

## Supporting Information

# Polyoxovanadate catalysts for oxidation of 1-phenyl ethanol: from the discrete $[V_4O_{12}]^{4-}$ and $[V_{10}O_{28}]^{6-}$ anions, to the anionic $[V_6O_{17}]_n^{4n-}$ coordination polymer

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**Table S1.** the BVS calculations of the vanadium and oxygen atoms in **1**.

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**Table S2.** the BVS calculations of the vanadium and oxygen atoms in **2**.

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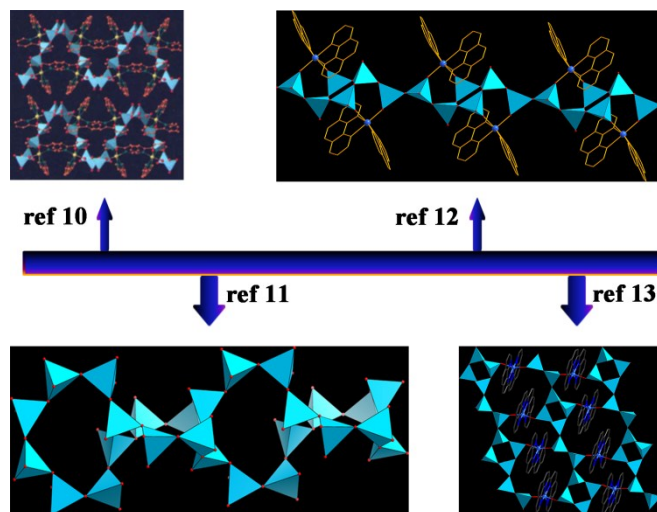
**Fig. S5.** Supramolecular structure of compound **3** (a) C–H···O hydrogen bonding interactions in **3**. (b)  $\pi\cdots\pi$  interactions in **3**.

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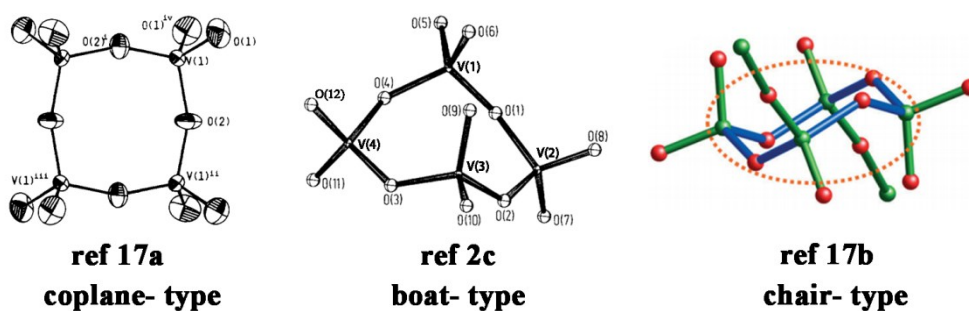
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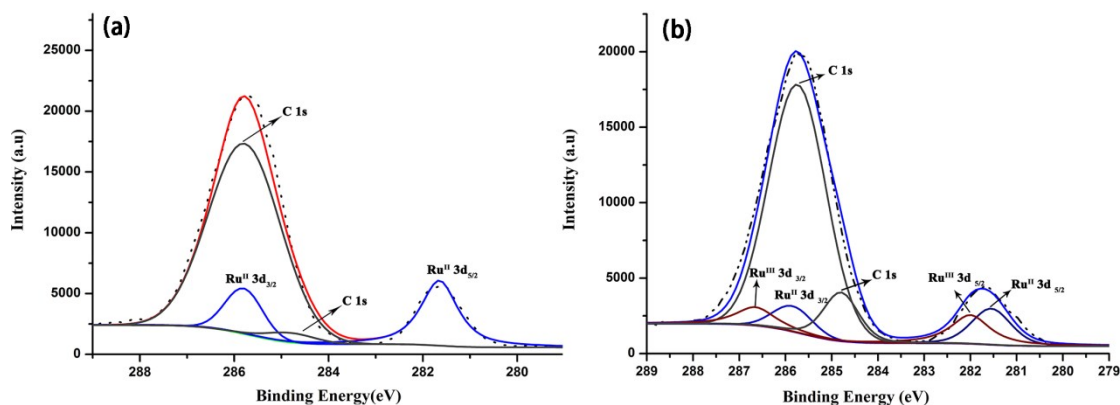
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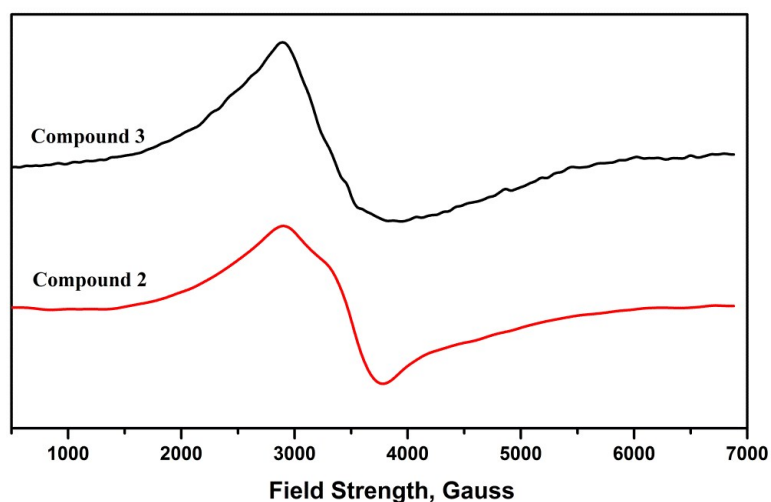
Atom	BVS
V1	5.295
V2	5.241
O1	2.179
O2	1.537
O3	1.667
O4	1.541
O5	1.508
O6	2.103



