

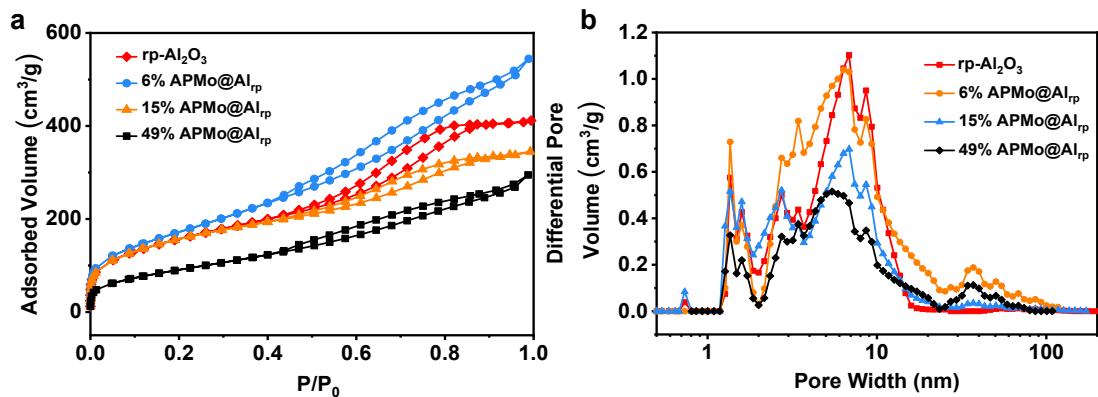
## Supporting Information

### Pentacoordinated Al<sup>3+</sup> stabilized polyoxometalates for the efficient catalytic valorization of biomass-derived feedstocks

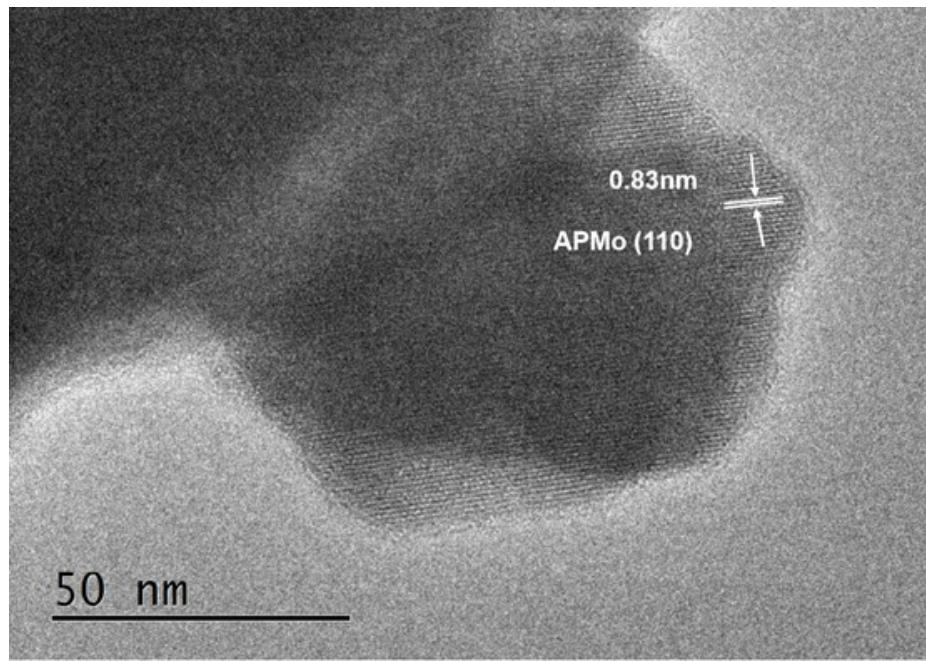
Lihua Wang<sup>a</sup>, Shuangxiu Ma<sup>a</sup>, Chunhong Chen<sup>a</sup>, Bing Lu<sup>a</sup>, Zhe Wang<sup>a</sup>, Yong Wang<sup>a</sup>, and Shanjun Mao<sup>\*a</sup>

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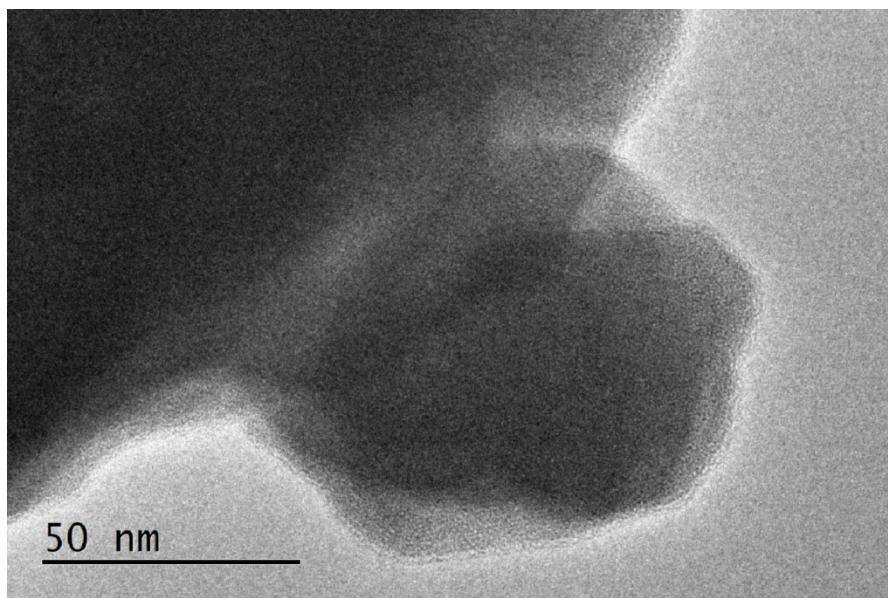
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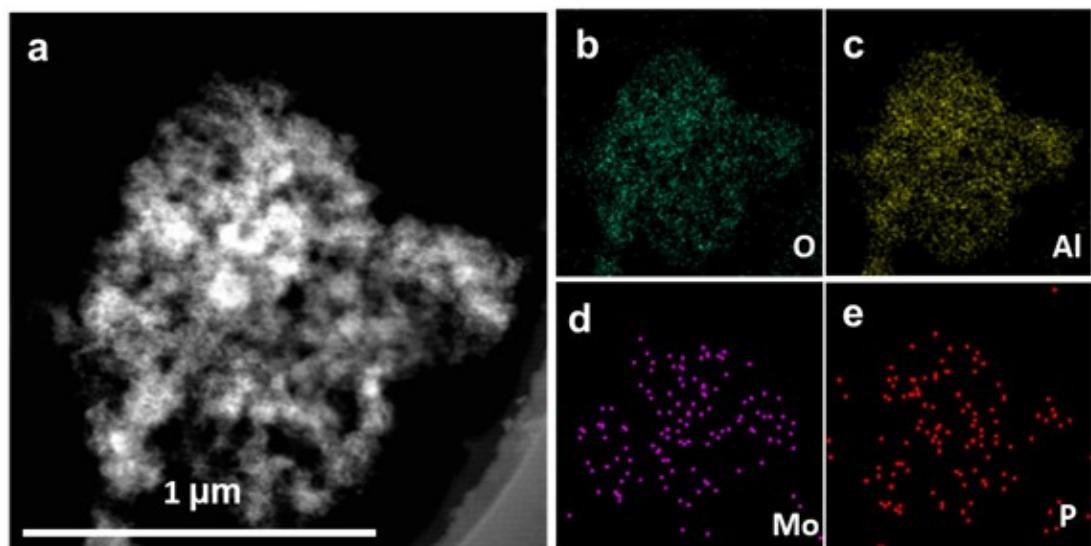
**Fig. S1.** (a)  $\text{N}_2$  adsorption and desorption isotherms, and (b) Pore size distributions of the catalysts.



