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Supporting information

Surfactant decorated hydrotalcite-supported polyoxometalates for aerobic oxidation of 5-hydroxymethylfurfural and monosaccharides

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Fig. S8 The Energy-dispersive spectroscopy (EDX) mapping of HPMoV@Mg_4Al-Surf (23)

Fig. S9 The EDAX of Mg_4Al-LDH (a) and HPMoV@Mg_4Al-Surf (5-28) (b-f)

Fig. S10 IR spectra of pyridine adsorption of HPMoV@Mg_nAl-Surf (23) (n = 1-3) (a-c) and HPMoV@Mg_4Al-Surf (5-28) (d-h)

Fig. S11 IR spectra of HPMoV@Mg_4Al-Surf (5-28) (a-e) and HPMoV@Mg_4Al-Surf (5-28) (a1-e1) after absorption of 5-HMF

Fig. S12 The carbon balance for HPMoV, HPMoV@Mg_4Al-LDH (23) and HPMoV@Mg_4Al-Surf (5-28) for oxidation of 5-HMF. Reaction conditions: 100 mg of 5-HMF, 30 mg of catalyst, 4 mL of DMSO, 140 °C, 1.0 MPa of O_2, 12 h

Fig. S13 The generation of CO_2 was determined by GC-MS

Fig. S14 The content of DFF varied with time upon HPMoV, HPMoV@Mg_4Al-LDH (5-28) and HPMoV@Mg_4Al-Surf (5-28) at 140 °C with 1.0 MPa of O_2

Fig. S15 Oxidation of 5-HMF in different solvents under the reaction conditions of 100 mg of 5-HMF, 30 mg of catalyst, and 4 mL of solvent at 140 °C for 12 h with 1.0 MPa of O_2

Fig. S16 Oxidation of 5-HMF under different oxygen pressure. Reaction conditions: 100 mg of 5-HMF, 30 mg of catalyst, and 4 mL of DMSO at 140 °C for 12 h

Fig. S17 Optimization of reaction conditions on 5-HMF conversion at atmospheric O_2 (0.1 MPa) as (a) reaction temperature, (b) reaction time, (c) usage of catalyst on the oxidation of 5-HMF. Reaction conditions: 100 mg of 5-HMF, 4 mL of DMSO

Fig. S18 UV-Vis spectrum of the reaction mixture after separating HPMoV@Mg_4Al-Surf (23)

Fig. S19 The structure characterization of reused HPMoV@Mg_4Al-Surf (23). (a) DR-UV-vis, (b) IR, (c) ^{31}P MAS NMR, (d) XPS, (e) SEM, and (f) HRTEM

Table S1 Oxidation of 5-HMF under various reaction conditions by different catalysts

Table S2 Elementary analysis, BET surface area, acid content and base content for HPMoV, Mg_nAl-LDH and HPMoV@Mg_nAl-Surf (n = 1-4)

Scheme S1 Reaction pathways for production of 5-HMF then to DFF from glucose in presence of multi-functional catalysts

S1. Materials

All chemicals and solvents were purchased from commercial supplies without further purification. In this paper, $H_5PMo_{10}V_2O_{40}$ (HPMoV) were prepared according to the well-established method[1] and characterized by IR spectroscopy. Mg_nAl-LDH (n represents Mg: Al = n: 1) with different proportions of magnesium and aluminum were synthesized according to Ref. [2].

S2. Physical measurements

The elemental analysis was determined by a Leeman Plasma Spec (I) ICP-ES. IR spectra (4000-400 cm^{-1}) were recorded on a Nicolet Magna 560 IR spectrometer (KBr disks). UV-vis spectra (200-800 nm) were performed on a Cary 500 UV-vis-NIR spectrophotometer. DR-UV-vis spectra (200-800 nm) were collected on a UV-2600 UV-vis spectrophotometer (Shimadzu). The structure of samples was characterized using a Japan Rigaku Dmax 2000 X-ray diffractometer with Cu Kα radiation (λ = 0.154178 nm). The ^{31}P MAS NMR were acquired by using a Bruker AM500 spectrometer at 202.5 MHz. XPS spectra were recorded on an Escalab-MK II photoelectronic spectrometer equipped with a micro-focus monochromatic Al Ka X-ray source. SEM micrographs and EDX spectra were obtained using a XL30 ESEM FEG at 25 kV (PhilipsXL-30). EDX was carried out to prove the existence of the Mg, Al, O, P, Mo and V elements. TEM micrographs were measured on a JEM-2100F instrument. Nitrogen adsorption-desorption isotherms and Brunauer-Emmet-Teller (BET) surface area were measured using an ASAP 2010M surface analyzer (the samples were degassed at 100 °C overnight). The acidic and basic properties were detected by a ZDJ-4B automatic potentiometric titrator. The product analysis was detected by using a high-performance liquid chromatography (HPLC) that equipped with a reversed-phase C18 column and a UV detector at the wavelength of 278 nm. Acetonitrile and ultrapure water (V/V = 2: 1) were used as mobile phase with a flow rate of 0.8 mL/min. The total organic carbon (TOC) was measured by a TOC Analyzer (TOC-LCPH, Shimadzu, Japan).

S3. Aerobic oxidation of 5-HMF

Aerobic oxidation of 5-HMF was carried out in Teflon-lined autoclave equipped with a magnetic stirrer. Typically, 100 mg of 5-HMF and 30 mg of catalyst were added into 4 mL of DMSO, then the mixture was heated up to 140 °C. During the reaction, the reactor was maintained at 1.0 MPa of oxygen pressure. After the reaction, the reactor was cooled to room temperature. The catalyst was separated from the mixture by centrifuge, then washed with ethanol several times and dried in oven at 60 °C for 12 h for reuse. Meanwhile, the reused experiment was carried out as the catalyst was separated by centrifuge and reused without any treatment.

$$\text{5-HMF conversion} = \text{moles of converted 5-HMF}/\text{moles of initial 5-HMF} \times 100\ \%$$

$$\text{DFF yield} = \text{moles of DFF}/\text{moles of initial 5-HMF} \times 100\ \%$$

S4. Aerobic oxidation of fructose or glucose

Aerobic oxidation of fructose or glucose was carried out in Teflon-lined autoclave equipped with a magnetic stirrer. In the experiment, fructose or glucose (100 mg) and catalyst 30 mg) were added to 4 mL of DMSO, and the mixture was heated up to 140 °C under 0.8 MPa of O_2. After the reaction, the reactor was cooled to room temperature, then the reused experiment was carried out in accordance with the above method in S3.

S5. Determination of the acidic and basic properties

The total acid content of catalysts was determined by automatic potentiometric titration. 50 mg catalyst was suspended in 50 mL of acetonitrile with stirring vigorously for 3 h. Then the resulting mixture was titrated with the solution of n-butylamine in acetonitrile (0.01 M). The titration end-point could be detected from the potentiometric titration curve and the total acid content of the catalysts could be calculated. IR spectra of pyridine adsorption was used for recognizing the Lewis and Brønsted acid sites. Pyridine was adsorbed by catalysts for 12 h under the condition of vacuum and 60 °C. The capacity of acidity was calculated by Lambert-Beer formula: $A = (\varepsilon \times W \times c)/S$. (A: absorbance, cm^{-1}, ε: extinction coefficient, $m^2 \cdot mol^{-1}$, W: the sample weight, kg, c: the concentration of acid, $mmol \cdot g^{-1}$, S: the sample disk area, m^2). The amount of Lewis and Brønsted acid sites was estimated from the integrated area of the adsorption bands at 1450 and 1540 cm^{-1}, respectively. The base content of the catalysts was measured by using the conductivity titration method. 50 mg catalyst was suspended in 50 mL of diluted 0.001 M HCl with stirring vigorously for 3 h. Then the resulting mixture was titrated with the solution of 0.01 M NaOH. The titration end-point could be detected by a sudden increase in conductivity.

