Incorporating highly-basic polyoxometalate anions comprising Nb or Ta into nanoscale reaction fields of porous ionic crystals

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Materials

Cr(NO₃)₃·9H₂O, KOH, KCl, KHCO₃, NaOH, NaClO₄, Na₂CO₃, Na₂WO₄·2H₂O, Nb₂O₅, conc. HCl, conc. H₃PO₄, conc. HNO₃, hydrogen peroxide, distilled water, ethanol, formic acid, and benzaldehyde were purchased from Kanto Chemical Co. Inc. Ethyl cyanoacetate, biphenyl, ethyl α -cyanocinnamate, malononitrile and benzalmalononitrile were purchased from TCI Co. Ltd. MgO and Ta₂O₅ was purchased from FUJIFILM Wako Pure Chemical Corporation. All the chemicals were used without further purification. [Cr₃O(OOCH)₆(H₂O)₃](OOCH)·*n*H₂O,¹ [Cr₃O(OOCH)₆(H₂O)₃](NO₃),² K₈H[P₂W₁₅(NbO₂)₃O₅₉]·12H₂O³, K₇[P₂W₁₇(NbO₂)O₆₁]·8H₂O,³ K₅Na₄[P₂W₁₅(TaO₂)₃O₅₉]·17H₂O,⁴ and K₆[α -P₂W₁₈O₆₂]·14H₂O⁵ were synthesized according to the literature methods.

Synthesis of K₅H[Cr₃O(OOCH)₆(H₂O)₃]₂[P₂W₁₇NbO₆₂](NO₃)·34H₂O (1)

 $[Cr_3O(OOCH)_6(H_2O)_3](OOCH) \cdot nH_2O$ (0.1 g, 0.028 mmol) was dissolved in 10 mL of aqueous HNO₃ solution (0.01 M, pH = 2). K₇[P₂W₁₇(NbO₂)O₆₁]·8H₂O (0.46 g, 0.098 mmol) and KCl (0.3 g) were added to the solution followed by stirring for 2 min. The solution was kept at 277 K for 3 days and green block crystals were obtained. Elemental analysis (%): Calcd: C 2.35, N 0.22, P 1.01, K 3.19, Cr 5.08, W 50.94. Found: C 2.49, N 0.29, P 0.99, K 3.37, Cr 4.93, W 52.10. The molar ratio of Nb : W according to X-ray fluorescence analysis (XRF) was 1 : 15.39, and fairly agreed with the calculation (1 : 17). FT-IR (KBr pellet, cm⁻¹, Fig. S1): v_{asym}(OCO) 1641, v_{sym}(OCO) 1374, v_{asym}(P–O_a) 1088, v_{asym}(W–O_a) 947, v_{asym}(W–O_b–W) 908, v_{asym}(W–O_c–W) 772.

Synthesis of K₅[Cr₃O(OOCH)₆(H₂O)₃]₂[P₂W₁₇NbO₆₂]·18H₂O (2)

 $[Cr_3O(OOCH)_6(H_2O)_3]OOCH \cdot nH_2O(0.1 \text{ g}, 0.028 \text{ mmol})$ was dissolved in 10 mL of aqueous HCl solution (0.01 M, pH = 2). K₇[P₂W₁₇(NbO₂)O₆₁] \cdot 8H₂O (0.46 g, 0.098 mmol) and KCl (0.2 g) were added to the solution followed by stirring for 2 min. The solution was kept at 277 K for 3 days and green block crystals were obtained. Elemental analysis (%): Calcd: C 2.49, P 1.07, K 3.38, Cr 5.39, W 54.03. Found: C 2.36, P 1.22, K 3.60, Cr 5.05, W 53.62. The molar ratio of Nb : W according to XRF was 1 : 15.46, and fairly agreed with the calculation (1 : 17). FT-IR (KBr pellet, cm⁻¹, Fig. S1): v_{asym}(OCO) 1633, v_{sym}(OCO) 1378, v_{asym}(P–O_a) 1092, v_{asym}(W–O_a) 957, v_{asym}(W–O_b–W) 908, v_{asym}(W–O_c–W) 781.

