Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

One-step solvent-free aerobic oxidation of aliphatic alcohols to esters using a tandem Sc–Ru⊂MOF catalyst

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S1. Materials

Chromium(III) nitrate nonahydrate ($Cr(NO_3)_3·9H_2O$, Aladdin, 99%), 1,4-dicarboxybenzene (BDC, Aladdin, 99%), Trimesic acid (H_3BTC, Alfa Aesar, 98%), Zirconium(IV) dichloride octahydrate ($ZrOCl_2·8H_2O$, Acros Organics, 98%), Ruthenium(III) chloride hydrate ($RuCl_3•xH_2O$, AccelaChem, 99.9%), Methanol (SCRC, 99.5%), Formic Acid (SCRC, 98%), Dichloromethane (DCM, SCRC, 99.5%), Toluene (SCRC, 99.5%), Tetrahydrofuran (THF, TEDIA, 99.8%), N,N-dimethylformamide (DMF, SCRC, 99.5%), Petroleum ether (SCRC, boiling range 60-90 °C), Scandium(III) trifluoromethesulfonate ($Sc(OTf)_3$, Adamas-beta, 99%), Indium(III) trifluoromethesulfonate ($In(OTf)_3$, Adamas-beta, 96%), Hafnium(III) trifluoromethesulfonate ($Hf(OTf)_3$, Adamas-beta, 98%), Iron(III) trifluoromethesulfonate ($Fe(OTf)_3$, Adamas-beta, 95%), Ruthenium on carbon (Ru/C, URchem, Ru 5%), 1-butanol (Aladdin, 99%), Butanal (TCI, 98%), Butyric acid (Amethyst Chemicals, 98%), Butyl butyrate (Macklin, 99%), 1-pentanol (SCRC, 99%), 1-hexanol (Aladdin, 99%), 1-heptanol (Adamas-beta, 99%), Capryl alcohol (1-octanol, Adamas-beta, 99%), 1-decanol (Aladdin, 98%), n-dodecane (Macklin, 99%), n-octadecane (Alfa Aesar, 99%), isobutanol (Macklin, 99%), isopentanol (Macklin, 99%), 3-pyridylmethanol (Adamas-beta, 98%), Cyclohexanemethanol (Macklin, 99%), Cyclohexylmethanol (Macklin, 98%), Benzyl alcohol (Aladdin, 99%), 4-methylbenzyl alcohol (Adamas-beta, 98%), 2-phenylethanol (Macklin, 99%), 3-phenylpropanol (Macklin, 99%)

1,1-dibutoxybutane (DBB was synthesized, purified and determined by ^1H NMR)

S2. Experimental Procedures

Acetal Synthesis[1]

1,1-dibutoxybutane (C4-acetal): 100mg MIL-101(Cr) catalyst was dispersed in a 1-butanol/butanal (9ml : 1ml) mixed solution by sonication. The mixture was then transferred to a 20ml glass bottle with a lid and heated at 100 °C for 3 h while stirring with a magnetic stirrer. After cooling to room temperature, the mixture was centrifuged and the supernatant was distillated under reduced pressure at 80 °C. The light-yellow remnant liquid was then collected.

Catalysts Preparation[1]

MIL-101(Cr): $Cr(NO_3)_3·9H_2O$ (1 g, 2.5 mmol) and 1,4-dicarboxybenzene (BDC) (415 mg, 2.5 mmol) were dispersed in 10 mL distilled water at room temperature. The mixture was then transferred to a 25 mL Teflon-lined autoclave and heated in a 200 °C oven for 7 h. After cooling down to room temperature, the product was collected by centrifugation and washed with DMF and methanol multiple times. The collected green powder was dispersed in methanol for later use.

MOF-808: Trimesic acid (H_3BTC, 3.75 mmol, 0.786 g) and $ZrOCl_2\cdot8H_2O$ (3.75 mmol, 1.209 g) were mixed in DMF (150 mL) and formic acid (150 mL). The mixture was placed in a closed 1 L Schott DURAN bottle and heated at 130 °C for 7 h. After cooling down, the obtained white powder was washed by DMF (3X), methanol (3X) and collected by centrifugation. The MOF-808 was activated at 150 °C for 20 h before performing experiments.

Ru⊂MOF-808: 300 mg of MOF-808 was placed into a 250 ml round bottom flask. Ruthenium(III) chloride hydrate ($RuCl_3\bullet xH_2O$, 90.3 mg) was dissolved in a DI water/ethanol (370 µl : 3.7 ml) mixed solvent and added to the flask. Dichloromethane (DCM, 15 mL) was added to the mixture and sonicated for 5 min to achieve a clear solution. After adding 30 ml petroleum ether, black precipitate was formed leaving a light-brown transparent supernatant. After drying the precipitate in a 70 ℃ oven, the solid was reduced into a U-shaped glass tube under atmospheric hydrogen atmosphere (H_2, 200 ℃) for 2 hours. The product was then washed with methanol (3X) and collected by centrifugation. The Ru⊂MOF-808 was activated at 150 °C for 20 h before performing experiments.

Sc-Ru⊂MOF-808: 300 mg of Ru⊂MOF-808 and 50 mg of $Sc(OTf)_3$ was dispersed in 5 ml of methanol and kept for 12 h at room temperature. The obtained black sediment was then washed with methanol (3X) and collected by centrifugation. The Sc-Ru⊂MOF-808 was activated at 150 °C for 20 h before performing experiments. **In-Ru⊂MOF-808**, **Hf-Ru⊂MOF-808** and **Fe-Ru⊂MOF-808** were prepared likewise.

