930	21.457744
41	H	25.207358	20.653771	20.690182
42	H	23.050679	14.615814	19.175759
43	H	20.684976	11.817405	16.177377
44	H	19.942838	13.118076	15.635778
45	H	25.175554	24.921321	18.699873
46	H	21.266192	22.070188	19.113105
47	H	25.514560	21.957127	15.871252
48	H	27.137412	16.876409	18.549823
49	H	22.984255	17.596784	21.759178
50	H	19.365165	16.839137	17.563917
51	H	23.275432	15.594400	14.270846
52	H	23.891256	10.689691	16.603559
53	H	20.170889	12.195410	20.527204
54	H	21.034582	10.783588	18.170778
55	H	29.005452	23.386585	19.373254
56	H	24.715242	23.349091	23.450162
57	Cu	21.631701	19.135668	17.741825
58	O	19.882277	19.531918	17.434742
59	C	19.371910	20.835346	17.509159
60	H	19.250507	21.149486	18.558693
61	H	20.053381	21.560113	17.036597
62	C	18.017103	20.907651	16.815091
63	H	17.316143	20.211981	17.281505
64	H	17.600749	21.915978	16.880909
65	H	18.116072	20.640108	15.760932

TS-5

S.No.	Atoms	Coordinates (Angstroms) X	Y	Z
1	O	23.016930	12.480505	17.112615
2	O	20.583149	10.947676	19.138096
3	O	21.136943	13.130912	19.054241
4	O	21.866028	10.571451	16.916437
5	O	20.389512	12.785360	16.457122
6	C	22.923238	11.239871	16.876425
7	C	20.649204	12.144452	19.609553
8	O	26.002542	18.526568	18.728722
9	O	22.236399	14.592827	15.690736
10	O	21.358924	17.058389	17.783075
11	O	23.097049	16.844757	19.960736
12	O	20.303481	15.111342	17.514326
13	O	23.871302	18.896406	20.469290
14	O	25.221832	16.469974	18.234477
15	O	23.507009	16.391171	16.137975
16	Al	21.761464	13.868982	17.360910
17	Al	23.346242	16.725271	18.029145
18	O	23.414854	18.500587	17.819310
19	C	26.132149	17.301326	18.486929
20	O	22.968858	14.903452	18.282348
21	C	20.320055	16.355538	17.650697
22	C	22.996368	15.548291	15.369884
23	C	23.344888	17.792851	20.749959
24	O	28.137000	24.380781	20.754992
25	O	25.040179	20.533372	17.151493
26	O	23.153837	22.722806	19.646196
27	O	25.049352	22.780351	21.574061
28	O	22.702953	20.752329	18.688870
29	O	26.384940	24.320586	22.524203
30	O	27.160332	22.760857	19.532308
31	O	25.154391	22.702746	17.730612
32	Al	24.447042	19.645438	18.733862
33	Al	25.147813	22.833827	19.671847
34	O	25.134086	24.610242	19.614229
35	C	28.098893	23.508245	19.812589
36	O	25.241774	20.952744	19.768234
37	C	22.371044	21.874407	19.199873
38	C	25.215154	21.754469	16.913213
39	C	25.450862	23.500764	22.535012
40	H	27.300484	24.361544	21.396249
41	H	25.289048	20.685581	20.692056
42	H	23.076519	14.655506	19.206706
43	H	20.653974	11.868273	16.246451
44	H	19.907636	13.170968	15.714450
45	H	25.164857	24.961654	18.721817
46	H	21.298056	22.088810	19.231093
47	H	25.438221	22.017740	15.871608
48	H	27.155110	16.907271	18.502867
49	H	23.070164	17.633681	21.800224
50	H	19.366601	16.891247	17.649881
51	H	23.221657	15.645886	14.302393
52	H	23.860527	10.731517	16.616855
53	H	20.219302	12.242819	20.607512
54	H	21.035305	10.832230	18.233337
55	H	29.023636	23.454397	19.229435
56	H	24.907103	23.361961	23.482085
57	Cu	21.647254	19.196258	17.800518
58	O	19.889041	19.598657	17.531667
59	C	19.432154	20.907710	17.329167
60	H	18.363269	20.858633	17.076634
61	H	19.491559	21.496040	18.259258
62	C	20.173738	21.641672	16.216285
63	H	20.076644	21.096406	15.275099
64	H	19.781199	22.652308	16.077826
65	H	21.238962	21.720509	16.450749