Synthesis of $K_6H[Cr_3O(OOCH)_6(H_2O)_3]_2[P_2W_{15}(NbO_2)_3O_{59}]_{0.5}[P_2W_{15}Nb_3O_{62}]_{0.5} \cdot 17H_2O$ (3_Nb)

 $[Cr_3O(OOCH)_6(H_2O)_3]OOCH \cdot nH_2O$ (0.06 g, 0.017 mmol) was dissolved in 10 mL of aqueous HNO₃ solution (0.01 M, pH = 2). K₈H[P₂W₁₅(NbO₂)₃O₅₉] · 12H₂O (0.23 g, 0.05 mmol) and KCl (0.05 g) were added to the solution followed by stirring for 1 min. The solution was kept at 277 K for 3 days and green hexagonal plate crystals were obtained. Elemental analysis (%): Calcd: C 2.55, P 1.10, K 4.15, Cr 5.52, W 48.82. Found: C 2.60, P 1.38, K 4.35, Cr 5.07, W 49.33. The molar ratio of Nb : W according to XRF was 1 : 5.9, and fairly agreed with the calculation (1 : 5). FT-IR (KBr pellet, cm⁻¹, Fig. S2): v_{asym}(OCO) 1639, v_{sym}(OCO) 1382, v_{asym}(P–O_a) 1092, v_{asym}(W–O_a) 960, v_{asym}(W–O_b–W) 912, v_{asym}(W–O_c–W) 799.

Synthesis of $K_7[Cr_3O(OOCH)_6(H_2O)_3]_2[P_2W_{15}(TaO_2)_3O_{59}]_{0.25}[P_2W_{15}Ta_3O_{62}]_{0.75} \cdot 21H_2O$ (3_Ta) [Cr₃O(OOCH)₆(H₂O)₃](OOCH) $\cdot n$ H₂O (0.2 g, 0.056 mmol) was dissolved in 10 mL of aqueous HNO₃ solution (0.01 M, pH = 2). K₃Na₄[P₂W₁₅(TaO₂)₃O₅₉] $\cdot 17H_2O$ (0.6 g, 0.12 mmol) and KCl (0.25 g) were added to the solution followed by stirring for 5 min. The solution was kept at 277 K for 1 days and grey powder was obtained. Elemental analysis (%): Calcd: C 2.40, P 1.03, K 4.55, Cr 5.19, W 45.87. Found: C 2.52, P 0.98, K 4.50, Cr 5.23, W 45.44. The molar ratio of Ta : W was 1 : 5.2, and fairly agreed with the calculation (1 : 5). FT-IR (KBr pellet, cm⁻¹, Fig. S3): $v_{asym}(OCO)$ 1640, $v_{sym}(OCO)$ 1375, $v_{asym}(P-O_a)$ 1090, $v_{asym}(W-O_a)$ 952, $v_{asym}(W-O_b-W)$ 907, $v_{asym}(W-O_c-W)$ 773.

Characterization

Elemental analysis was performed by combustion analysis (vario MICRO cube, Elementar) for C and N, inductively coupled plasma optical emission spectrometry (ICP-OES) (ICP-OES720, Agilent Technologies) for P and W, X-ray fluorescence analysis (ZSX Primus IV and EDXL300, Rigaku) for Nb and Ta, and atomic absorption spectrometry (AAS) (Hitachi, ZA3000) for K and Cr. Prior to the ICP-OES and AAS measurements, conc. HNO₃ (3 mL) was added to ca. 10 mg (accurately weighed) of the PICs to dissolve the solid completely into water (50 mL). FT-IR spectra were recorded by the KBr pellet method with a JASCO FT-IR 4100 spectrometer (JASCO) equipped with a TGS detector. Thermogravimetry (TG) was conducted with a Thermo Plus 2 thermogravimetric analyzer (Rigaku) with α -Al₂O₃ as a reference under a dry N₂ flow (100 mL min⁻¹) in the temperature range of 298–773 K and an increasing rate of 10 K min⁻¹. Powder XRD (PXRD) patterns were measured with a D8 advance X-ray diffractometer (Bruker) by using Cu K α radiation ($\lambda = 1.54056$ Å, 40 kV–40 mA) in the range of 3–50°. ¹H-NMR spectra were recorded with a Bruker AVANCE III 500 MHz spectrometer. ³¹P solid-state magic angle spinning (MAS) NMR spectra (MAS rate = 10 kHz) were recorded with a Bruker AVANCE 400WB spectrometer, and 85% H₃PO₄ (0 ppm) was used as an external standard for the calibration of chemical shifts. Water and CO₂ adsorption isotherms were measured at 298 K and 268 K, respectively, using a volumetric gas sorption apparatus Belsorp-max (MicrotracBEL Corp.). Prior to the measurements, about 0.1 g of the compounds (accurately weighed) were treated under vacuum at 298 K for 3 h to remove the water of crystallization. Absorption equilibrium was judged by the following criteria: $\pm 0.3\%$ of pressure change in 300 s (water) or $\pm 0.3\%$ of pressure change in 2000 s below 10 kPa and ± 10 Pa of pressure change in 2000 s in the range of 10–100 kPa (CO₂). In situ IR spectra under methanol vapor were recorded on a FT/IR-6600 (JASCO) by transmission method with a sample-coated Si disk. On one side of the Si disk (20 mm $\phi \times 0.5$ mmt), samples suspended in water were dropped and air dried. Prior to the measurements, the Si disks were treated under vacuum for 90 min and exposed to methanol vapor (10 kPa) at 298 K. Then, the pressure was reduced to 10 Pa to remove the physisorbed methanol molecules.

