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Electronic Supplementary Information

Two New Isopolyoxovanadates Based on V_{10} and V_6: Structural Assembly and Dual Catalytic Applications

Linmeng Lu[1], Ziyi Hu[1], Qichao Yan, Xinyao Gao, Chaonan Liu, Ruikang Zhang, Li Ma[*], and Yuanzhe Gao[*]

Hebei Key Laboratory of Inorganic Nano-materials, National Demonstration Center for Experimental Chemistry Education, Hebei Engineering Research Center of Thin Film Solar Cell Materials and Devices, College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang, 050024, P. R. China.

[*]Correspondence authors

Email: yzgao@hebtu.edu.cn; mali0801@hebtu.edu.cn

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Experimental Methods

1.1 Materials and methods

All chemicals were used as purchased without purification. Hydrothermal synthesis was carried out with a 23 mL Teflon-lined autoclave under autogenous pressure; the reaction vessels were filled to approximately 25% of their volume capacity. FT-IR spectra were recorded in KBr pellets with FTIR-8900 IR spectrometer in the range of 4000-500 cm^{-1}. Powder X-ray diffraction (PXRD) was performed on a Bruker AXS D8 Advance diffractometer. TGA analyses were performed on a Perkin-Elmer Pyris Diamond TG/DTA instrument in flowing N_2 with a heating rate of 10°C min^{-1}. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250 X-ray photoelectron spectrometer. The reaction products were analyzed by GC (Agilent, GC-7980B with an FID detector equipped with a DB-FFAP capillary column).

1.2 X-ray crystallography

Single crystal samples of compounds **1-2** with regular shapes were collected under an optical microscope. Crystallography data were collected at 298(2)K temperature using the XtaLAB Synergy Dualflex HyPix diffractometer equipped with A Cu Kα radiation source (λ = 1.54056 A). Compounds **1-2** maintained a constant temperature of 293(2)K during the data acquisition process. The crystal structure was solved by Shelxtl

software, and the structure was refined by using the XL refinement package optimized by the least square method. The crystallography data and structural refinement details of compounds **1-2** are detailed in Table S1. Their characteristic bond lengths (A) and bond angles (°) data are listed in Table S2 respectively.

1.2 Experiment of sulfide oxidation reaction and Knoevenagel condensation reaction

1.2.1 Experiment of sulfide oxidation reaction

The catalytic activities of compounds **1-2** were systematically evaluated using the methyl phenyl sulfide/tert-butyl hydroperoxide (TBHP) reaction system. The reaction process is as follows: 0.40 mmol of methylphenyl sulfide, 0.56 mmol of tert-butyl hydrogen peroxide (TBHP), 0.40 mmol of 1-bromo-2-fluorobenzene (GC internal standard), 2.0 mL of methanol and 10 mg of catalyst are added successively to the sample tube. At room temperature, stirring was carried out on a parallel reactor. The reaction process was quantitatively monitored using a gas chromatograph (GC), and the catalyst after the reaction was washed multiple times with methanol by a centrifuge and then dried in the air for the next use.

1.2.2 Experiment of Knoevenagel condensation reaction

Benzaldehyde and malonitrile were selected as reactants to test and evaluate the catalytic performance of compounds **1-2**. The reaction process is as follows: 1.00 mmol of benzaldehyde, 2.00 mmol of malonitrile, 1.00

mmol of 1-bromo2-fluorobenzene (GC internal standard), 2.0 mL of ethanol and 10 mg of catalyst are added successively to the sample tube. Under room temperature conditions, the reaction system was carried out on a parallel reactor. A gas chromatograph (GC) was used, and the reaction process was quantitatively monitored by the internal standard method. The catalyst after the reaction was washed multiple times with ethanol by a centrifuge and then dried in the air for the next use.