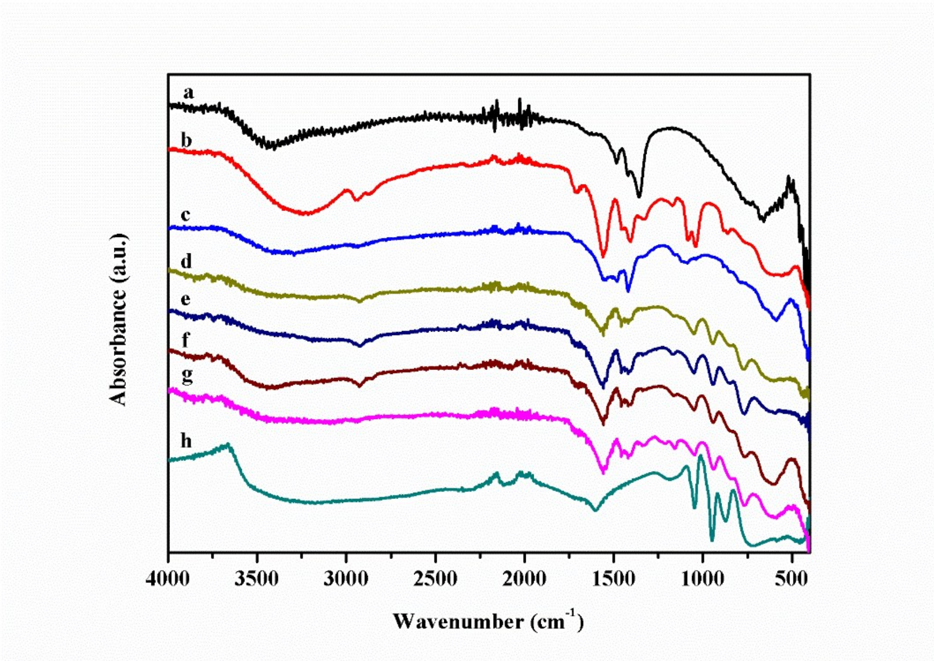


Fig. S1 IR spectra of Mg_4Al-LDH (a), Mg_4Al-COOH (b), Mg_4Al-NH_2 (c), HPMoV@Mg_1Al-Surf (23) (d), HPMoV@Mg_2Al-Surf (23) (e), HPMoV@Mg_3Al-Surf (23) (f), HPMoV@Mg_4Al-Surf (23) (g), and HPMoV (h)

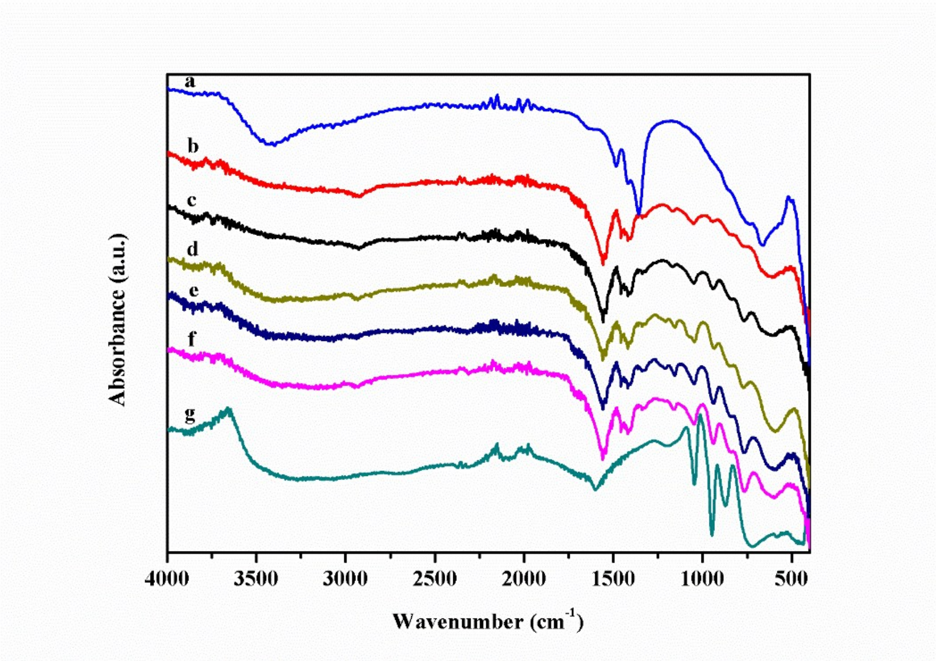


Fig. S2 IR spectra of HPMoV@Mg_4Al-Surf with different loading amount: Mg_4Al-LDH (a), HPMoV@Mg_4Al-Surf (5) (b)， HPMoV@Mg_4Al-Surf (12) (c)， HPMoV@Mg_4Al-Surf (17) (d)， HPMoV@Mg_4Al-Surf (23) (e), HPMoV@Mg_4Al-Surf (28) (f), and HPMoV (g)

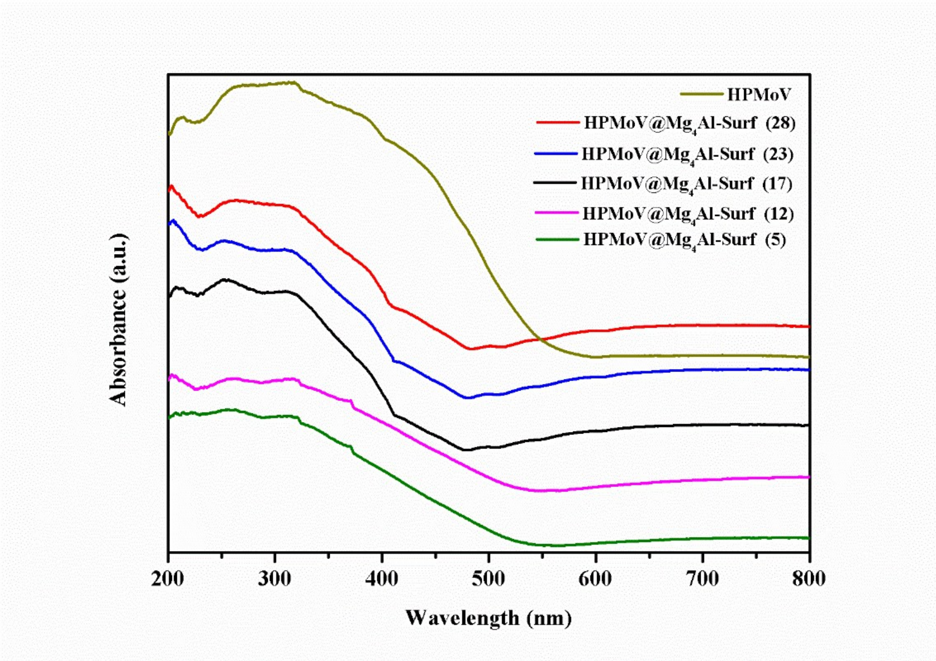


Fig. S3 DR-UV-vis spectra of the HPMoV@Mg_4Al-Surf (5-28)

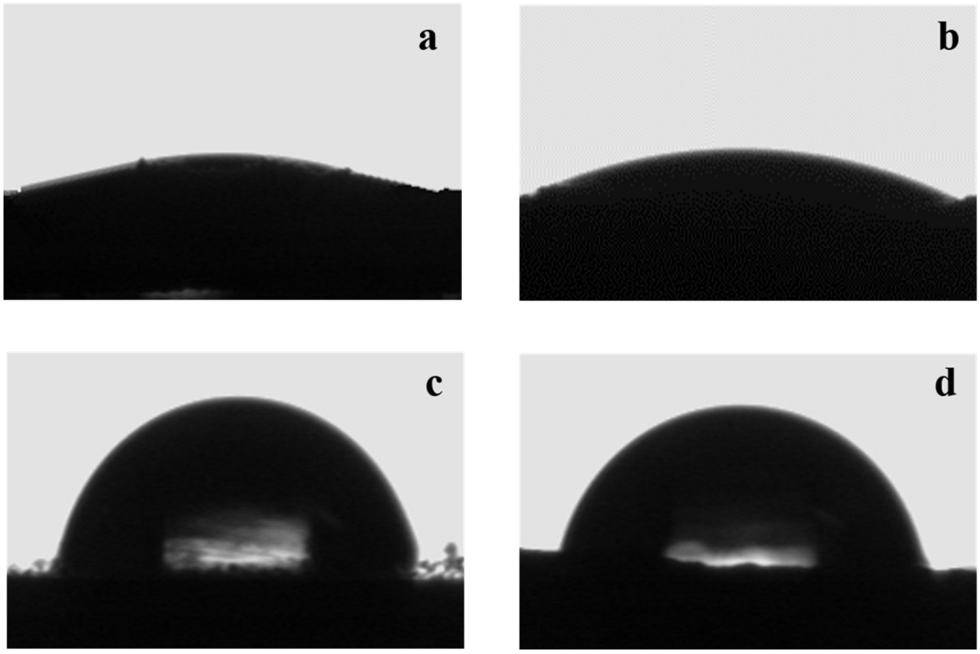


Fig. S4 Water contact angle of Mg_4Al-LDH (a), Mg_4Al-NH_2 (b), Mg_4Al-Surf (c) and HPMoV@Mg_4Al-Surf (23) (d)