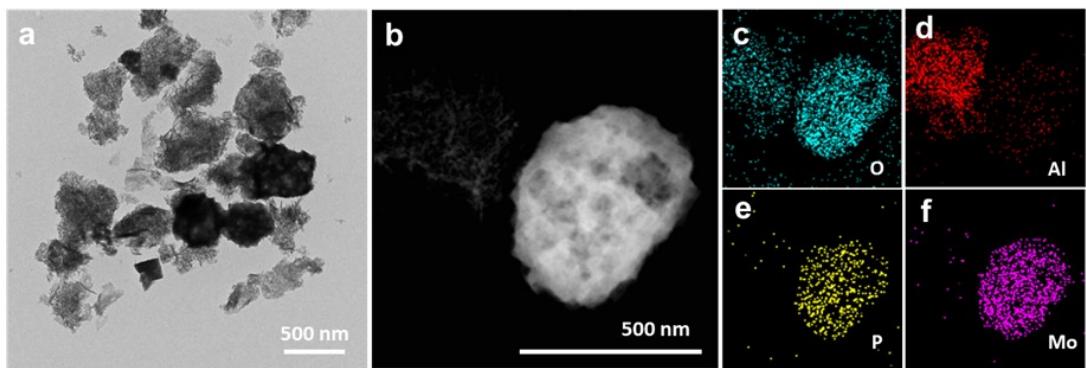
**Fig. S2.** HRTEM image of pure APMo.



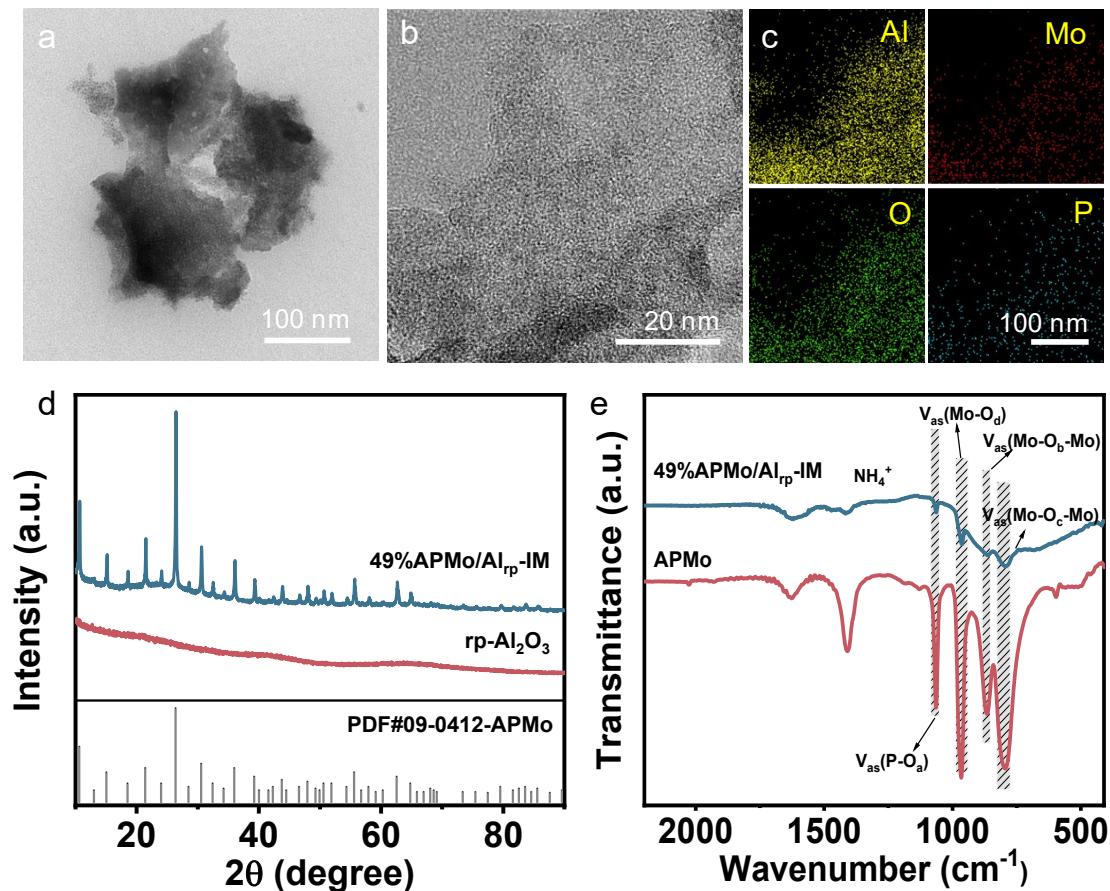
**Fig. S3.** HRTEM image of pure APMo after a few seconds. The lattice fringes disappear.



**Fig. S4.** (a-e) HAADF-STEM image and corresponding EDS maps of 12%APMo@Al<sub>rp</sub> for O, Al, P, and Mo.

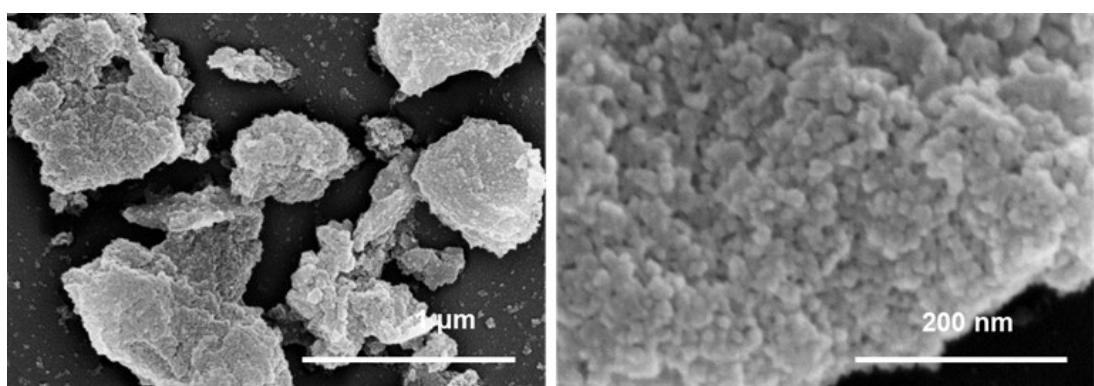


**Fig. S5.** (a)TEM image of 49%APMo/Al<sub>2</sub>O<sub>3</sub>-IM, (b-f) HAADF-STEM image and corresponding EDS maps of 49%APMo/Al<sub>2</sub>O<sub>3</sub>-IM for O, Al, P, and Mo.