Section S2 Supplementary Tables

Table S1. Detailed crystallographic parameters of compounds **1-2**

Compound	**1**	**2**
Empirical formula	$C_8H_{32}Cu_2N_8O_{25}V_{10}$	$C_4H_{12}CuN_4O_{16}V_6$
Formula weight	1276.89	741.36
Temperature/K	293(2)	293(2)
Crystal system	triclinic	orthorhombic
space group	*P***Error!**	*Cmca*
a/Å	6.7442(2)	18.5683(2)
b/Å	8.9299(2)	15.3038(2)
c/Å	15.9661(3)	6.6179(1)
α/°	105.040(2)	90
β/°	91.170(2)	90
γ/°	106.320(2)	90
Volume/Å^3	886.67(4)	1880.58(4)
Z	1	4
Calculated density(mg·m^{-3})	2.391	2.618
μ/mm^{-1}	23.195	26.033

Reflections collected	10638	7583
Reflections unique	3540	970
$R_{(int)}$	0.0361	0.0352
parameters	245	81
GOOF on F^2	1.055	1.059
R_1 *[I>2sigama (I)]*	0.0335	0.0226
wR_2 *[I>2sigama(I)]*	0.0896	0.0656
R_1 (all data)	0.0346	0.0229
wR_2 (all data)	0.0905	0.0659

Table S2. The select bonds and angles of compounds **1-2**.

Compound **1**					
Cu(1)-N(3)	2.011(3)	V(3)-O(7)	1.588(3)	N(3)#1-Cu(1)-N(3)	180.000(1)
Cu(1)-N(4)	2.030(3)	V(3)-O(8)	1.922(2)	N(3)#1-Cu(1)-N(4)	96.13(11)
Cu(1)-O(6)	2.489(33)	V(3)-O(12)#4	2.075(2)	N(3)-Cu(1)-N(4)	83.87(11)
Cu(2)-O(13)	2.442(50)	V(4)-O(2)#6	2.941(6)	N(4)#1-Cu(1)-N(4)	180.000(1)
V(1)-O(10)	1.695(2)	V(3)-O(7)	1.588(3)	O(10)-V(1)-O(12)	109.38(10)
V(1)-O(11)	1.606(2)	V(3)-O(8)	1.922(2)	O(10)-V(1)-O(13)	111.04(10)
V(1)-O(12)	1.791(2)	V(4)-O(3)#6	1.928(2)	O(11)-V(1)-O(10)	108.13(12)
V(1)-O(13)	1.820(19)	V(4)-O(5)	1.873(3)	O(11)-V(1)-O(12)	107.07(11)
V(2)-O(8)	1.916(2)	V(4)-O(6)	1.586(3)	O(11)-V(1)-O(13)	107.87(11)
V(2)-O(10)	1.937(2)	V(4)-O(8)#6	1.937(2)	O(12)-V(1)-O(13)	113.15(9)
V(2)-O(12)#4	1.973(2)	V(4)-O(13)#4	2.007(2)	V(4)#3-V(2)-V(3)	75.519(16)

V(2)-O(13)#5	1.988(19)	V(5)-O(1)	1.752(5)	O(8)-V(2)-V(3)	36.35(6)
V(3)-O(4)	1.876(2)	V(5)-O(2)	1.611(3)	O(8)-V(2)-V(4)#3	40.51(6)
V(3)-O(5)	1.703(2)	V(5)-O(3)	1.690(2)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z+1 #3 -x+1,-y+1,-z+1 #4 -x,-y+1,-z+1 #5 x-1,y,z #6 x+1,y,z

Compound **2**

Cu(1)-N(1)	2.008(19)	N(1)-Cu(1)-N(1)#2	95.24(11)	O(2)-V(1)-O(5)	106.53(5)
V(1)-O(2)	1.613(19)	O(3)-V(2)-O(5)	106.03(7)	O(1)-V(1)-O(5)	94.16(5)
V(1)-O(1)	1.703(19)	O(3)-V(2)-O(4)#4	110.29(7)	O(5)-V(1)-O(5)#2	142.39(10)
V(1)-O(1)#6	2.103(19)	O(5)-V(2)-O(4)#4	98.38(6)	O(2)-V(1)-O(1)#6	100.27(9)
V(2)-O(3)	1.596(13)	O(3)-V(2)-O(4)	108.39(7)	O(1)-V(1)-O(1)#6	154.66(5)
V(2)-O(5)	1.728(13)	O(5)-V(2)-O(4)	94.76(6)	O(5)-V(1)-O(1)#6	78.46(5)
V(2)-O(4)	1.883(13)	O(4)#4-V(2)-O(4)	133.52(6)	V(2)#6-O(4)-V(2)	135.83(8)
V(2)-O(4)#5	2.059(14)	O(3)-V(2)-O(4)#5	100.29(6)	V(2)-O(4)-V(2)#5	105.87(6)
N(1)-Cu(1)-N(1)#1	180.0	O(4)-V(2)-O(4)#5	74.05(6)		
N(1)#1-Cu(1)-N(1)#2	84.76(11)	O(2)-V(1)-O(1)	105.07(11)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+1,y,z #4 x,-y+3/2,z-1/2 #5 -x+3/2,y+0,-z+1/2
#6 -x+1,-y+3/2,z-1/2

