Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Furthering the Reaction Mechanism of Cationic Vanadium Clusters towards Oxygen

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S1. Small V_n^+ clusters reacting with oxygen

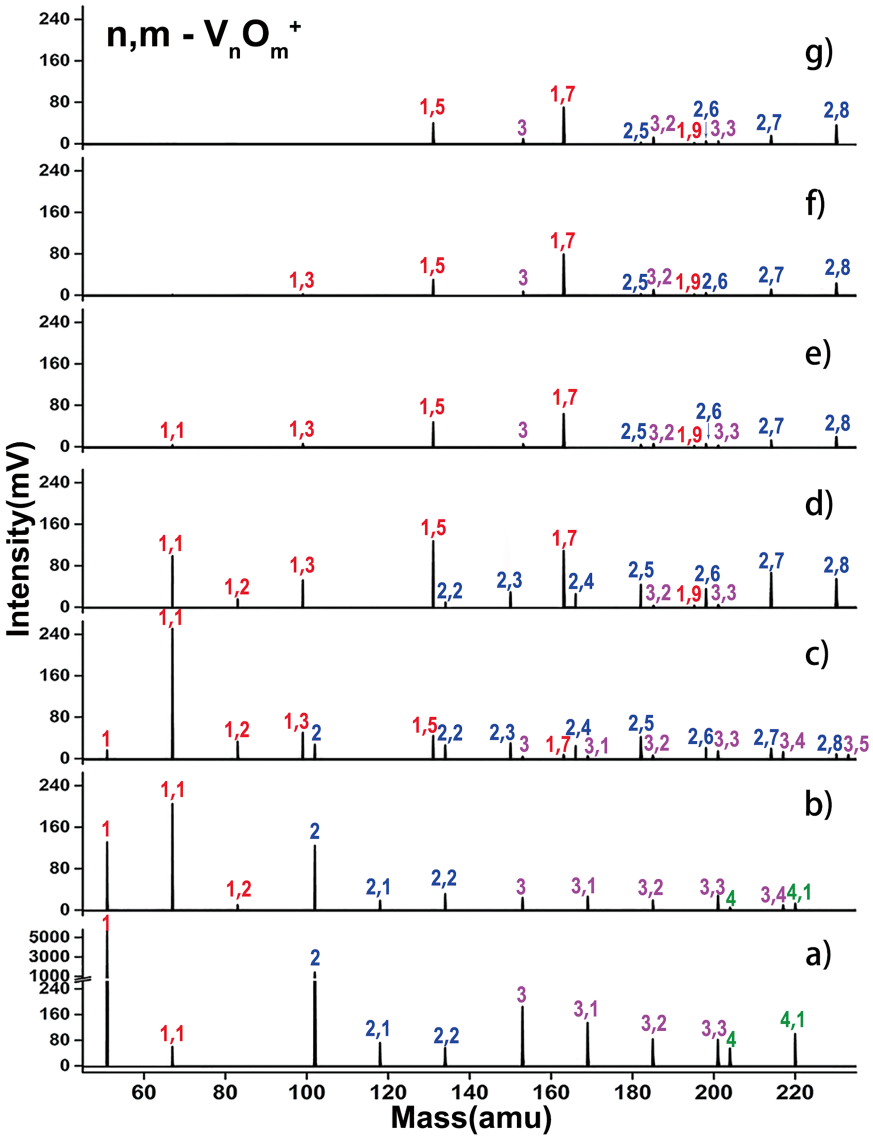

Fig. S1 Full mass spectra of small V_n^+ (n=1-4) clusters produced via a 1.0 cm nozzle at the absence **(a)** and presence **(b-g)** of oxygen introduced into the reaction tube. The amount of oxygen (0.1 MPa 3%O_2/He) is controlled by the on-time width of a pulsed valve: 210, 220, 230, 240, 250, 270 μs, respectively.

S2. Small neutral V_n^0 reacting with oxygen

Neutral V_n clusters are obtained by vacuum ultraviolet laser (VUV 118nm) ionization, after removing the charged species by the deflection plates downstream the reaction tube. Details of the instrumentation method can be found in our recently published studies.[1-3]

