Supporting Information

Figure Caption:

Section 1: Synthesis of **1**.

Section 2: Structure determination for **1**.

Section 3: Detalied conditions of the selective catalytic oxidation reaction.

Section 4: Detailed description of the stability test of catalyst 1.

Fig. S1. View of the crown-shaped borovanate anionic partial structure.

Fig. S2. The EDS spectrum of **1**.

Fig. S3. The simulated/experimental powder X-ray diffraction for **1** and catalyst after four runs of catalytic reaction.

Fig. S4. The IR spectrum for **1**.

Fig. S5. The TG and DTG curves for **1**.

Fig. S6. The XPS spectra for B_{1s}(c) and O_{1s}(d) in **1**.

Fig. S7. The XPS spectra for N_{1s}(e) and C_{1s}(f) in **1**.

Table S1. The results of BVS calculations for V, Cu and B sites in **1**.

Table S2. The selected bond distances(Å) and angles(°) for **1**.

Section 1: Synthesis of 1:

1 was prepared from a mixture of V_2O_5, $NH_4B_5O_8$, $Cu(CO_2CH_3)_2 \cdot H_2O$, H_3BO_3, $C_2H_8N_2$ (en) and H_2O in a molar ratio of 1:9:6:10:36:300 by means of hydrothermal method. The above mixture was stirred for 30 min, and transferred into a 50 mL Teflon-lined stainless steel autoclave and kept at 180 °C for 6 days. After the mixture was cooled to RT in a rate of 6°C/h, black block crystals were obtained. The crystals were collected by washed with deionized water and dried in air. Yield: 78 % (based on V_2O_5). The collected crystals were used for subsequent structural characterizations and various performance researches. It is worth noting that H_3BO_3, $NH_4B_5O_8$ and ethylenediamine (en) play a vital role during the synthesis process. We tried not to add H_3BO_3 in the synthesis process under the same other conditions, unfortunately, the target compound **1** could not be obtained, and we could only get the known black block compound $(enH_2)_5[(VO)_{12}O_6B_{18}O_{36}(OH)_6] \cdot 2(H_3O) \cdot 6H_2O$ (H.N. Wang and Z.X. Huang. *Chem. Res.*, 2006, **4**, 17). If only H_3BO_3 was introduced into the reaction and $NH_4B_5O_8$ was not added, we could only obtain previously reported borovanadate $\{[Cu(en)_2]_3[Cu(en)_2B(OH)_3]_2[(V^VO)_2(V^{IV}O)_{10}O_6(B_{18}O_{36}(OH)_6)(H_2O)]\} \cdot 13H_2O$ (Y.Q. Feng, Z.G. Zhong, H.W. Wang, H.T. Fan, D.Q. Bi, L. Wang, Z.Z. Xing and D.F. Qiu. *Chem.-Eur. J.*, 2017, **23**, 9962). It may be probably due to the polyboron anions $(B_5O_8)^-$ and $(BO_3)^{3-}$ provided more opportunities for the synthesis of borovanadates with high B/V ratio. Meanwhile, ethylenediamine not only acts as reactant and structure directing agent, but also plays the roles of reducing V^{5+} to V^{4+} cation and acid-base reconciliation of the system. In addition, we once tried to synthesize 3D open-framework borovanadates using other TM^{2+} cations (Co^{2+}, Ni^{2+} and Zn^{2+}) instead of Cu^{2+} cation under the same reaction conditions, however, which has not been successful up to now. This reveals that the Cu^{2+} cation with John-teller effect is very conducive to build 3D open-framework structures.

Section 2: Structure determination for 1:

The data for the crystal (0.32 × 0.28 × 0.26 mm) were collected on a Bruker APEX-II CCD diffractometer (Mo-Kα, λ = 0.71073 Å) at 293(2) K. A total of 17414 reflections were collected, of which 3205 reflections were unique (R_{int} = 0.0691). The structure was solved by the direct method and refined by the full-matrix least-squares on F^2 using the *SHELXL*-97 soft-ware. Hydrogen atoms on C/N from organic ligands (en) and protonated O(1) sites have been added by means of geometric hydrogenation. The H atoms bonded to isolated water molecules O1W, O2W and O3W were not added due to their slight disorders. All the non-hydrogen atoms were refined anisotropically.