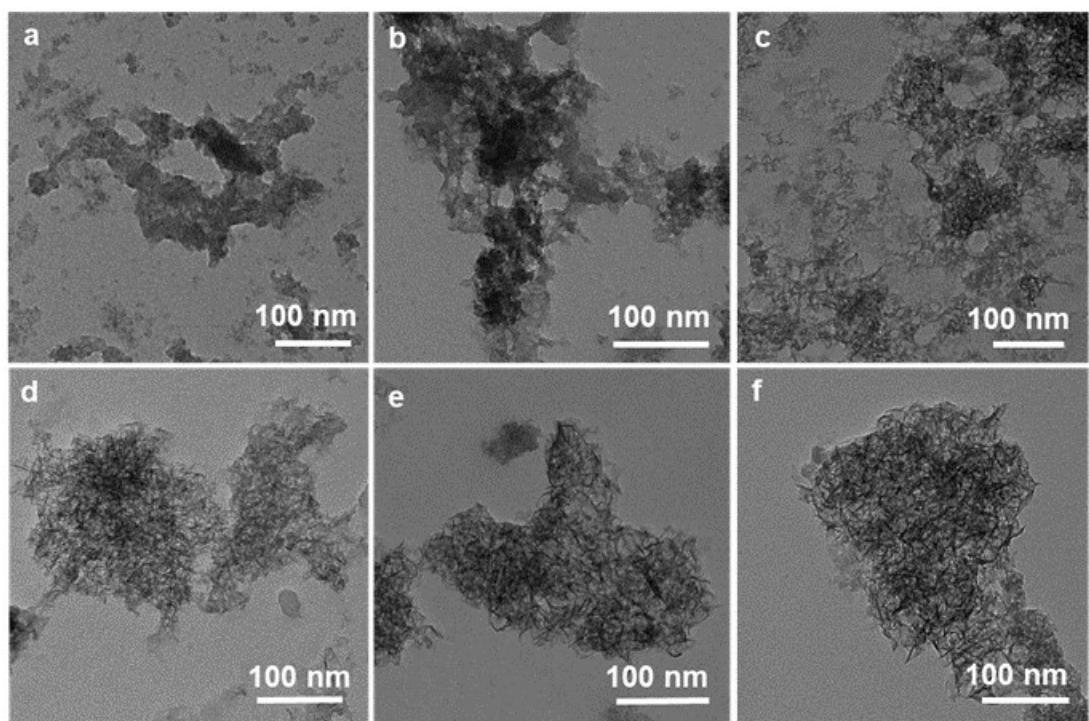


**Fig. S6.** (a)TEM, (b) HRTEM images, and (c) EDS maps of 49%APMo/Al<sub>rp</sub>-IM for Al, Mo, O, and P. (d) XRD patterns and (e) FT-IR spectra of 49%APMo/Al<sub>rp</sub>-IM.

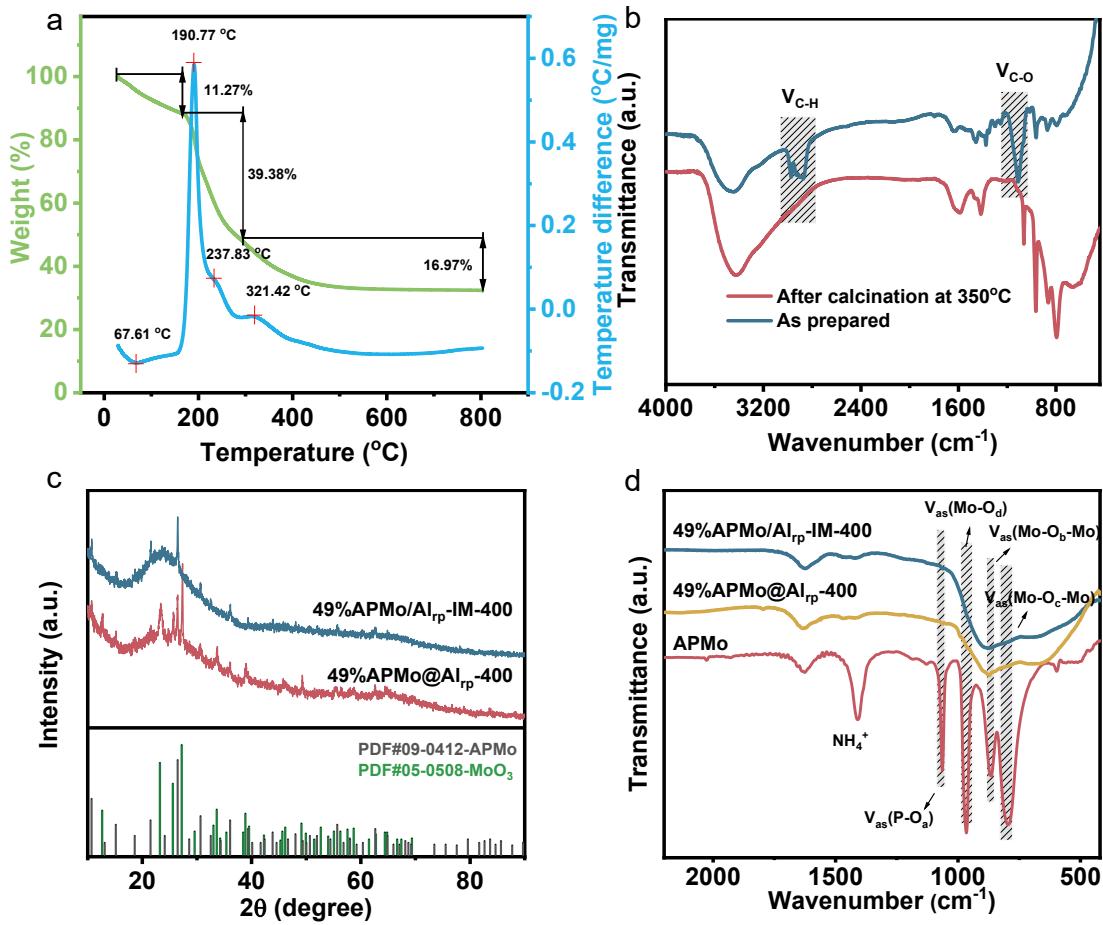
49%APMo/Al<sub>rp</sub>-IM exhibits irregular morphology with uniform distribution of Al, O, Mo, and P elements. Powder X-ray diffraction (XRD) shows peaks assigned to the parent crystalline APMo (JCPDS No. 09-0412), proving the successful loading of APMo along with the FT-IR results exhibiting finger-print peaks of APMo.



**Fig. S7.** SEM images of rp-Al<sub>2</sub>O<sub>3</sub>.

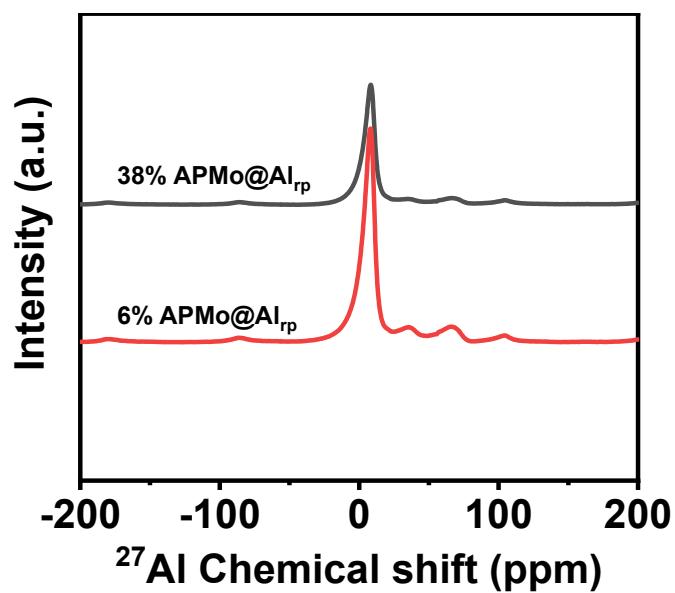


**Fig. S8.** TEM images of n%APMo@Al<sub>rp</sub> (n=0, 2, 6, 15, 38, 49).

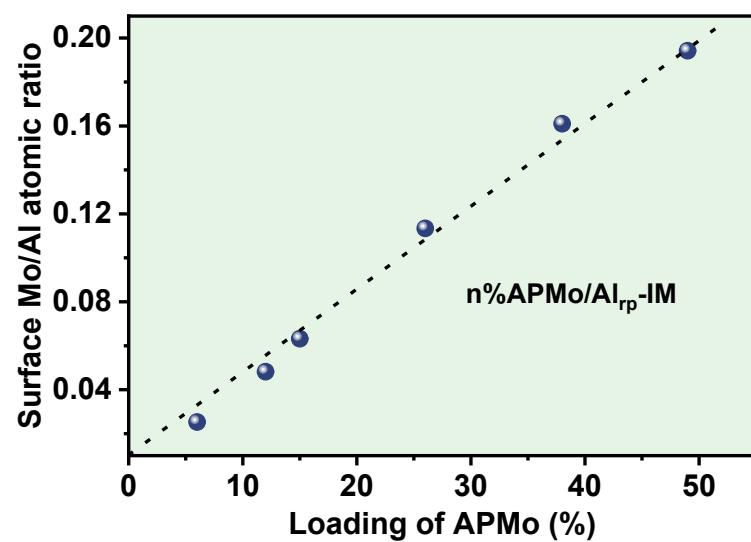


**Fig. S9.** (a) TGA-DTA curves of as-prepared 49%APMo@Al<sub>rp</sub>. (b) FT-IR spectra of as-prepared and calcined 49%APMo@Al<sub>rp</sub>. XRD patterns (c) and FT-IR spectra (d) of 49%APMo@Al<sub>rp</sub> and 49%APMo/Al<sub>rp</sub>-IM calcined at 400 °C.