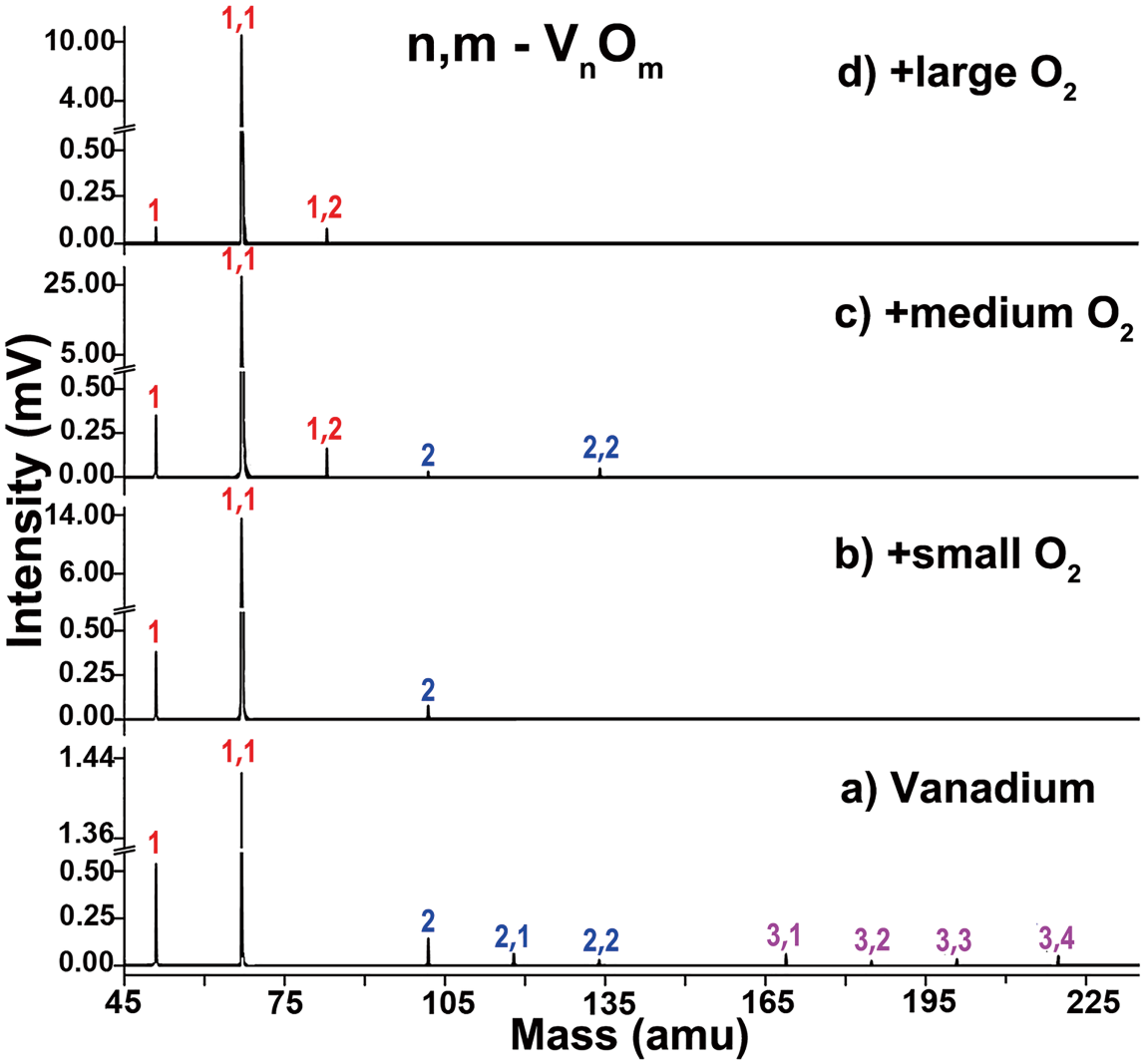

Fig. S2 TOF mass spectra of small V_n (n=1-4) clusters produced via a 1.0 cm nozzle at the absence **(a)** and presence **(b-d)** of oxygen added into the reaction tube. The amount of oxygen (0.1 MPa 3%O_2/He) is controlled by the on-time width of pulsed valve: 200, 220, 250μs, respectively.