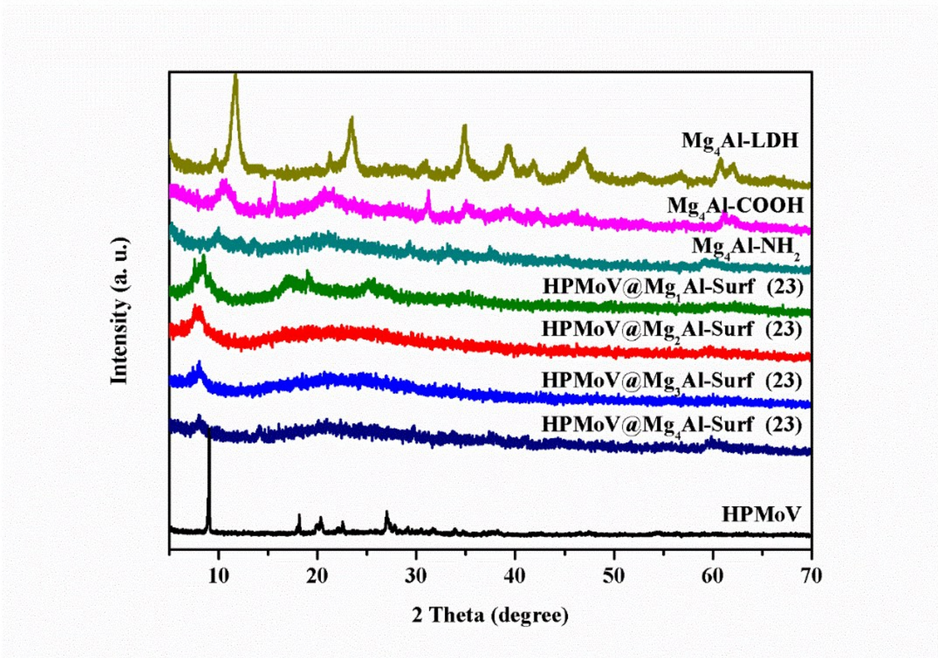


Fig. S5 XRD patterns of Mg_4Al-LDH, Mg_4Al-COOH, Mg_4Al-NH_2, HPMoV@Mg_nAl-Surf (23) (n = 1, 2, 3, 4) and HPMoV

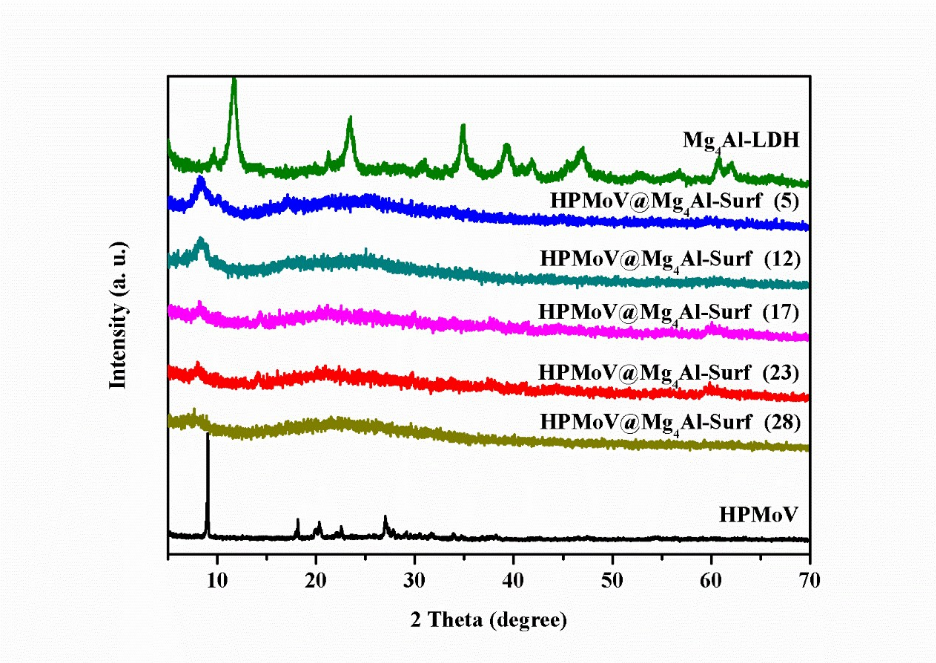


Fig. S6 XRD patterns of Mg_4Al-LDH, HPMoV@Mg_4Al-Surf (5-28) and HPMoV

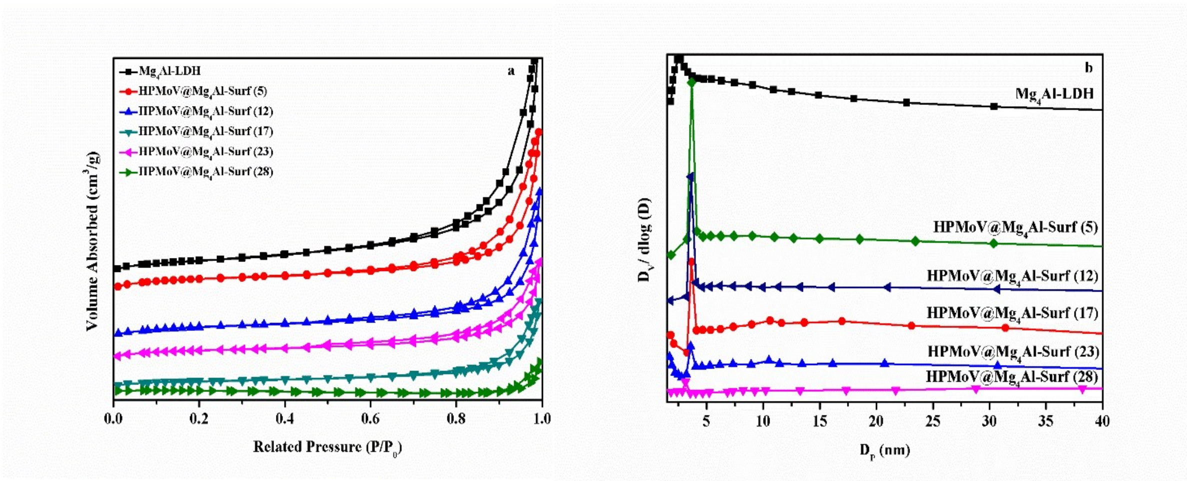


Fig. S7 Nitrogen adsorption-desorption isotherms (a) and pore size distribution profiles according to BJH desorption dV/dD pore volume (b) of Mg_4Al-LDH and HPMoV@Mg_4Al-Surf (5-28)