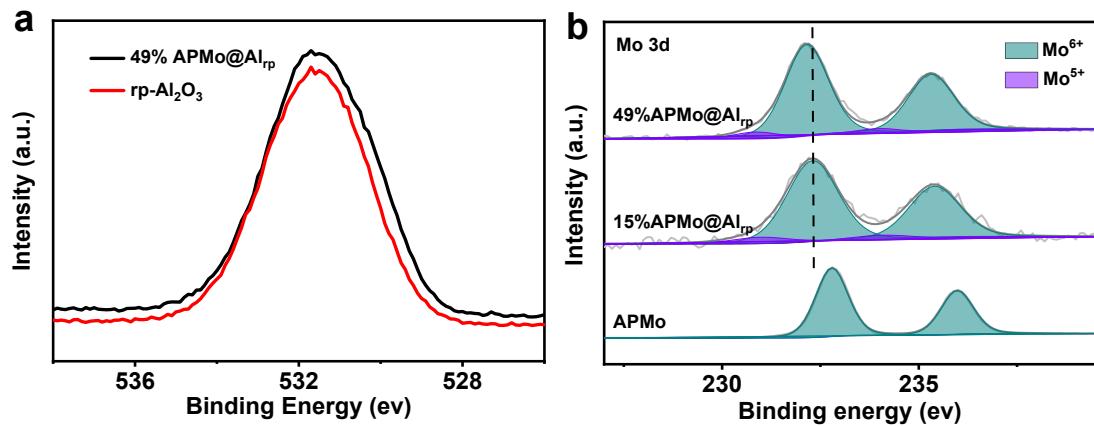
The obvious exothermic peaks at 190.77 °C and 237.83 °C are attributed to the composition of P123, accompanied with significant weight loss (**Fig. S9a**). After calcination at 350 °C, the identical C-O stretching vibration bands (1000-1125 cm<sup>-1</sup>) and C-H symmetrical and asymmetric stretching vibration bands (2876 and 2930 cm<sup>-1</sup> respectively) of isopropanol and P123 disappeared<sup>1</sup> (**Fig. S9b**), implying the removal of isopropanol and P123. Further increasing the calcination temperature to 400 °C, APMo would decompose to produce MoO<sub>3</sub> species (**Fig. S9c**), with the disappearance of FT-IR finger-print peaks (**Fig. S9d**).



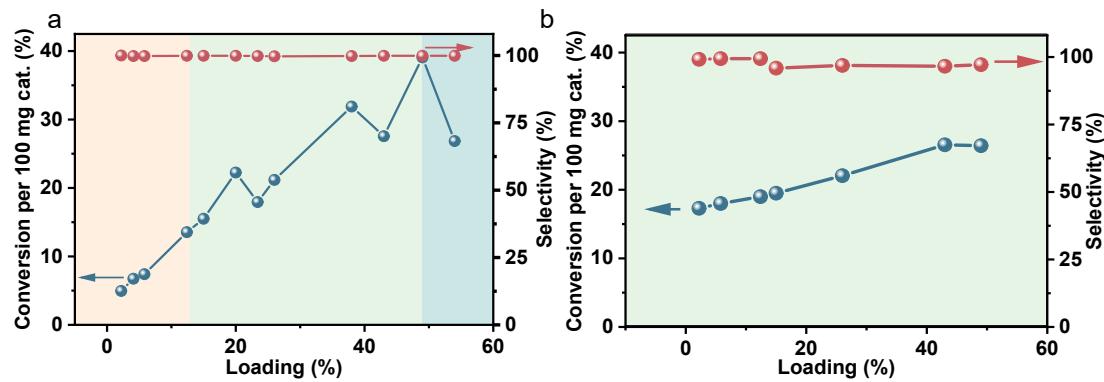
**Fig. S10.**  $^{27}\text{Al}$  MAS NMR spectra of 6%APMo@Al<sub>rp</sub> and 38%APMo@Al<sub>rp</sub>.



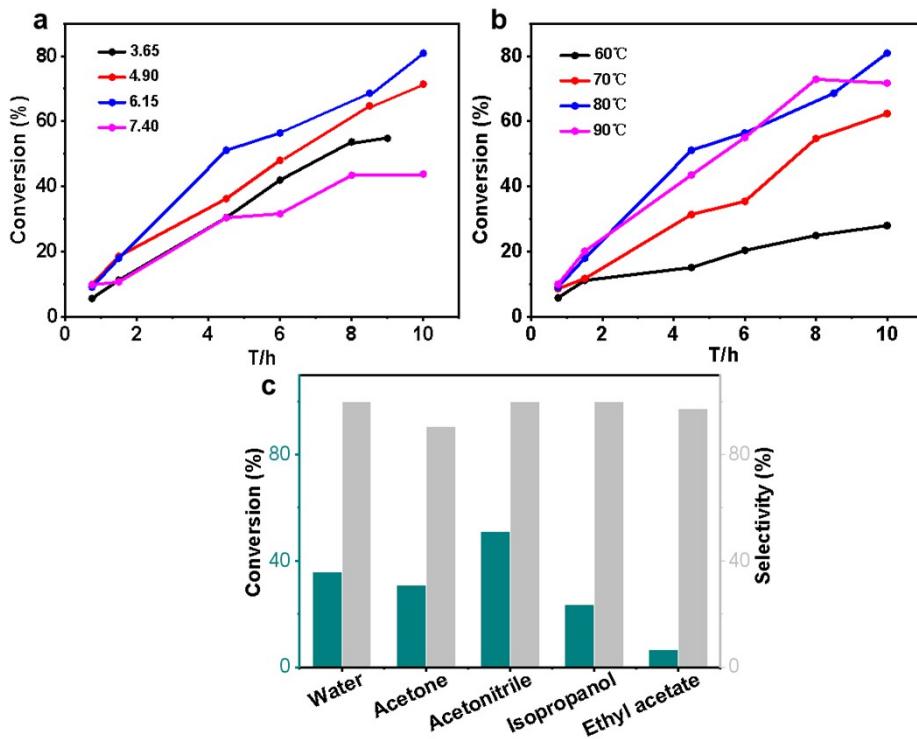
**Fig. S11.** XPS-measured surface Mo/Al atomic ratios of n%APMo/Al<sub>rp</sub>-IM.