INT-9

S.No.	Atoms	Coordinates (Angstroms) X	Y	Z
1	O	23.057589	12.422511	17.066548
2	O	20.651281	10.831565	19.083347
3	O	21.156339	13.026584	19.000195
4	O	21.942262	10.493898	16.857500
5	O	20.424338	12.676578	16.400738
6	C	22.987939	11.181073	16.826702
7	C	20.690621	12.029455	19.555225
8	O	25.934142	18.489831	18.721832
9	O	22.232895	14.518446	15.644137
10	O	21.288000	16.980817	17.734043
11	O	23.049214	16.769250	19.925151
12	O	20.292669	14.999740	17.471978
13	O	23.790747	18.829955	20.446808
14	O	25.188714	16.426097	18.202214
15	O	23.472161	16.336140	16.099707
16	Al	21.771596	13.783482	17.311941
17	Al	23.313017	16.666219	17.991509
18	O	23.346777	18.433366	17.791926
19	C	26.084246	17.269498	18.470497
20	O	22.948908	14.843045	18.240798
21	C	20.270846	16.241760	17.614617
22	C	22.976019	15.488709	15.327592
23	C	23.280947	17.717252	20.720212
24	O	27.974019	24.353450	20.838115
25	O	24.976002	20.477127	17.131115
26	O	23.044335	22.688075	19.532111

27	O	24.860289	22.744722	21.539892
28	O	22.627796	20.675006	18.653903
29	O	26.145277	24.302223	22.530937
30	O	27.058081	22.719014	19.587593
31	O	25.124004	22.646582	17.704822
32	Al	24.359422	19.591123	18.708589
33	Al	25.035153	22.789085	19.642333
34	O	25.031019	24.565882	19.576385
35	C	27.980444	23.472245	19.902485
36	O	25.135011	20.909158	19.750739
37	C	22.277357	21.817792	19.096907
38	C	25.185145	21.692680	16.893733
39	C	25.217206	23.475956	22.510307
40	H	27.109797	24.337158	21.440125
41	H	25.170565	20.644962	20.675813
42	H	23.049163	14.601444	19.167803
43	H	20.711939	11.763565	16.199346
44	H	19.957835	13.050618	15.642352
45	H	25.101958	24.911894	18.684139
46	H	21.202204	22.026985	19.075592
47	H	25.442333	21.946525	15.857506
48	H	27.112679	16.889860	18.492376
49	H	23.005765	17.547781	21.768887
50	H	19.295244	16.736002	17.633081
51	H	23.198814	15.595345	14.260451
52	H	23.935896	10.690019	16.572823
53	H	20.258594	12.117809	20.553171
54	H	21.105226	10.727438	18.178691
55	H	28.930578	23.417441	19.361591
56	H	24.635809	23.340970	23.435445
57	Cu	21.538121	19.099901	17.816653
58	H	20.119710	19.636007	17.722699

5. X-ray absorption spectroscopic analysis. X-ray Near-Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) measurements have been carried out at the Energy-Scanning EXAFS beamline (BL-9) at the Indus-2 Synchrotron Source at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India.[13] All the measurements were performed at room temperature. This beamline operates in the energy range of 4 keV to 25 keV. The beamline optics consist of a Rh/Pt coated collimating meridional cylindrical mirror and the collimated beam reflected by the mirror is monochromatized by a Si (111) based double crystal monochromator (DCM). The second crystal of the DCM is a sagittal cylindrical crystal which is used for horizontal focusing of the beam while another Rh/Pt coated bendable post mirror facing downward is used for vertical focusing of the beam at the sample position. Two ionization chambers (300 mm length each) have been used for data collection in the transmission mode; one ionization chamber for measuring incident flux, the second one for measuring transmitted flux. For energy calibration, standard metal foils were used. Appropriate gas pressure and gas mixture have been chosen to achieve 10-20% absorption in the first ionization chamber and 70-90% absorption in the second ionization chamber to obtain a better signal-to-noise ratio. Pellets were made from powder samples for recording absorption spectra. Sample powder was mixed homogeneously with cellulose powder in appropriate proportion and pressed (2 Ton) into a 15 mm diameter disc. The amount of the sample was estimated such that to get a reasonable edge jump at a particular absorption edge of the element to be probed. Spectra were collected at the copper K-edge in transmission mode and were calibrated against the reference spectrum of metallic copper (8978.9 eV). Data were processed using Demeter software.[14] A metallic copper foil standard was used as a reference for energy calibration and was measured simultaneously with experimental samples.

XANES analysis. The oxidation states of the Cu species within MIL-53(Al)-Cu(OH) and MIL-53(Al)-Cu after oxidation of methane were determined by the comparison of the energy of its K-edge positions to that of $CuCl_2$. The positions of the Cu K-edge of MIL-53(Al)-CuCl, MIL-53(Al)-Cu(OH), MIL-53(Al)-Cu after oxidation of methane aligned well with that of $CuCl_2$ (8985.3 eV). We, therefore, concluded that Cu ion in MIL-53(Al)-Cu(OH) and MIL-53(Al)-Cu after oxidation of methane has +2 oxidation state.