Sc⊂MOF-808: 300 mg of MOF-808 and 50 mg of $Sc(OTf)_3$ was dispersed in 5 ml of methanol and kept for 12 h at room temperature. The obtained white sediment was then washed with methanol (3X) and collected by centrifugation. The Sc⊂MOF-808 was activated at 150 °C for 20 h before performing experiments.

Catalysis

The oxidation reactions were conducted in a 10 ml stainless-steel autoclave equipped with a magnetic stirrer, a pressure gauge and an automatic temperature controller. In a typical experiment, 4.35 mmol of alcohol and 10 mg of catalyst were loaded into the reactor. The reactor was then sealed, pressurized to 12 bar with O_2, and heated up to the target temperature under constant stirring. After reaction, the autoclave was cooled down, the pressure was vented and the solution was separated by filtration and analyzed by gas chromatography (GC) with n-dodecane as the internal standard. In some experiments different substrate and catalysts have been used for the reaction.

The products were analyzed by GC (Agilent Technologies 7820A) equipped with a polar column of CYCLOSIL-B and flame ionization detector (FID), with inlet temperature of 250 ºC. The products have been separated by starting from 40 °C and hold for 2 min with subsequent heating to 150 °C at a rate of 20 °C/min, then to 250 °C at a rate of 30 °C/min. GC-MS analysis (Agilent Technologies 5977A MSD with

Agilent Technologies 7890B GC system equipped with HP-5 capillary column) was used to identify the organic compounds.

The conversion of carbonyl compound, selectivity and yield to corresponding products were defined as follows:

$$Conversion\ (\%) = 1 - n_A/n_A^0$$

$$Selectivity\ (\%) = 1 - n_p/(n_A^0 - n_A)$$

, where n_A , n_A^0 and n_p refers to the final, initial moles of alcohol and final moles of product, respectively. n-dodecane was used as internal standard for the GC analysis.

S3. Instrumentation

ICP experiment was carried out on an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES Icap7400). The calculation method of the loading of Ru and Sc in MOFs as follows:

$$m_{Ru}\% = \frac{a_{Ru}}{a_M} * \frac{N_M}{M_M} * 100\%$$

$$m_{Sc}\% = \frac{a_{Sc}}{a_M} * \frac{N_M}{M_M} * 100\%$$

Here, a_{Ru} - constituent content of Ru by ICP-OES, a_{Sc} - constituent content of Sc by ICP-OES, a_M - constituent content of metal (MOFs) by ICP-OES, N_M - the number of metal in molecular formula [MOF-808: $Zr_6O_4(OH)_4[C_6H_3(CO_2)_3]_2(HCOO)_6$], M_M – the molecular formula weight of MOF.

Transmission electron microscope (TEM) images were taken on a JEM 2100 plus (200 kV) or JEM 1400 plus (120 kV). Powder samples were first evenly dispersed in methanol. Then, a 2.0 μl solution droplet was added onto a carbon-coated copper grid.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image were taken on an 80 kV aberration-corrected JEOL GrandARM.

Energy-dispersive X-ray spectroscopy (EDS) elemental mapping images and line scan were collected on a JEM 2100 plus (200 kV) or JEM 1400 plus (120 kV)

Powder X-ray diffraction (PXRD) patterns were collected on an X-ray diffractometer (Bruker D8 PHASER) with Cu K radiation, operated at 40 kV and 40 mA.

Scanning electron microscope (SEM) images were obtained using a JSM-7800F Prime Scanning Electron Microscopy at 5 kV. The samples were pre-coated with Au for 10 seconds using an SBC-12 sputter coater.

Gas sorption. N_2 adsorption isotherms were collected by a volumetric gas adsorption analyzer (Quantachrome Instruments Autosorb-iQ-MP-AG). Typically, a 30-80 mg powder sample was loaded in a 6 mm large bulb sample cell and degassed under vacuum at 120 °C for 8 h. The BET surface area was determined using the data points in the pressure range of 0.01−0.1 P/P_0 from the N_2 adsorption isotherms at 77 K.

Gas chromatography. An Agilent Technologies 7820A equipped with a polar column of CYCLOSIL-B and flame ionization detector (FID) was used to quantify reaction products. The inlet temperature was set at 250 ºC. The column condition is as follows. The initial oven temperature was set and kept at 40 °C for 2 min. Subsequently, the temperature was ramped to 150 °C at a rate of 20 °C/min, then to 250 °C at a rate of 30 °C/min.

^{1}H-NMR spectra were recorded on a Bruker AVANCE III HD 400MHz spectrometer

X-ray photoelectron spectroscopy (XPS) data were determined by Thermo Fisher ESCALAB 250 Xi.

Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) was collected on PerkinElmer Frontier FT-IR in the range of 400-4000 cm^{-1} at a resolution of 1 cm^{-1}.

Thermogravimetric analysis (TGA) experiments were performed on a PerkinElmer TGA 8000. Typically, samples were firstly heated to 150 ºC and retained at that temperature for 30 minutes under N_2 atmosphere to remove residual solvent and then heated to 800 ºC at a rate of 20 ºC/min under oxygen (O_2) atmosphere, and then kept 800 ºC for 30 min.