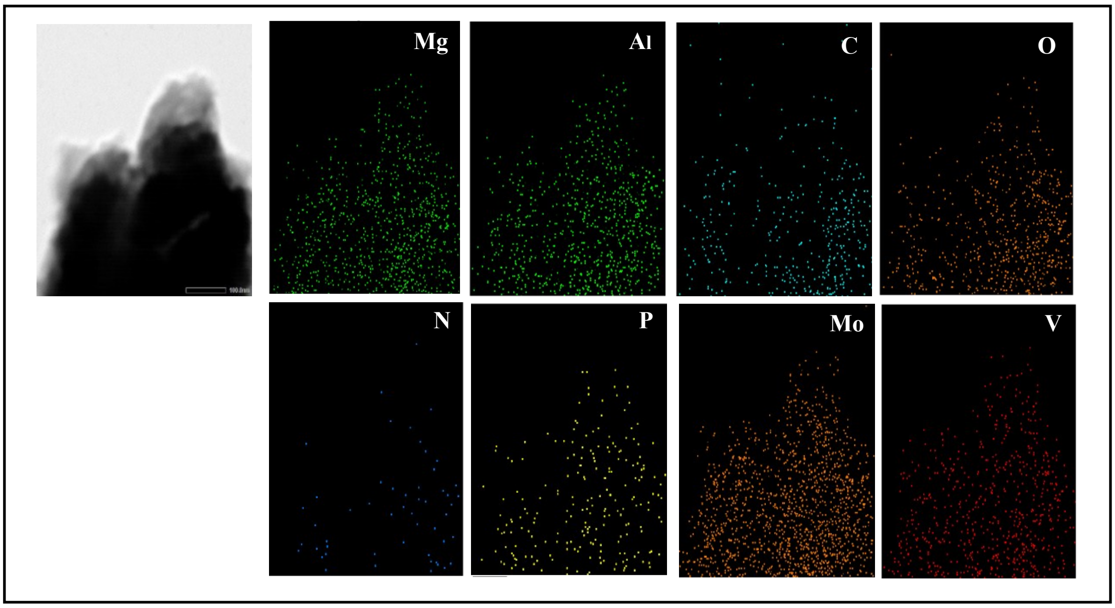


Fig. S8 The Energy-dispersive spectroscopy (EDX) mapping of HPMoV@Mg_4Al-Surf (23)

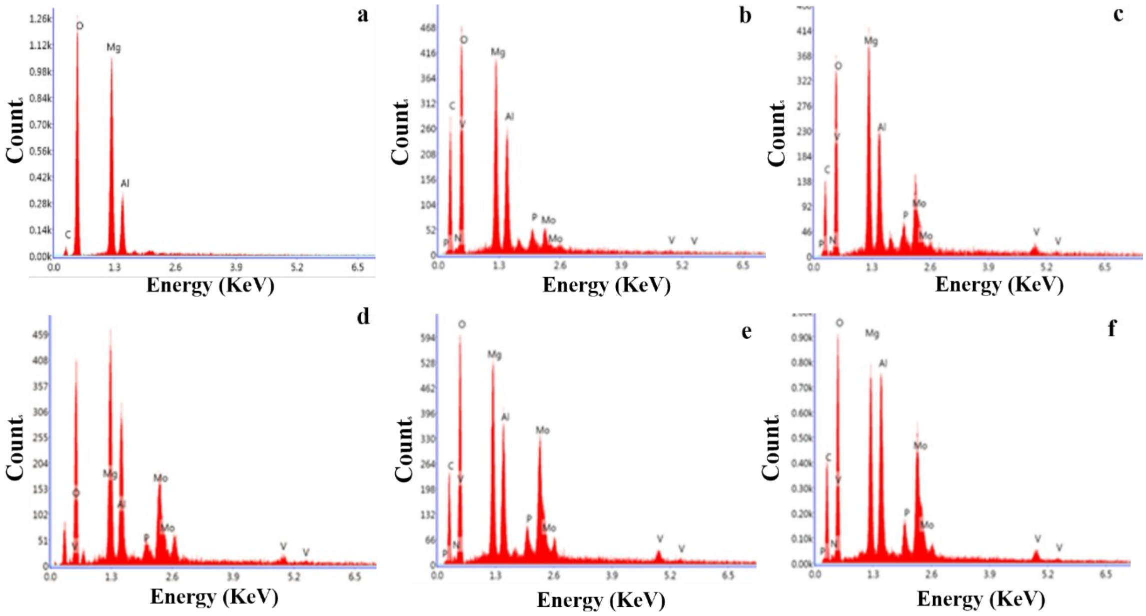


Fig. S9 The EDAX of Mg_4Al-LDH (a) and HPMoV@Mg_4Al-Surf (5-28) (b-f)

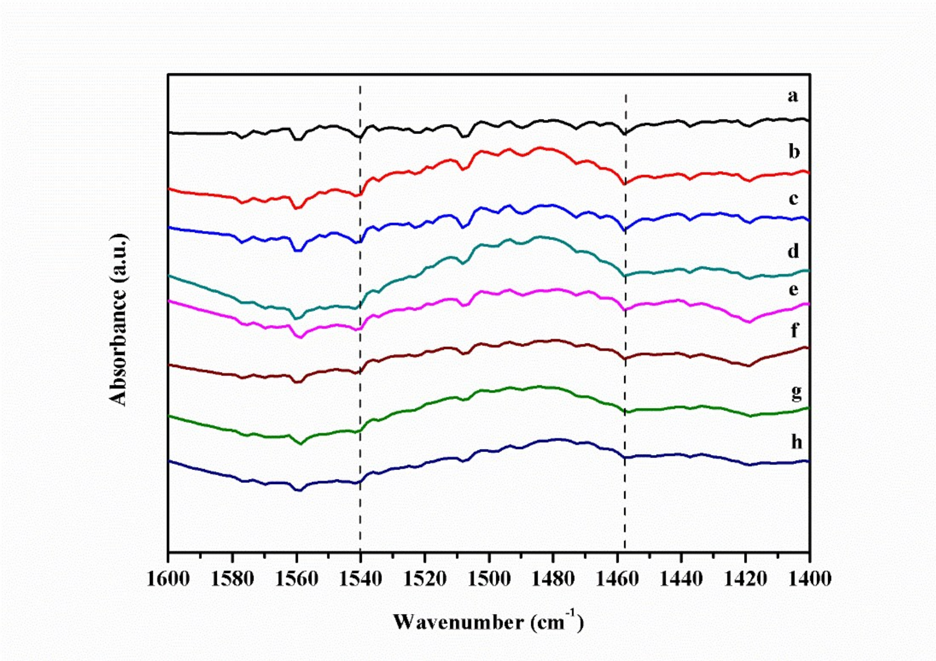


Fig. S10 IR spectra of pyridine adsorption of HPMoV@Mg_nAl-Surf (23) (n = 1-3) (a-c) and HPMoV@Mg_4Al-Surf (5-28) (d-h)

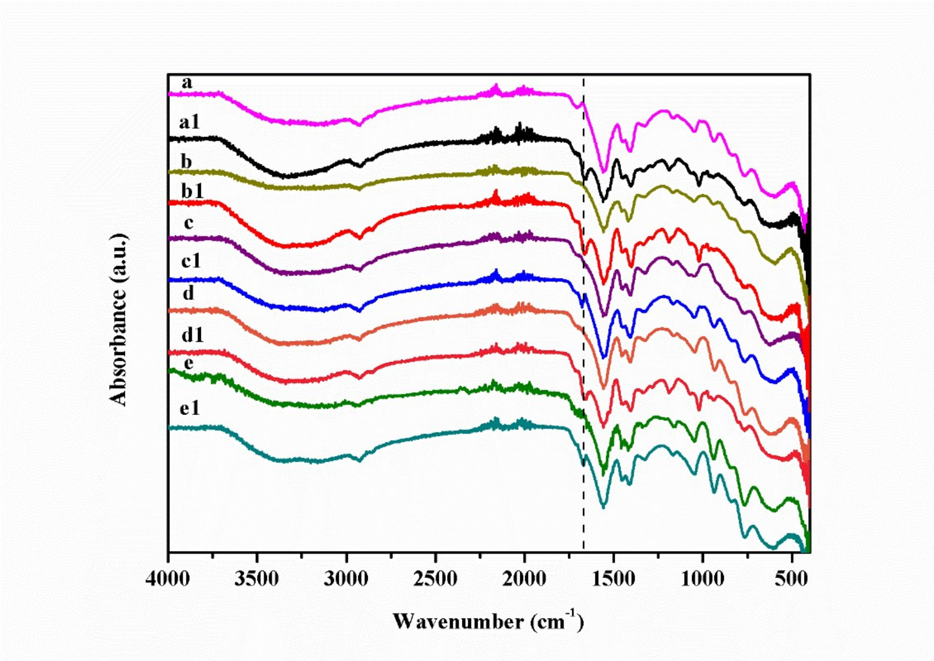


Fig. S11 IR spectra of HPMoV@Mg_4Al-Surf (5-28) (a-e) and HPMoV@Mg_4Al-Surf (5-28) (a1-e1) after absorption of 5-HMF