S3. Optimized structures of $V_{1\text{-}4}^{0,+}$ and their oxides

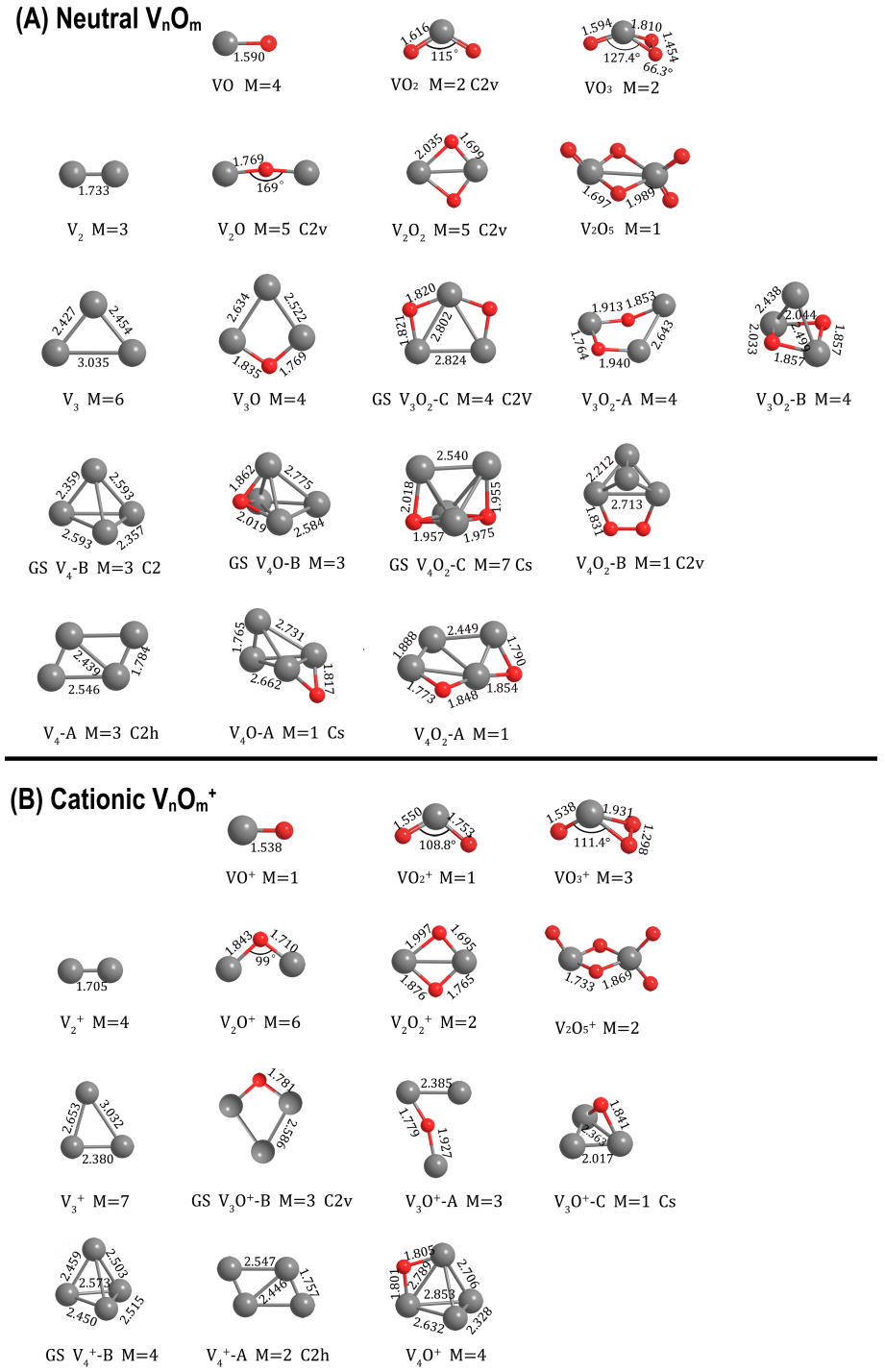

Fig. S3 The optimized stuctrues of $V_{1\text{-}4}^{0,+}$ and $V_{1\text{-}4}O_x^{0,+}$ at B3LYP-D3/TZVP level.

S4. Energy calculations

Table S1. ZPVE-corrected energies (E/eV) of $V_nO_m^{+/0}$ species calculated at B3LYP-D3/TZVP level (lowest lying isomers in bold).

	M=1	M=3	M=5	M=7
O	2.759	**0.000**	\	\
O_2	\	**0.000**	\	\
V^+	2.549	1.082	**0.000**	33.984
VO^+	**0.000**	0.226	2.341	\
VO_2^+	**0.000**	1.378	3.696	\
V_2	0.397	**0.000**	1.151	\
V_2O	5.229	0.175	**0.000**	0.164
V_2O_2	1.530	0.566	**0.000**	\
V_3^+	1.528	0.287	0.031	**0.000**
V_3O^+-A	2.167	0.564	1.153	2.467
V_3O^+-B	1.633	**0.000**	0.439	\
V_3O^+-C	2.167	\	\	\
V_4-A	1.116	0.611	0.850	\
V_4-B	1.983	**0.000**	0.331	\
V_4O-A	1.507	\	\	\
V_4O-B	1.312	**0.000**	0.343	\
V_4O_2-A	2.501	\	\	\
V_4O_2-B	7.886	\	\	\
V_4O_2-C	2.109	0.910	0.736	**0.000**

	M=2	M=4	M=6	M=8
V	1.901	**0.000**	0.041	\
VO	1.306	**0.000**	3.449	\
VO_2	**0.000**	1.737	4.052	\
V_2^+	0.327	**0.000**	0.653	\
V_2O^+	3.138	0.202	**0.000**	0.281
$V_2O_2^+$	**0.000**	0.348	0.018	\
V_3	0.660	0.116	**0.00**	1.384
V_3O	0.301	**0.000**	0.550	\
V_3O_2-A	1.197	0.568	1.293	\
V_3O_2-B	0.993	0.888	1.135	\
V_3O_2-C	0.327	**0.000**	0.464	\
V_3O_2-D	0.657	\	\	\
V_4^+-A	0.836	1.071	\	\
V_4^+-B	1.643	**0.000**	0.148	2.069
V_4O^+	**0.000**	0.405	0.017	\

