Supporting Information

Size-dependent reactivity of $V_n O^+$ (*n* =1-9) clusters with ethane

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Figure S1. Time-of-flight (TOF) mass spectra for the reactions of mass-selected V_n^+ (a1–5) and V_nO^+ (c1–5) with C₂H₆. The pressures of C₂H₆ are shown. The reaction times are around 1.8 ms for $V_{5,6}^+$, 1.9 ms for $V_{5,6}O^+$, 4.8 ms for V_7^+ , 1.9 ms for $V_{8,9}^+$, and 2.0 ms for $V_{7-9}O^+$. The V_nX^+ and V_nOX^+ (X = C₂H₂, C₂H₄, C₂H₆, etc) species are labeled as +X, respectively. Peaks marked with asterisks are due to water impurities in the gas handling system.



Figure S2. Variation of relative ion intensities with respect to the C_2H_6 pressures in the reaction of V_2O^+ with C_2H_6 . The solids lines are fitted to the experimental data points by using the equations derived with the approximation of the pseudo-first-order reaction mechanism.



Figure S3. Variations of relative ion intensities with respect to the effective C_2H_6 pressures in the reaction of V_nO^+ (n = 3-7) and V_5^+ with C_2H_6 . The solid lines are fitted to the experimental data points by using the equations derived with the approximation of the pseudo-first-order reaction mechanism.



Figure S4. BPBE optimized structures of V⁺ (a), V₂⁺ (b), V₃⁺ (c), V₄⁺ (d), V₅⁺ (e), and V₆⁺ (f). The relative energies are given in eV. Superscripts denote the spin multiplicity.



Figure S5. BPBE optimized structures of V_7^+ (a), V_8^+ (b), and V_9^+ (c). The relative energies are given in eV. Superscripts denote the spin multiplicity.



Figure S6. BPBE optimized structures of VO⁺ (a), V_2O^+ (b), V_3O^+ (c), and V_4O^+ (d).

The relative energies are given in eV. Superscripts denote the spin multiplicity.



Figure S7. BPBE optimized structures of V_5O^+ (a) and V_6O^+ (b). The relative energies are given in eV. Superscripts denote the spin multiplicity.



Figure S8. BPBE optimized structures of $V_7O^+(a)$, $V_8O^+(b)$, and $V_9O^+(c)$. The relative energies are given in eV. Superscripts denote the spin multiplicity.



(a)

Figure S9. BPBE-calculated potential-energy curves (PECs) for spin conversions occurring in the first C-H activation of ethane by V_2^+ (⁴I1 \rightarrow ²TS1) and the first C-H activation of ethane by V_2O^+ (⁸I3 \rightarrow ⁶TS2), respectively.



Figure S10. Molecular orbital interactions in the reaction of V_3O^+ with C_2H_6 (see I15 in Figure 5 in the main text).

		С-Н	V-C	V-H	H-H	V-V	V-O
Experiment	Value Ref.	3.507 1	4.384 2	2.169 3	4.519 1	2.791 4	6.602 5
Pure Functionals	BPBE	3.407	4.402	2.555	4.288	3.012	6.942
	BPW91	3.420	4.392	2.570	4.312	3.016	6.938
	BP86	3.603	4.663	2.852	4.563	3.663	7.214
	TPSS	3.571	4.358	2.922	4.619	3.083	6.758
	BLYP	3.500	4.550	2.869	4.469	3.749	7.113
	M06L	3.357	4.707	2.531	4.215	2.102	6.717
Hybrid Functionals	X3LYP	3.476	3.621	2.800	4.473	1.406	6.229
	B1LYP	3.423	3.338	2.766	4.442	1.117	5.946
	B3LYP	3.485	3.655	2.793	4.497	1.498	6.255
	B3P86	3.581	3.817	2.743	4.575	1.372	6.390
	PBE1PBE	3.375	3.404	2.512	4.247	0.657	5.959
	B1B95	3.351	2.766	2.532	4.379	0.737	5.985
	M06	3.415	3.914	2.596	4.379	2.208	6.377

Table S1. DFT calculated and experimental bond dissociation energies of C–H, V–C, V–H, H–H, V–V and V–O. The values are in units of eV.

References

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