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Electronic Supplementary Information

Exploring the Brønsted Acidity of UiO-66 (Zr, Ce, Hf) Metal-Organic Frameworks for Efficient Solketal Synthesis from Glycerol Acetalization

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1. General information

1.1. Reagents

Hafnium chloride ($HfCl_4$, 98%) was purchased from Sigma-Aldrich. Ammonium ceric nitrate ($(NH_4)_2[Ce\ (NO_3)_6$, 98%]), Acetic acid (CH_3COOH, 98.5-100.5%), Acetone (C_3H_6O, 99%), Methanol (CH_4O, 99%), 1, 4-benzenedicarboxylate (H_2BDC, 98%) and hydrochloric acid (HCl, 98%) were brought from SDFCL, Mumbai, India. Zirconium Chloride ($ZrCl_4$, 98%), Glycerol (98%), Sodium hydroxide (NaOH, 99%) and Potassium bromide (KBr, 98.5%) were purchased from Merck Life Science Pvt. Ltd. Mumbai, India. *N, N*-dimethylformamide (DMF, 99 wt %) was supplied by Avra Synthesis Pvt. Ltd. Hyderabad, India. Ethanol (C_2H_60, 99.9%) was supplied by Fine Chemical Co. Ltd. Sodium nitare ($NaNO_{3,}$ 99%) purchased from NICE chemicals, India. All chemicals were used without further purification.

1.2. Characterization

Powder X-ray diffraction (PXRD) patterns were recorded on Bruker with Cu Kα radiation (λ = 1.5418 Å) operating at 20 kV and 10 mA. The specific surface area, pore volume and pore size of catalysts were measured using a BEL Sorp II BET (Brunauer-Emmett-Teller) instrument.

2. Synthesis methods

2.1. Synthesis of UiO-66(Hf) MOF

In a typical solvothermal synthesis, [1] 300 mg (0.94 mmol) of $HfCl_4 \cdot 6H_2O$ and 174 mg (1.04 mmol) of H_2BDC were dissolved in 10 mL of DMF solvent containing 0.1M H_2O in a 30 mL screw capped bottle and sealed. The synthesis was carried out in a pre-heated oven at 100˚C for 24 h. On completion of the reaction time, the reaction mixture was brought to room temperature and the supernatant was decanted. The solid product was washed with fresh DMF (50 mL) once, twice with ethanol (2 x 50 mL) using centrifuge. Finally, the powder was dried under vacuum at room temperature.

2.2. Synthesis of UiO-66(Zr) MOF

In a typical procedure, UiO-66(Zr) material synthesized according reported literature. [2] 50 mg of H_2BDC (0.31 mmol), 66.8 mg of $ZrCl_4$(0.28 mmol) and 1.4 mL of acetic acid were dissolved in 20 mL of DMF solvent in a 30 mL screw capped bottle. It is sonicated for 10 minutes for complete dissolution and placed in preheated oven at 120 ˚C for 24 hours. After the completion of reaction time, the mixture was brought to room temperature, centrifuged and the supernatant was decanted. The product was first washed with DMF and then with methanol twice (2 x 15 mL). It was then dried under vacuum at room temperature.

2.3. Synthesis of UiO-66(Ce) MOF

In a typical procedure, UiO-66(Ce) material synthesized according reported literature. [3] 212.4 mg terepthalicacid (1.279 mmol) was dissolved in approximately 7.2 mL of DMF. The solute was dissolved by sonicating for 5 mins. Exactly 2.4 mL of 0.533M $[Ce(NH_4)_2(NO_3)_6]$ was added using a micropipette. It is then kept in an oil bath at 100˚C and stirred for 15 min using a magnetic stirrer. Yellow colored precipitate was formed. After the completion of reaction time, the mixture was brought to room temperature, centrifuged and the supernatant was decanted. Washed two times using fresh DMF (7mL) followed by washing with acetone 3 times.