S5. Reaction channels of $V_n^{+,0}$ (n=1-4) towards O_2

Table S2. Calculated reaction energies (ΔE/eV, ZPVE Corrected energies) and Gibbs free energies (ΔG_{298k}/eV) for the different dissociation channels of cationic V_n^+ (n=1-4) clusters with oxygen at B3LYP-D3/TZVP Level.

Entrance Channel	Products Channel	ΔE/eV	ΔG_{298k}/eV
$^5V^+ + {}^3O$	(1a) $^1VO^+$	-9.698	-4.103
$^5V^+ + {}^3O_2$	(1b) $^1VO_2^+$	-4.053	-3.742
	(1c) $^1VO^+ + {}^3O$	0.722	0.738
$^4V_2^+ + {}^3O_2$	(2a) $^5V^+ + {}^2VO_2$	-4.818	-4.818
	(2b) $^1VO^+ + {}^4VO$	-3.981	-4.002
$^7V_3^+ + {}^3O_2$	(3a) $^4VO^+ + {}^6V_2O$	-5.896	-5.892
	(3b) $^5V^+ + {}^5V_2O_2$	-5.599	-5.474
	(3c) $^4V_2^+ + {}^2VO_2$	-4.127	-4.063
	(3d) $^5V_2O + {}^1VO^+$	-2.429	-2.353
$^4V_4^+ + {}^3O_2$	(4a) $^5V^+ + {}^4V_3O_2$	-6.624	-7.478
	(4b) $^4VO + {}^3V_3O^+$	-6.586	-7.559
	(4c) $^3V_2 + {}^2V_2O_2^+$	-5.284	-6.180
	(4d) $^4V_2^+ + {}^5V_2O_2$	-4.798	-5.739
	(4e) $^6V_2O^+ + {}^5V_2O$	-4.234	-5.264

[a] Spin multiplicities are marked as pre-superscripts.
[b] ZPVE Corrected Energies for the isomers of the above species are given in Table S1.
[c] The structures of the selected isomers are given in Fig. S3.

Table S3. Calculated reaction energies (ΔE/eV, ZPVE Corrected energies) and Gibbs free energies (ΔG_{298k}/eV) for the different dissociation channels of neutral V_n (n=1-4) clusters with oxygen at B3LYP-D3/TZVP Level.

Entrance Channel	Products Channel	Δ E/eV	Δ G_{298k}/eV
$^4V + {}^3O$	(1a) ^4VO	-6.303	-6.059
$^4V + {}^3O_2$	(1b) $^1VO_2$	-6.418	-6.138
	(1c) $^1VO + {}^3O$	-1.192	-1.128
$^3V_2 + {}^3O_2$	(2a) $^5V_2O_2$	-8.334	-7.994
	(2b) $^4V + {}^2VO_2$	-5.262	-5.263
	(2c) $^4VO + {}^4VO$	-6.339	-6.403
	(2d) $^5V_2O + {}^3O$	-0.774	-0.770
$^6V_3 + {}^3O_2$	(3a) $^4V_3O_2$	-10.166	-9.653
	(3b) $^4V + {}^5V_2O_2$	-6.741	-6.594
	(3c) $^4VO + {}^5V_2O$	-5.484	-5.430
	(3d) $^2VO_2 + {}^4V_2$	-4.825	-4.738
	(3e) $^4V_3O + {}^3O$	-2.532	-2.389
$^3V_4 + {}^3O_2$	(4a) $^7V_4O_2$	-10.050	-8.807
	(4b) $^4V + {}^4V_3O_2$	-8.149	-8.040
	(4c) $^4VO + {}^4V_3O$	-6.817	-6.835
	(4d) $^3V_2 + {}^5V_2O_2$	-5.879	-5.856
	(4e) $^6V_3 + {}^2VO_2$	-4.440	-4.524
	(4f) $^5V_2O + {}^5V_2O$	-4.205	-4.243
	(4g) $^3V_4O + {}^3O$	-2.225	-2.113

[a] Spin multiplicities are marked as pre-superscripts.
[b] ZPVE Corrected Energies for the isomers of the above species are given in Table S1.
[c] The structures of the selected isomers are given in Fig. S3.