Single crystal X-ray diffraction (SXRD) analysis

Single crystal X-ray diffraction data of **1** and **2** was collected at 153 K with a HyPix-6000 area detector by using a Rigaku Saturn diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Single crystal X-ray diffraction data of **3_Nb** was collected at 93 K with a CCD plate detector by using a Rigaku XtaLAB AFC12 (RINC): Kappa dual offset/far diffractometer with mirror monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The data reduction and correction were processed with CrysAlisPro software. All the structures are solved by intrinsic phase method (SHELXT)⁶ and refined by the full-matrix least-squares method on F^2 using SHELXL-2018/3 crystallographic software package⁷ through Olex2⁸. All the atoms were refined anisotropically, and the position of hydrogen atoms on the formic acid are theoretically calculated and refined isotropically. The Platon/Squeeze program⁹ was used to mask the electron density of the disordered water molecules and K⁺ in the voids of **1** and **3_Nb**. The program suggested that 80

and 408.5 electrons are found in the solvent-accessible volume per formula, roughly consistent with the unassigned lattice water molecules and K^+ in the voids.

Catalytic reaction

Knoevenagel condensation reaction was carried out in a glass tube equipped with a magnetic stirrer. In a typical run of reaction, a mixture of benzaldehyde (106 mg, 1.0 mmol), active methylene compounds (ethyl cyanoacetate: 113.1 mg, 1.0 mmol or malononitrile: 66.1 mg, 1.0 mmol), biphenyl (10 mg, internal standard), and catalyst (0.01 mmol) in ethanol (1.0 mL for reaction with ethyl cyanoacetate or 3.0 mL for reaction with malononitrile) was stirred at 353 K. The mole ratio (catalyst/reactant) was varied from 0.5–1.5% during the optimization process. The amounts of products (ethyl α -cyanocinnamate or benzalmalononitrile) were followed by gas chromatography using a GC-2014 (Shimadzu) fitted with a HP-5 column (60 m × 0.32 mm × 0.25 µm) and a flame ionization detector (FID). The reaction solution (with the solid catalyst) was sampled periodically and injected directly into the GC system.

Computation details

The density functional theory (DFT) calculations were performed using Gaussian 09 program package.¹⁰ The geometric structures of $[P_2W_{17}NbO_{62}]^{7-}$, $[P_2W_{15}Nb_3O_{62}]^{9-}$ and $[P_2W_{15}Ta_3O_{62}]^{9-}$ were optimized with B3LYP hybrid functional.¹¹ The LANL2DZ¹² was applied for Nb, W, and Ta atoms, and 6-31G(d)¹³ was used to describe P and O atoms. The solvent effect was included with the polarizable continuum model (PCM)¹⁴ and water solvent.

Compound	1	2	3_Nb
Empirical formula	C ₁₂ H ₅₅ NP ₂ K ₅ Cr ₆ Nb	$C_{12}H_{60}P_2K_5Cr_6NbW_1$	$C_{12}H_{59}P_2K_6Cr_6Nb_3$
	W ₁₇ O ₁₁₃	7 O 113	W ₁₅ O _{112.5}
Formula weight	5809.06	5784.14	5648.36
Temperature (K)	153	153	93
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Hexagonal	Trigonal
Space group	$P2_{1}/n$	$P6_3/mmc$	<i>P</i> -3 <i>m</i> 1
<i>a</i> (Å)	15.8007(2)	15.8474(3)	16.1712(4)
<i>b</i> (Å)	26.9370(4)	15.8474(3)	16.1712(4)
<i>c</i> (Å)	29.2946(6)	21.4754(6)	24.9066(7)
α (°)	90	90	90
β (°)	96.5576(16)	90	90
γ (°)	90	120	120
Volume ($Å^3$)	12386.9(4)	4670.8(2)	5640.7(3)
Ζ	4	2	2
F(000)	9936	4862	4963
θ range (°)	4.696 to 61.168	4.816 to 60.904	4.906 to 60.022
Reflections collected	140475	27338	40304
GoF on F^2	1.040	1.230	1.076
$R_1^a [I > 2\sigma(I)]$	0.0589	0.0736	0.0454
$wR_2^{b}[I > 2\sigma(I)]$	0.1522	0.1791	0.0883