S4. Figures and Tables

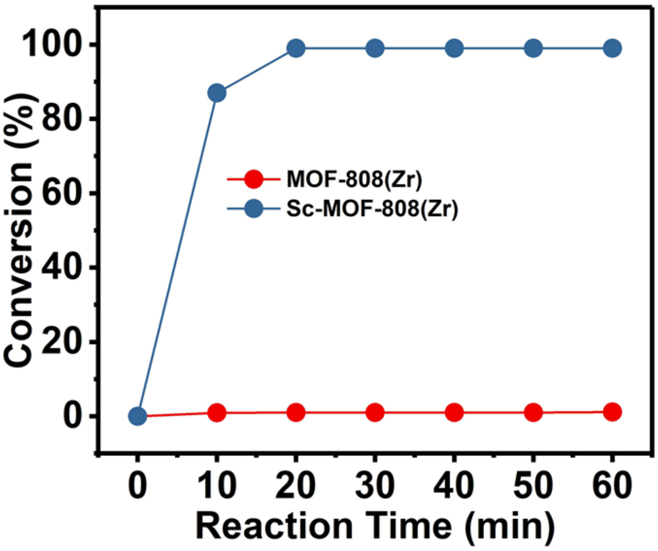


Figure S1. Conversion of butanal under acetalization process using MOF-808 (red) and Sc-MOF-808 (blue) catalysts. Reaction condition: 500 µl 1-butanol and 50 µl butanal, 10 mg catalysts, 100°C, 4 bar N_2.

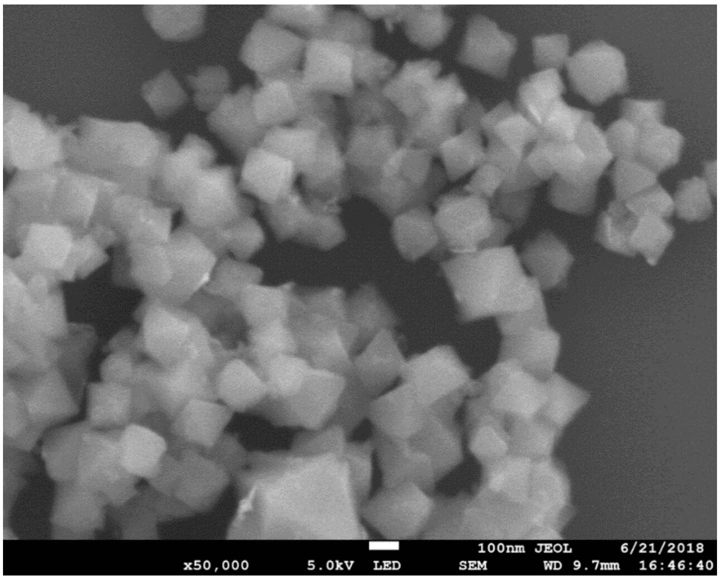


Figure S2. SEM image of MOF-808 particles.

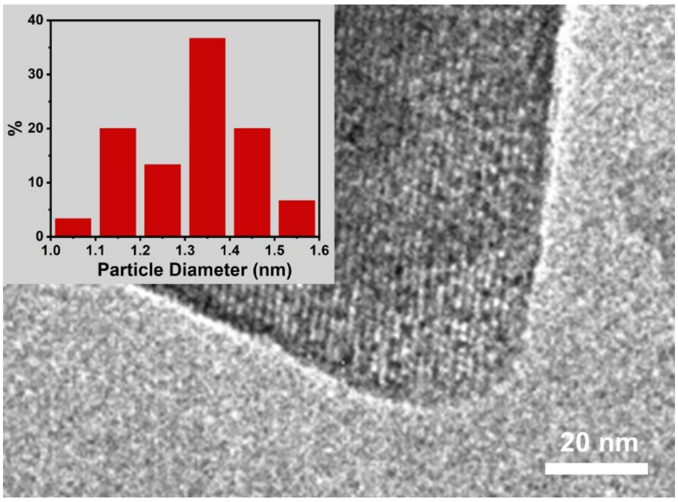


Figure S3. TEM image of Sc-Ru⊂MOF-808. Inset shows the size distribution of Ru NPs.

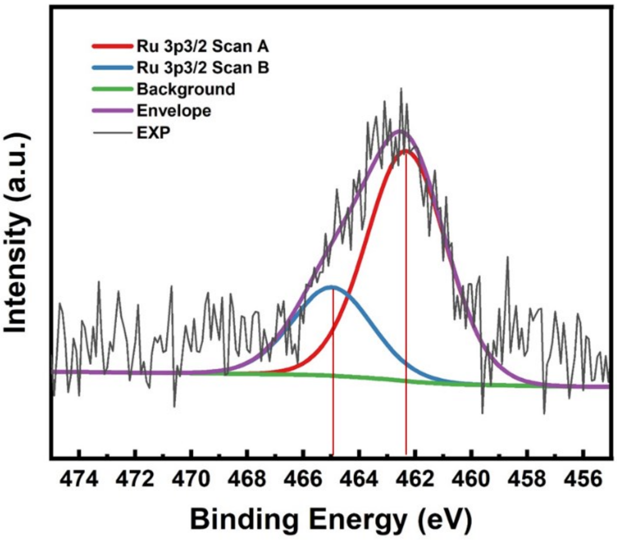


Figure S4. XPS spectrum of Ru in Sc-Ru⊂MOF-808. Peaks at 462.2 and 464.9 eV can be respectively assigned to Ru(0)[2] and non-stoichiometric oxide RuOx[3].