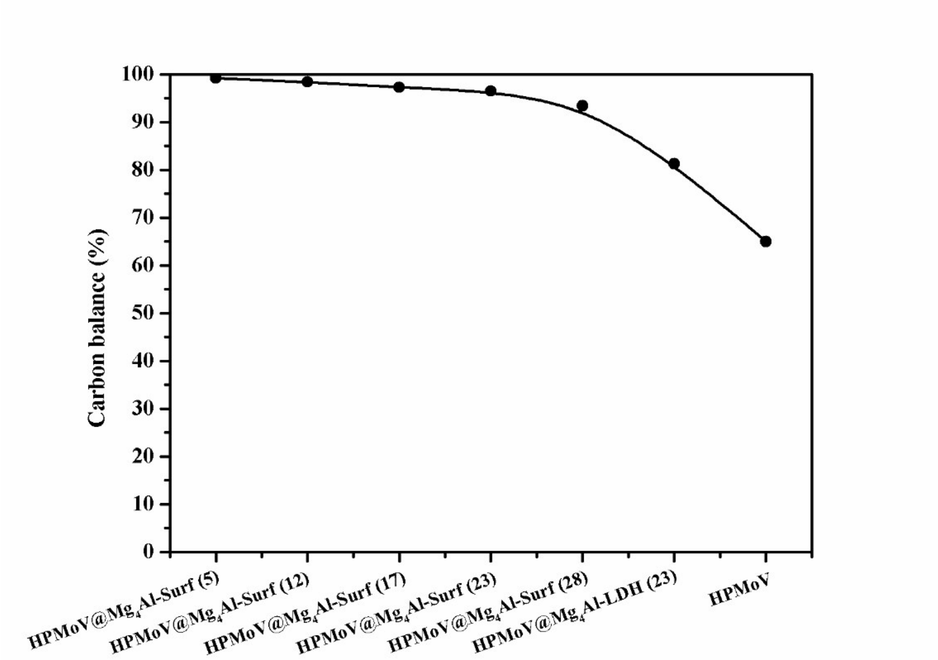


Fig. S12 The carbon balance for HPMoV, HPMoV@Mg_4Al-LDH (23) and HPMoV@Mg_4Al-Surf (5-28) for oxidation of 5-HMF. Reaction conditions: 100 mg of 5-HMF, 30 mg of catalyst, 4 mL of DMSO, 140 °C, 1.0 MPa of O_2, 12 h

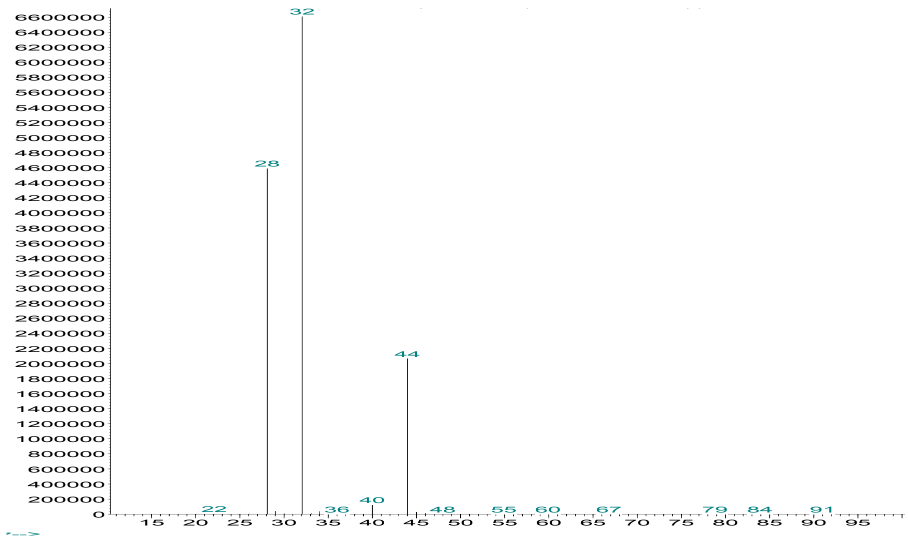


Fig. S13 The generation of CO_2 was determined by GC-MS

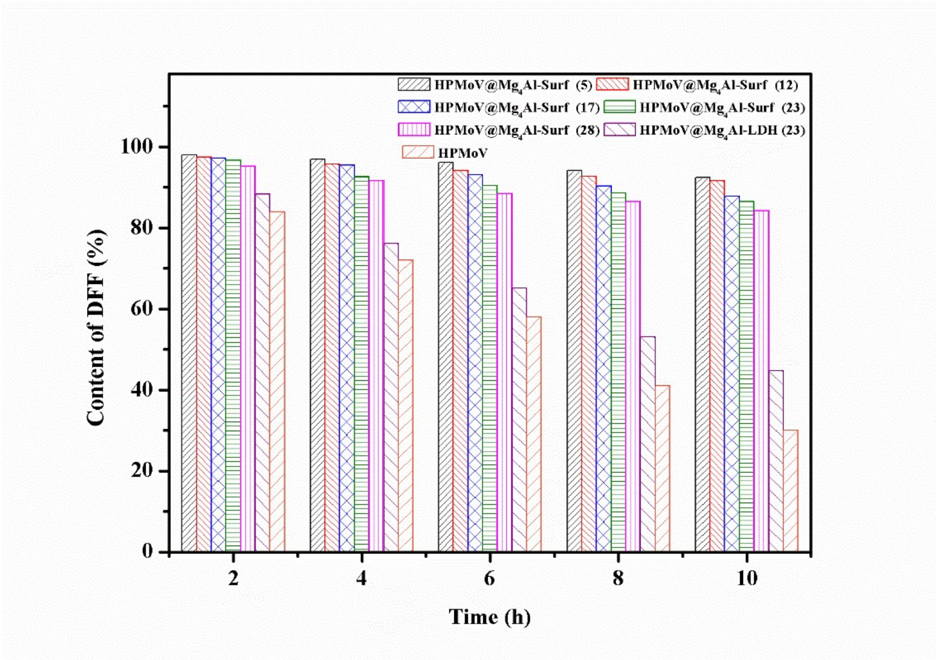


Fig. S14 The content of DFF varied with time upon HPMoV, HPMoV@Mg_4Al-LDH (5-28) and HPMoV@Mg_4Al-Surf (5-28) at 140 °C with 1.0 MPa of O_2

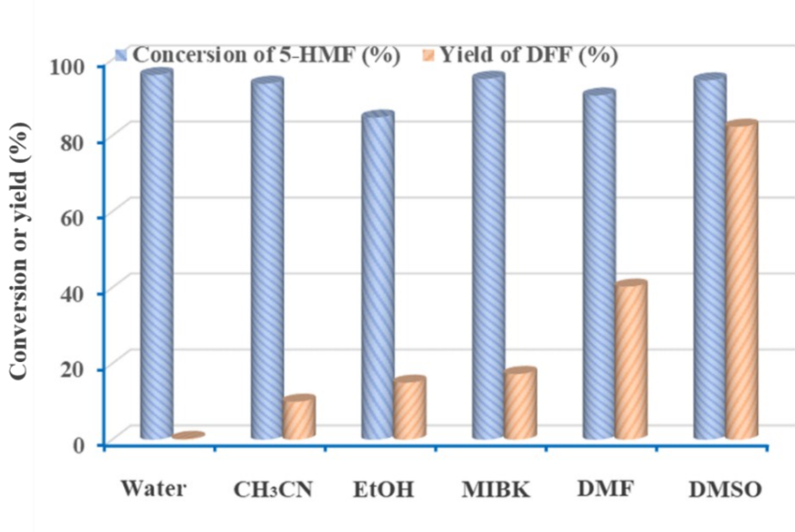


Fig. S15 Oxidation of 5-HMF in different solvents under the reaction conditions of 100 mg of 5-HMF, 30 mg of catalyst, and 4 mL of solvent at 140 °C for 12 h with 1.0 MPa of O_2