Table S1 Crystallographic data of 1, 2 and 3_Nb

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|;$ ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$

Mole ratio	Solvent	Time	Temp.	Conversion	Yield ^b	Selectivity ^c
/ %		/ h	/ °C	/ %	/ %	/ %
1	Ethanol	6	80	79	78	99
1	Toluene	6	80	_	0	_
1	Acetonitrile	6	80	_	1	_
1	Methanol	6	80	85	76	90
1	Ethanol	6	60	66	65	99
1	Ethanol	6	40	55	54	99
1	Ethanol	6	20	42	41	99
1	Ethanol	3	80	67	66	99
1	Ethanol	9	80	84	79	94
0.5	Ethanol	6	80	59	56	95
1.5	Ethanol	6	80	83	82	99

Table S2 Optimization of reaction conditions in Knoevenagel condensation^a

^aReaction conditions: PIC **3**_N**b** as catalyst, 1.0 mmol benzaldehyde, 1.0 mmol ethyl cyanoacetate, 10 mg biphenyl (internal standard), 1 mL solvent. ^bYield of ethyl α -cyanocinnamate. ^cSelectivity to ethyl α -cyanocinnamate.

Entry	Catalyst	Conversion / %	Yield ^d / %	Selectivity ^e / %
1	$P_2W_{15}Nb_3$	49	32	65
2	$P_2W_{17}Nb$	88	48	54
3	$P_2W_{15}Ta_3$	92	72	78
4	$\mathbf{P_2W_{18}}^{\mathrm{b}}$	44	9	21
5	\mathbf{Cr} - $\mathbf{H}^{\mathrm{b},\mathrm{c}}$	31	10	31
6	$Cr-H^{b,c} + P_2W_{15}Nb_3$	27	6	21
7	$Cr-H^{b,c} + P_2W_{17}Nb$	22	7	32
8	$Cr-H^{b,c} + P_2W_{15}Ta_3$	84	56	67

Table S3 Catalytic results for POMs and macrocations^a

^aReaction conditions: 0.01 mmol catalyst, 1.0 mmol benzaldehyde, 1.0 mmol ethyl cyanoacetate, 10 mg biphenyl (internal standard), 1 mL ethanol. ^bCatalysts dissolved in the reaction solution. ^cAmount of **Cr-H** in the reaction is 2 mol% because there are two macrocations in the chemical formulae of PICs. ^dYield of ethyl α -cyanocinnamate. ^eSelectivity to ethyl α -cyanocinnamate.

Catalyst	Temp	Solvent	Time	Yield ^a	Reference
-	/ K			/ %	
3 Nb	353	Ethanol	6 h	78	This work
3_Та	353	Ethanol	6 h	82	This work
Commercial Nb ₂ O ₅	353	Ethanol	6 h	38	This work
Commercial Ta ₂ O ₅	353	Ethanol	6 h	11	This work
Commercial MgO ^b	353	Ethanol	6 h	97	This work
$K_7HNb_6O_{19}$ ·13 H_2O	353	Ethanol	6 h	98	This work
$K_8Ta_6O_{19}$ ·16 H_2O^b	353	Ethanol	6 h	99	This work
$Na_{16}[SiNb_{12}O_{40}]$	343	Methanol	2 h	67	1
Nb ₂ O ₅ ·xH ₂ O	343	Methanol	2 h	7	1
SiO_2	343	Methanol	2 h	6	1
$H_4SiW_{12}O_{40}$	343	Methanol	2 h	14	1
$Na_{3}PW_{12}O_{40}$	343	Methanol	2 h	23	1
Na_2WO_4	343	Methanol	2 h	52	1
$Na_8H[PW_9O_{34}]$	298	Methanol	6 h	80	2
$(NH_4)_{17}Na_7H_{12}[Co(H_2O)TeMo_6O_{21}]$	343	Methanol	3 h	92	3
$\{N(CH_2PO_3)_3\}]_6.42H_2O$					
K ₇ HNb ₆ O ₁₉ ·13H ₂ O	333	Ethanol	2 h	98	4
SiO_2	413	_	5 h	58	5
Al_2O_3	413	_	5 h	34	5
Nb ₂ O ₅	413	_	5 h	27	5
ZnO	353	_	1 h	58	6
MgO	293	DMF	2 h	84	7
Ηβ	413	_	6 h	65	8
ΗβΤDΑ	413	_	6 h	31	8
Znβ	413	_	6 h	73	8
HY	413	_	6 h	27	8
ZnY	413	_	6 h	60	8
$TBA_6[\gamma-H_2GeW_{10}O_{36}]^c$	305	Acetonitrile	2 h	98	9
$TBA_6[\gamma - H_2GeW_{10}O_{36}]^c$	313	_	5 min	85	9
$TBA_8[\alpha-H_2GeW_{10}O_{36}]^c$	305	Acetonitrile	3 h	96	10