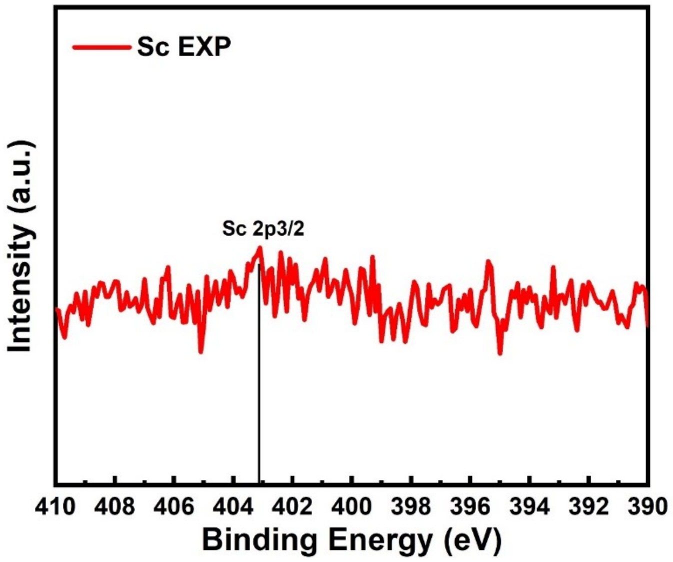


Figure S5. XPS spectrum of Sc in Sc-Ru⊂MOF-808. No evident signal of Sc could be observed.

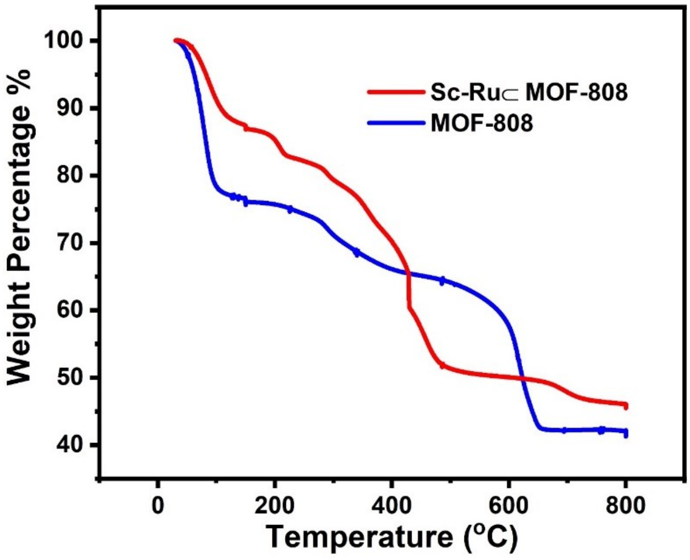


Figure S6. TGA spectra of MOF-808 and Sc-Ru⊂MOF-808 catalysts. Samples were activated at 150ºC and thermally decomposed under nitrogen atmosphere.

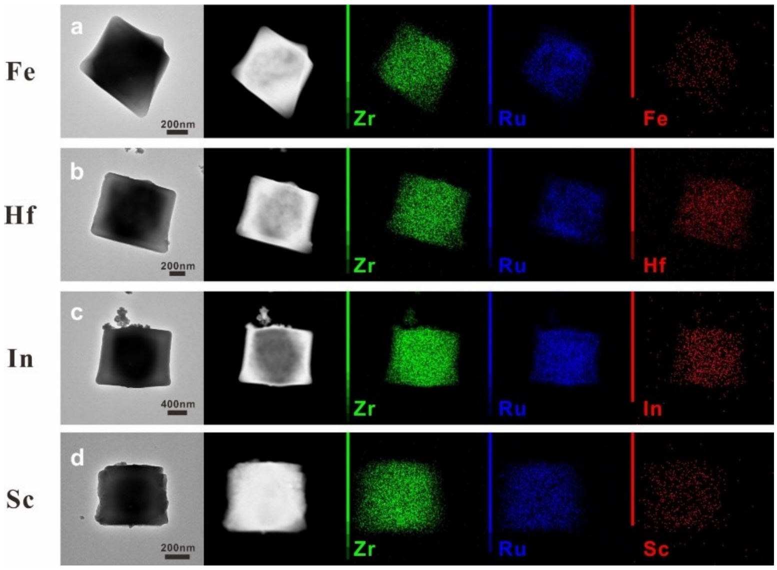


Figure S7. TEM image and STEM-EDS elemental mapping of M-Ru⊂MOF-808 (M = Sc, In, Hf, Fe) catalysts.

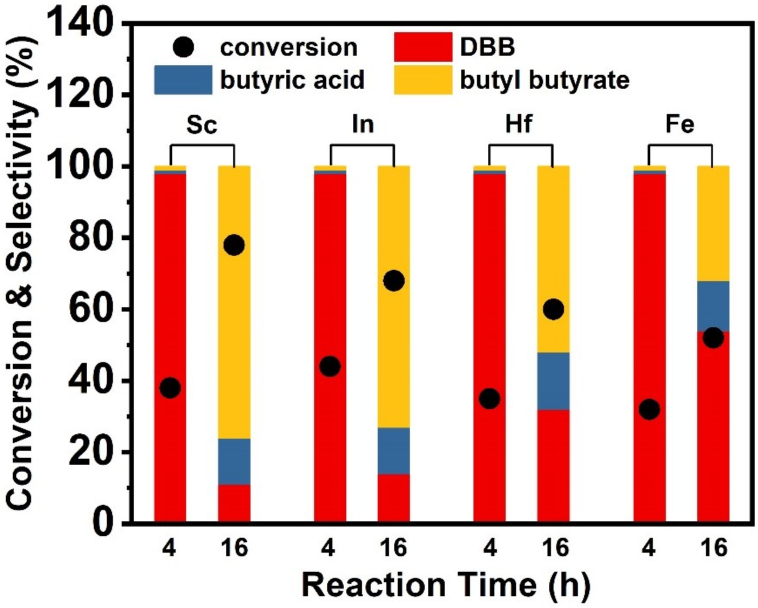


Figure S8. Conversion and product distribution of 1-butanol oxidation reaction on 0.1 mol% M-Ru⊂MOF-808 (based on Ru, M = Sc, In, Hf, Fe) with different reaction time. Reaction condition: 4.35 mmol 1-butanol, 120 ºC, 12 bar O_2. Catalysts are prepared by immersing Ru⊂MOF in 10mg/ml $M(OTf)_3$ ($M(OTf)_4$ for Hf) methanol solution for 12 h, then collected through centrifuging and washed with methanol for 3 times.