S6. Reaction Dynamics

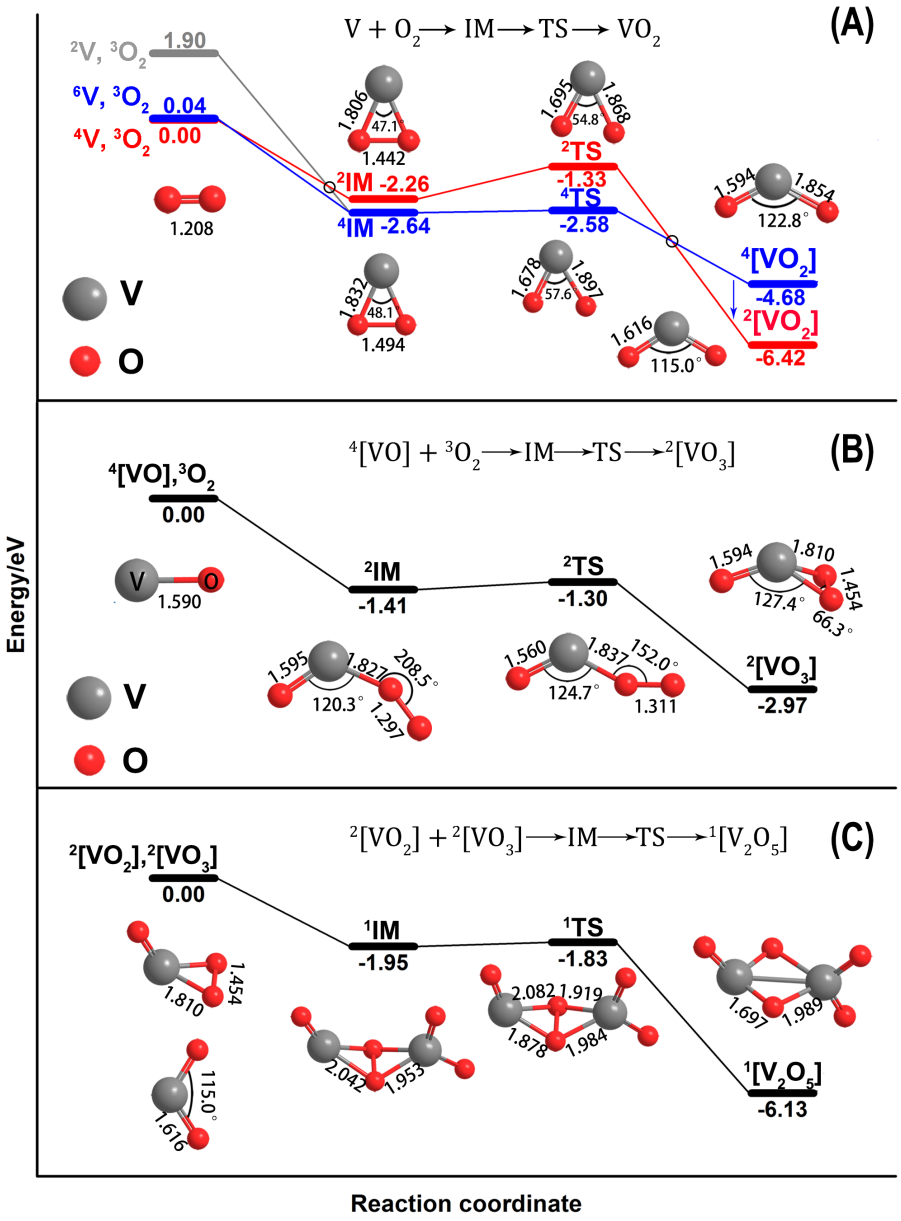

Fig. S4. Reaction energy diagrams of **(A)** V+O_2→VO_2, **(B)** VO + O_2 → VO_3, and **(C)** VO_3 + VO_2→V_2O_5, calculated at B3LYP/TZVP level with DFT-D3 dispersion correction. The energy values are relative to the entrance channel, denoted as zero-point vibration corrected energies, and given in eV. Spin multiplicity is marked as pre-superscript. Hollow circle denotes a possible spin inversion point for reaction paths.