3. Characterization of catalysts

3.1. Scanning electron microscopy (SEM) analysis of MOFs

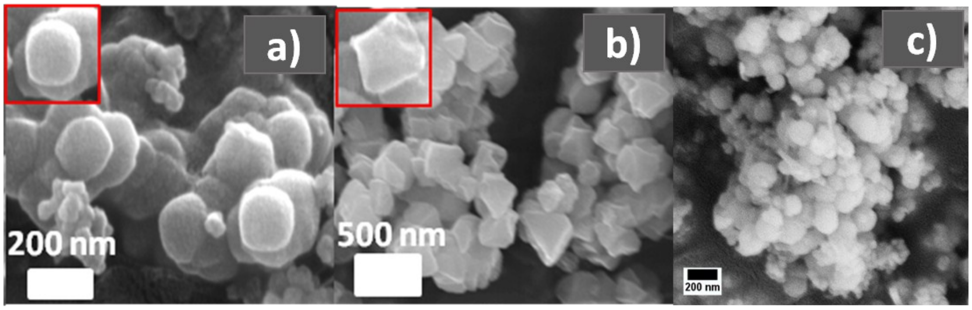


Figure S1: Scanning electron microscopy images of a) UiO-66(Zr), b) UiO-66(Ce) and c) UiO-66(Hf). The morphology and size distribution of UiO-66(Zr), UiO-66(Ce) and UiO-66(Hf), MOFs are nearly spherical, 50-200 nm; deformed octahedral, 100-270 nm; nearly spherical 50-220 nm, respectively.

3.2 Estimation of acidity of MOFs

In a typical procedure, 100 mg of catalyst (MOF) was stirred with 10 ml 0.2 M $NaNO_3$ solution for 8 h to undergo ion exchange at room temperature. Then the mixture was centrifuged to separate the catalyst and ion-exchanged solution. Later, the liberated HCl was titrated against

0.0025 M NaOH using phenolphthalein as an indicator.[4] The total H^+ ions liberated was calculated and tabulated in the Table S1.

Catalyst	Acidity (mmol/g)
UiO-66 (Hf)	1.26
UiO-66 (Ce)	0.82
UiO-66 (Zr)	0.25

Table S1: Total H^+ calculation using acid-base titration.

3.3 Potentiometric titration to calculate the linker defects and strength of acidity in each isostructural UIO-66 MOFs

The linker defects of three UiO-66 MOFs have been calculated by ion exchange followed by acid-base pH titration. [5] In a typical procedure, 50 mg of catalyst (MOF) was soaked in 60 mL of 0.01M $NaNO_3$ solution and kept it for stirring for 18 h to undergo ion exchange at room temperature. The pH of the each ion exchanged MOF solution is measured before the titration and values were noted as 3.5, 4.6 and 5.8 for UIO-66(Hf), UIO-66(Ce) and UIO-66 (Zr) respectively, using pH electrode (EUTECH PC510). In the next step, each titrant pH value adjusted to 3 by adding 0.1M aq. HCl. Finally, it was titrated against 0.1 M aq. NaOH by adding dropwise (0.05mL) until pH become 11. The low pH of UiO-66(Hf) however suggests high acidity among other MOFs. This low pH/high acidity of UiO-66(Hf) might be due to more oxophilic nature of Hf (IV) metal ion leads to labile nature of proton at SBU in the ion exchange method. Results suggest that UiO-66(Hf) had shown more acidic nature than UiO-66(Ce) and UiO-66(Zr). Moreover, the Brønsted acidity arised form SBU /metal node associated with μ_3-OH, M-OH_2 and M-OH are in well accordance with the literature reports. [5, 6, 7] On the other hand, their M-O bond dissociation energies are to be 801 kJ/mol, 790 kJ/mol, and 766 kJ/mol of UiO-66(Hf), UiO-66(Ce) and UiO-66(Zr), respectively, suggests that Hf(IV) has more oxophilic nature among others.

Table S2: Calculated pKa values for isotructural UiO-66 MOFs

MOF	pH(before titration)	pKa1	pKa2	pKa3
		μ_3-OH	-OH_2	-OH
UiO-66 (Hf)	3.51	3.30	4.94	6.25
UiO-66 (Ce)	4.57	3.44	4.93	7.30
UiO-66 (Zr)	5.81	3.68	5.75	7.43