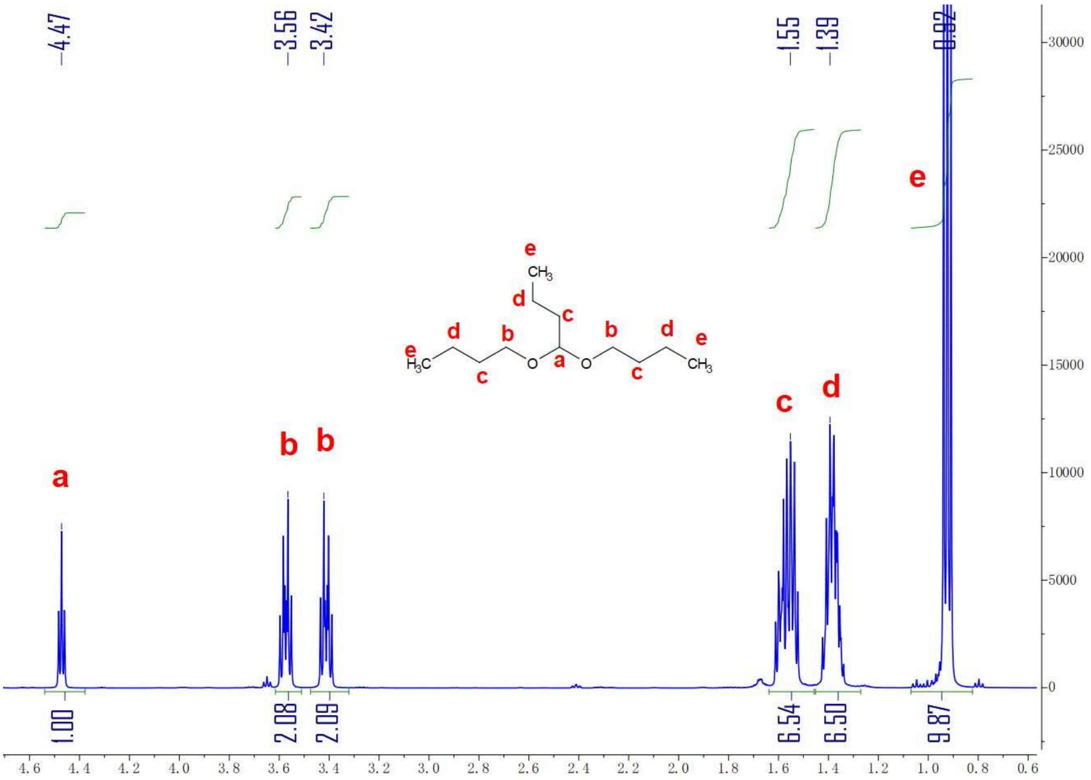


Figure S9. ^{1}H NMR spectrum of 1,1-dibutoxybutane (DBB).

