<Supporting Information>

Ru(III)-based polyoxometalate tetramer as highly efficient heterogeneous catalyst for alcohol oxidation reactions at room temperature

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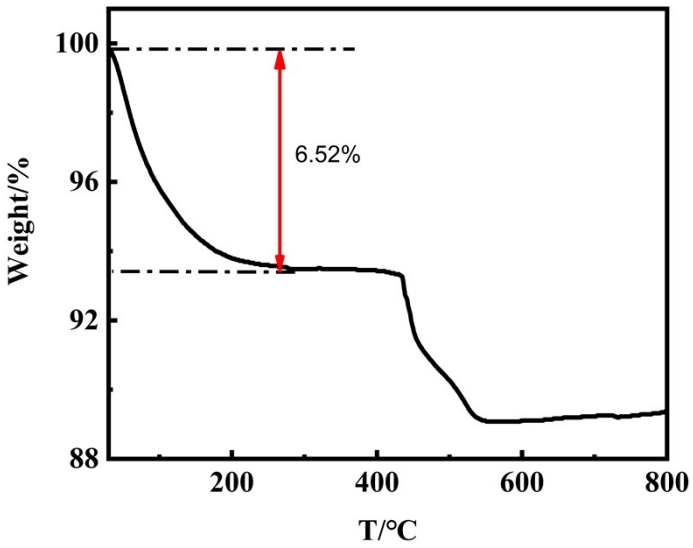

Fig. S1 The thermogravimetric curves of **1**.

TG analysis

The thermal stability of **1** has been explored under a nitrogen flow between room temperature and 800 °C by thermogravimetric analysis (TGA). The TGA curve reveals two-step weight loss process. The first weight loss of 6.52% from 30 to 240 °C is attributed to forty-two lattice water molecules (calc. 6.59%). The second weight loss corresponds to the partial collapse of POM skeleton and the oxidation of imidazole ligands.

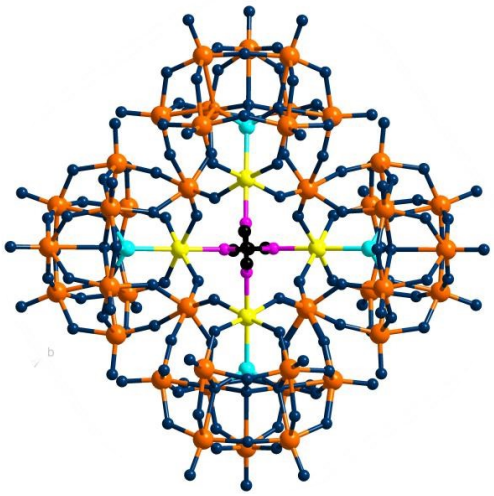

Fig. S2 Ball-and-stick representation of polyanion **1**. Color code: Ru, yellow; As, aqua; O, dark blue; C, black; N, pink; all hydrogen atoms have been omitted for clarity.

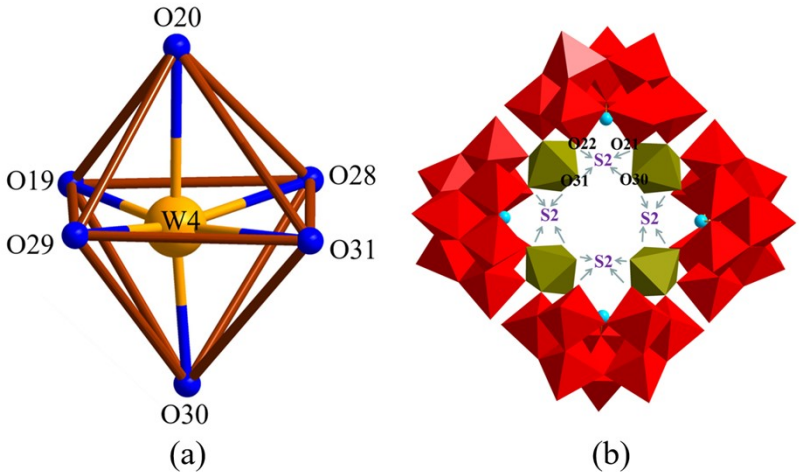

Fig. S3 (a) Ball-and-stick representation of the {WO_6} octahedron. Color code: W, light orange; O, blue; (b) Ball-and-stick representation of the polyanion $[(AsW_9O_{33})_4(WO_2)_4]^{28-}$ with the S2 sites. S2 means the remaining vacant site. Color code: WO_6 octahedron, red; bridging group WO_6 octahedron, dark yellow; As, aqua; O, dark blue; all hydrogen atoms have been omitted for clarity.