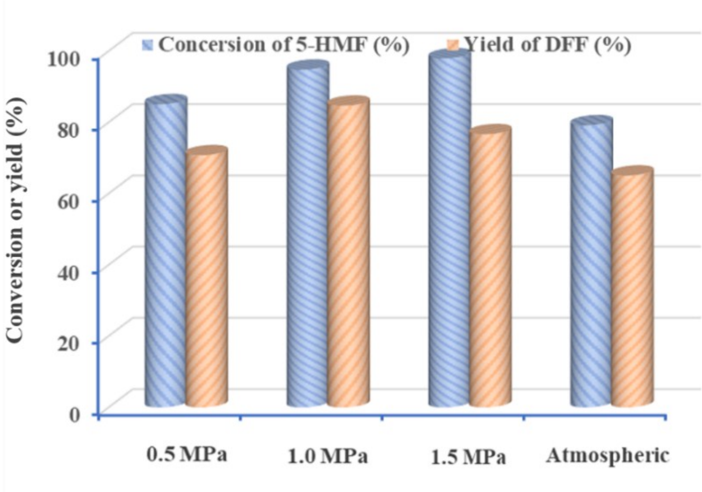


Fig. S16 Oxidation of 5-HMF under different oxygen pressure. Reaction conditions: 100 mg of 5-HMF, 30 mg of catalyst, and 4 mL of DMSO at 140 °C for 12 h

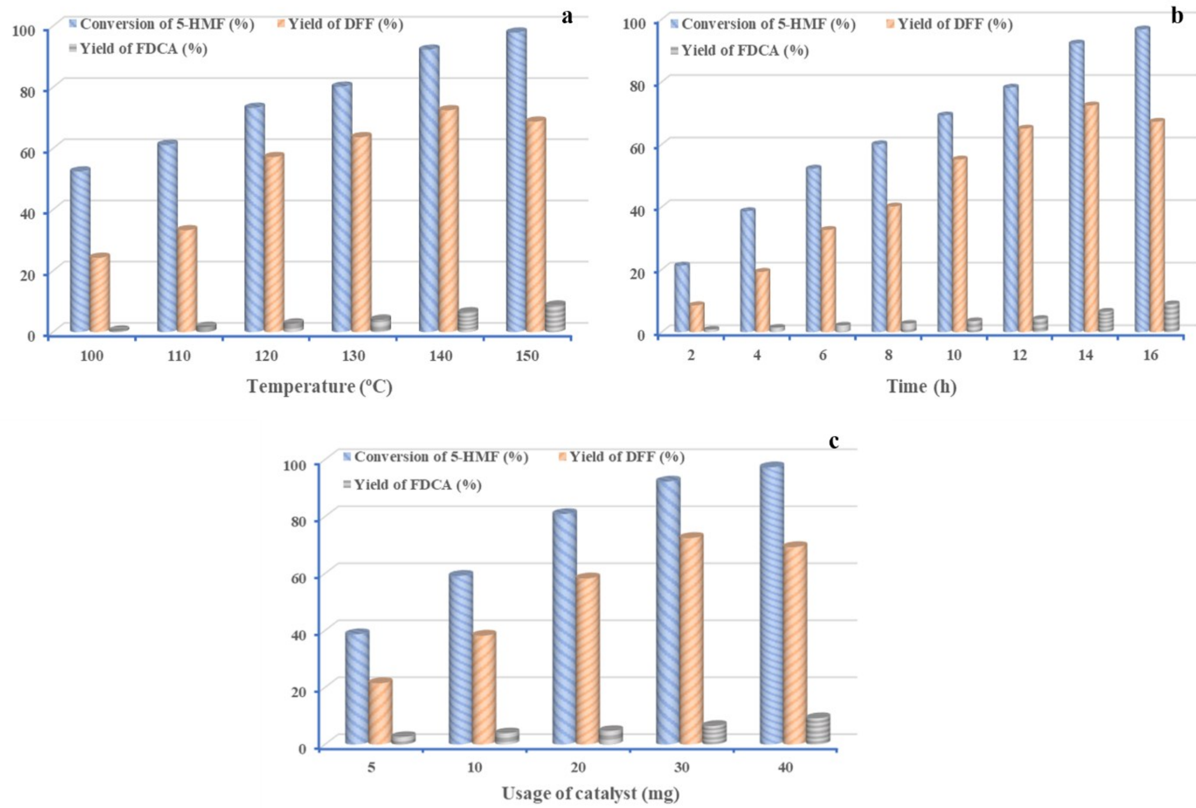


Fig. S17 Optimization of reaction conditions on 5-HMF conversion at atmospheric O_2 (0.1 MPa) as (a) reaction temperature, (b) reaction time, (c) usage of catalyst on the oxidation of 5-HMF. Reaction conditions: 100 mg of 5-HMF, 4 mL of DMSO

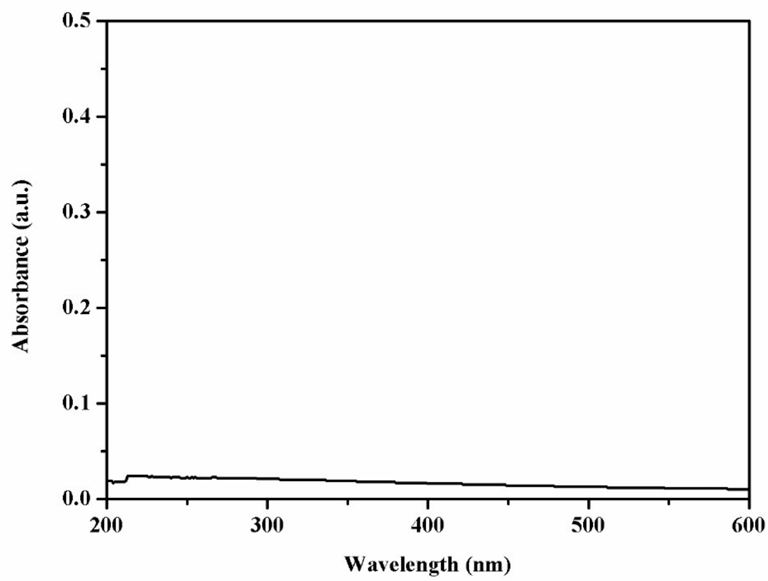


Fig. S18 UV-Vis spectrum of the reaction mixture after separating HPMoV@Mg_4Al-Surf (23)