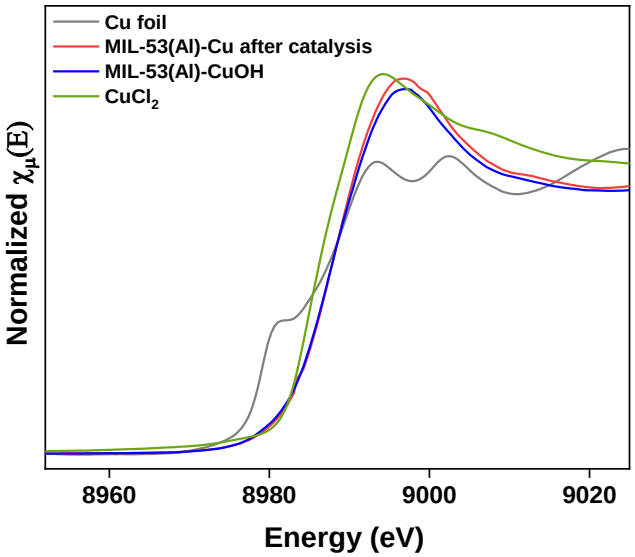

Figure S11. μ(E) XAS spectra of metallic Cu(0) (grey), $CuCl_2$ (green), MIL-53(Al)-Cu(OH) (blue), MIL-53(Al)-Cu after catalysis (red).

EXAFS fitting using DFT optimized structures. The spectra were calibrated against the reference spectra and aligned to the first peak in the smoothed first derivative of the absorption spectrum, the background noise was removed, and the spectra were processed to obtain a normalized unit edge step. The fitting parameters of MIL-53(Al)-Cu(OH) and MIL-53(Al)-Cu after oxidation of methane are summarized in Table S7 and Table S8, respectively.

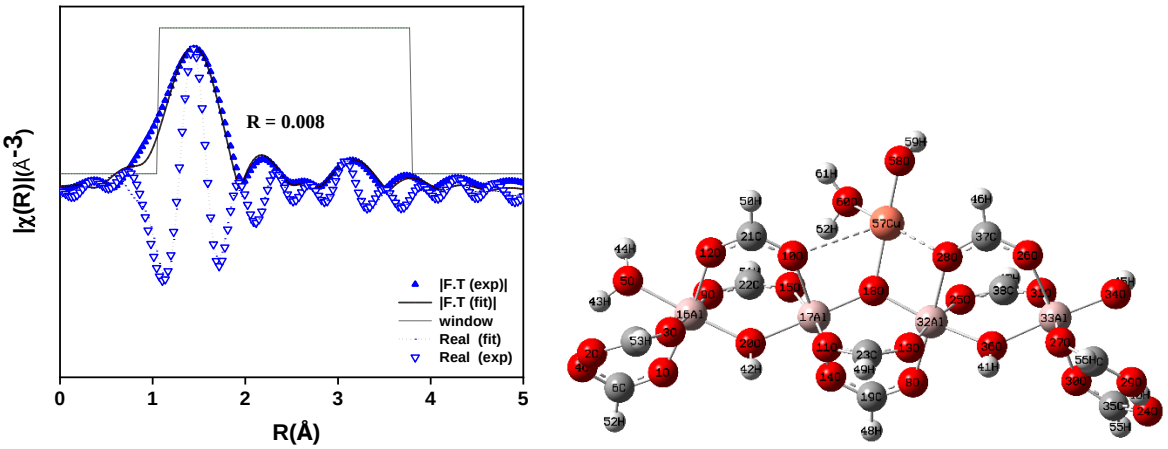

Figure S12. (a) EXAFS spectrum and fit of MIL-53(Al)-Cu(OH). (b) DFT-optimized structure of MIL-53(Al)-Cu(OH).

Table S7. Summary of EXAFS fitting parameters of MIL-53(Al)-Cu(OH).