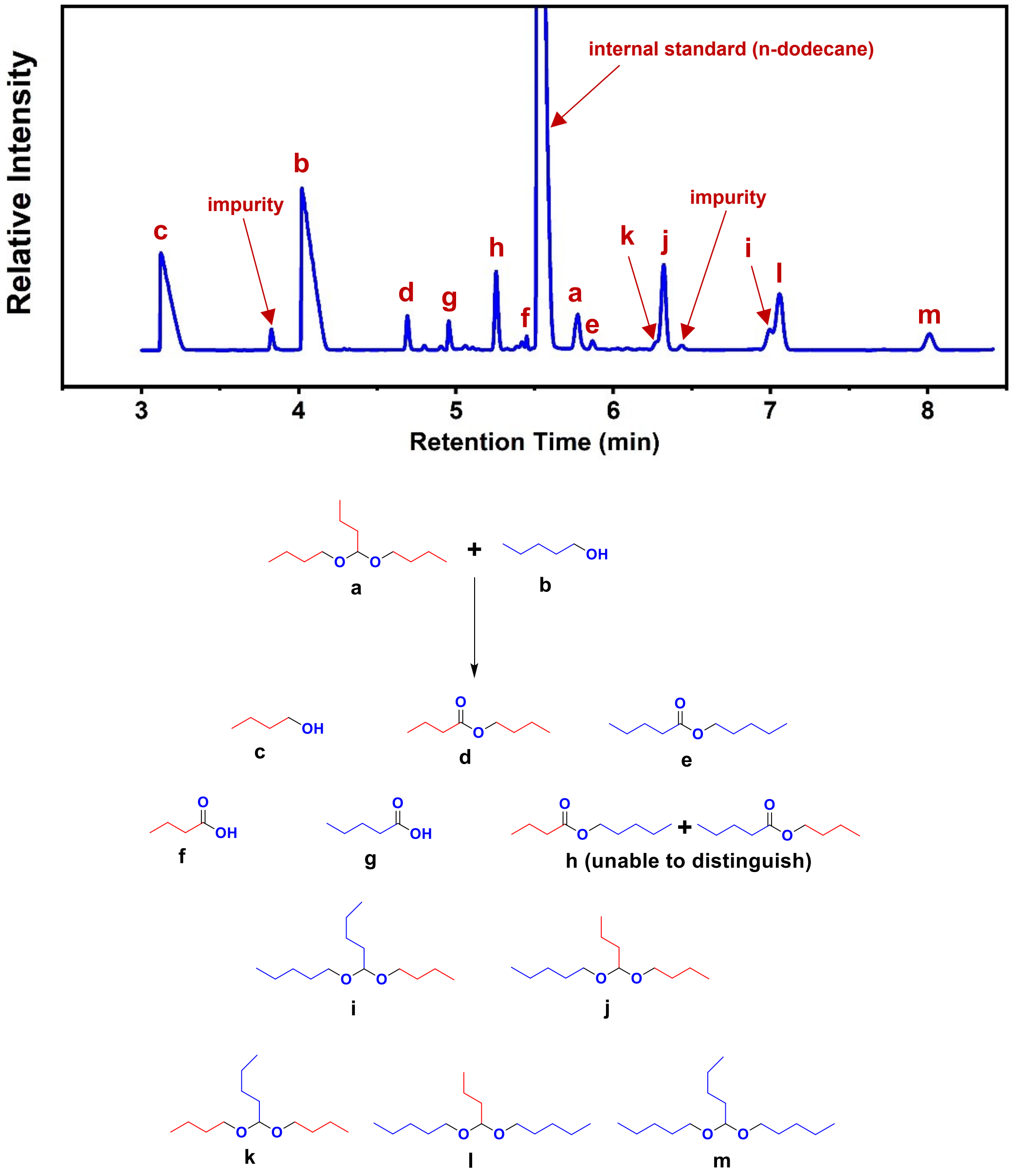


Figure S10. GC-FID peak analysis of catalytic conversion of a DBB/1-pentanol mixture (1:3 n/n). Reaction condition: 4.35mmol 1-pentanol + 1.45mmol DBB, 120 °C, 12 bar O_2, 10 mg Sc-Ru⊂MOF-808, 4 h.

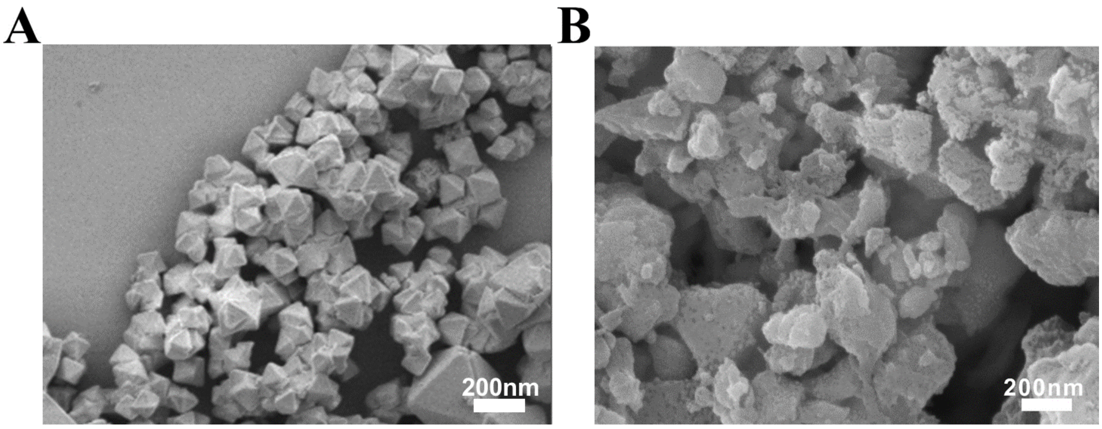


Figure S11. SEM image of Sc-Ru⊂MOF-808 before (A) and after (B) DAEC reaction of 1-butanol at 120℃ for 24 h.

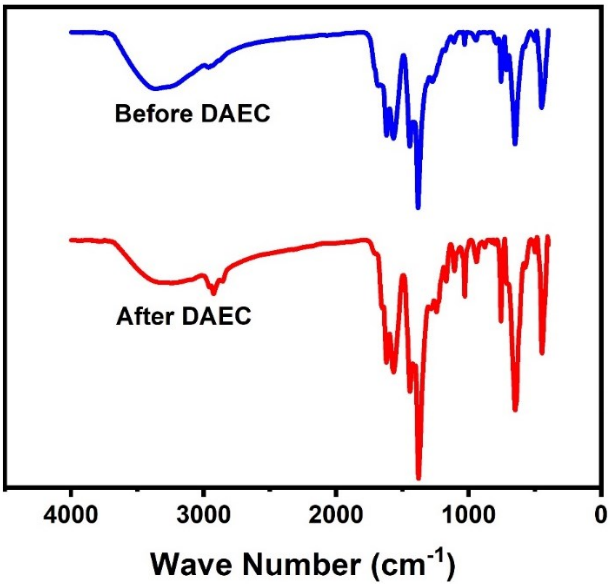


Figure S12. FTIR spectra of Sc-Ru⊂MOF-808 before and after DAEC reaction of 1-butanol at 120℃ for 24 h.