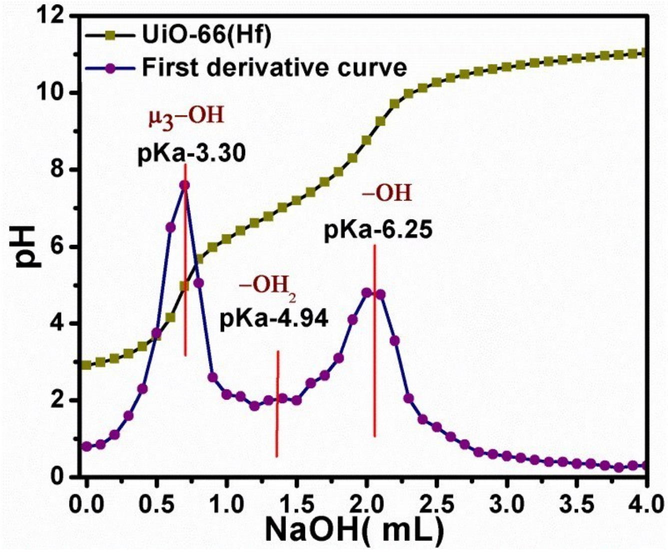


Figure S2. Acid-base titration curve and first derivative curve for UiO-66(Hf).

μ_3-OH	0.5996 mL	mL NaOH
	0.05996 mmol	mmol protons from μ_3-OH
Hf -OH$_2$	0.7972 mL	mL NaOH
EP2-EP1	0.07972 mmol	mmol protons from Hf -OH$_2$
Hf -OH	0.6596 mL	mL NaOH
EP3-EP2	0.06596 mmol	mmol protons from Hf -OH
	0.145270	**Total mmol of protons**

Table S3: Calculation of linker defects in UIO-66 (Hf) MOF.

Missing linkers	Molecular formula	M.Wt.	mmol of taken for 0.0510g	Acidity (moles)	Acidity (mmol) for 0.050 g
0	$Hf_6O_4(OH)_4(BDC)_6$	2200.74	2.3174E-05	0	0
1	$Hf_6O_4(OH)_4(BDC)_5[H_2O(OH)]_2$	2106.41	2.42118E-05	0.0001452	0.145270
1.05	$Hf_6O_4(OH)_4(BDC)_5[H_2O(OH)]_2$	2099.94	2.42864E-05	0.00015300	0.15300
1.1	$Hf_6O_4(OH)_4(BDC)_{4.9}[H_2O(OH)]_{2.1}$	2093.47	2.43614E-05	0.00016078	0.16078
1.2	$Hf_6O_4(OH)_4(BDC)_{4.8}[H_2O(OH)]_{2.2}$	2080.54	2.45128E-05	0.00017649	0.17649
1.3	$Hf_6O_4(OH)_4(BDC)_{4.7}[H_2O(OH)]_{2.3}$	2067.61	2.46661E-05	0.00019239	0.19239
1.4	$Hf_6O_4(OH)_4(BDC)_{4.6}[H_2O(OH)]_{2.4}$	2054.67	2.48214E-05	0.00020850	0.20849
1.5	$Hf_6O_4(OH)_4(BDC)_{4.5}[H_2O(OH)]_{2.5}$	2041.74	2.49786E-05	0.00022480	0.22480

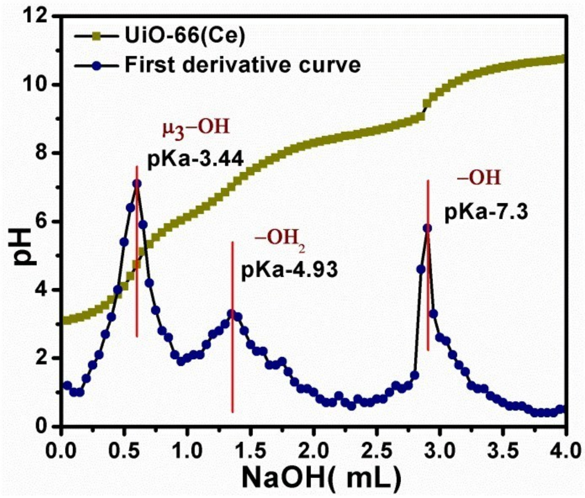


Figure S3. Acid-base titration curve and first derivative curve for UiO-66(Ce).

μ_3-OH	0.6015mL	mL NaOH
	0.06015mmol	mmol protons from μ_3-OH
Ce -OH_2	0.75064 mL	mL NaOH
EP2-EP1	0.075064	mmol protons from Ce-OH_2
Ce -OH	1.55065 mL	mL NaOH
EP3-EP2	0.155064	mmol protons from Ce-OH
	0.230128	**Total mmol of protons**

Table S4: Calculation of linker defects in UIO-66 (Ce) MOF.