Section S3 Supplementary Figures

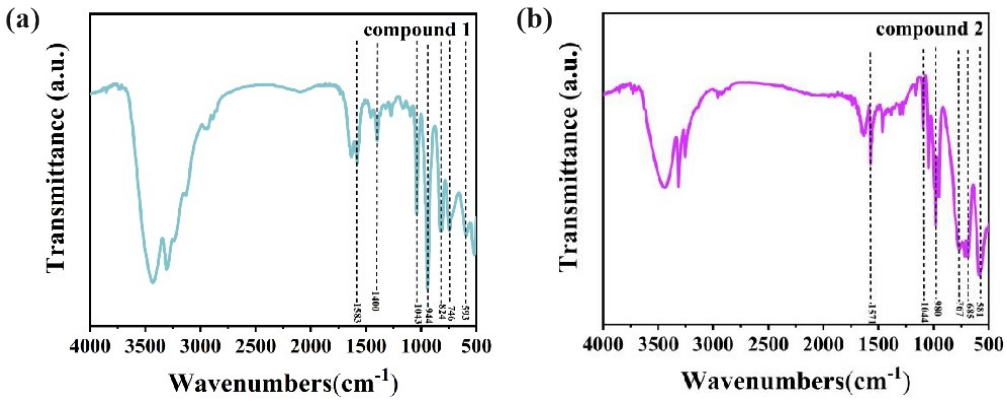

Fig. S1. FT-IR spectra of compounds **1-2**.

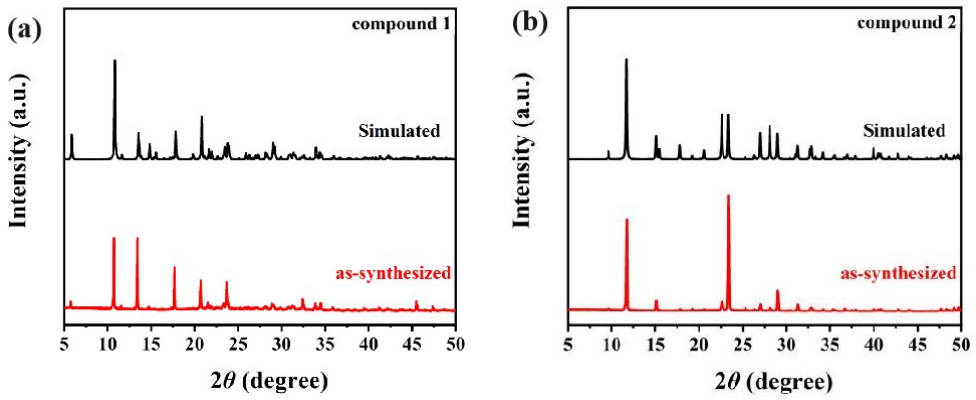

Fig. S2. Simulated and experimental PXRD patterns of compounds **1-2**.

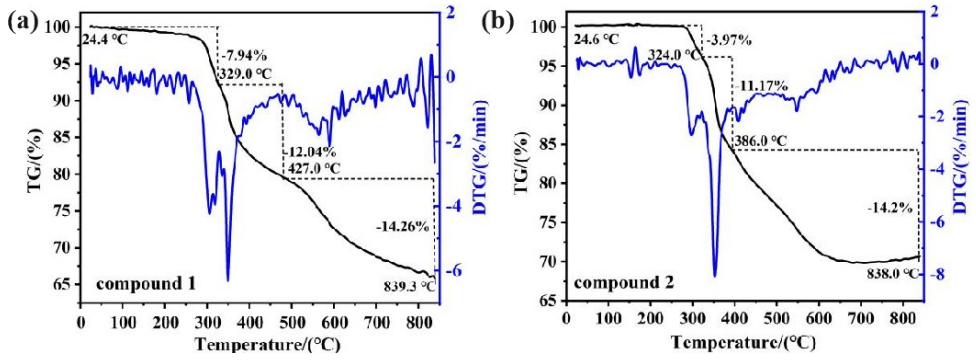

Fig. S3. TG curves of compounds **1-2**.