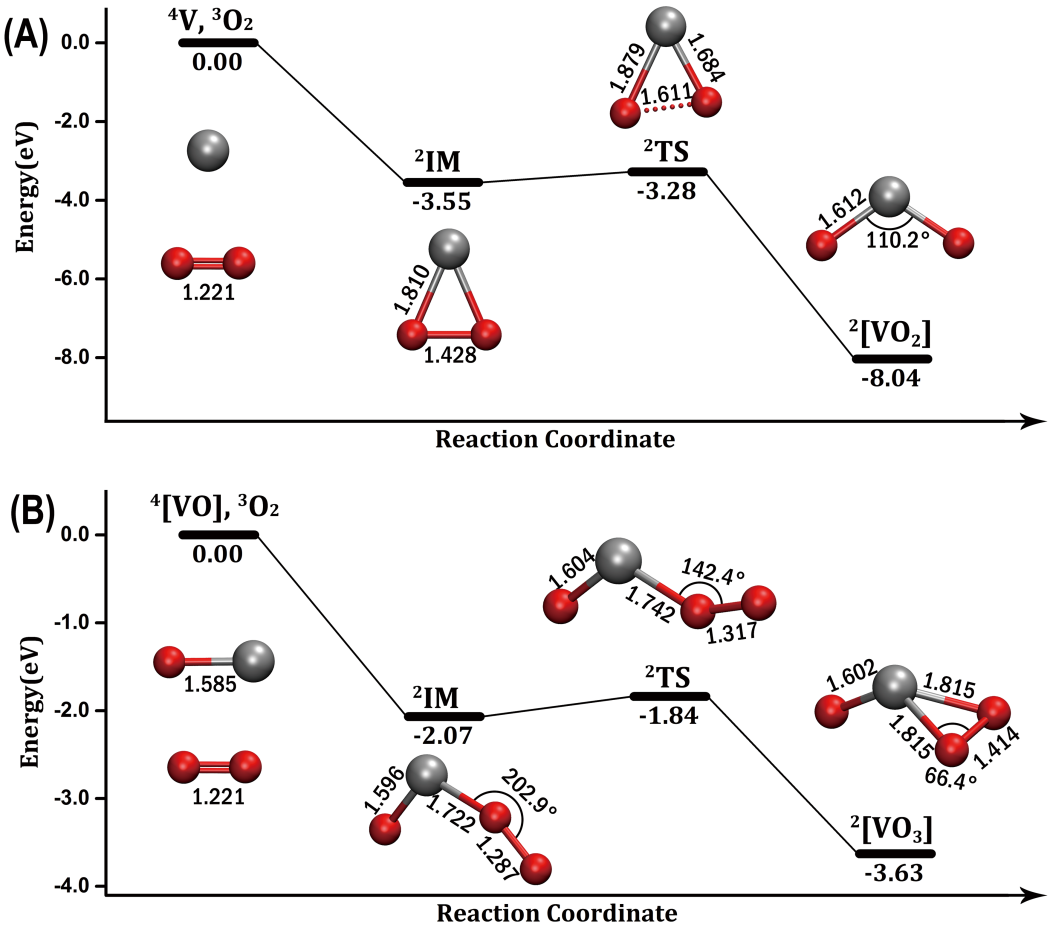

Fig. S5 The calculated Reaction energy diagrams at BP86/def2TZVP level of theory. (A) *V* + O_2 → VO_2, (B) *VO* + O_2 → VO_3. The energy values are relative to the entrance channel, denoted as zero-point vibration corrected energies, and given in eV. Spin multiplicity is marked as pre-superscript**.**

S7. Charge Decomposition Analysis (CDA)

Table S4. Charge Decomposition Analysis (CDA) result of VO_3^+

d = the number of electrons donated from fragment.1 to fragment.2 **fragment.1=VO^+ fragment.2=O_2**

b = the number of electrons back donated from fragment.2 to fragment .1 **Occ.=1.0 occupied Occ.=0.0 unoccupied**

r = the number of electrons involved in repulsive polarization **Orb. =molecular orbitals of VO_3^+**