Missing linkers	Molecular formula	M.Wt	mmol of taken for 0.050g	Acidity (moles)	Acidity (mmol) for 0.050 g
0	$Ce_6O_4(OH)_4(BDC)_6$	1969.92	2.53817E-05	**0**	**0**
1	$Ce_6O_4(OH)_4(BDC)_5[H_2O(OH)]_2$	1875.59	2.66582E-05	0.00015994	0.15994
1.1	$Ce_6O_4(OH)_4(BDC)_{4.9}[H_2O(OH)]_{2.1}$	1862.66	2.68433E-05	0.00017716	0.17716
1.2	$Ce_6O_4(OH)_4(BDC)_{4.8}[H_2O(OH)]_{2.2}$	1849.73	2.70310E-05	0.00019462	0.19462
1.3	$Ce_6O_4(OH)_4(BDC)_{4.7}[H_2O(OH)]_{2.3}$	1836.79	2.72213E-05	0.00021232	0.21232
1.4	$Ce_6O_4(OH)_4(BDC)_{4.6}[H_2O(OH)]_{2.4}$	1823.86	2.74143E-05	0.00023028	0.23028
1.5	$Ce_6O_4(OH)_4(BDC)_{4.5}[H_2O(OH)]_{2.5}$	1810.93	2.76101E-05	0.00024849	0.24849

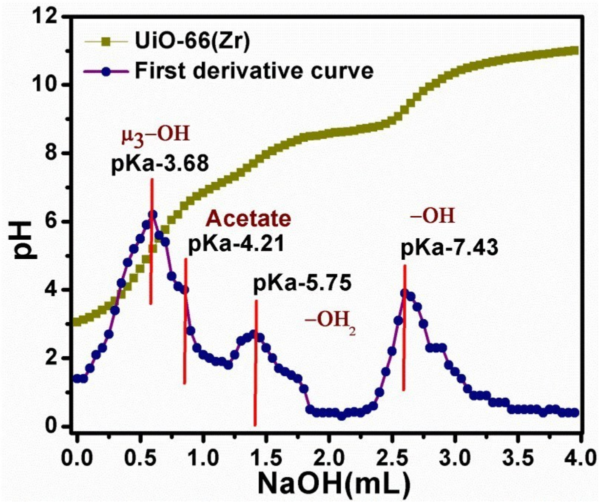


Figure S4. Acid-base titration curve and first derivative curve for UiO-66(Zr)

μ_3-OH	0.589mL	mL NaOH
	0.0589 mmol	mmol protons from μ_3-OH
Acetate	0.309	mL NaOH
EP_2-EP_1 =	0.0309	mmol protons from AA
Zr -OH_2	1.198	mL NaOH
EP_3-EP_2 =	0.1198	mmol protons from Zr OH_2
Zr -OH	1.648	mL NaOH
EP_4-EP_3 =	0.1648	mmol protons from Zr-OH

Total mmol of protons from AA and [(OH_2)(OH)]	0.3155
Amount of [(OH_2)(OH)] protons	0.2846
Relative amount from AA	9.47 %
Relative amount of [(OH_2)(OH)]	90.20 %

Table S5: Calculation of linker defects in UiO-66 Zr MOF.

No. of missing linkers	Total number of BDC linkers	MW (g/Mol)	Protons from AA	Protons from OH/OH_2	Amount of protons from 0.05 g sample (mmoles)
0	6	1664.03	0	0	0
1	5	1580.25	0.19587	5.4123	0.19606
1.1	4.9	1571.88	0.21546	5.9535	0.21567
1.2	4.8	1563.50	0.23505	6.4948	0.23528
1.3	4.7	1555.12	0.25464	7.0360	0.25489
1.4	4.6	1546.74	0.27423	7.5773	0.27450
1.5	4.5	1538.36	0.29381	8.1185	0.29410
1.6	4.4	1529.98	0.31340	8.6597	0.31371
1.7	4.3	1521.60	0.33299	9.2010	0.33332

4. Catalysis

Table S6: Esterification of levulinic acid with methanol and ethanol with different MOFs.