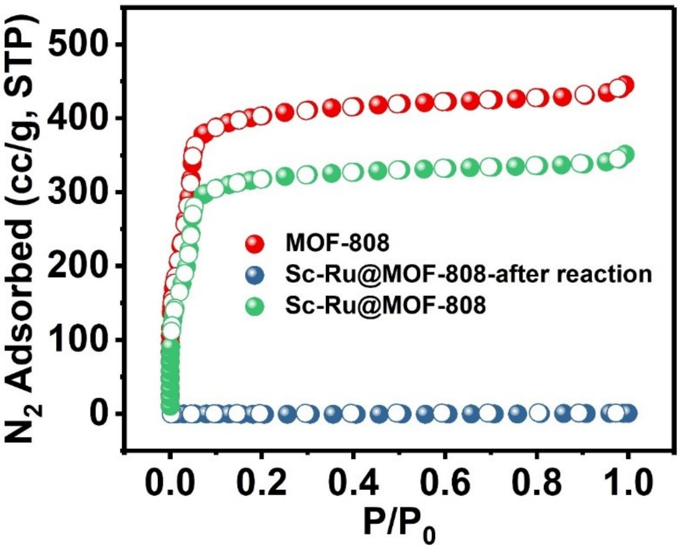


Figure S13. N_2 sorption isotherms at 77K of Sc-Ru⊂MOF-808 before and after DAEC reaction of 1-butanol at 120℃ for 24 h.

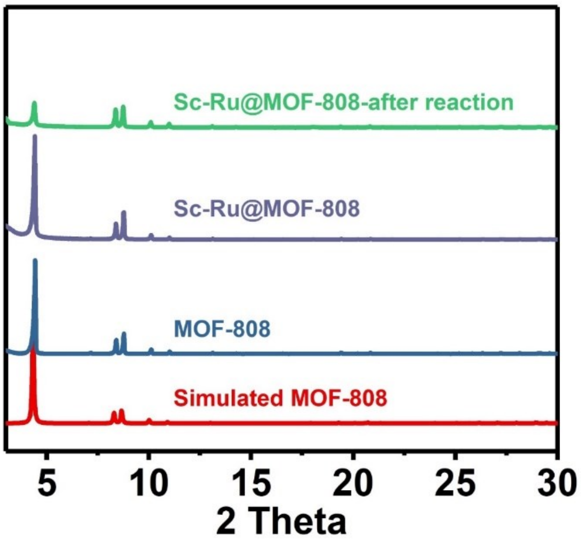


Figure S14. PXRD spectra of Sc-Ru⊂MOF-808 before and after DAEC reaction of 1-butanol at 120℃ for 24 h.

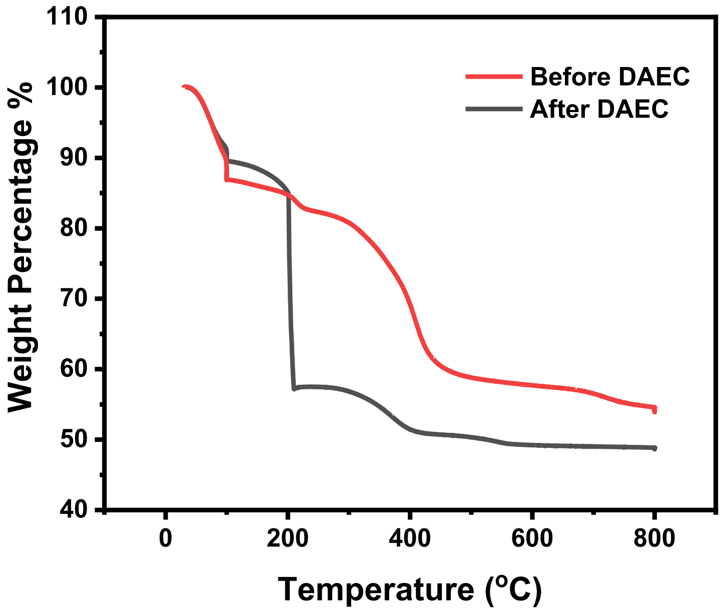


Figure S15. TGA spectra of Sc-Ru⊂MOF-808 before and after DAEC reaction of 1-butanol at 120°C for 24 h. Samples were activated at 100°C under nitrogen atmosphere before thermally decomposed in O_2.

By calculation, the weight fraction of polymers in the solid mixture recycled after DAEC reaction is 12%.

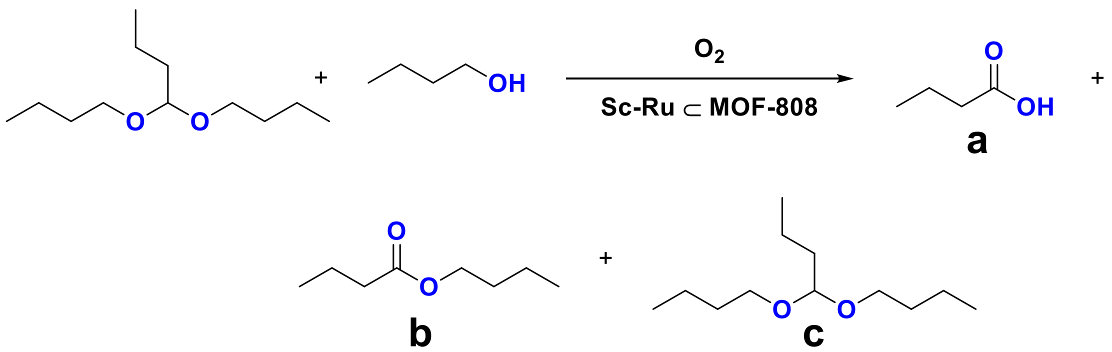
Table S1. Conversion and product distribution of 1-butanol oxidation reaction on 0.1 mol% Sc-Ru⊂MOF-808 (based on Ru). Reaction condition: 4.35 mmol 1-butanol, 120 °C, 24 h. (The conversion and selectivity were determined by gas chromatography with n-dodecane as the internal standard.)