**Fig. S3.** XPS for C 1s and Ru 3d. Peak deconvolution of the Ru 3d core-level energy region yields two ruthenium intensities (a) at 281.65 eV (3d<sub>5/2</sub>) and 285.80 eV (3d<sub>3/2</sub>) for Ru<sup>II</sup> 3d in **1** (b) 282.0 eV (3d<sub>5/2</sub>) and 286.65 eV (3d<sub>3/2</sub>) for Ru<sup>III</sup> 3d in **3**, 281.6 eV (3d<sub>5/2</sub>) and 285.85 eV (3d<sub>3/2</sub>) for Ru<sup>II</sup> 3d in **3**. Carbon from phen ligands and graphitic carbon intensity are located at 284.8 eV and 285.8 eV, respectively.

**Table S2.** the BVS calculations of the vanadium and oxygen atoms in **2**.

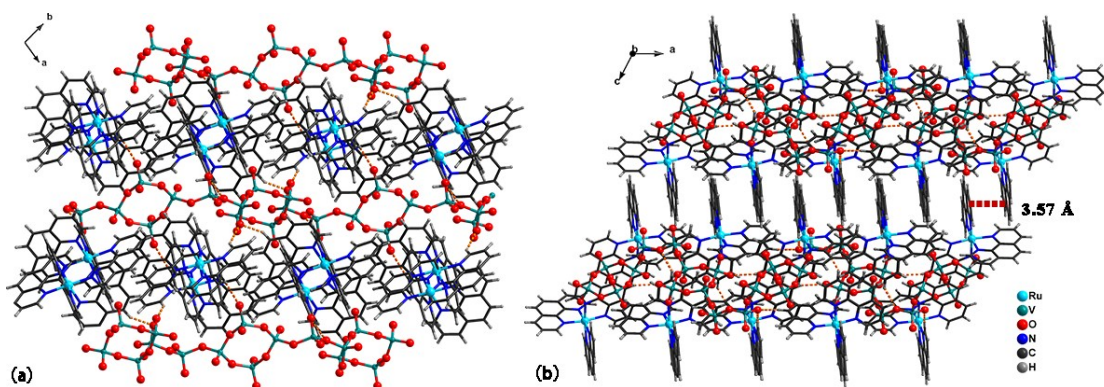
Atom	BVS	Atom	BVS	Atom	BVS	Atom	BVS
V1	5.073	O1	1.908	O6	1.671	O11	1.948
V2	5.059	O2	1.754	O7	1.809	O12	1.869
V3	5.043	O3	1.740	O8	1.919	O13	1.371
V4	5.110	O4	1.908	O9	1.826	O14	1.938
V5	5.126	O5	2.004	O10	1.745		