Catalyst	Reaction condition		LA:MeOH mole ratio	Levulinic acid (LA)con.(%)	LA:EtOH mole ratio	Levulinic acid con.(%)
	Time	Temp.				
UiO-66(Hf)	4h	80˚C	1 : 15	84.1	1 : 15	44.5
UiO-66(Ce)	4h	80˚C	1 : 15	50.4	1 : 15	18.8
UiO-66(Zr)	4h	80˚C	1 : 15	15.7	1 : 15	7.5
Blank	4h	80˚C	1 : 15	8.3	1 : 15	4.2

Reaction conditions: Levulunic acid (116.12 mg, 1 mmol), alcohol (480.6 mg, 15 mmol), catalyst amount 20 mg and reaction carried for 4h at 80˚C. Products were analyzed by Agilent-GC (HP-5 column).

4.1. Solketal synthesis from glycerol and acetone with different MOFs

In a typical catalysis procedure, 1g of glycerol and 2.52 g of acetone(glycerol to acetone mole ratio to be 1:4) were transferred into 25 mL of round bottem flask and then 10 wt% of catalyst (with respect to glycerol weight) was transferred into reactants mixture.Finally reaction carried at room temperature for 1h under stirring. On completion of reaction time, small amount of methanol was added to the reaction mixture and the product mixture was then seperated from catalyst by centrifuge. The product identification was analyzed by gas chromatography (GC-2014, Shimadzu, column: DB-WAX, 30 m × 0.25 mm × 0.25 µm).

Table S7: Turnover frequency (TOF) values comparison for different catalysts.

Catalyst	**Glycerol conversion (%)**	**Reaction conditions**		**TOF(h^{-1})***	**Ref.**
		Temp.(C)	**Time (min)**		
UiO-66(Hf)(a)	**48.4**	**R.T**	**5**	**13886.9**	**This work (a)**
UiO-66(Zr)	0.7	R.T	5	153.0	This work
UiO-66(Ce)	14.4	R.T	5	3801.0	This work
A-15 [b]	15.0	R.T	30	689	[8]
MoO_3/SiO_2 0.5	0.5	R.T	30	68	[8]
K-10	1.2	R.T	30	236	[8]
H-ZSM-5	1.0	R.T	30	108	[8]
H-Beta	11.5	R.T	30	1656	[8]
$MP-SO_3H-24$	60.5	R.T	30	5682	[8]
$SO_{4}{}_{2-}/ZrO_2$	3.5	R.T	30	687	[8]
$Meso-SnO_2-T-350$(c)	51.3	60 ˚C	30	506	[9]

Meso-SnO$_2$-TF-350 (c)	29.0	60 ˚C	30	420	9
Al-MCM-41 (c)	35.5	60 ˚C	30	154	9
Al-SBA-15 (c)	26.1	60 ˚C	30	142	9
Al-TUD-1(c)	10.2	60 ˚C	30	45	9
Zr-TUD-1(d)	46	80 ˚C	120	339	10
Hf-TUD-1(d)	52	80 ˚C	120	320	10
Al-TUD-1(d)	28	80 ˚C	120	105	10
Sn-MCM-41(d)	42	80 ˚C	120	319	10
USY (d)	36	80 ˚C	120	54	10
Nb$_2$O$_5$-573(e)	73	70 ˚C	120	480	11
AC-S-18M(f)	36	RT	30	153	12
SCS1/0.3(g)	76	70 ˚C	30	39	13
BAIL-1 (h)	63	R.T	30	661	14
SnCl$_2$ [I]	81	25° C	90	59.7	15
H$_2$SO$_4$ [I]	51	25° C	90	33.9	15
PTSA [I]	65	25° C	90	39.3	15
MIL -100(V) [j]	83	25° C	90	70.7	16
Co[II](Co[III]$_{1.25}$ Al$_{0.75}$)O$_4$ [k]	69.2	130 °C	180	139	17
V-MCM-41	84	-	-	10.2	18

[a] **Reaction conditions**: Glycerol = 2.0 g, Acetone = 5.04g, glycerol: acetone = 1:4, catalyst = 0.25wt% (referred to glycerol weight).

[b] **Reaction conditions:** Glycerol = 2.5g, Acetone = 1.6g, Glycerol: acetone = 1:1, catalyst =0.1wt% (referred to glycerol weight).

[c] **Reaction conditions:** glycerol (27 mmol = 2.5 g), acetone (27 mmol = 1.6 g), catalystamount = 0.125g, temp = 60 °C, time = 30 min.