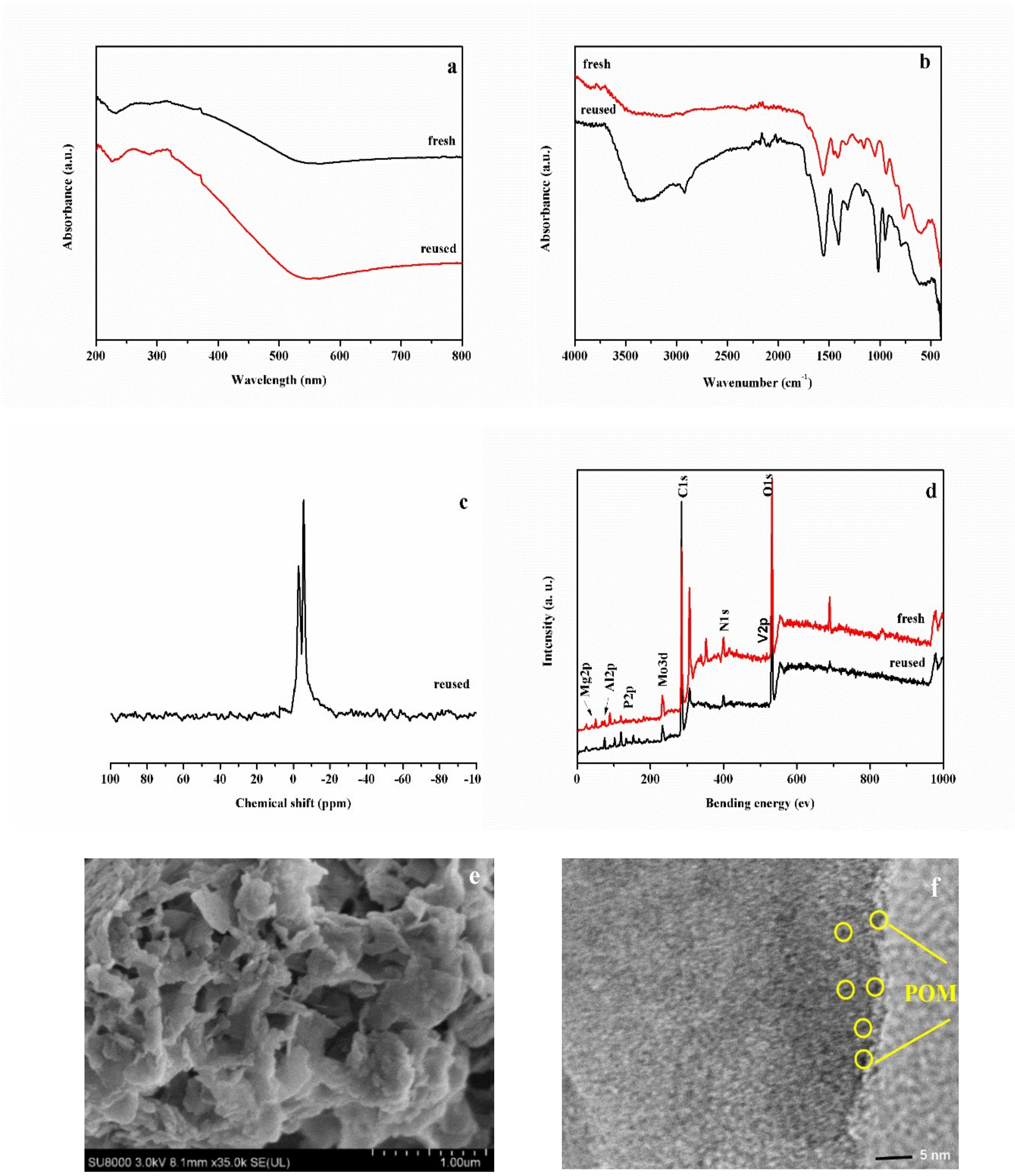


Fig. S19 The structure characterization of reused HPMoV@Mg_4Al-Surf (23). (a) DR-UV-vis, (b) IR, (c) ^{31}P MAS NMR, (d) XPS, (e) SEM, and (f) HRTEM

Table S1 Oxidation of 5-HMF under various reaction conditions by different catalysts

Catalysts	Reaction Condition	Oxidant	T (°C)	Time (h)	Con.%	Yield of DFF %	Yield of FDCA%	Yield of FFCA%	Ref.
$Mn_6Fe_1O_x$	1 mmol HMF, 5 mL DMF	O_2 1.5 MPa	110	5	97	91	-	-	3
Co-Mn/N@C	0.5 mmol HMF, 10 mL H_2O	O_2 1 bar	85	12	99.7	-	96.1		4
Cs/MnO_x	63 mg HMF, 10 mL DMF	O_2 10 bar	100	12	98.4	94.7	-	-	5
Au/HAP	0.2513 g HMF, 20 mL CH_3OH	Air 2.4 MPa	130	6	99.1	-	89.3		6
Pt/Fe_3O_4/rGO	0.50 mmol HMF, 20 mL H_2O	O_2 0.5 MPa	95	0.5	100	-	98		7
MnOx/P25 (TiO_2)	1mmol 5-HMF, 10 g ethanol	Air 30 bar	140	2	33	32	-	-	8
Pd-Au/HT (1 : 4)	200 mg HMF, 50 ml H_2O	O_2 60 mL/min.	60	6	99.9	-	90	-	9
Pt/PVP	0.5 mmol HMF, 10 mL H_2O	O_2 1.0 MPa	110	5	99.9	-	99.9	-	10
Au/CeO_2	0.5 mmol HMF, 20 ml H_2O	O_2 0.5 MPa	130	2.5	99.9	-	90	-	11
Pd/CC	0.1 g HMF， 5 mL H_2O	O_2 20 mL/min	140	30	93	-	85	-	12
MgO·CeO_2	0.14 M 5-HMF, 7 mL H_2O	O_2 0.9 bar	100	9	97.8	96	-		13
Ru/AC	0.3 mmol HMF, 14.5 mL H_2O,	O_2 1 bar	75,	1	100		-	92	14
Au-Ru/rGO	0.5 mmol of HMF, 10 ml toluene,	O_2 5 bar	80	8	90.9	-	-	95.7	15
Pt–Ni/AC-15ALD	0.015 g HMF, 3 mL H_2O	O_2 0.8 MPa	100	15	100	-	97.5	-	16
NiFe-LDH	10 mmol HMF, 1M KOH	-	25	1.5	98	-	98	-	17
NC-T	0.5 mmol HMF, 10 mL acetonitrile	O_2 10 bar	100	4	100	95.1	-	-	18
Ru/ZrO_2	0.5 mmol HMF, 10 mL H_2O	O_2 10 bar	120	16	100	-	97	3	19

2 mmol HMF, O_2

$MnCo_2O_4$	15 mL toluene	1.0 MPa							
Fe_3O_4@SiO_2	0.4 mmol HMF, 5 mL H_2O	O_2 10 bar	110	48	92	-	73.6	-	21
$MnCo_2O_4$	0.2 mmol HMF, 5 mL H_2O	O_2 1 MPa	100	24	99.9	-	70.9	-	22
$MnFe_2O_4$	1 mmol HMF, 20 ml acetonitrile	-	100	5	99	-	85	-	23
Cu/NG, TEMPO	126 mg HMF, 15 mL acetonitrile	O_2 0.4 MPa	70	8	99.8	99.2	-	-	24
$MgO{\cdot}MnO_2{\cdot}CeO_2$	0.015 M 5-HMF, 7 mL of H_2O	O_2 2.0 MPa	110	10	98.9	-	94	-	25
CoPz/g-C_3N_4	100.8 mg HMF, 40 mL buffer solution	Air 20 mL/min	25	14	99.6	-	96.1	-	26
$ZnFe_{1.65}Ru_{0.35}O_4$	0.5 mol HMF, 3 mL DMF	O_2 20 mL/min	110	4	94	82.2	3.4	_	27
Ru/$MnCo_2O_4$	2 mmol HMF, 20 mL H_2O	Air 0.7 MPa	120	10	100	_	99.1	_	28
$Ni_{0.9}Pd_{0.1}$	2 mmol HMF, 10 mL H_2O	O_2 1.0 MPa	80	4	>99	_	86	_	29
Co/Mn/Br	2.2-2.3 mmol HMF, 2.5 mL HOAc	O_2 0.76 MPa	180	1/6	>99	_	92.9	_	30
α-CuV_2O_6	1mol HMF, 4 mL DMSO	O_2 1 bar	130	3	100	99.9	_	_	31
V_2O_5/ceramic	63 mg HMF, 4 mL DMSO	O_2 40 mL/min	140	5	100	87.5	_	_	32
MnO_2	0.2 mmol HMF, 5 mL H_2O	O_2 1.0 MPa	100	24	≥99	_	91	_	33
CC-SO_3H-NH_2	200 mg HMF, 2 mL DMSO	O_2 20 mL/min	140	9	85	85	_	_	34
PMA-MIL-101	0.5 mol HMF, 5 mL DMSO	O_2 20 mL/min	140	20	90.8	88.2	_	_	35
SBA-15-Biimidazole-Ru	0.5 mol HMF 8 mL 4-chlorotoluene	O_2 20 mL/min	110	11	96.9	88.7	_	_	36
Ru/C	1 mmol HMF, 10 mL H_2O	O_2 0.5 MPa	120	10	100	_	88	_	37
Au-Pd/ZOC	0.5 mmol HMF, 10 mL H_2O	O_2 3 bar	80	4	>99	_	>99	_	38