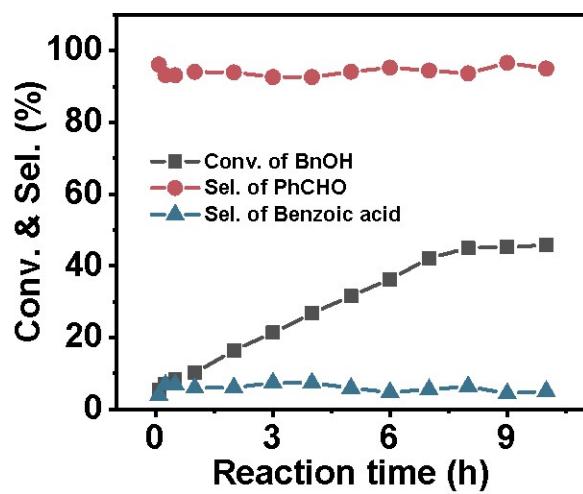
**Fig. S12.** (a-b) XPS spectra of 49%APMo@Al<sub>rp</sub>, 15%APMo@Al<sub>rp</sub>, APMo, and rp- Al<sub>2</sub>O<sub>3</sub>. High-resolution spectra for the O 1s peak (a), Mo 3d peak (b).



**Fig. S13.** (a-b) Conversion and selectivity of benzyl alcohol oxidation per 100 mg catalyst for n%APMo@Al<sub>rp</sub> (a), and n%APMo/Al<sub>2</sub>O<sub>3</sub>-IM (b) as a function of APMo loading (%). Reaction conditions: 100 mg catalyst, 5 mL CH<sub>3</sub>CN, 3.10 mL 30% H<sub>2</sub>O<sub>2</sub>, 2 mmol Benzyl alcohol, 80 °C, 4 h.



**Fig. S14.** Conversion of benzyl alcohol oxidation versus time with different volume of 30%H<sub>2</sub>O<sub>2</sub> (a) and different temperatures (b) with 49%APMo@Al<sub>rp</sub>, (c) conversion and selectivity with different solvents.



**Fig. S15.** Reaction kinetic curves of 49%APMo/Al<sub>rp</sub>-IM. Reaction conditions: 100 mg catalyst, 5 mL CH<sub>3</sub>CN, 6.15 mL 30% H<sub>2</sub>O<sub>2</sub>, 4 mmol Benzyl alcohol, 80 °C, 10 h.

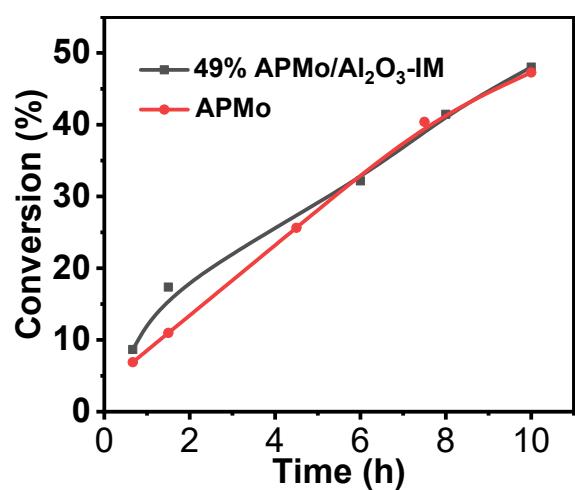


Fig. S16. Reaction kinetics curve of 49%APMo/Al<sub>2</sub>O<sub>3</sub>-IM and pure APMo.

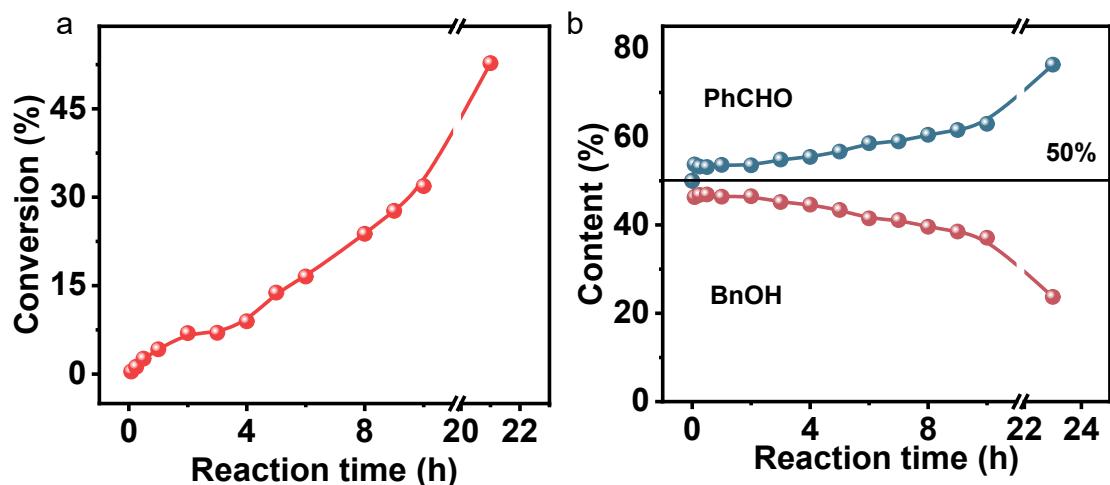
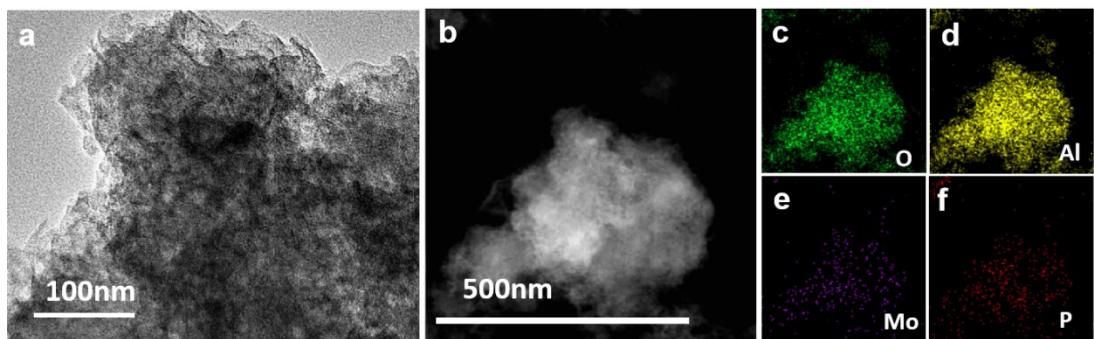
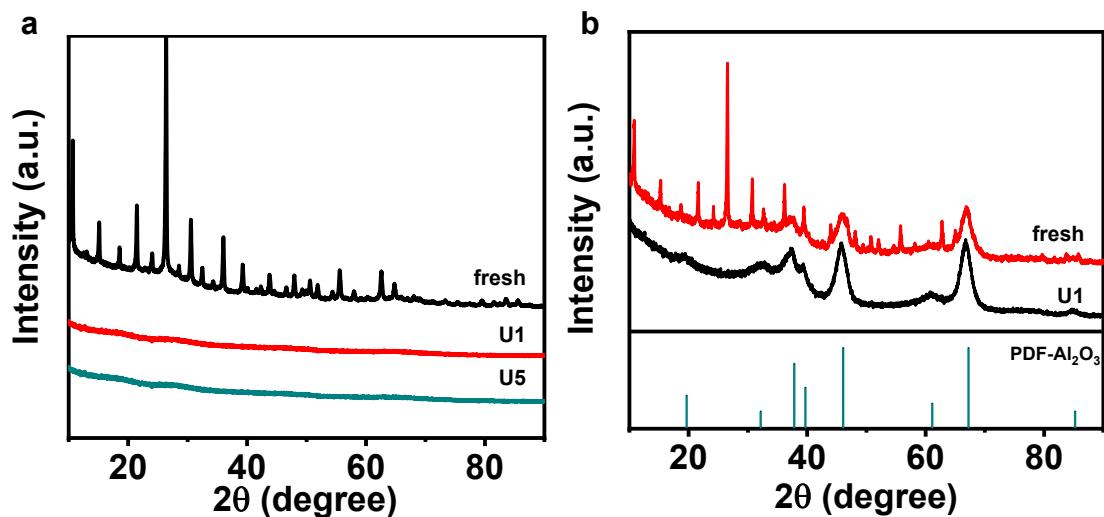