Section 3: Detalied conditions of the selective catalytic oxidation reaction:

MeOH solvent (2mL), catalyst **1** (0.017mmol), 30% H_2O_2 (0.60 mmol) and methyl phenyl sulfide (0.5 mmol) were added to the flask in order, and refluxed at 40 °C for 6 hours. The filtrate was extracted with ethyl acetate, the obtained organic phase was dried with anhydrous $MgSO_4$, filtered, and the results were detected by gas chromatography mass spectrometer to determine the conversion and selectivity of the reaction. Each conversion/selectivity is depended on the average of three parallel experimental results.

Section 4: Detailed description of the stability test of catalyst 1:

After the reaction is completed, the catalyst **1** is separated by centrifugation and filtration, washed with ethyl acetate and distilled water, and dried under vacuum for subsequent recycling. In order to confirm the stability of catalyst **1**, we collected and treated the catalyst after each round of catalytic reaction in the same method as above, and carried out X-ray powder diffraction test. The test results showed that the structure of the catalyst was stable (Fig. S3). Meanwhile, we also performed the experiment of atomic absorption to analyze the mixture after the fourth run. The results showed that there was no corresponding signal of vanadium element in the mixture, indicating that the catalyst was stable during the catalytic reaction.
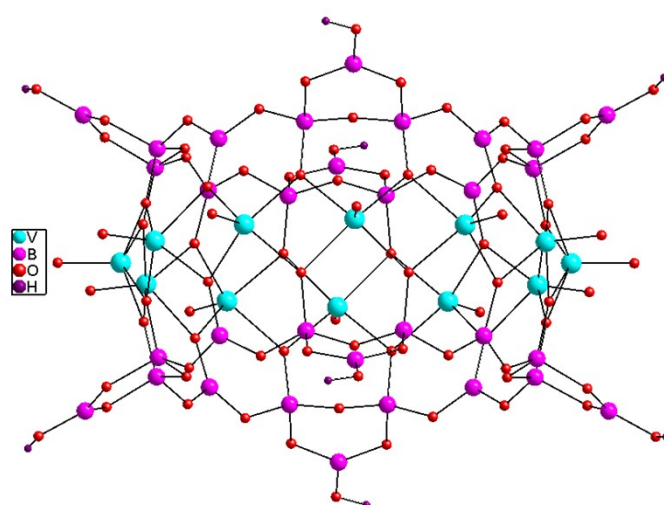