Result for alpha electrons						Result for beta electrons					
Orb.	**Occ.**	**d**	**b**	**d-b**	**r**	**Orb.**	**Occ.**	**d**	**b**	**d-b**	**r**
1	1.0	-0.000001	0.000000	-0.000001	-0.000001	**1**	1.0	-0.000001	0.000000	-0.000001	-0.000001
2	1.0	0.000039	-0.000001	0.000040	0.000047	**2**	1.0	0.000043	-0.000001	0.000044	0.000040
3	1.0	-0.000010	-0.000787	0.000777	-0.000050	**3**	1.0	-0.000011	-0.000794	0.000784	-0.000030
4	1.0	-0.000010	-0.000778	0.000768	-0.000046	**4**	1.0	-0.000011	-0.000784	0.000773	-0.000030
5	1.0	0.000006	-0.000001	0.000007	0.000003	**5**	1.0	0.000006	-0.000001	0.000007	0.000002
6	1.0	0.000076	-0.000039	0.000115	0.000064	**6**	1.0	0.000080	-0.000040	0.000120	0.000062
7	1.0	0.000041	0.000000	0.000042	0.000003	**7**	1.0	0.000037	-0.000002	0.000038	0.000014
8	1.0	0.000019	-0.000010	0.000029	0.000020	**8**	1.0	0.000020	-0.000010	0.000030	0.000019
9	1.0	-0.000147	-0.000048	-0.000099	0.004788	**9**	1.0	0.000005	-0.000032	0.000037	0.004447
10	1.0	0.001421	-0.001038	0.002459	0.028525	**10**	1.0	0.001756	-0.001077	0.002834	0.027940
11	1.0	0.000194	-0.000083	0.000277	0.002128	**11**	1.0	0.000164	-0.000103	0.000267	0.002225
12	1.0	0.002175	-0.000065	0.002239	0.002512	**12**	1.0	0.000429	-0.000164	0.000594	0.006086
13	1.0	0.000305	0.017789	-0.017484	-0.041010	**13**	1.0	-0.000446	0.024372	-0.024818	-0.053270
14	1.0	0.000221	0.000079	0.000142	-0.000780	**14**	1.0	0.000215	0.000085	0.000130	-0.000782
15	1.0	0.001109	0.001117	-0.000009	0.028148	**15**	1.0	-0.000193	0.022198	-0.022390	-0.010923
16	1.0	0.000316	0.016375	-0.016059	0.021693	**16**	1.0	0.000036	0.026043	-0.026007	0.001422
17	1.0	0.008185	0.028053	-0.019868	-0.044462	**17**	1.0	0.004605	0.029425	-0.024819	-0.044062
18	1.0	-0.001213	0.023781	-0.024994	0.076923	**18**	1.0	0.000288	0.036023	-0.035735	0.046549
19	1.0	0.013176	-0.000865	0.014041	-0.010550	**19**	1.0	0.001851	0.004329	-0.002477	0.007003
20	1.0	-0.000198	0.004669	-0.004867	-0.010083	**20**	1.0	-0.000054	0.002608	-0.002662	-0.006562
21	1.0	0.010489	0.012145	-0.001656	-0.085938	**21**	1.0	-0.002291	0.012903	-0.015194	-0.061964
22	1.0	0.045743	0.003172	0.042571	-0.057248	**22**	1.0	-0.000911	0.036206	-0.037118	-0.018735
23	1.0	-0.007386	-0.001276	-0.006110	0.000713	**23**	1.0	-0.000415	0.028443	-0.028857	-0.018222
24	0.0	0.000000	0.000000	0.000000	0.000000	**24**	0.0	0.000000	0.000000	0.000000	0.000000
25	0.0	0.000000	0.000000	0.000000	0.000000	**25**	0.0	0.000000	0.000000	0.000000	0.000000
26	0.0	0.000000	0.000000	0.000000	0.000000	**26**	0.0	0.000000	0.000000	0.000000	0.000000
27	0.0	0.000000	0.000000	0.000000	0.000000	**27**	0.0	0.000000	0.000000	0.000000	0.000000
			.....						**.....**		

Table S5. Charge Decomposition Analysis (CDA) result of $V_2O_5^+$

d = the number of electrons donated from fragment.1 to fragment.2 **fragment.1=VO_3^+ fragment.2=VO_2**

b = the number of electrons back donated from fragment.2 to fragment .1 **Occ.=1.0 occupied Occ.=0.0 unoccupied**

r = the number of electrons involved in repulsive polarization **Orb. =molecular orbitals of $V_2O_5^+$**