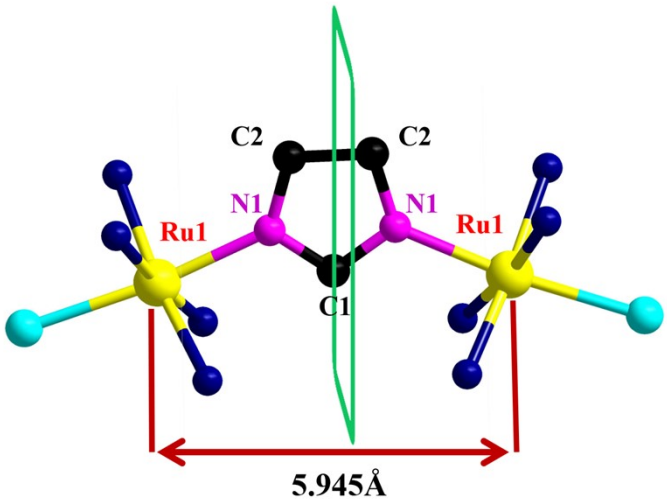

Fig. S4 Ball-and-stick representation of the polyanion of $\{Ru_{1.6}(C_3H_3N_2)\}^{3.8+}$, and the distance of Ru···Ru is 5.945 Å. Color code: Ru, yellow; As, aqua; O, dark blue; C, black; N, pink; all hydrogen atoms have been omitted for clarity.

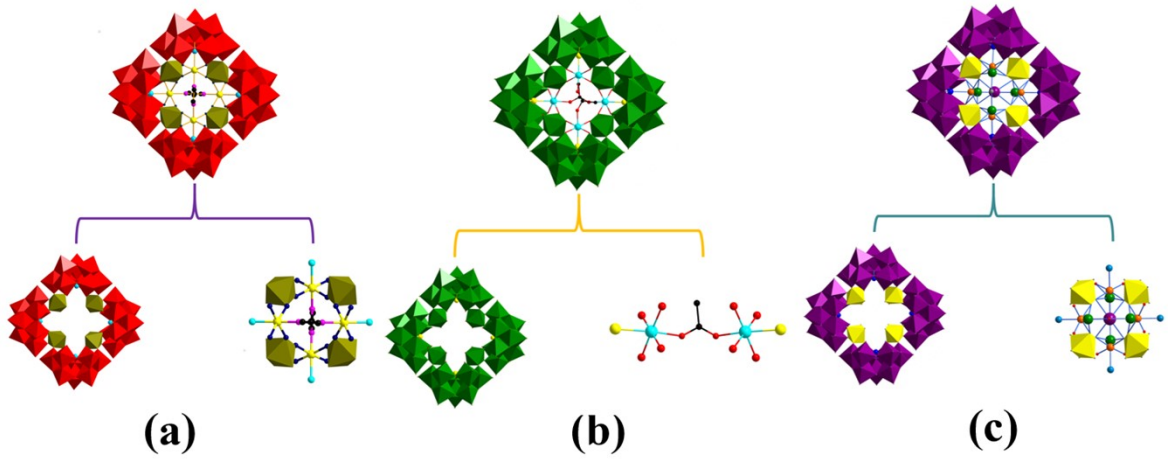

Fig. S5 (a) Combined polyhedral/Ball-and-stick representation of polyanion **1**. Color code: WO_6 octahedron, red; bridging group WO_6 octahedron, dark yellow; Ru, yellow; As, aqua; O, dark blue; C, black; N, pink; all hydrogen atoms have been omitted for clarity; (b) Combined polyhedral/Ball-and-stick representation of $[As_4W_{40}O_{140}\{Ru_2(CH_3COO)\}_2]^{28-}$ Color code: WO_6 octahedron, green; As, yellow; Ru, aqua; C, black; O, red; (c) Combined polyhedral/Ball-and-stick representation of $[Pd_2Na_2K(AsW_9O_{33})_4(WO_2)_4(H_2O)]^{21-}$ Color code: WO_6 octahedron, violet; bridging group WO_6 octahedron, yellow; K, violet; Na, green; Pd, orange; As, blue; O, red.