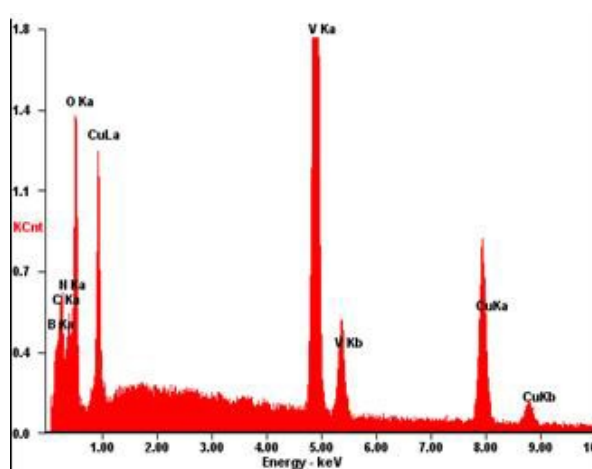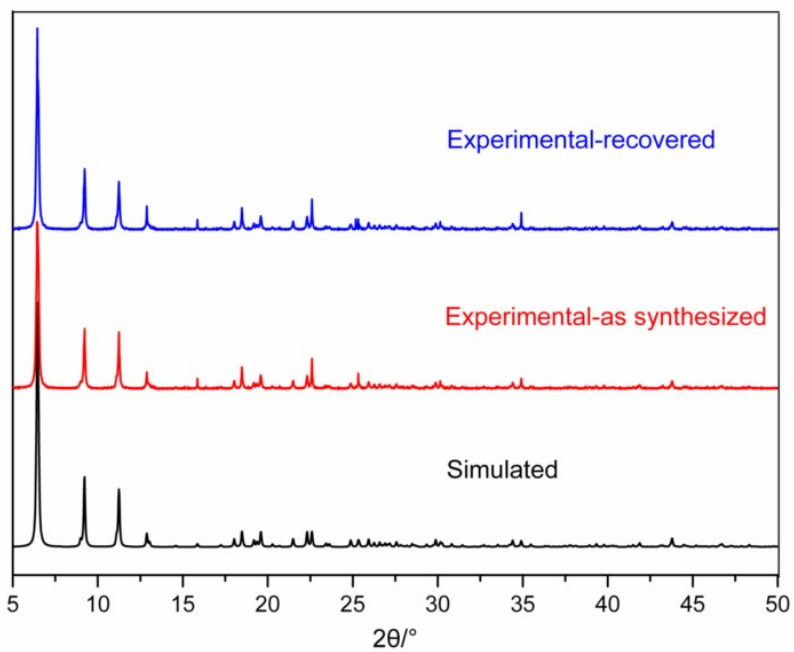**Fig. S1.** View of the crown-shaped borovanate anionic partial structure.
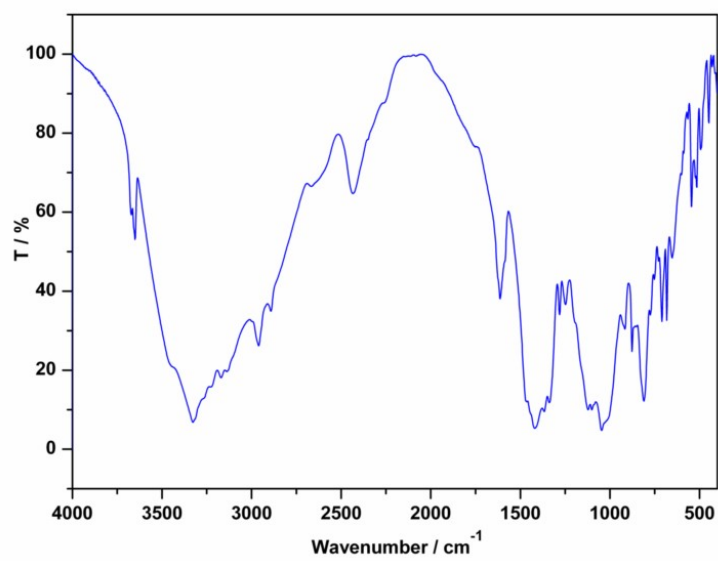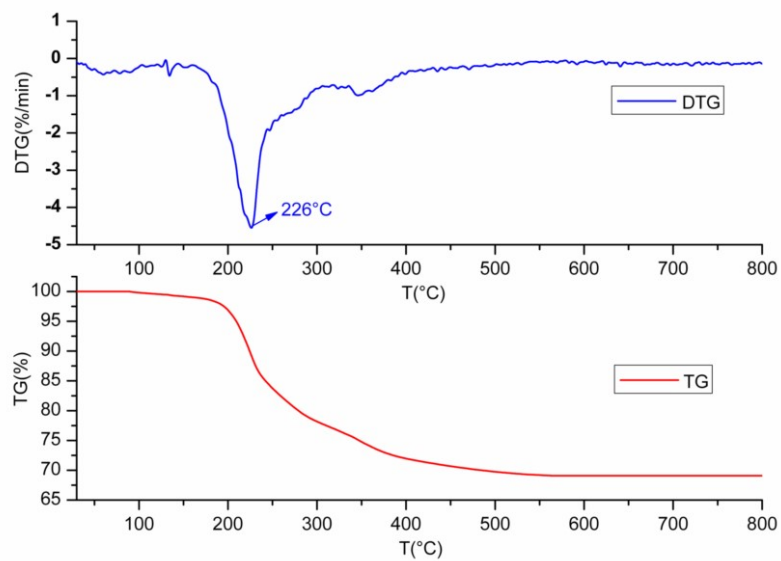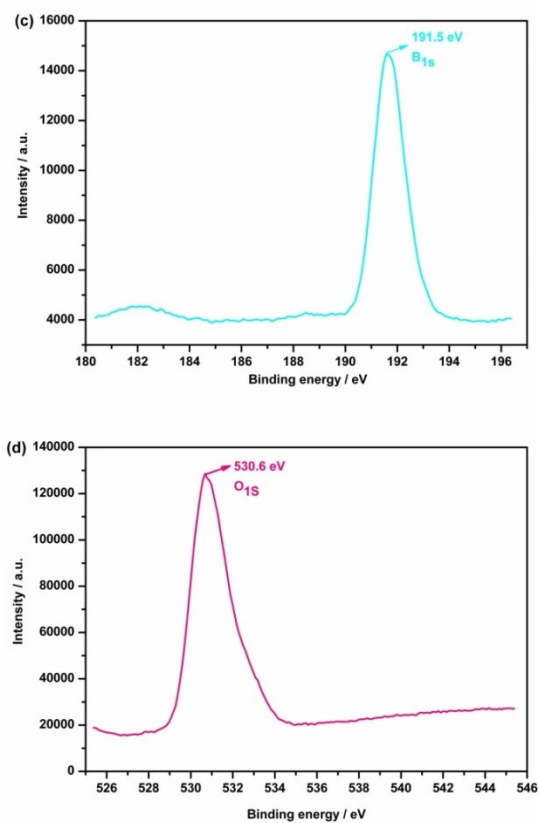