Sample	MIL(Al)Cu-OH	Fitting range	*k* 2-10 Å^{-1} R 1.0-3.8 Å
Independent points	10	**R-factor**	0.008
Variables	6	**S_0^2**	0.71
Reduced chi-square	179	**ΔE_0(eV)**	3.11
R(Cu-O58) (Å)	1.88±0.07	**σ^2 (Cu-O58) (Å^2)**	0.004±0.003
R(Cu-O18) (Å)	1.91±0.07	**σ^2 (Cu-O18) (Å^2)**	0.004±0.003
R(Cu-O10) (Å)	1.95±0.07	**σ^2 (Cu-O10) (Å^2)**	0.004±0.003
R(Cu-O28) (Å)	1.95±0.07	**σ^2 (Cu-O28) (Å^2)**	0.004±0.003
R(Cu-O60) (Å)	2.42±0.09	**σ^2 (Cu-O60) (Å^2)**	0.002±0.001
R(Cu-H59) (Å)	2.32±0.09	**σ^2 (Cu-H59) (Å^2)**	0.002±0.001
R(Cu-H60) (Å)	2.66±0.09	**σ^2 (Cu-H60) (Å^2)**	0.002±0.001
R(Cu-H61) (Å)	2.66±0.09	**σ^2 (Cu-H61) (Å^2)**	0.002±0.001
R(Cu-Al17) (Å)	3.1±0.04	**σ^2 (Cu-Al17) (Å^2)**	0.01±0.001
R(Cu-Al32) (Å)	3.1±0.04	**σ^2 (Cu-Al32) (Å^2)**	0.01±0.001
R(Cu-C21) (Å)	3.31±0.04	**σ^2 (Cu-C21) (Å^2)**	0.01±0.001
R(Cu-C37) (Å)	3.31±0.04	**σ^2 (Cu-C37) (Å^2)**	0.01±0.001
R(Cu-O11) (Å)	3.42±0.04	**σ^2 (Cu-O11) (Å^2)**	0.01±0.001
R(Cu-O13) (Å)	3.42±0.04	**σ^2 (Cu-O13) (Å^2)**	0.01±0.001
R(Cu-C23) (Å)	3.66±0.04	**σ^2 (Cu-C23) (Å^2)**	0.01±0.001

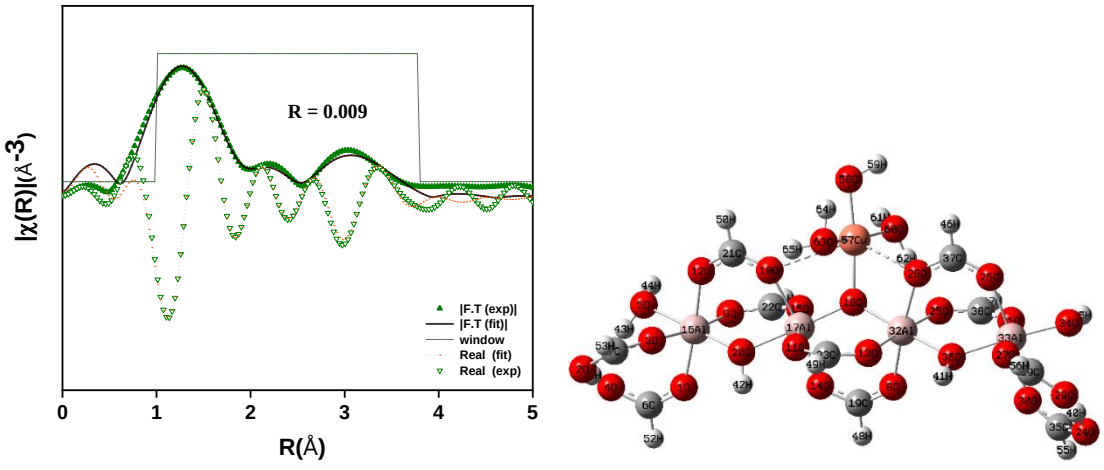

Figure S13. (a) EXAFS spectrum and fit of MIL-53(Al)-Cu after catalysis. (b) DFT-optimized structure of MIL-53(Al)-Cu after catalysis.

Table S8. Summary of EXAFS fitting parameters of MIL-53(Al)-Cu after catalysis.

Sample	**MIL(Al)Cu-OH**	**Fitting range**	**k 2-10 Å-1 R 1.0-3.8 Å**
Independent points	10	**R-factor**	0.009
Variables	6	**S_o^2**	0.74
Reduced chi-square	168	**ΔE_0 (eV)**	1.11
R(Cu-O58) (Å)	1.88±0.003	**σ^2 (Cu-O58) (Å^2)**	0.003±0.001
R(Cu-O18) (Å)	1.91±0.003	**σ^2 (Cu-O18) (Å^2)**	0.003±0.001
R(Cu-O10) (Å)	1.95±0.003	**σ^2 (Cu-O10) (Å^2)**	0.003±0.001
R(Cu-O28) (Å)	1.95±0.003	**σ^2 (Cu-O28) (Å^2)**	0.003±0.001
R(Cu-O60) (Å)	2.42±0.09	**σ^2 (Cu-O60) (Å^2)**	0.002±0.001
R(Cu-O63) (Å)	2.42±0.09	**σ^2 (Cu-O63) (Å^2)**	0.002±0.001
R(Cu-H59) (Å)	2.32±0.09	**σ^2 (Cu-H59) (Å^2)**	0.002±0.001
R(Cu-H61) (Å)	2.66±0.09	**σ^2 (Cu-H61) (Å^2)**	0.002±0.001
R(Cu-H65) (Å)	2.66±0.09	**σ^2 (Cu-H65) (Å^2)**	0.002±0.001
R(Cu-H64) (Å)	2.66±0.09	**σ^2 (Cu-H64) (Å^2)**	0.002±0.001
R(Cu-Al17) (Å)	3.27±0.06	**σ^2 (Cu-Al17) (Å^2)**	0.01±0.004
R(Cu-Al32) (Å)	3.27±0.06	**σ^2 (Cu-Al32) (Å^2)**	0.01±0.004
R(Cu-C21) (Å)	3.36±0.06	**σ^2 (Cu-C21) (Å^2)**	0.01±0.004
R(Cu-C37) (Å)	3.36±0.06	**σ^2 (Cu-C37) (Å^2)**	0.01±0.004
R(Cu-O11) (Å)	3.44±0.06	**σ^2 (Cu-O11) (Å^2)**	0.01±0.004
R(Cu-O13) (Å)	3.44±0.06	**σ^2 (Cu-O13) (Å^2)**	0.01±0.004
R(Cu-C23) (Å)	3.7±0.04	**σ^2 (Cu-C23) (Å^2)**	0.01±0.004