[d] **Reaction conditions:** 1.00 × 10−2 mol of glycerol, 1.00 × 10−2 mol ofacetone (acetone :glycerol = 1 : 1), 1.50 × 10−3 mol of dioxane and 2.00× 10−2 mol of tert-butanol, 25 mg of catalyst (3 wt% relative to glycerol), 2 h at 80 °C.

[e] **Reaction conditions:** Temperature = 343 K, glycerol: acetone =1:1.5, Catalyst = 6.4 wt% (wrt glycerol), Solvent free

[f] **Reaction conditions:** Temperature = room temperature, glycerol: acetone =1: 4, Catalyst = 2.7 wt%.

[g] **Reaction conditions:** Glycerol = 5 g, acetone = 18.91, Glycerol: acetone = 1:6 , Temperature = 70 °C

[h] **Reaction conditions:** Glycerol: acetone = 1:3, Temperature = R.T, Catalyst = 0.4 wt% (w.r.t glycerol)

[I] **Reaction conditions:** 4.79 mmol of glycerol and 19.64 mmol of acetone, 1 mol % of catalyst in 15 ml of CH$_3$CN, 25°C, 90 min

[j] **Reaction conditions:** 4.79 mmol of glycerol and 19.64 mmol of acetone, 2.5wt % of catalyst in 15 ml of CH$_3$CN, 25°C, 90 min

[k] **Reaction condition:** 2 g glycerol, 12.72 g acetone, 0.1 g catalyst, 130 °C, 3 h

TOF (h^{-1}) = Moles of reactant /(Total no. of active sites in catalyst × Time in hour)

4.2. Controlled experiments

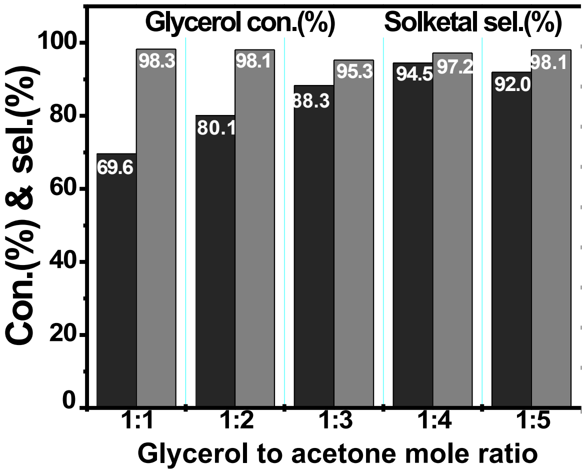


Figure S5: Effect of reactants molar ratio o solketal synthesis over UiO-66(Hf). Reaction conditions: Glycerol = 1.0 g, Acetone =2.52g, Glycerol, catalyst = 10.0 wt% (referred to glycerol weight), reaction carried at R.T for 1h.

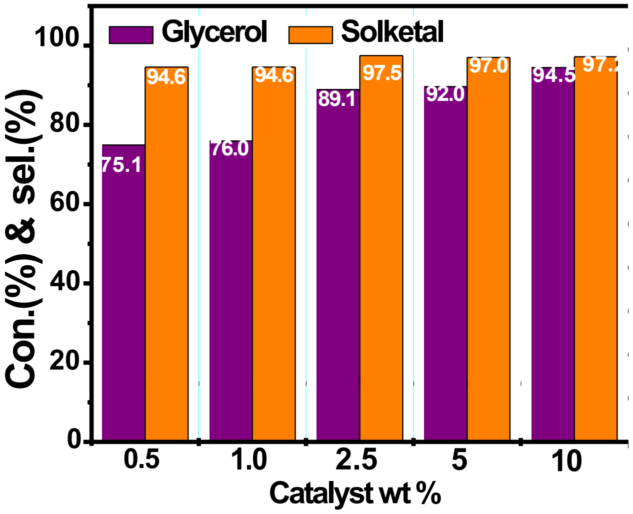


Figure S6: Effect of catalyst weight % on solketal synthesis over UiO-66(Hf). Reaction conditions: Glycerol = 1.0 g, Acetone =2.52g, Glycerol: acetone = 1:4, catalyst = 0.5 wt%, 1.0 wt%, 2.5 wt% and 10.0 wt% (referred to glycerol weight), reaction carried at R.T for 1h.