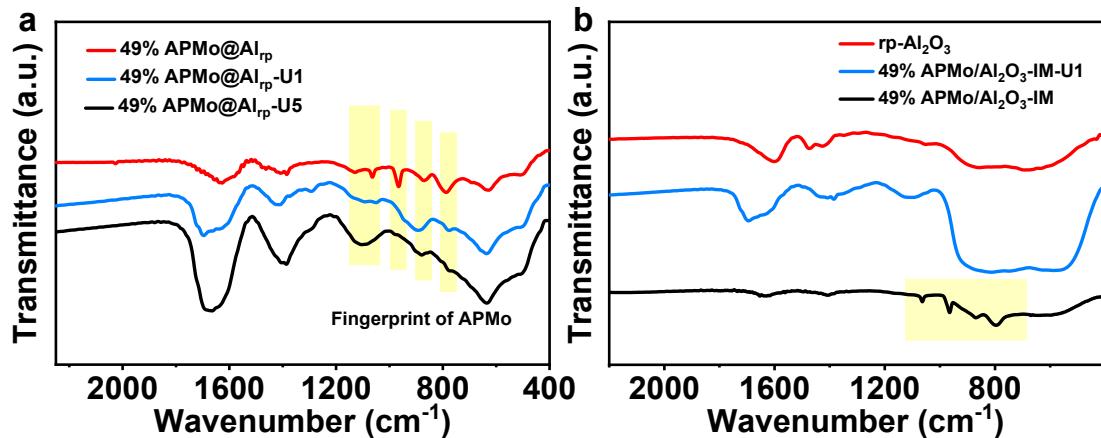
Fig. S17. Reaction kinetic curves of 49%APMo@Al<sub>rp</sub> using pure PhCHO (a) and a mixture of BnOH/PhCHO in a 50/50 ratio (b) as substrates. Reaction conditions: 100 mg catalyst, 5 mL CH<sub>3</sub>CN, 6.15 mL 30% H<sub>2</sub>O<sub>2</sub>, 4 mmol substrates, 80 °C, 21 h/23 h.



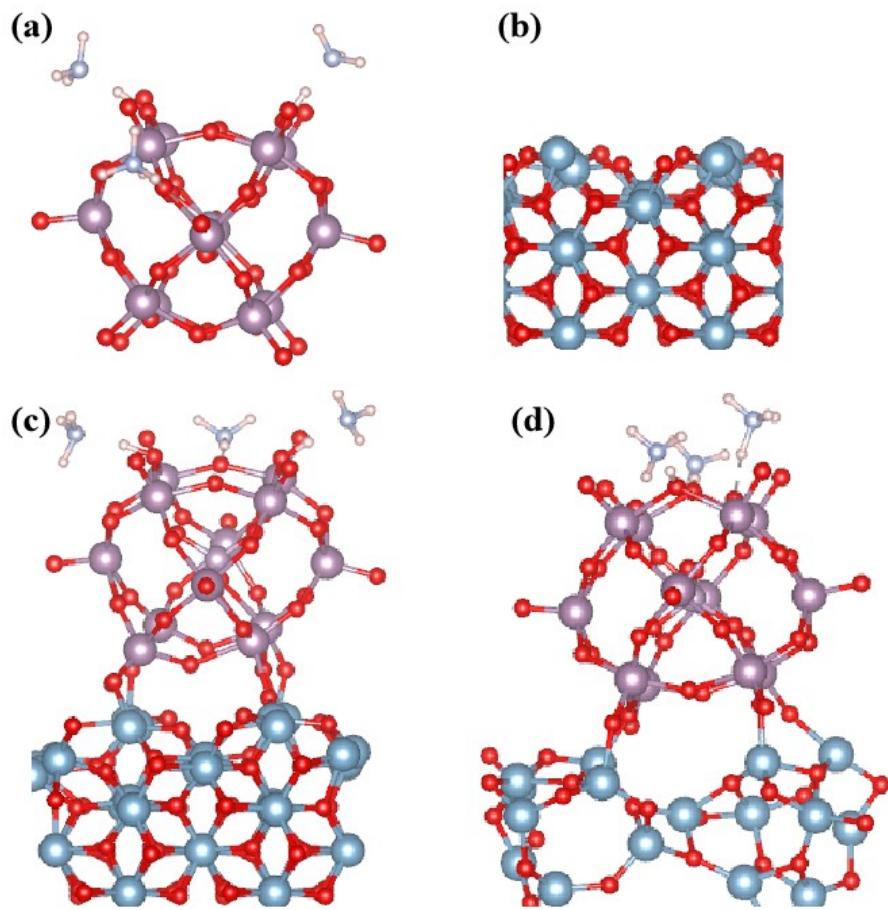
**Fig. S18.** (a)TEM image of 49%APMo@ $\text{Al}_{\text{rp}}$ -U5, (b-f) HAADF-STEM image and corresponding EDS maps of 49%APMo@ $\text{Al}_{\text{rp}}$ -U5 for O, Al, P, and Mo.



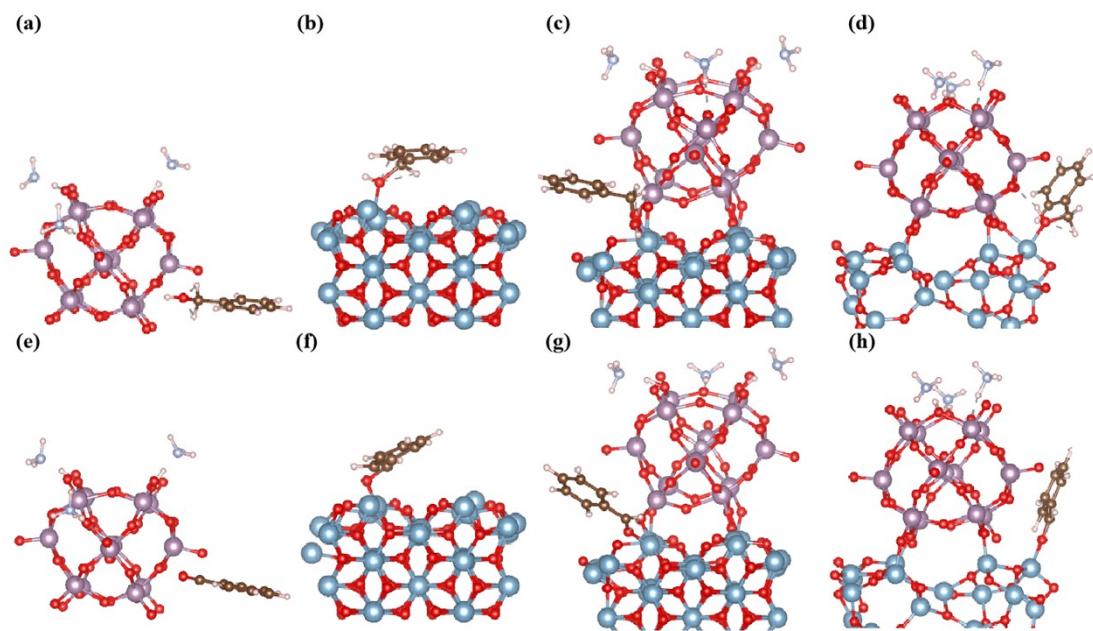
**Fig. S19.** (a) XRD patterns of fresh and reused 49%APMo@ $\text{Al}_{\text{rp}}$ , (b) XRD patterns of fresh 49%APMo/ $\text{Al}_2\text{O}_3$ -IM and 49%APMo/ $\text{Al}_2\text{O}_3$ -IM-U1.