Table S4 Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate over various catalysts

^aYield of ethyl α-cyanocinnamate. ^bCatalyst decomposed or dissolved in the reaction. ^cCatalytic reaction is homogeneous. 1) *Catal. Sci. Technol.* 2016, **6**, 460. 2) *Appl. Catal., A* 2014, **475**, 140. 3) *Inorg. Chem.* 2020, **59**, 10665, 4) *Mol. Catal.* 2018, **453**, 93. 5) *Catal. Today* 2009, **142**, 278. 6) *J. Catat.* 2019, **369**, 157. 7) *Catal. Sci. Technol.* 2016, **6**, 1903. 8) *Appl. Catal., A* 2006, **298**, 8. 9) *Chem. Commun.* 2012, **48**, 8422. 10) *Chem. Eur. J.* .2014, **20**, 5946.

Catalyst	Temp / K	Solvent	Time	Yield ^a / %	Reference
3_Nb	353	Ethanol	0.5 h	91	This work ^b
3_Nb	353	Ethanol	1 h	99	This work ^b
3_Ta	353	Ethanol	0.5 h	92	This work ^b
3_Ta	353	Ethanol	1 h	96	This work ^b
$Na_{16}[SiNb_{12}O_{40}]$	298	Methanol	0.5 h	98.5	1
$Na_{16}[SiNb_{12}O_{40}]$	298	Methanol	2 h	99.8	1
$Na_8H[PW_9O_{34}]$	298	Methanol	6 h	92	2
$K_7HNb_6O_{19}$ ·13 H_2O	333	Ethanol	45 min	99	3
$TBA_2[W_6O_{19}]$	reflux	Ethanol	7 min	92	4
$TBA_6[\gamma-H_2GeW_{10}O_{36}]^c$	305	Acetonitrile	0.5 h	99	5
$TBA_{4}[\gamma-SiW_{10}O_{34}(H_{2}O)_{2}]^{c}$	305	Acetonitrile	2.5 h	90	6

 Table S5 Knoevenagel condensation of benzaldehyde and malononitrile over various catalysts

^aYield of benzalmalononitrile. ^bReaction conditions: 0.01 mmol catalyst, 1.0 mmol benzaldehyde (internal standard), 1.0 mmol malononitrile, 10 mg biphenyl, 3 mL C₂H₅OH. ^cCatalytic reaction is homogeneous. 1) *Catal. Sci. Technol.* 2016, **6**, 460. 2) *Appl. Catal., A* 2014, **475**, 140. 3) *Mol. Catal.* 2018, **453**, 93. 4) *Synth. React. Inorg. Met.-Org. Chem.* 2012, **42**, 1022. 5) *Chem. Commun.* 2012, **48**, 8422. 6) *J. Organomet. Chem.* 2007, **692**, 455.



Table S6 NBO charges of oxygens in $[P_2W_{17}NbO_{62}]^{7-}$ in 1

Atomic number	Charge	Atomic number	Charge
O ₂₀	-1.02968	O ₅₁	-0.73035
O_{21}	-0.69653	O ₅₂	-0.69914
O_{22}	-0.69846	O ₅₃	-0.71530
O ₂₃	-0.69862	O ₅₄	-0.71148
O ₂₄	-0.70434	O ₅₅	-0.71895
O ₂₅	-0.69844	O ₅₆	-1.02957
O_{26}	-0.70048	O ₅₇	-0.71854
O ₂₇	-0.69896	O ₅₈	-0.70707
O_{28}	-0.71351	O59	-0.71474
O ₂₉	-0.71075	O_{60}	-0.70813
O ₃₀	-0.69851	O ₆₁	-1.03277
O ₃₁	-0.69998	O ₆₂	-1.03680
O ₃₂	-0.71437	O ₆₃	-0.55235
O ₃₃	-0.70518	O ₆₄	-0.55527
O ₃₄	-0.71135	O ₆₅	-0.56056
O ₃₅	-0.69693	O_{66}	-0.55298
O ₃₆	-0.71430	O ₆₇	-0.55540
O ₃₇	-1.02948	O_{68}	-0.55861
O ₃₈	-1.02895	O ₆₉	-0.55327
O ₃₉	-0.70598	O_{70}	-0.55880
O_{40}	-0.71438	O ₇₁	-0.56069
O_{41}	-0.70838	O ₇₂	-0.55659
O_{42}	-0.71158	O ₇₃	-0.55234
O_{43}	-0.71343	O_{74}	-0.55657