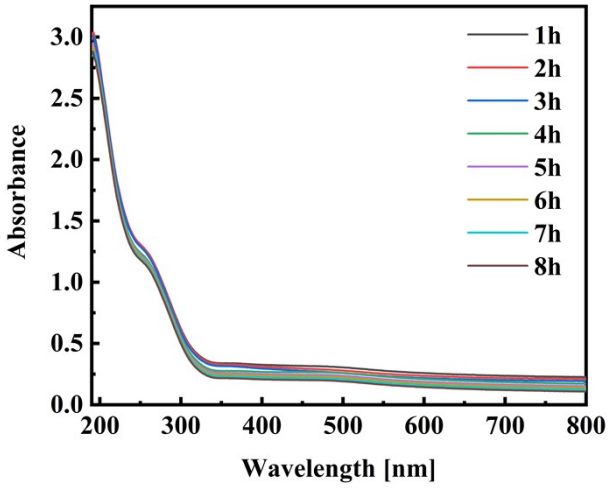

Fig. S6 The UV-Vis spectra of compound **1** with time intervals.

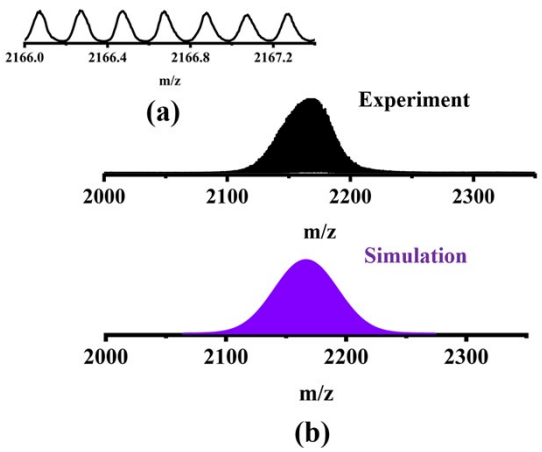

Fig S7 Catalyst **1** dissolved in water: (a) Zoom-in of the peaks at around m/z 2166.67; (b)The simulated isotope pattern (bluish violet) and experimental data (black) at around m/z 2166.67.

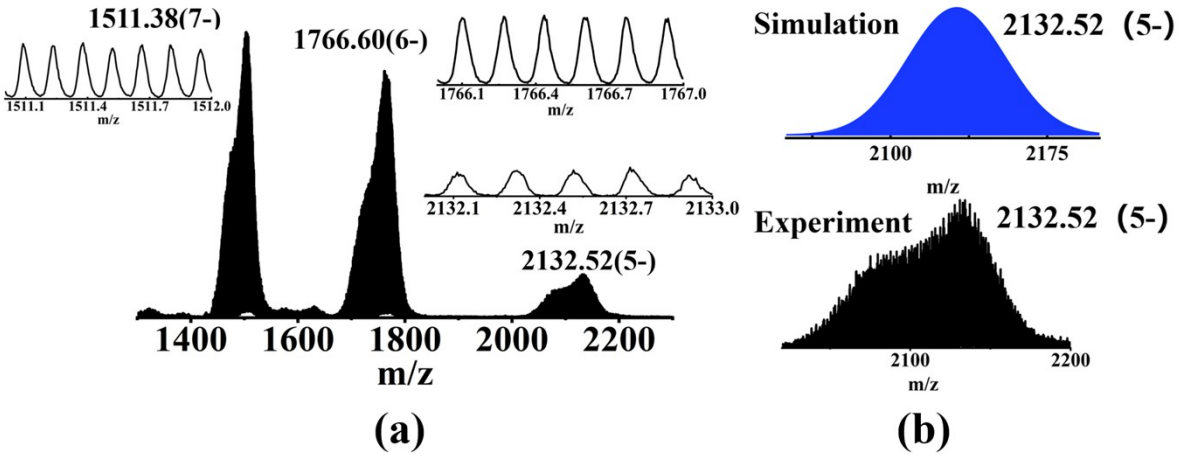

Fig. S8 After catalysis **1** dissolved in water (a) ESI mass spectrum corresponding to the intact cluster at around 1511.38, 1766.60 and 2132.52; (b) Simulated (blue) and experimental (black) patterns at around m/z 2132.52.