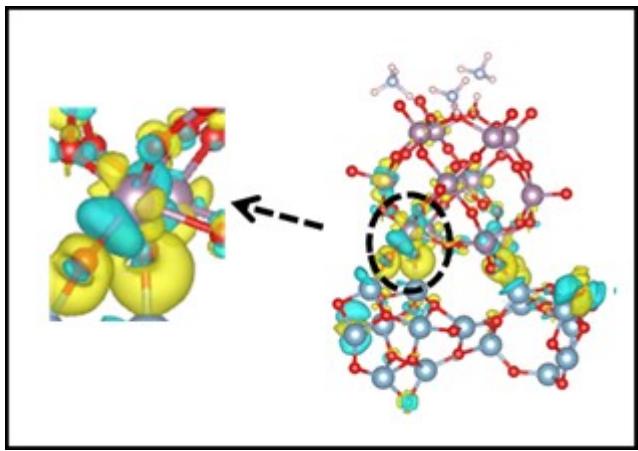
**Fig. S20.** (a) FT-IR spectra of 49%APMo@Al<sub>rp</sub> and reused samples, (b) FT-IR spectra of rp-Al<sub>2</sub>O<sub>3</sub>, 49%APMo/Al<sub>2</sub>O<sub>3</sub>-IM, and 49%APMo/Al<sub>2</sub>O<sub>3</sub>-IM-U1.



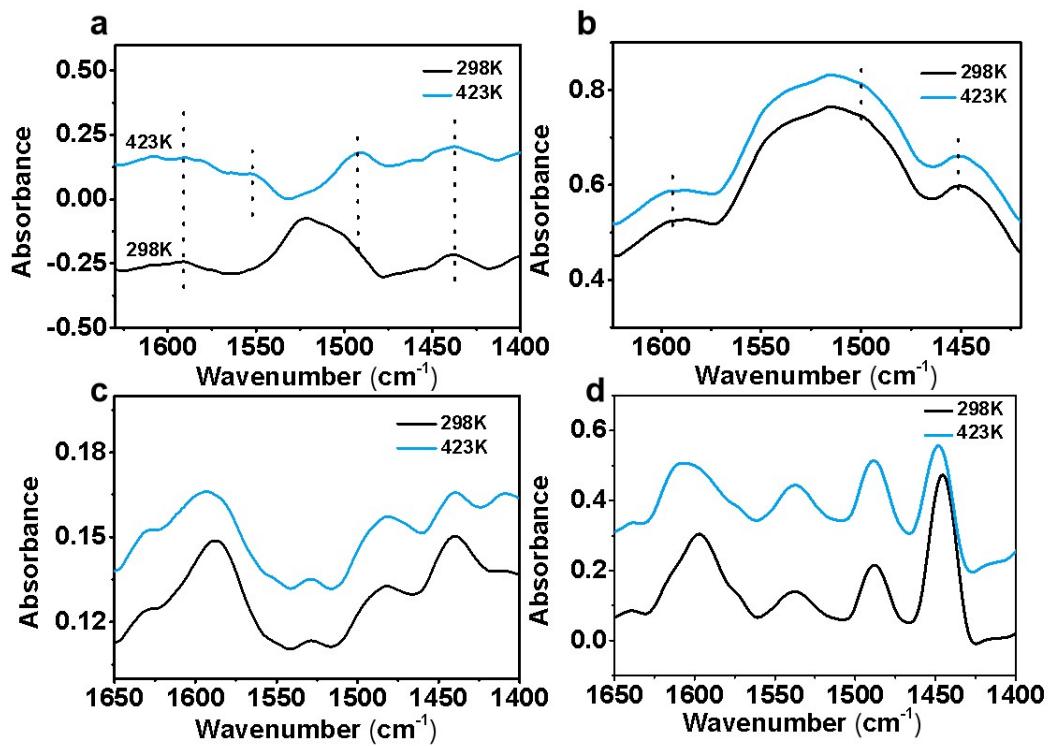
**Fig. S21.** (a-b) Catalyst structures of APMo (a),  $\text{Al}_2\text{O}_3$ -com (b), APMo/ $\text{Al}_2\text{O}_3$ -IM(c) and APMo@ $\text{Al}_{\text{rp}}$ (d).



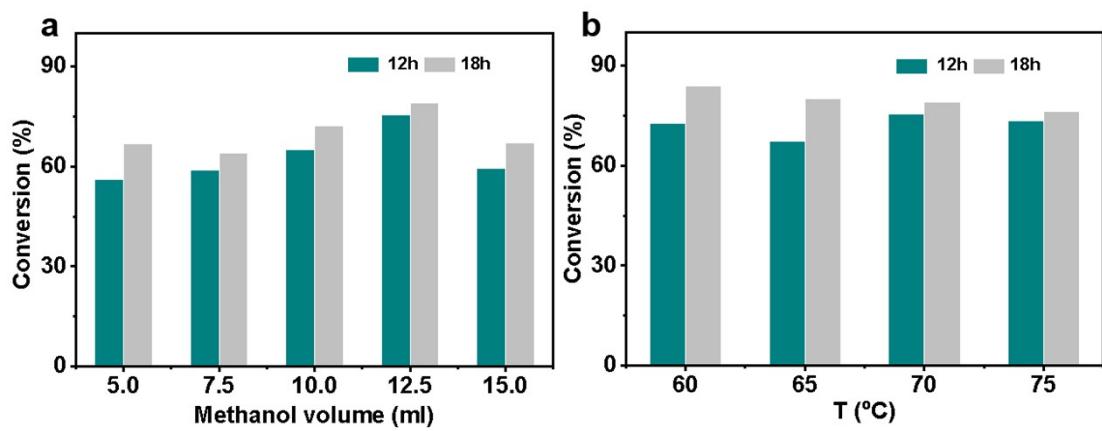
**Fig. S22.** Typical binding geometries of Benzyl alcohol (a-d) and Benzaldehyde (e-h) on different catalysts.



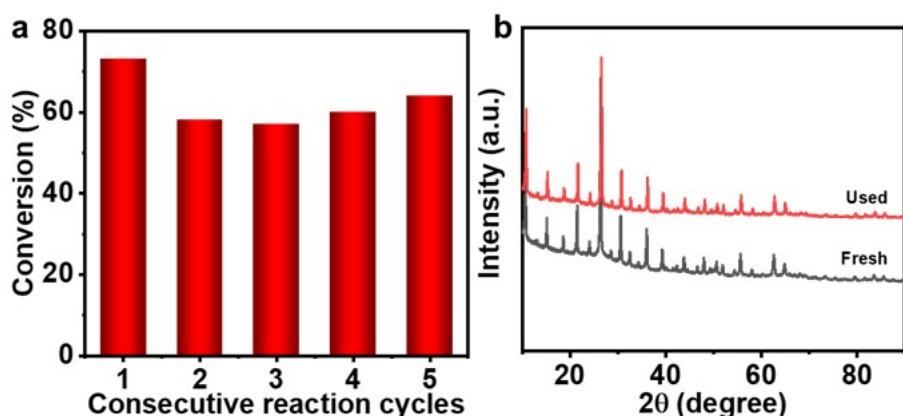
**Fig. S23.** The charge density difference between the POM and the amorphous  $\text{Al}_2\text{O}_3$  surfaces, (dark purple: Mo, light purple: P, silver: Al, red: O, blue: N, and white: H), the yellow and blue colors indicate electron accumulation and depletion, respectively, the value of the iso-surfaces was set to  $\pm 0.003 \text{ e/Bohr}^3$ .