O ₄₄	-0.71659	O ₇₅	-0.56817
O_{45}	-0.70756	O ₇₆	-0.56281
O_{46}	-0.70756	O ₇₇	-0.56414
O_{47}	-1.02969	O ₇₈	-0.56403
O_{48}	-0.72957	O ₇₉	-0.69827
O_{49}	-1.02967	O_{80}	-0.65822
O_{50}	-0.71620	O ₈₁	-0.56285



Table S7 NBO charges of oxygens in $[P_2W_{17}NbO_{62}]^{7-}$ in 2

Atomic number	Charge	Atomic number	Charge
O ₂	-0.71094	O ₄₉	-0.70449
O_3	-0.55875	O_{50}	-0.65818
O_5	-0.70836	O ₅₂	-1.03277
O_6	-0.55314	O ₅₄	-1.03682
O_8	-0.71143	O ₅₅	-0.69643
O_9	-0.55526	O ₅₆	-0.69857
O_{11}	-0.70716	O ₅₇	-0.70053
O ₁₂	-0.55231	O ₅₈	-0.69852
O_{14}	-0.70595	O ₅₉	-0.70049
O ₁₅	-0.55657	O_{60}	-0.69635
O ₁₇	-0.71531	O ₆₁	-0.71444
O_{18}	-0.56062	O ₆₂	-1.02960
O_{20}	-0.71557	O ₆₃	-0.71443
O ₂₁	-0.56062	O ₆₄	-1.02962
O ₂₃	-0.70722	O ₆₅	-0.71336
O_{24}	-0.55229	O ₆₆	-1.02895
O_{26}	-0.70596	O_{67}	-0.71433
O ₂₇	-0.55659	O ₆₈	-1.02967
O ₂₉	-0.70838	O69	-0.73024
O_{30}	-0.55318	O_{70}	-0.71338
O ₃₂	-0.71144	O ₇₁	-1.02945
O ₃₃	-0.55525	O ₇₂	-0.71459
O ₃₅	-0.71089	O ₇₃	-0.71434

O ₃₆	-0.55876	O_{74}	-1.02971
O_{38}	-0.69877	O_{75}	-0.73019
O_{40}	-0.69832	O_{76}	-0.56833
O_{42}	-0.69829	O_{77}	-0.56278
O_{44}	-0.69895	O_{78}	-0.56282
O_{45}	-0.56408	O_{79}	-0.71860
O_{47}	-0.69894	O_{80}	-0.71858
O_{48}	-0.56408	O_{81}	-0.71674



Table S8 NBO charges of oxygens in $[P_2W_{15}Nb_3O_{62}]^{9\text{--}in}\,\textbf{3_Nb}$

Atomic number	Charge	Atomic number	Charge
O ₃	-0.69821	O ₄₆	-0.70405
O_4	-0.72127	O_{47}	-0.61597
O_5	-0.69549	O_{48}	-0.70364
O_6	-0.59146	O ₅₁	-0.71297
O_7	-0.59240	O ₅₂	-0.70459
O_{10}	-0.69818	O ₅₃	-0.61601
O_{11}	-0.72117	O ₅₄	-0.70362
O ₁₂	-0.69590	O ₅₇	-0.71289
O ₁₃	-0.59128	O ₅₈	-0.70457
O_{14}	-0.59218	O ₅₉	-0.61586
O ₁₇	-0.69767	O_{60}	-0.70353
O_{18}	-0.72155	O ₆₃	-1.02207
O ₁₉	-0.69584	O_{64}	-1.03895
O_{20}	-0.59129	O ₆₅	-0.73777
O_{21}	-0.59223	O_{66}	-0.73788
O_{24}	-0.69795	O ₆₇	-0.73792
O ₂₅	-0.72122	O_{68}	-1.02740
O_{26}	-0.69599	O69	-1.02604
O_{27}	-0.59127	O_{70}	-0.72583
O_{28}	-0.59226	O_{71}	-0.78530
O_{31}	-0.69789	O ₇₂	-0.72728
O ₃₂	-0.72117	O ₇₃	-1.02732
O ₃₃	-0.69632	O_{74}	-1.02597
O ₃₄	-0.59100	O ₇₅	-0.72584