Fig. S2. The EDS spectrum of **1**.

Fig. S3. The simulated/experimental powder X-ray diffraction for **1** and catalyst after four runs of catalytic reaction.

Fig. S4. The IR spectrum for **1**.

Fig. S5. The TG and DTG curves for **1**.

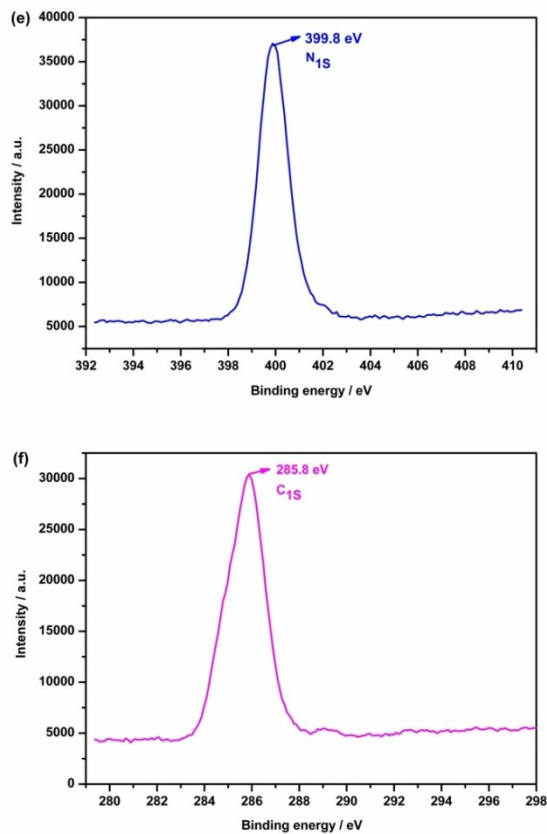**Fig. S6.** The XPS spectra for B_{1s}(c) and O_{1s}(d) in **1**.

Fig. S7. The XPS spectra for N_{1s}(e) and C_{1s}(f) in **1**.

Table S1. The results of BVS calculations for V, Cu and B sites in **1**.

Bond	Distance	BVS	$V_{(Sum)}$	Bond	Distance	BVS	$V_{(Sum)}$
V1-O11	1.602(10)	1.63		Cu2-N3	1.85(3)	0.52	
V1-O5	1.908(6)	0.71		Cu2-N3#6	1.85(3)	0.52	
V1-O5#1	1.908(6)	0.71	4.23	Cu2-N2	1.87(3)	0.49	2.08
V1-O8#2	1.981(7)	0.59		Cu2-N2#6	1.87(3)	0.49	
V1-O8#3	1.981(7)	0.59		Cu2-O9	2.969(71)	0.03	
V2-O12	1.586(9)	1.70		Cu2-O9#3	2.969(71)	0.03	
V2-O6	1.931(6)	0.67		B1-O1	1.348(13)	1.06	
V2-O6#1	1.931(6)	0.67	4.32	B1-O2	1.358(13)	1.04	3.13
V2-O5#1	1.948(7)	0.64		B1-O3	1.361(13)	1.03	
V2-O5	1.948(7)	0.64		B2-O4	1.447(13)	0.81	
V3-O10	1.614(10)	1.83		B2-O9#3	1.449(12)	0.81	3.10
V3-O6	1.894(7)	0.75		B2-O5	1.461(13)	0.78	
V3-O6#1	1.894(7)	0.75	4.73	B2-O2	1.505(12)	0.70	
V3-O8	1.953(7)	0.70		B3-O4	1.443(13)	0.82	
V3-O8#1	1.953(7)	0.70		B3-O7	1.461(13)	0.78	3.09