**Fig. S24.** In situ FTIR of pyridine adsorption profiles of rp-Al<sub>2</sub>O<sub>3</sub> (a), 15% APMo@Al<sub>rp</sub> (b), commercial Al<sub>2</sub>O<sub>3</sub> (c), and 49%APMo/Al<sub>2</sub>O<sub>3</sub>-IM (d).



**Fig. S25.** Conversion of palmitic acid upon esterification with different volume of methanol (a), and different temperatures (b) catalyzed by 49%APMo@Al<sub>rp</sub>.



**Fig. S26.** (a) Conversion of palmitic acid esterification over consecutive reaction cycles with 49%APMo@Al<sub>rp</sub>, (b) XRD patterns of fresh and reused 49%APMo@Al<sub>rp</sub>.

**Table S1.** Physical-chemical properties of the catalysts.

Sample	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Total pore volume ( $\text{cm}^3/\text{g}$ )	Average pore diameter (nm)
rp-Al <sub>2</sub> O <sub>3</sub>	567	0.637	4.49
6%APMo@Al <sub>rp</sub>	640	0.842	5.27
15%APMo@Al <sub>rp</sub>	560	0.533	3.81
26%APMo@Al <sub>rp</sub>	518	0.499	3.85
49%APMo@Al <sub>rp</sub>	339	0.456	5.37
49%APMo/Al <sub>rp</sub> -IM	217	0.134	2.48
Al <sub>2</sub> O <sub>3</sub> -com	135	0.802	23.80
49%APMo/Al <sub>2</sub> O <sub>3</sub> -IM	124	0.528	17.93

**Table S2.** ICP-AES results of APMo loading for n%APMo@Al<sub>rp</sub>.

Catalysts	Actual loading/%
2%APMo@Al <sub>rp</sub>	2.2
4%APMo@Al <sub>rp</sub>	4.1
6%APMo@Al <sub>rp</sub>	5.8
12%APMo@Al <sub>rp</sub>	12.4
15%APMo@Al <sub>rp</sub>	15.0
23%APMo@Al <sub>rp</sub>	23.4
20%APMo@Al <sub>rp</sub>	19.8
26%APMo@Al <sub>rp</sub>	25.54
38%APMo@Al <sub>rp</sub>	38.0
43%APMo@Al <sub>rp</sub>	42.6
49%APMo@Al <sub>rp</sub>	48.7
54%APMo@Al <sub>rp</sub>	54.1

**Table S3.** <sup>27</sup>Al MAS Percentage of aluminum with different coordination numbers.

Entry	Catalysts	Al <sub>T</sub> /%	Al <sub>p</sub> /%	Al <sub>o</sub> /%
1	rp-Al <sub>2</sub> O <sub>3</sub>	11	15	74
2	6%APMo@Al <sub>rp</sub>	10	10	80
3	15%APMo@Al <sub>rp</sub>	12	20	68
4	38%APMo@Al <sub>rp</sub>	8	9	83
5	49%APMo@Al <sub>rp</sub>	7	2	91

**Table S4.** ICP-AES results of 49%APMo@Al<sub>rp</sub> and the used ones.

Entry	Catalysts	APMo loading/%
1	49%APMo@Al <sub>rp</sub>	48.7
2	49%APMo@Al <sub>rp</sub> -U5 <sup>a</sup>	34.3
3	49%APMo@Al <sub>rp</sub> -U5 <sup>b</sup>	37.0
4	49%APMo@Al <sub>rp</sub> <sup>c</sup>	45.8

a: after five cycles of benzyl alcohol oxidation;

b: after five cycles of palmitic acid esterification;

c: after repeated washing with water.

**Table S5.** Comparison of results obtained over different Keggin-type POM catalysts in the selective oxidation of benzyl alcohol with H<sub>2</sub>O<sub>2</sub>.

Entry	Catalyst	Reaction	Reaction	Mol ratio	Mol ratio	Conv.	Sel.	Ref.
		Time(h)	Temperature(°C)	(H <sub>2</sub> O <sub>2</sub> /alc ohol)	(Alcohol/cat)	(%)	(%)	
1	49%APMo@Al <sub>rp</sub>	10	80	15	155	81	100	This work
2	{3CD@SiW <sub>12</sub> }	24	85	5	250	96	25	2
3	[SiW <sub>12</sub> O <sub>40</sub> ] <sup>4-</sup>	24	85	5	250	19	15.8	2
4	[PW <sub>12</sub> O <sub>40</sub> ] <sup>3-</sup>	6	95	1.5	77	48	67	3
5	[PW <sub>11</sub> ZnO <sub>39</sub> ] <sup>5-</sup>	8	85	10	20	34	100	4
6	[BW <sub>11</sub> O <sub>39</sub> H]	6	90	2	66.7	98	83	5
7	H <sub>5</sub> PV <sub>2</sub> W <sub>10</sub> O <sub>40</sub>	8	80	>20	2.6	75	93	6
8	PIPA-13	6	95	1.5	77	96	86	3
9	[TMGOH] <sub>2.2</sub> H <sub>0.8</sub> P W	6	90	1.5	333.3	90	89.2	7
10	[PyHA] <sub>3</sub> PW	6	90	1.5	6	72	95.8	7
11	PW-NH <sub>2</sub> -IL-SBA- 15	6	100	3.0	-	72	91	8
12	(PW <sub>11</sub> ) <sub>3</sub> /MCM-41	20	80	3.0	-	30	90	9

The amount of H<sub>2</sub>O<sub>2</sub> used in the reaction is relatively high, mainly because the support of our catalyst 49%APMo@Al<sub>rp</sub> is essentially amorphous AlOOH. AlOOH (especially AlOOH with surface defects) tends to absorb H<sub>2</sub>O<sub>2</sub> via Al-O-H structure interacting with the oxygen atom of H<sub>2</sub>O<sub>2</sub><sup>10</sup>. Besides, AlOOH has been reported to be the support material of H<sub>2</sub>O<sub>2</sub> electrochemical sensing<sup>11</sup>. The support adsorbs a large amount of H<sub>2</sub>O<sub>2</sub>, resulting in the need to provide much H<sub>2</sub>O<sub>2</sub> to ensure the formation of adequate [Mo(O)(O<sub>2</sub>)<sub>2</sub>] intermediates on APMos. The relatively high reaction temperature and high APMo loading may also account for the high H<sub>2</sub>O<sub>2</sub> dosage.

**Table S6.** Comparison of results obtained over different reported catalysts in palmitic acid esterification.

Catalyst	Reaction condition	Conv. (%)	Ref.
49%APMo@Al <sub>rp</sub>	60 °C 18 h	89	This work
49%APMo/Al <sub>2</sub> O <sub>3</sub> -IM	60 °C 18 h	47	This work
ZrO <sub>2</sub> -TiO <sub>2</sub>	100 °C 5 h	93	12
PIL-3	65 °C 10 h	91	13
SBA-15-SO <sub>3</sub> H	85 °C 3 h	85	14
Zr-SBA15-08	160 °C 6 h	64	15
ZeoA@MesoS	60 °C 50 h	75	16
Al-MCM-41	130 °C 2 h	79	17

**Table S7** Acidity properties of the catalysts.

Catalyst	Total acid site (mmol <sub>NH3</sub> /g) <sup>a</sup>	B/L ratio <sup>b</sup>
49%APMo@Al <sub>rp</sub>	2.17	0.08
49%APMo/Al <sub>rp</sub> -IM	1.75	0.15
rp-Al <sub>2</sub> O <sub>3</sub>	1.54	0.04
49%APMo/Al <sub>2</sub> O <sub>3</sub> -IM	1.30	0.56
Al <sub>2</sub> O <sub>3</sub> -com	0.31	0.24

<sup>a</sup>Determined from NH<sub>3</sub>-TPD results.

<sup>b</sup>Determined from the integral area ratios of absorbance bonds at 1543 and 1447 cm<sup>-1</sup>, respectively.

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