Result for alpha electrons						Result for beta electrons					
Orb.	Occ.	d	b	d-b	r	Orb.	Occ.	d	b	d-b	r
1	1.0	0.000006	0.000000	0.000006	0.000001	1	1.0	0.000006	0.000000	0.000007	0.000000
2	1.0	-0.000001	0.000008	-0.000009	0.000004	2	1.0	-0.000002	0.000008	-0.000010	0.000004
3	1.0	-0.000517	-0.000032	-0.000485	-0.000161	3	1.0	-0.000580	-0.000019	-0.000562	-0.000036
4	1.0	-0.000096	-0.000545	0.000449	-0.000369	4	1.0	-0.000116	-0.000534	0.000418	-0.000333
5	1.0	-0.000001	0.000001	-0.000002	-0.000001	5	1.0	-0.000002	0.000001	-0.000002	-0.000001
6	1.0	-0.000001	-0.000001	0.000000	-0.000001	6	1.0	-0.000001	-0.000001	0.000000	0.000000
7	1.0	-0.000429	-0.000014	-0.000414	-0.000277	7	1.0	-0.000547	-0.000009	-0.000538	-0.000037
8	1.0	-0.000268	-0.000001	-0.000267	-0.000003	8	1.0	-0.000267	-0.000001	-0.000267	-0.000003
9	1.0	0.000006	-0.000001	0.000006	0.000001	9	1.0	0.000006	0.000000	0.000006	0.000000
10	1.0	0.000001	0.000000	0.000001	-0.000001	10	1.0	0.000001	0.000000	0.000001	-0.000001
11	1.0	-0.000004	0.000000	-0.000004	0.000000	11	1.0	-0.000004	0.000000	-0.000004	0.000000
12	1.0	-0.000008	-0.000001	-0.000007	-0.000002	12	1.0	-0.000009	0.000000	-0.000008	-0.000001
13	1.0	-0.000001	0.000035	-0.000036	0.000009	13	1.0	-0.000001	0.000035	-0.000037	0.000009
14	1.0	-0.000004	0.000047	-0.000051	0.000023	14	1.0	-0.000005	0.000048	-0.000053	0.000025
15	1.0	0.000000	0.000000	0.000000	-0.000001	15	1.0	0.000000	0.000000	0.000000	-0.000001
16	1.0	-0.002252	0.000063	-0.002315	-0.000486	16	1.0	-0.002457	0.000117	-0.002574	0.000117
17	1.0	-0.000194	-0.003015	0.002821	-0.000577	17	1.0	-0.000284	-0.003122	0.002838	-0.000714
18	1.0	0.000214	0.000180	0.000034	0.005494	18	1.0	0.000259	0.000232	0.000027	0.007527
19	1.0	0.000206	-0.000068	0.000274	0.000435	19	1.0	0.000123	-0.000071	0.000194	0.000313
20	1.0	0.000012	0.000000	0.000012	0.000267	20	1.0	0.000011	0.000002	0.000009	0.000331
21	1.0	-0.000103	0.000030	-0.000133	0.001047	21	1.0	-0.000059	0.000056	-0.000116	0.000225
22	1.0	-0.000167	0.000027	-0.000194	0.002424	22	1.0	-0.000194	0.000047	-0.000241	0.001366
23	1.0	-0.000152	0.001698	-0.001850	0.005664	23	1.0	-0.000117	0.001695	-0.001812	0.005464
24	1.0	0.015284	-0.000511	0.015796	0.009842	24	1.0	0.022492	-0.000855	0.023347	-0.017897
25	1.0	0.012489	-0.000656	0.013144	-0.007581	25	1.0	0.013296	-0.000682	0.013978	-0.008425
26	1.0	-0.002767	-0.002582	-0.000186	-0.023242	26	1.0	0.000268	-0.000347	0.000615	0.000465
27	1.0	-0.000925	-0.000686	-0.000239	-0.004966	27	1.0	-0.002771	-0.002616	-0.000155	-0.012159
28	1.0	0.001041	0.000104	0.000937	0.000123	28	1.0	-0.000405	-0.000299	-0.000107	-0.001284
29	1.0	0.011133	0.002575	0.008558	0.006116	29	1.0	0.020719	0.002562	0.018157	-0.003260
30	1.0	0.020051	0.001205	0.018846	-0.007671	30	1.0	0.020830	0.000456	0.020373	-0.008125
31	1.0	0.006402	0.001775	0.004627	0.055699	31	1.0	0.012083	0.001524	0.010559	0.048049
32	1.0	-0.005235	0.001109	-0.006344	0.058974	32	1.0	0.025879	0.001800	0.024079	-0.000297
33	1.0	0.011626	-0.001284	0.012911	-0.013598	33	1.0	0.003456	0.002927	0.000528	0.014626
34	1.0	0.001419	0.004266	-0.002848	0.020320	34	1.0	0.004125	0.002850	0.001276	0.022835
35	1.0	0.002228	0.003905	-0.001677	0.025353	35	1.0	-0.001332	0.001618	-0.002950	-0.008065
36	1.0	0.004649	-0.000892	0.005541	-0.027816	36	1.0	0.002247	-0.000128	0.002376	-0.007591
37	1.0	-0.002492	0.001794	-0.004285	0.018063	37	1.0	0.005203	0.000467	0.004736	0.002408

38	1.0	0.003744	0.009121	-0.005377	-0.024793	**38**	1.0	-0.000189	0.010124	-0.010313	-0.016329
39	1.0	0.000698	-0.006910	0.007607	-0.024851	**39**	1.0	0.001104	-0.007052	0.008157	-0.060265
40	1.0	0.004914	-0.003172	0.008086	-0.025061	**40**	1.0	0.009127	-0.004382	0.013509	-0.024923
41	1.0	0.009169	-0.008491	0.017659	-0.023653	**41**	1.0	0.019121	-0.001117	0.020239	-0.030607
42	1.0	0.027002	-0.001542	0.028545	-0.053971	**42**	1.0	-0.001290	-0.017208	0.015918	-0.009553
43	1.0	0.000394	-0.014118	0.014512	-0.009914	**43**	0.0	0.000000	0.000000	0.000000	0.000000
44	0.0	0.000000	0.000000	0.000000	0.000000	**44**	0.0	0.000000	0.000000	0.000000	0.000000
45	0.0	0.000000	0.000000	0.000000	0.000000	**45**	0.0	0.000000	0.000000	0.000000	0.000000
46	0.0	0.000000	0.000000	0.000000	0.000000	**46**	0.0	0.000000	0.000000	0.000000	0.000000
47	0.0	0.000000	0.000000	0.000000	0.000000						
			.....						**.....**		

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