Pd/HT-5	0.4 mmol HMF, 10 mL H_2O	O_2 100mL/min	100	8	100	_	99	_	39
Fe_3O_4@C @Pt	15 mg HMF, 0.2 mmol Na_2CO_3	O_2 100mL/min	90	4	100	_	100	_	40
Pt/C-O-Mg	0.5 mmol HMF, 10 mL H_2O	O_2 1.0 MPa	110	12	100	_	97	_	41
FeCo/C	1mol HMF, 2 mL toluene	O_2 1.0 MPa	100	6	99	99	_	_	42
Co/Mn/Br	13.2 mmol 5-HMF, 5 mL HOAc	N_2/O_2 = 1/1 (mol/mol)	160	0.5	100	_	78.1	_	43
$Bi(NO_3)_3·5H_2O$, cellulose-Cu-NP	126 mg HMF, 10 mL MeCN	Air	80	2	96.5	82	_	_	44
$Ni_3(BTP)_2$	1.8 mmol HMF, 25 mL H_2O	O_2 30 bar	120	24	100	99	_	_	45
SBA-NH_2-VO^{2+} SBA-NH_2-Cu^{2+}	100 mg HMF 7 mL 4-chlorotoluene	O_2 0.28 MPa	110	12	98.8	62.7	_	_	46
V_2O_5	2.0 mmol HMF 10 mL acetic acid	O_2 10 bar	100	4	99	_	_	75	47
N-doped graphene NG-800	1mol HMF, 30 mL acetonitril	O_2 1.0 MPa	100	6	100	99.5	_	_	48
NNC-900	0.63 mmol HMF, 10 mL H_2O	O_2 100mL/min	80	48	100	_	80	_	49
GO	2 mmol HMF, 4 mL DMSO	O_2 20 mL/min	140	24	100	90	_	_	50
$[EMIM]_4Mo_8O_{26}$	9 mmol HMF, 18 mmol NaOH 20 mL H_2O	25 ml 6 % H_2O_2	100	2	96.2	_	92.7	_	51
Ru/CTF	1mmol HMF, 15 mL MTBE	Air 20 bar	80	1	86.3	63.6	_	_	52
Ru/CTF	1mmol HMF, 15 mL H_2O	Air 20 bar	140	3	100	0.1	77.6	_	53
C-Fe_3O_4-Pd	0.4 mmol HMF, 8 mL H_2O	O_2 30 mL/min	80	4	98.2	_	91.8	_	54
Pt/TiO_2	2 g HMF, $NaHCO_3$/5-HMF=2	Air 0.1 MPa	100	6	>99.9	_	>99.9	_	55
Pt/CNT	0.5 mmol HMF,	O_2	90	14	100		98		56

	20 ml H_2O	0.5 MPa								
Polyaniline-VO(acac)$_2$	100 mg HMF, 8 mL 4-chlorotoluene	O_2 20 mL/min	110	12	99.2	86.2	_	_		57
VO_2-PANI/CNT	1mol HMF, 2 mL DMSO	O_2 1.0 MPa	120	11	>99	96	_	_		58
Fe_3O_4-CoO_x	70 mg HMF, 4 mL DMSO	t-BuOOH 0.5 mL	80	15	97.2	_	68.6	_		59
GO	1mol HMF, 30 mL acetonitrile	_	100	18	100	99.6	_	_		60
GO_{ase} $M_{3\text{-}5}$ PaoABC	0.3 mmol 5-HMF, 0.3 mL MeCN	Air 1.0 MPa	37	10	100	_	86.9	_		61
$Cs_3HPMo_{11}VO_{40}$	1mol 5-HMF, 2 mL DMSO	O_2 0.8 MPa	110	6	99	99	-	-		62
Au-Pd/CNT	0.50 mmol HMF, 20 mL H_2O	O_2 0.5 MPa	100	12	99	-	99	-		63
Ag-OMS-2	315 mg HMF, 40 mL isopropyl alcohol	Air 15 atm	165	6	99	99	-	-		64
FeIII–POP-1	1.58 mmol HMF, 10 ml H_2O	Air 10 bar	100	10	100	-	79	-		65
K-OMS-2	100 mg HMF, 3 mL DMSO	O_2 10 mL/min	110	6	99	99	-	-		66
Au/HT	1 mmol HMF, 6 ml H_2O	O_2 50 mL/min	95	7	99	-	99	-		67
Fe_3O_4/Mn_3O_4	126 mg HMF, 7 mL DMF	O_2 20 mL/min	120	4	99.8	82.1	-	-		68
RuCo(OH)$_2$-CeO_2	126 mg HMF, 7 mL MIBK	O_2 20 mL/min	120	12	96.5	82.6	8.9	-		69
Ru/hydroxyapatite	100 mg HMF, 7 mL 4-chlorotoluene	O_2 20 mL/min	90	4	100	89.1	9.3	-		70

Table S2 Elementary analysis, BET surface area, acid content and base content for HPMoV, Mg_nAl-LDH and HPMoV@Mg_nAl-Surf (n = 1-4)

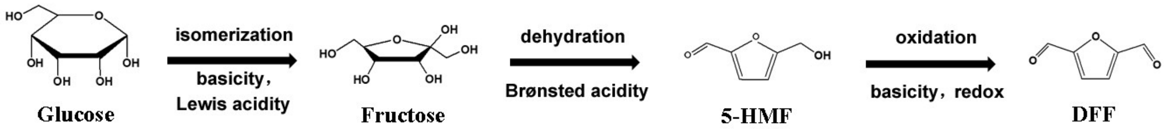
Catalyst	Elementary results (calculated values in parenthesis)[a]/%					Loading amount wt %	S_{BET} (m^2/g)	Acidity (mmol/g)			Basicity[d] (mmol/g)
	P	Mo	V	Al	Mg			Total acidity[b] (mmol/g)	B-acidity[c] (mmol/g)	L-acidity[c] (mmol/g)	
HPMoV	1.80	55.20	5.85	-	-	-	3.90	2.66	2.60	-	-
Mg_1Al-LDH	-	-	-	18.03	16.31	-	78.5	0.21	-	0.20	0.68
Mg_2Al-LDH	-	-	-	13.02	23.38	-	75.4	0.18	-	0.17	0.74
Mg_3Al-LDH	-	-	-	10.09	27.45	-	71.2	0.16	-	0.14	0.86
Mg_4Al-LDH	-	-	-	8.31	30.00	-	68.6	0.12	-	0.11	0.94
HPMoV@Mg_1Al-Surf (23)	0.59	18.04	1.93	8.82	7.95	23.0	36.0	0.73	0.51	0.16	0.11
HPMoV@Mg_2Al-Surf (23)	0.63	19.98	2.13	4.92	8.83	23.0	32.6	0.70	0.50	0.14	0.13
HPMoV@Mg_3Al-Surf (23)	0.59	18.70	2.01	4.63	12.35	23.0	29.5	0.67	0.51	0.11	0.14
HPMoV@Mg_4Al-Surf (5)	0.19	5.42	0.54	6.10	21.92	5.0	45.4	0.21	0.08	0.10	0.56
HPMoV@Mg_4Al-Surf (12)	0.38	11.39	0.23	5.38	19.25	12.0	38.0	0.37	0.22	0.09	0.42
HPMoV@Mg_4Al-Surf (17)	0.49	14.85	1.57	4.95	17.76	17.0	33.6	0.47	0.34	0.08	0.28
HPMoV@Mg_4Al-Surf (23)	0.57	18.35	1.98	4.52	16.19	23.0	23.4	0.62	0.51	0.07	0.20
HPMoV@Mg_4Al-Surf (28)	0.71	20.85	2.23	4.21	15.08	28.0	13.4	0.68	0.57	0.06	0.13

[a]The elementary results were calculated by the ICP-AES.

[b]The total acidity was measured by potentiometric titration.

[c]The B and L acidity were valued by the IR spectra of adsorbed pyridine and calculated by Lambert-Beer equation.

[d]The basicity was measured by conductivity titration method.



Scheme S1 Reaction pathways for production of 5-HMF then to DFF from glucose in presence of multi-functional catalysts

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