O ₃₅	-0.59208	O ₇₆	-0.78498
O_{38}	-0.69797	O_{77}	-0.72711
O39	-0.72132	O_{78}	-1.02820
O_{40}	-0.69525	O ₇₉	-1.02668
O_{41}	-0.59163	O_{80}	-0.72554
O_{42}	-0.59256	O_{81}	-0.78508
O ₄₅	-0.71223	O_{82}	-0.72690



Table S9 NBO charges of oxygens in $[P_2W_{15}Ta_3O_{62}]^{9-}$ in 3_Ta

Atomic number	Charge	Atomic number	Charge
O ₃	-0.72930	O ₄₅	-0.70413
O_4	-0.72082	O_{46}	-0.61410
O_5	-0.69649	O_{47}	-0.80891
O_6	-0.58865	O ₄₉	-0.71274
O_7	-0.58718	O_{50}	-0.70425
O_{10}	-0.72947	O ₅₁	-0.61392
O ₁₁	-0.72078	O ₅₂	-0.80889
O ₁₂	-0.69587	O ₅₄	-0.71212
O ₁₃	-0.58865	O55	-0.70364
O_{14}	-0.58703	O_{56}	-0.61409
O_{17}	-0.72949	O ₅₇	-0.80892
O_{18}	-0.72039	O_{60}	-1.02231
O ₁₉	-0.69602	O ₆₁	-1.05017
O_{20}	-0.58864	O ₆₂	-0.73712
O_{21}	-0.58709	O ₆₃	-0.73716
O_{24}	-0.72922	O ₆₄	-0.73732
O_{25}	-0.72063	O ₆₅	-1.02758
O ₂₆	-0.69592	O ₆₆	-1.02675
O_{27}	-0.58871	O_{67}	-0.72477
O_{28}	-0.58713	O ₆₈	-0.88435
O ₃₁	-0.72956	O ₆₉	-0.72524
O_{32}	-0.72069	O_{70}	-1.02775
O ₃₃	-0.69624	O ₇₁	-1.02689
O ₃₄	-0.58868	O ₇₂	-0.72435
O ₃₅	-0.58725	O ₇₃	-0.88464
O_{38}	-0.72921	O ₇₄	-0.72471
O ₃₉	-0.72078	O ₇₅	-1.02754
O_{40}	-0.69572	O ₇₆	-1.02685

O ₄₁	-0.58876	O ₇₇	-0.72475
O_{42}	-0.58709	O_{78}	-0.88445
O_{44}	-0.71276	O_{79}	-0.72527



Fig. S1 IR Spectra of (a) $[Cr_3O(OOCH)_6(H_2O)_3](OOCH) \cdot nH_2O$, (b) $K_7[P_2W_{17}(NbO_2)O_{61}] \cdot 8H_2O$, (c) **1** and (d) **2**. The bands around 1575 cm⁻¹ and 1320 cm⁻¹ in (a), which correspond to the $v_{asym}(OCO)$ and $v_{sym}(OCO)$, respectively, of the formate anion have disappeared in (c) and (d), showing that formate anion is successfully exchanged with POM in the synthetic procedures of **1** and **2**.



Fig. S2 IR Spectra of (a) $[Cr_3O(OOCH)_6(H_2O)_3](OOCH) \cdot nH_2O$, (b) $K_8H[P_2W_{15}(NbO_2)_3O_{59}] \cdot 12H_2O$, and (c) **3_Nb**. The bands around 1575 cm⁻¹ and 1320 cm⁻¹ in (a), which correspond to the $v_{asym}(OCO)$ and $v_{sym}(OCO)$, respectively, of the formate anion have disappeared in (c), showing that formate anion is successfully exchanged with POM in the synthetic procedure of **3_Nb**.



Fig. S3 IR Spectra of (a) $[Cr_3O(OOCH)_6(H_2O)_3](OOCH) \cdot nH_2O$, (b) $K_5Na_4[P_2W_{15}(TaO_2)_3O_{59}] \cdot 17H_2O$, and (c) **3_Ta**. The bands around 1575 cm⁻¹ and 1320 cm⁻¹ in (a), which correspond to the $v_{asym}(OCO)$ and $v_{sym}(OCO)$, respectively, of the formate anion have disappeared in (c), showing that formate anion is successfully exchanged with POM in the synthetic procedure of **3_Ta**.