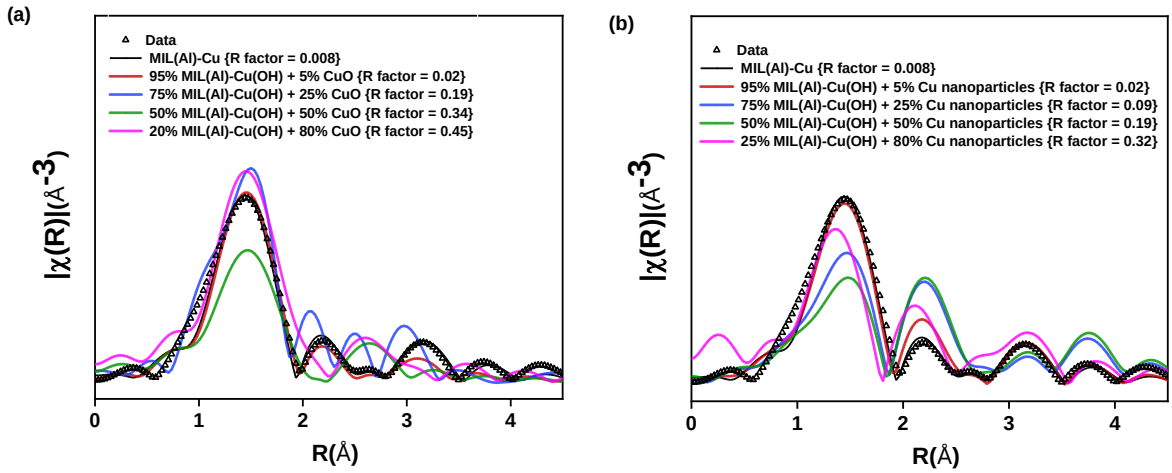

Figure S14. (a) EXAFS spectrum of MIL-53(Al)-Cu(OH) fitted with 5% CuO and 95% MIL-53(Al)-Cu(OH) (red); 25% CuO and 75% MIL-53(Al)-Cu(OH) (blue); 50% CuO and 50% MIL-53(Al)-Cu(OH) (green); 80% CuO and 20% MIL-53(Al)-Cu(OH) (magenta). (b) EXAFS spectrum of MIL-53(Al)-Cu(OH) fitted with 5% Cu (0) and 95% MIL-53(Al)-Cu(OH) (red); 25% Cu (0) and 75% MIL-53(Al)-Cu(OH) (blue); 50% Cu (0) and 50% MIL-53(Al)-Cu(OH) (green) and 80% Cu (0) and 20% MIL-53(Al)-Cu(OH) (magenta). The significant misfits indicates that MIL-53(Al)-Cu(OH) does not contain any Cu dimers/oligomers or Cu-nanoparticles.