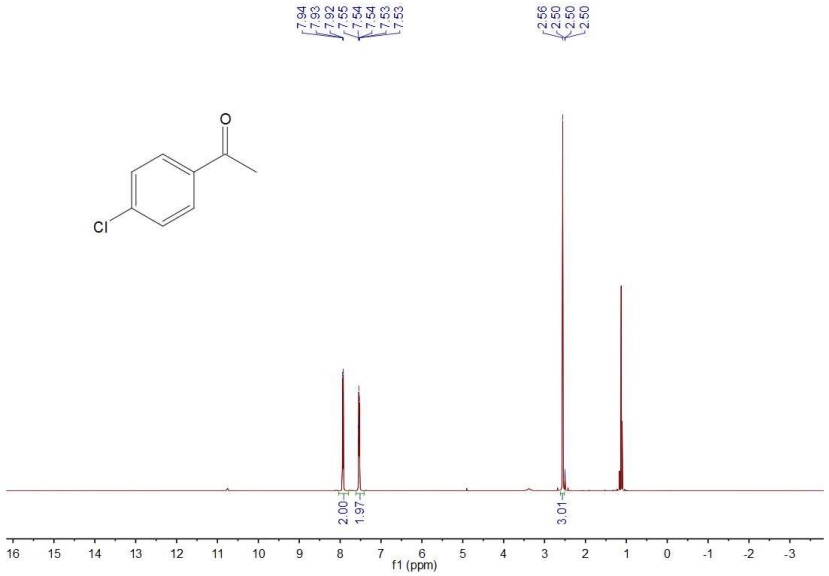

Fig. S9 The ^{1}HNMR spectrum of post-catalyzed solution.

Table S1 Crystallographic data parameters for **1**.

	1
empirical formula	$C_6H_6As_4K_4N_4Na_9O_{158}Ru_{3.2}W_{40}$
formula weight	11004.08
temperature (K)	150.0
crystal system	tetragonal
space group	I-4
a /Å	19.7922(4)
b /Å	19.7922(4)
c /Å	26.1324(6)
α /deg	90
β /deg	90
γ /deg	90
V /Å^3	10236.9(5)
Z	2
ρ_{calc} /g cm^{-3}	3.570
μ /mm^{-1}	23.427
2ϑ range/deg	4.858 to 56.612
index ranges	-24 ≤ h ≤ 26
	-22 ≤ k ≤ 26
	-34 ≤ l ≤ 34
reflns collected	41367
independent reflens	12357
R_{int}	0.0612
data/restraints/parameters	12357/198/519
GOF on F^2	1.079
R_1, wR_2 [$I > 2\sigma(I)$]	0.0409, 0.0946
R_1, wR_2 [all data]	0.0441, 0.0959

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

Table S2 Selected bonds distances of compound **1**.

Bond	Bond length	Bond	Bond length
Ru1–O21	2.072 (13)	W4–O19	2.097 (12)
Ru1–O22	2.071 (14)	W4–O20	2.067 (13)
Ru1–O30	2.031 (13)	W4–O28	1.977 (14)
Ru1–O31	2.049 (13)	W4–O29	1.907 (13)
Ru1–As1	2.394 (3)	W4–O30	1.767 (15)
Ru–N1	2.07 (2)	W4–O31	1.721 (13)

Table S3 Bond valence sum calculations of Ru, As and W of compound **1**.

Atom Code	Bond Valence	Valence State	Atom Code	Bond Valence	Valence State
Ru1/Ru2/Ru3/Ru4	3.271	+3	W5	6.199	+6
As1/As2/As3/As4	2.297	+3	W6	6.102	+6
W1	6.351	+6	W7	6.123	+6
W2	5.774	+6	W8	6.259	+6
W3	6.411	+6	W9	6.481	+6
W4	6.358	+6	W10	5.960	+6

Table S4 Assignment of peaks in negative mode mass spectra of **1** before and after catalysis and simulation.

Entry	**Charge**	**Observed M/z**	**Calculated M/z**	**Polyanion**
1	-7	1513.23	1513.19	$KNa_7H_{5.4}[(AsW_9O_{33})_4(WO_2)_4\{Ru_{3.2}(C_3H_3N_2)_2\}(H_2O)_2]^{7-}$
2	-6	1782.90	1782.93	$K_3Na_5H_{6.4}[(AsW_9O_{33})_4(WO_2)_4\{Ru_{3.2}(C_3H_3N_2)_2\}(H_2O)_6]^{6-}$
3	-5	2166.67	2166.53	$K_3Na_7H_{5.4}[(AsW_9O_{33})_4(WO_2)_4\{Ru_{3.2}(C_3H_3N_2)_2\}(H_2O)_{11}]^{5-}$
4	-7	1511.38	1511.45	$Na_9H_{4.4}[(AsW_9O_{33})_4(WO_2)_4\{Ru_{3.2}(C_3H_3N_2)_2\}(H_2O)]^{7-}$
5	-6	1766.60	1766.53	$Na_9H_{5.4}[(AsW_9O_{33})_4(WO_2)_4\{Ru_{3.2}(C_3H_3N_2)_2\}(H_2O)_2]^{6-}$
6	-5	2132.52	2132.52	$K_3Na_5H_{7.4}[(AsW_9O_{33})_4(WO_2)_4\{Ru_{3.2}(C_3H_3N_2)_2\}(H_2O)_4]^{5-}$