TG analysis

As shown in Fig. S3, the thermal stabilities of compounds **1**−**2** were investigated in the temperature range of 20.0−800.0°C under an atmosphere of N_2. For compound **1**, the first weight loss of 19.98% (calcd. 18.83%) occurring between 24.4-427.0°C corresponds to the loss of four ethylenediamine molecules. The second weight loss of 14.26% in the range of 427.0−839.3°C is attributed the collapse of the $\{V^{IV}_4V^{V}_6O_{25}\}$ cluster framework. For compound **2**, the first weight loss of 15.14% (calcd. 16.2%) occurring between 24.6−386.0°C is attributed to the loss of two

ethylenediamine molecules. The second weight loss of 14.2% in the range of 386.0-838.0°C is attributed to the collapse of the $\{V^{V}_{6}O_{16}\}$ cluster framework.

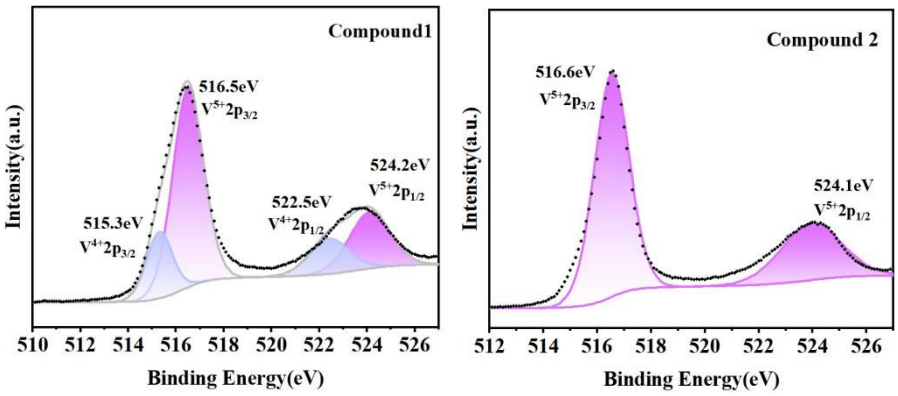

Fig. S4. XPS spectra of compound **1-2**.

XPS analysis

For compound **1**, the typical peaks with binding energies of 515.3 and 522.5 eV are assigned to V^{IV} $3p_{3/2}$ and V^{IV} $3p_{1/2}$, and those at 516.5 and 524.2 eV are attributed to V^{V} $2p_{3/2}$ and V^{V} $2p_{1/2}$, suggesting that the oxidation states of V ions in **1** are +4 and +5, respectively. For **2**, the typical peaks with binding energies of 516.6 and 524.1 eV are assigned to V^{V} $2p_{3/2}$ and V^{V} $2p_{1/2}$, suggesting that all V ions are in the +4 state (Fig. S4).

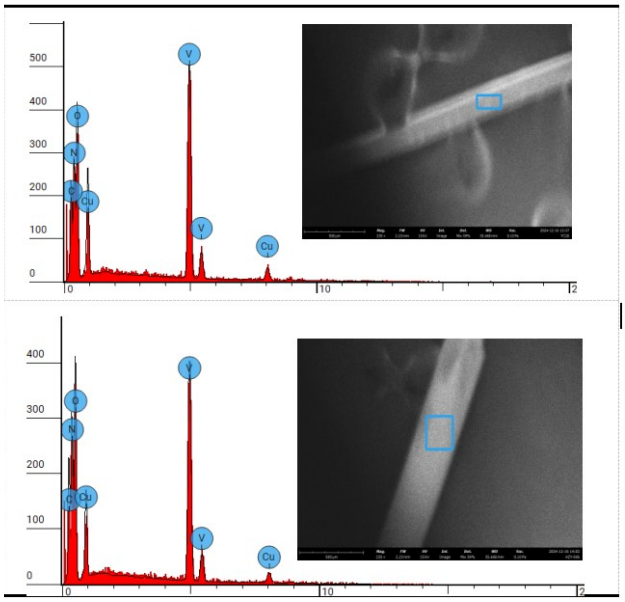

Fig. S5. EDS trial of compound **1-2**.