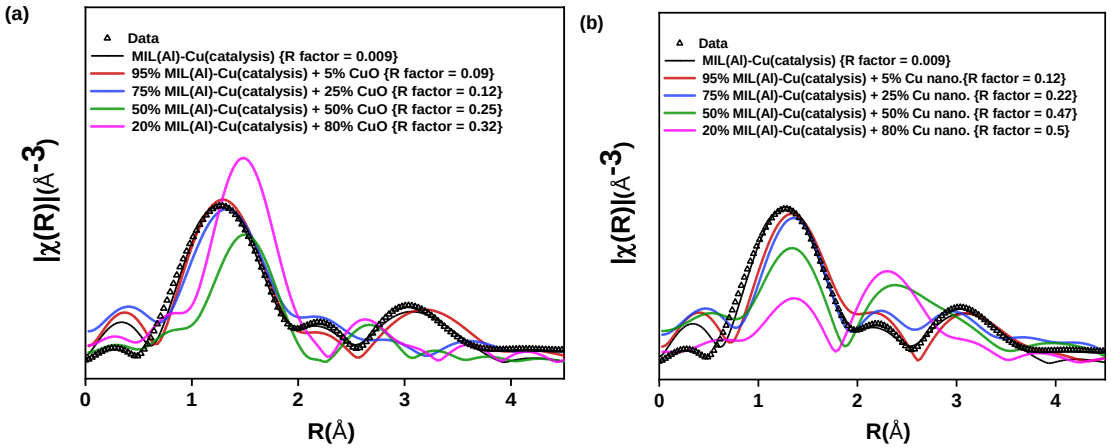

Figure S15. (a) EXAFS spectrum of MIL-53(Al)-Cu after catalysis fitted with 5% CuO and 95% MIL-53(Al)-Cu(OH) (red); 25% CuO and 75% MIL-53(Al)-Cu(OH) (blue); 50% CuO and 50% MIL-53(Al)-Cu(OH) (green); 80% CuO and 20% MIL-53(Al)-Cu(OH) (magenta). (b) EXAFS spectrum of MIL-53(Al)-Cu after catalysis fitted with 5% Cu (0) and 95% MIL-53(Al)-Cu(OH) (red); 25% Cu (0) and 75% MIL-53(Al)-Cu(OH) (blue); 50% Cu (0) and 50% MIL-53(Al)-Cu(OH) (green) and 80% Cu (0) and 20% MIL-53(Al)-Cu(OH) (magenta). The significant misfits indicates that MIL-53(Al)-Cu(OH) does not contain any Cu dimers/oligomers or Cu-nanoparticles.

5.1.1. XPS analysis of MIL-53(Al)-Cu(OH).

All the binding energies were corrected with reference to the C1s peak at 284.8 eV. MULTIPAK software was used for peak analysis and de-convolution studies.

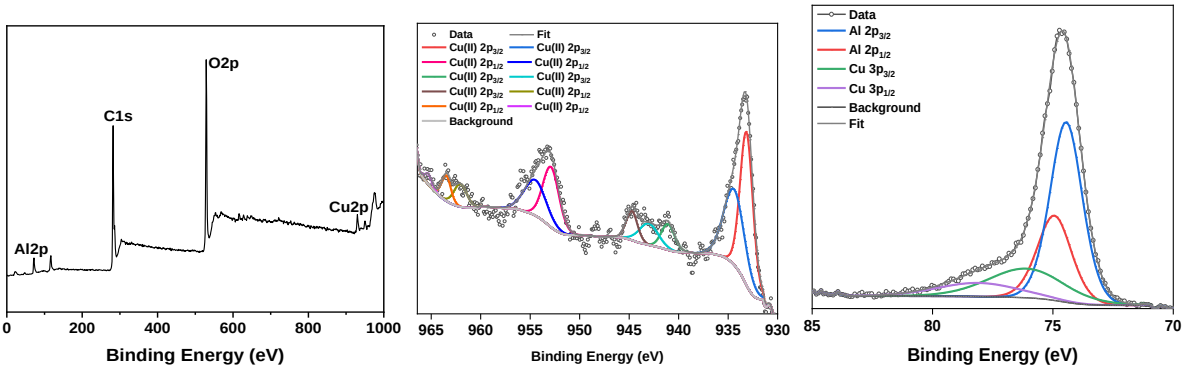

Figure S16. (a) Raw XPS data of MIL-53(Al)-Cu(OH). (b) XPS fitting of copper in MIL-53(Al)-Cu(OH). (c) XPS fitting of aluminium in MIL-53(Al)-Cu(OH).

Table S9. XPS fitting parameters for Cu(II) in MIL-53(Al)-Cu(OH) MOF

Component	Position (eV)	FWHM (eV)	Area	Area%
Cu(II) 2p	933.13	1.35	745.08	23.46
Cu(II) 2p	934.37	2.48	761.72	23.97
Cu(II) 2p	941.05	1.44	129.14	4.05
Cu(II) 2p	943.00	2.50	255.04	7.05
Cu(II) 2p	944.79	1.35	151.00	4.73
Cu(II) 2p	952.92	1.80	372.54	11.63
Cu(II) 2p	954.41	2.64	380.86	11.88
Cu(II) 2p	961.52	0.35	24.88	0.77
Cu(II) 2p	962.96	2.88	344.03	10.69
Cu(II) 2p	965.49	0.8	56.86	1.76