Oxygen Pressure (bar)	**Conversion (%)**	**Selectivity (%)**			
		Butanal	Butyl butyrate	Butyric acid	DBB
9	77	0	83	11	6
12	87	0	88	11	1
15	93	0	87	13	0

Table S2. Conversion and product distribution of 1-butanol oxidation reaction on various amount of Sc-Ru⊂MOF-808. Reaction condition: 4.35 mmol 1-butanol, 120 °C, 12 bar O_2, 24 h. (The conversion and selectivity were determined by gas chromatography with n-dodecane as the internal standard.)

Amount of catalyst (mol% based on Ru with respect to 1-butanol)	**Conversion (%)**	**Selectivity (%)**			
		Butanal	Butyl butyrate	Butyric acid	DBB
0.2	90	0	87	13	0
0.1	87	0	88	11	1
0.05	81	0	88	8	4
0.025	67	1	81	11	7

Table S3. The catalytic results of 1-butanol (2.18mmol) and 1,1-dibutoxybutane (2.18/3mmol) mixed substrate by Sc-Ru⊂MOF-808.
Reaction condition: 120 ºC, 2.18 mmol 1-butanol and 0.73 mmol DBB, 0.1 mol% Sc-Ru⊂MOF-808 (based on Ru), 12 bar O_2.



Reaction time (h)	Weight Percentage (%)			
	Butanol	a	b	c
0	52	0	0	48
0.5	54	0	1	45
1	56	2	1	41
2	61	5	2	32
4	61	10	2	27
8	64	10	14	11
16	46	15	34	4
24	22	17	59	2

Table S4. Conversion and product distribution in cyclic performance test of Sc-Ru⊂MOF-808 for DAEC reaction.
Solvent free, 4.35 mmol 1-butanol, 0.1 mol% Sc-Ru⊂MOF-808 (based on Ru), 120 °C, 12 bar O_2, 24 h.

Cycle number	**Conversion (%)**	**Selectivity (%)**			
		Butanal	Butyl butyrate	Butyric acid	DBB
1	87	0	88	11	1
2	32	0	1	5	94
3	29	0	1	3	96

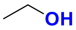
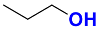
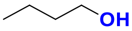
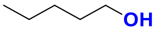
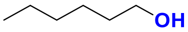
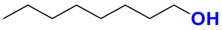
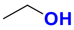
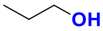
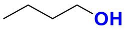
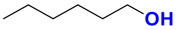
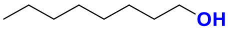
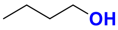
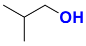
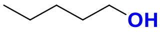
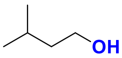
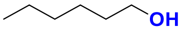
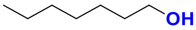
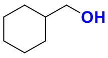
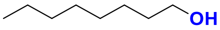
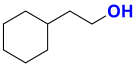
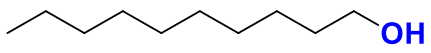
Table S5. Conversion, product distribution (determined by GC) and cumulative Sc leaching (determined by ICP-OES) in cyclic performance test of Sc-Ru⊂MOF-808 for sole esterification reaction.

Reaction condition: 2.18 mmol butyric acid and 4.35 mmol 1-butanol, 10 mg Sc-Ru⊂MOF-808 (based on Ru), 120 °C, 4 bar N_2, 24 h. Catalysts are recycled, dried, and outgassed after each cycle.

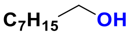
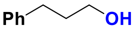
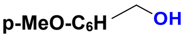
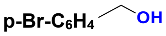
	Conversion of acid (%)	**Selectivity of Ester (%)**	**m_{Zr}/m_{Sc}**	**Cummulative Sc leaching (%)**
Before reaction	-	-	248	0
Cycle 1	88	100	265	6
Cycle 2	86	100	269	8
Cycle 4	83	100	273	9

Table S6: DAEC instances of aliphatic alcohols using heterogeneous catalysts.

Symmetric Ester Production

Catalysts	Substrates	Solvents	Solvent wt %	Yield of esters (%)	
Co_3O_4-based particles supported on carbon-nitrogen materials (Co_3O_4-N@C)[6]		n-heptane	~90	65	
		n-heptane	~95	71	
		n-heptane	~95	72	
		n-heptane	~95	73	
		n-heptane	~95	75	
		n-heptane	~94	75	
				Conversion %	Selectivity %
1-ethyl-3-methylimidazoliu-m acetate ([EMIM]OAc)[7]		[EMIM]OAc	~96	98	94
		[EMIM]OAc	~94	95	92
		[EMIM]OAc	~93	96	83
		[EMIM]OAc	~91	92	79
		[EMIM]OAc	~88	89	72
Sc-Ru⊂MOF-808 (this work)		None	N/A	87	88
		None	N/A	91	90
		None	N/A	93	83
		None	N/A	92	91
		None	N/A	86	86
		None	N/A	89	85
		None	N/A	90	84
		None	N/A	85	87
		None	N/A	88	87
		None	N/A	88	81

Asymmetric Ester Production

Catalyst	Substrates	Solvents	Substrate Concentration	Yield of esters (%)
Novel carbon-stabilized polymer-incarcerated bimetallic (Au-Pd) nanocluster catalysts (PI-CB/Au-Pd)[8]	, Methanol	$MeOH/H_2O$ (1:2)	0.125M	78
	, Methanol	$MeOH/H_2O$ (1:2)	0.125M	81
	, Methanol	$MeOH/H_2O$ (2:1)	0.125M	96
	, Methanol	$MeOH/H_2O$ (2:1)	0.125M	97

S5. Supplementary References

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