Cu1-N1	2.04(2)	0.32		B3-O6	1.476(13)	0.75	
Cu1-N1#1	2.04(2)	0.32		B3-O3	1.483(12)	0.74	
Cu1-N1#4	2.04(2)	0.32	1.66	B4-O7	1.327(13)	1.13	
Cu1-N1#5	2.04(2)	0.32		B4-O9	1.345(13)	1.07	3.15
Cu1-O12	2.360(9)	0.19		B4-O8	1.389(12)	0.95	
Cu1-O12	2.360(9)	0.19					

Symmetry transformations used to generate equivalent atoms:

#1: *x*, *y*, -*z*+2;   #2: *y*, -*x*+1, -*z*+2;   #3: *y*, -*x*+1, *z*;

#4: -*x*+1, -*y*+2, -*z*+2;   #5: -*x*+1, -*y*+2, *z*;   #6: -*x*+1/2, -*y*+3/2, -*z*+3/2.

Table S2. The selected bond distances (Å) and angles (°) for **1**.

Bond	Distance	Bond	Distance	Bond	Angle
V1-O11	1.602(10)	Cu2-N3	1.85(3)	O11-V1-O5	110.1(4)
V1-O5	1.908(6)	Cu2-N3#6	1.85(3)	O5-V1-O5#1	82.0(4)
V1-O5#1	1.908(6)	Cu2-N2	1.87(3)	O11-V1-O8#2	108.3(4)
V1-O8#2	1.981(7)	Cu2-N2#6	1.87(3)	O5-V1-O8#2	88.5(3)
V1-O8#3	1.981(7)	Cu2-O9	2.969(71)	O5#1-V1-O8#2	141.4(3)
V2-O12	1.586(9)	Cu2-O9#3	2.969(71)	O8#2-V1-O8#3	75.9(4)
V2-O6	1.931(6)	B1-O1	1.348(13)	O12-V2-O6	108.2(3)
V2-O6#1	1.931(6)	B1-O2	1.358(13)	O6-V2-O6#1	80.9(4)
V2-O5#1	1.948(7)	B1-O3	1.361(13)	O12-V2-O5#1	107.9(3)
V2-O5	1.948(7)	B2-O4	1.447(13)	O6-V2-O5#1	143.9(3)
V3-O10	1.614(10)	B2-O9#3	1.449(12)	O6-V2-O5	88.5(3)
V3-O6	1.894(7)	B2-O5	1.461(13)	O5#1-V2-O5	80.0(4)
V3-O6#1	1.894(7)	B2-O2	1.505(12)	O10-V3-O6#1	110.1(3)
V3-O8	1.953(7)	B3-O4	1.443(13)	O6#1-V3-O6	82.8(4)
V3-O8#1	1.953(7)	B3-O7	1.461(13)	O10-V3-O8	107.9(4)
Cu1-N1	2.04(2)	B3-O6	1.476(13)	O6#1-V3-O8	141.9(3)
Cu1-N1#1	2.04(2)	B3-O3	1.483(12)	O6-V3-O8	87.8(3)
Cu1-N1#4	2.04(2)	B4-O7	1.327(13)	O8-V3-O8#1	77.2(4)
Cu1-N1#5	2.04(2)	B4-O9	1.345(13)	N1#1-Cu1-N1	99.4(16)
Cu1-O12	2.360(9)	B4-O8	1.389(12)	N2-Cu2-N3	94.3(14)
Cu1-O12	2.360(9)	O1-H1#5	0.8200	N1-Cu1-O12#5	89.7(11)

Symmetry transformations used to generate equivalent atoms:

#1: *x*, *y*, -*z*+2;   #2: *y*, -*x*+1, -*z*+2;   #3: *y*, -*x*+1, *z*;

#4: -*x*+1, -*y*+2, -*z*+2;   #5: -*x*+1, -*y*+2, *z*;   #6: -*x*+1/2, -*y*+3/2, -*z*+3/2.