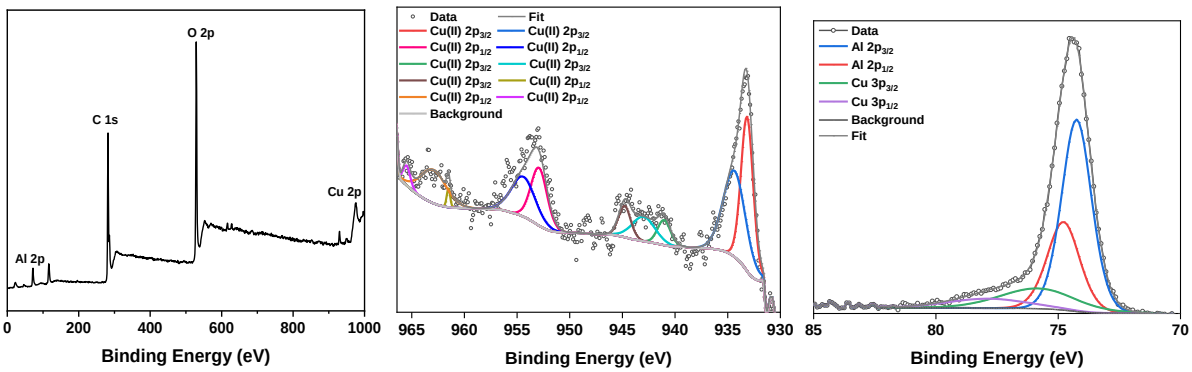

Figure S17. (a) Raw XPS data of MIL-53(Al)-Cu(OH) after catalysis. (b) XPS fitting of copper in MIL-53(Al)-Cu(OH) after catalysis. (c) XPS fitting of aluminium in MIL-53(Al)-Cu(OH) catalysis.

Table S10. XPS fitting parameters for Cu(II) in MIL-53(Al)-Cu MOF recovered after catalysis.

Component	Position (eV)	FWHM (eV)	Area	Area%
Cu(II) 2p	933.13	1.35	745.08	23.46
Cu(II) 2p	934.37	2.48	761.72	23.97
Cu(II) 2p	941.05	1.44	129.14	4.05
Cu(II) 2p	943.00	2.50	255.04	7.05
Cu(II) 2p	944.79	1.35	151.00	4.73
Cu(II) 2p	952.92	1.80	372.54	11.63
Cu(II) 2p	954.41	2.64	380.86	11.88
Cu(II) 2p	961.52	0.35	24.88	0.77
Cu(II) 2p	962.96	2.88	344.03	10.69
Cu(II) 2p	965.49	0.8	56.86	1.76

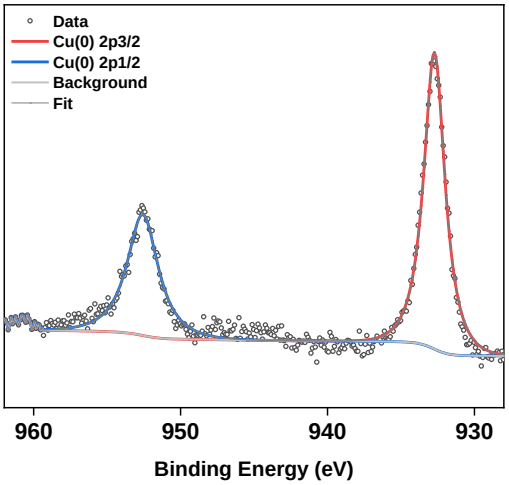

Figure S18. XPS fitting of copper in Cu@MIL-53(Al).

Table S11. XPS fitting parameters for Cu(0) in Cu@MIL-53(Al).

Component	Position (eV)	FWHM (eV)	Area	Area%
Cu(0) 2p	932.68	0.7	1263.1	62.74
Cu(0) 2p	952.52	1.6	757	37.26

Table S12. Simulated parameters of EPR spectroscopic spin-trapping experiments for MIL-53(Al)-Cu(OH) catalysed oxidation of methane.[a]

Adducts	g-factor	$A^{14}N$ (G)	$A^{a}H$ (G)	lw (mT)[b]
DMPO-CH_3	2.01	22.4	15.9	0.8

[a]Reaction conditions: 3.8 mg MIL-53(Al)-Cu(OH) (4.0 μmol Cu), 30 bar CH_4, 10 bar O_2, 50 μL DMPO, 32 h, 175°C. [b]The linewidth (lw, in mT) defines the FWHM (full width at half height) of the absorption Gaussian (first number)