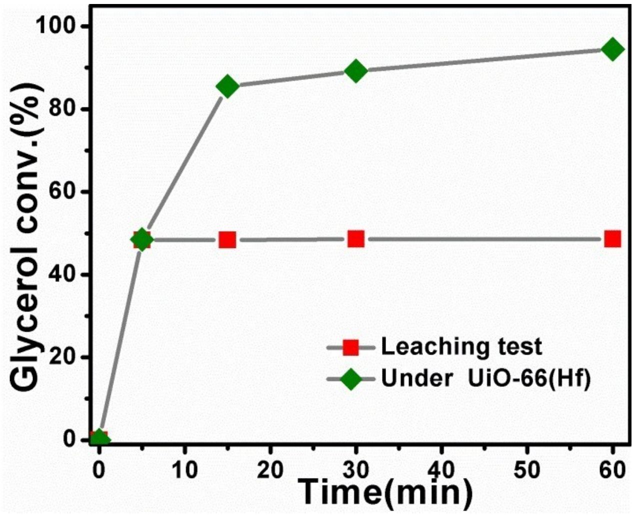


Figure S7: Catalyst heterogeneity (leaching) test for solketal synthesis over UiO-66(Hf). Reaction conditions: Glycerol = 1.0 g, Acetone =2.52g, Glycerol: acetone = 1:4, catalyst =10 wt% (referred to glycerol weight), reaction carried at R.T for 1h.

4.3. Leaching test

Leaching test was carried out in order to test the catalysts heterogeneity. In a typical procedure, glycerol and acetone has taken as 1:4 mole ratios and transferred into 25 mL of round bottom flask and then 10 wt% of catalyst was added into the reactants mixture. And reaction carried at room temperature under stirring for 5 minutes and after completion of reaction the product mixture was isolated from catalyst. The isolated product mixture was carried for reaction without catalyst and reaction samples were collected for 15, 30 min and 1h. Finally, products identification analyzed by gas chromatograms.

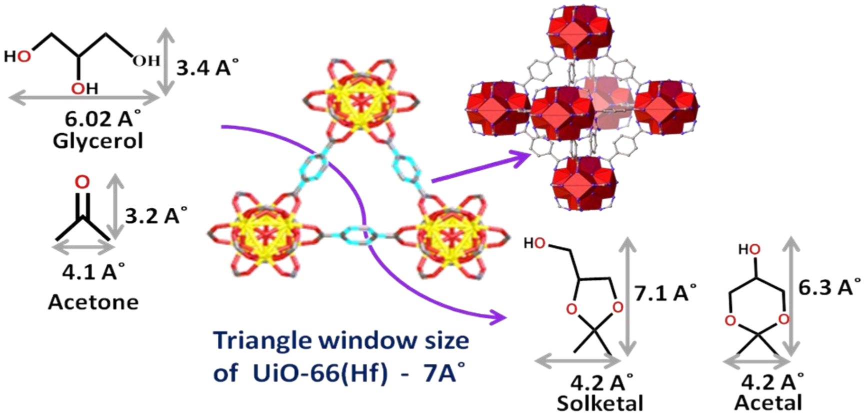
4.4. Recyclability of the catalyst

On completion of reaction, the catalyst was isolated from the reaction mixture using centrifugation. Then, initially the catalyst washed twice with water and four times with methanol in order to remove residuals of reactants/products from the active sites of catalyst. Finally, the catalyst was dried under vacuum at room temperature. The dried catalyst was used for 1st cycle for catalysis by following same procedure of fresh catalyst. And the same procedure followed for all cycles.

4.5. ICP analyses after catalytic reactions

The reaction mixtures were filtered through 0.2 μ syringe filters after completion of reactions. The isolated reaction supernatants were analysed by ICP-OES analysis for Hf, Ce, and Zr metal ions in the respective solutions. We did not observe any detectable amounts (<1 ppm) of these metal ions which confirms that these MOF catalysts were highly stable and the reactions were heterogeneous in nature.

4.7. MOF pore size comparison with the sizes of substrates



Scheme S1: Scheme: Comparison of molecular dimensions of substrates and products with window openings of UiO-66 MOFs in the glycerol acetalization. UiO-66 family of MOFs have tetrahedral (7.5 Å) and octahedral pores (12 Å) with window openings of ~7 Å. In comparison, the substrates glycerol and acetone dimensions are around 3.4 Å X 6.0 Å and 3.2 Å X 4.1 Å respectively. So, the substrates can enter the pores of UiO-66 quite easily. The product dimensions are also well within the sizes of pore/window openings.

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