EDS analysis

As shown in Fig. S5, the EDS analysis indicates that **1** and **2** both contain the elements O, V, and Cu, with the chemical stoichiometric ratio of V to Cu being consistent with the results obtained from single-crystal structure analysis. The inset images show the scanning electron microscopy (SEM) morphological characterization results of compounds **1-2**.

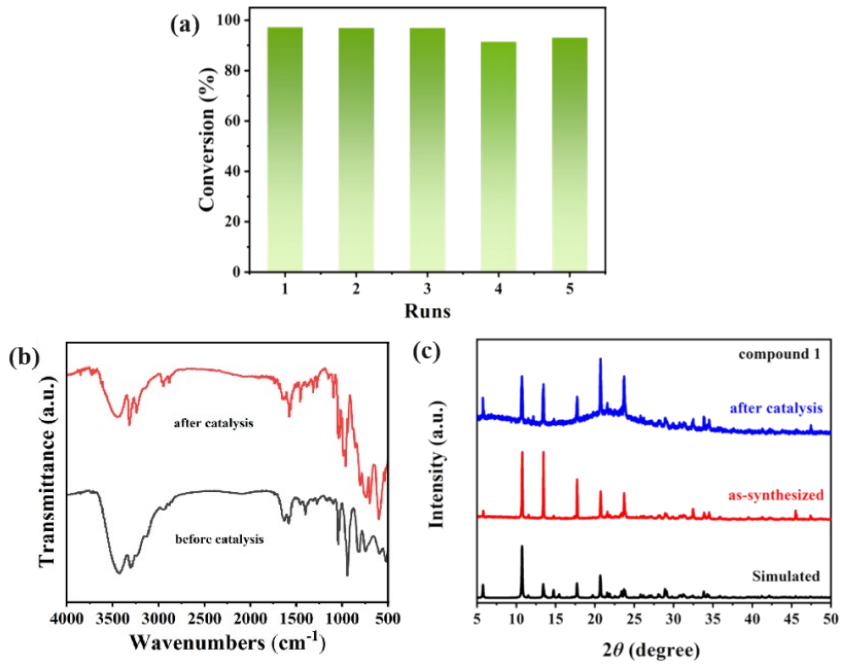

Fig. S6. The FT-IR spectra and PXRD patterns of the reused compound **1** in the sulfoxidation reaction.

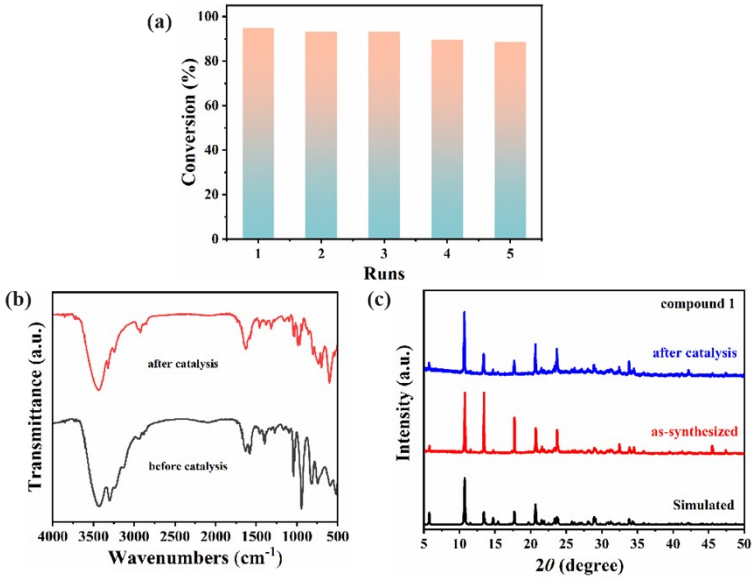

Fig. S7. The FT-IR spectra and PXRD patterns of the reused compound **2** in the Knoevenagel condensation**.**