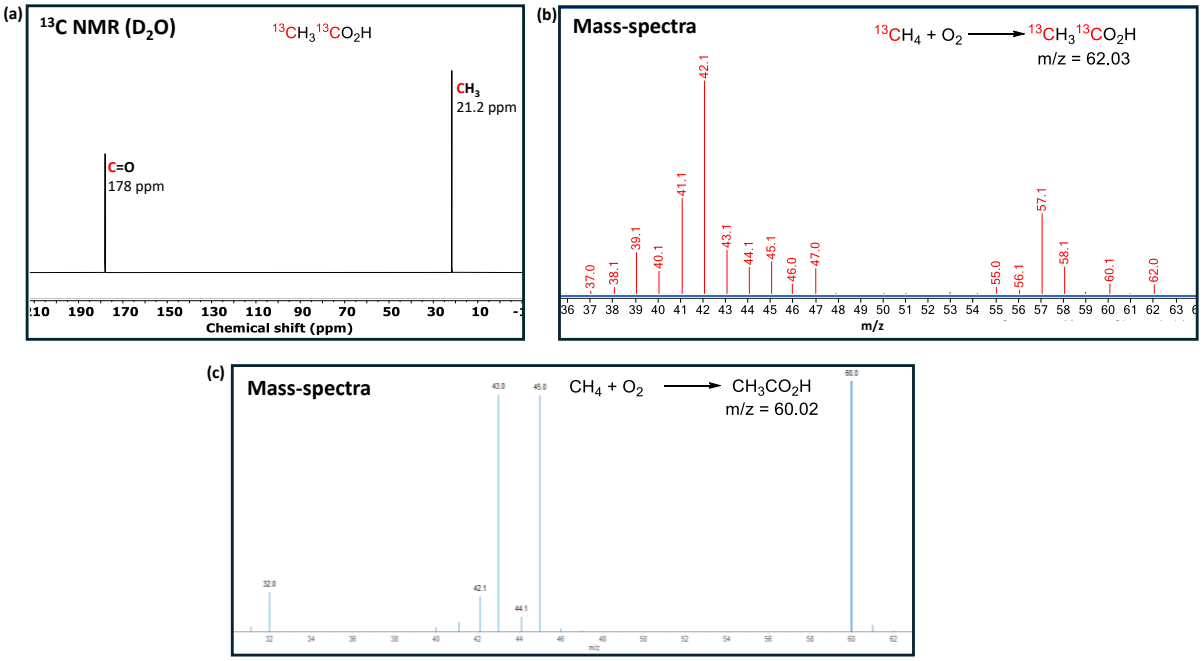

Figure S19. (a) ^{13}C NMR (400 MHz, D_2O) spectrum of the reaction mixture obtained after $^{13}CH_4$ oxidation by O_2 using MIL-53(Al)-Cu(OH) as the catalyst. Reaction conditions: 3.8 mg MIL-53(Al)-Cu(OH) (4.0 μmol Cu), 30 bar $^{13}CH_4$, 10 bar O_2, 32 h, 175°C. Signal centered at 21.2 ppm, corresponding to the sp^3 hybridized carbon and signal centred at 178 ppm corresponds to sp^2 hybridized carbon in $^{13}CH_3{}^{13}CO_2H$, confirms the involvement of CH_4-derived carbon atoms in the formation of acetic acid. (b) Mass spectra of the obtained $^{13}CH_3{}^{13}CO_2H$ after $^{13}CH_4$ oxidation using O_2. (c) Mass spectra of the obtained CH_3CO_2H after CH_4 oxidation using O_2 under identical reaction conditions.

Table S13. Comparison of catalytic activity of MIL-53(Al)-Cu(OH) catalysed oxidation of CH_4 to CH_3CO_2H using O_2 with other reported catalysts.

Reference	**Catalyst**	**Oxidant (Flow/Total pressure)**	**Condition**	**Temperature (°C)**	**CH_3CO_2H Selectivity**	**CH_3CO_2H Productivity**			
						µmol. g^{-1}_{cat}. h^{-1}	**mmol. mol_{metal}^{-1} h^{-1}**	**mmol. mol_{metal}^{-1}**	**µmol. g_{cat}^{-1}**
This Work	MIL-53(Al)-Cu(OH)	CH_4 (30 bar), O_2 (10 bar)	Batch	175	92	**12,418**	**11,796**	**3,77,472**	**3,97,368**
ACS Catal. **14**, 1797–1807 (2024).	Au/24h-ZSM5(DR-24)	CH_4 (20.7 bar), O_2 (3.5 bar)	Batch	240	21				12.1
Nat. Commun. **14**, 3047 (2023).	PdO/Pd–WO_3-2	CH_4 + H_2O	Flow/Light	r.t	91.6	90.7			
		CH_4 (10 bar) + H_2O	Batch/Light	r.t	60.2	62.5			
Appl. Catal. B **337**, 122983 (2023).	Ag/AgCl-WO_{3-X}	0.1 bar CH_4:N_2 (1:9), 0.1 bar O_2	Light	25	62.7	188.5			
ACS Catal. **13**, 7199–7209 (2023).	Au/ZSM-5+XC72R	CH_4 (20.7 bar), O_2 (3.5 bar)	Batch	240	2.5				31.4
J. Am. Chem. Soc. **145**, 6156–6165 (2023).	Ce-UiO-Cu(OH)	CH_4 (30 bar), O_2 (6 bar)	Batch	115	96				3,24,324
Nat. Catal. **5**, 45–54 (2022).	Au-ZSM-5	CH_4 (20.7 bar), O_2 (3.5 bar)	Batch	240	41	45.48			3.79

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