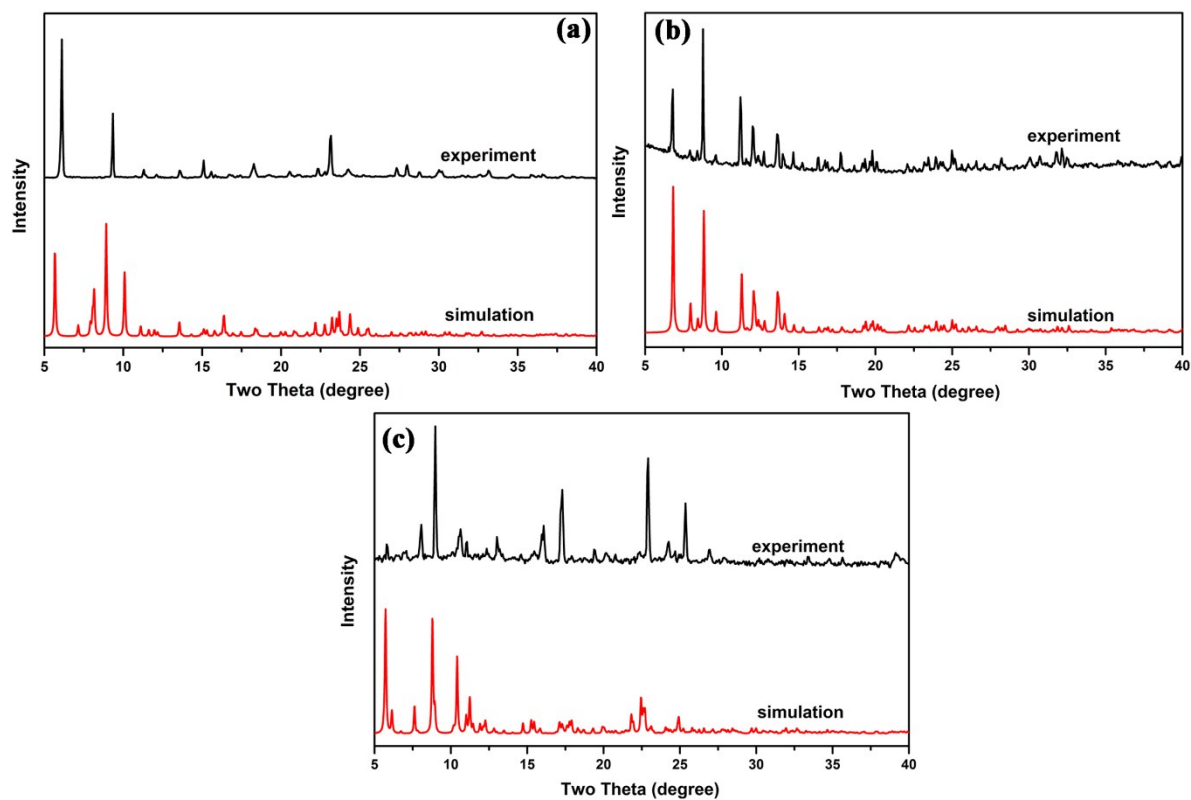
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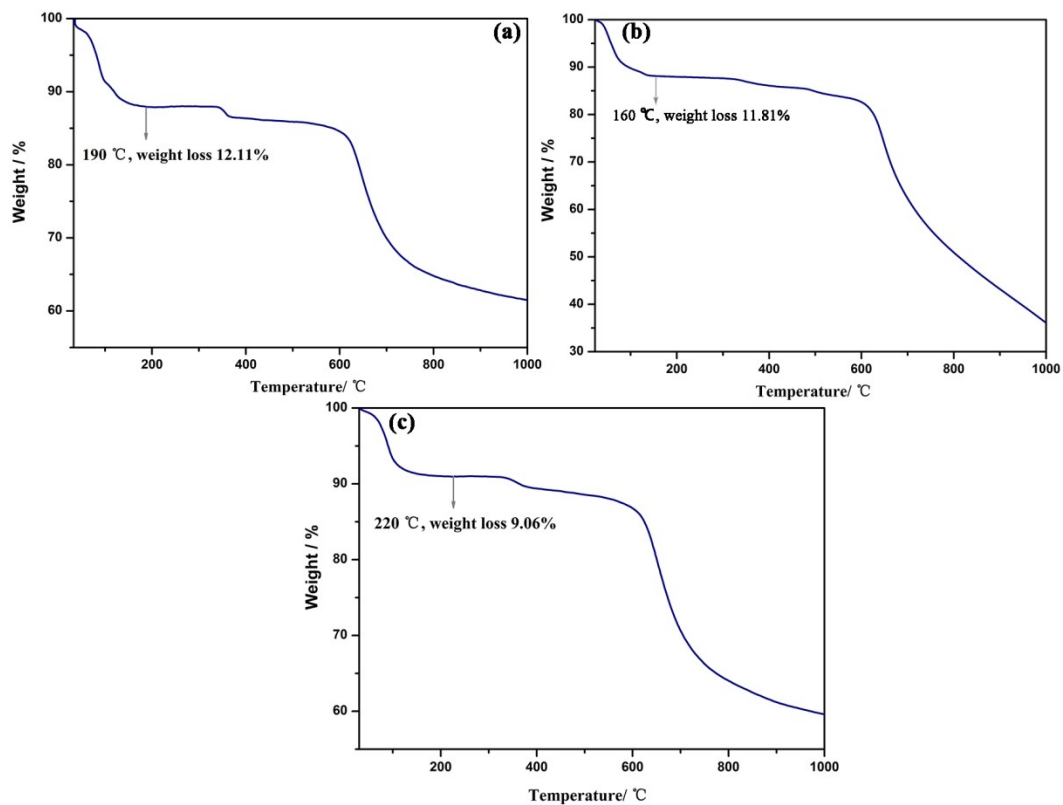
Atom	BVS	Atom	BVS	Atom	BVS	Atom	BVS
V1	5.303	O1	1.694	O7	1.847	O13	1.759
V2	5.372	O2	1.694	O8	1.754	O14	2.083
V3	5.721	O3	2.152	O9	2.226	O15	2.178
V4	5.382	O4	1.764	O10	1.658	O16	1.997
V5	5.332	O5	2.170	O11	1.712	O17	1.618
V6	5.486	O6	2.183	O12	2.107		