Fig. S4 TG-DTA analysis of 1.



Fig. S5 TG-DTA analysis of 2.



Fig. S6 TG-DTA analysis of 3_Nb.



Fig. S7 TG-DTA analysis of 3_Ta.



Fig. S8 Solid-state ³¹P-MASNMR spectra of (a) **1** and (b) **2**. The signals were reproduced with sum of two Gaussian-Lorentzian mixed functions. The reason why mixed functions were needed is probably due to the substitutional disorder of Nb/W in **1** and **2**. The peaks at the lower field (-10.2 ppm and -9.8 ppm for **1** and **2**, respectively) were assigned to the P in the half-anion containing Nb, and those at the higher field (-12.2 ppm and -11.9 ppm for **1** and **2**, respectively) were assigned to the other P.¹⁵



Fig. S9 Solid-state ³¹P-MASNMR spectra of (a) **3**_Nb and (b) **3**_Ta. The signals were reproduced with sum of two pairs (blue and orange peaks) of Gaussian-Lorentzian mixed functions. The reason why mixed functions were needed is probably due to the substitutional disorder of Nb(Ta)/W in the PICs. These results suggest the existence of POMs with and without peroxo groups in the PICs; specifically, the orange and blue peaks were assigned to the P atoms of $[P_2W_{15}(MO_2)_3O_{59}]^{9-}$ and $[P_2W_{15}M_3O_{62}]^{9-}$ (M = Nb or Ta), respectively.^{4,16,17}



Fig. S10 PXRD patterns of **1**. (a) Calculated, (b) experimental, (c) treated with ethanol at 353 K for 2 h, and (d) after catalytic reaction.



Fig. S11 PXRD patterns of **2**. (a) Calculated, (b) experimental, (c) treated with ethanol at 353 K for 2 h, and (d) after catalytic reaction.



Fig. S12 PXRD patterns of **3**_**Nb**. (a) Calculated, (b) experimental, (c) treated with ethanol at 353 K for 2 h, and (d) after catalytic reaction. The calculated pattern by the Pawley method (dotted line) was overlaid with the experimental pattern (solid line). Cell parameter: a = 16.131(18) Å. c = 25.096(72) Å. The difference between the experimental and calculated data was shown under the pattern.



Fig. S13 PXRD patterns of **3**_**Ta**. (a) Calculated from the CIF file of **3**_**Nb**, (b) experimental. (c) treated with ethanol at 353 K for 2 h, and (d) after catalytic reaction. The calculated patterns by the Pawley method (dotted lines) were overlaid with the experimental patterns (solid lines). Cell parameter: a = 16.113(1) Å. c = 25.269(5) Å for (b), a = 15.938(10) Å. c = 25.386(23) Å for (d). The difference between the experimental and calculated data was shown under each pattern.



Fig. S14 GC charts of Knoevenagel condensation (Left: entry 4; right: entry 7 in main text, after reaction).



Fig. S15 ¹H-NMR spectra of the solutions after reaction. Top: entry 4; bottom: entry 7. Assignment: a: C_2H_5OH ; b: aromatic hydrogen; c: $CHCl_3$; d - OCH_2 -; e: - CH_3 . The assignments are based on the Spectral Database for Organic Compounds (SDBS) of National Institute of Advanced Industrial Science and Technology (AIST), Japan. Compounds SDBS number: biphenyl: No. 1182; benzaldehyde: No. 672; ethyl cyanoacetate: No. 1306; ethyl α -cyanocinnamate: No. 1439; ethanol: No. 1300; chloroform: No. 894.



Fig. S16 Water adsorption/desorption isotherms of 1 (red), 2 (blue), 3_Nb (black), and 3_Ta (green). Solid and open circles indicate the adsorption and desorption branches, respectively.



Fig. S17 CO_2 adsorption/desorption isotherms of 1 (red), 2 (blue), 3_Nb (black), and 3_Ta (green). Solid and open circles indicate the adsorption and desorption branches, respectively.



Fig. S18 Calculated NBO charges of oxygen atoms in $[P_2W_{18}O_{62}]^{6-}$ in Cr-H-P₂W₁₈.



Fig. S19 Difference in-situ IR spectra of methanol adsorbed on PICs (a) 1, (b) 2, (c) 3_Nb, (d) 3_Ta, and (e) Cr-H-P₂W₁₈.



Fig. S20 In-situ IR spectra. PICs **3_Nb** and **3_Ta** were exposed to methanol vapor at 298 K then heated. The arrows indicate the v(C-O) band of adsorbed methanol.

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