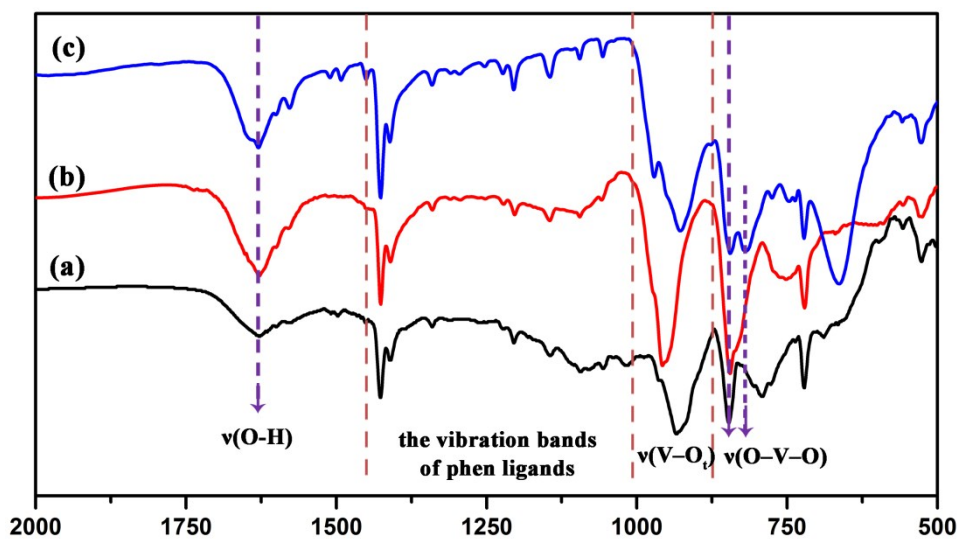
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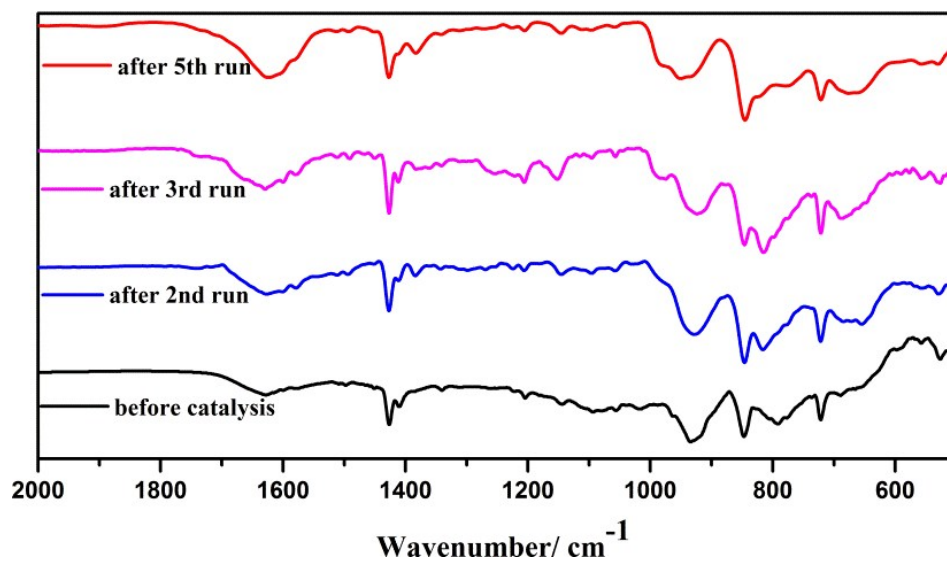
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