Supporting Information

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Table SI-2 Equilibrium free energies, lattice parameters, and Fermi energies of the $M_{0.0625}V_{0.9375}O_2$ (the DFT calculations are carried without spin-polarization, and the lattice parameters are scaled to four units of $M_{0.0625}V_{0.9375}O_2$)

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Figure SI-2 Distribution diagram of the transition metal doped VO_2 (M_1) on the plane of their decomposition enthalpies and entropies (the DFT calculations were carried out without spin-polarization)

Table SI-1 Thermal dynamic properties of the transition metal oxides and $M_{0.0625}V_{0.9375}O_2$ (the DFT calculation are carried out without spin-polarization, units: kJ·mol^{-1} for enthalpy and J·K^{-1}·mol^{-1} for entropy)

Oxides	$\Delta_f H$ [oxide] [a]	$\Delta_f H$ [$M_{0.0625}V_{0.9375}O_2$] [b]	ΔH [c]	ΔS [d]
Sc_2O_3	-1908.8	-729.08	0.44	4.47
TiO	-519.7	-723.69	22.22	10.88
Ti_2O_3	-1520.9	-723.69	7.17	4.47
TiO_2	-944.0	-723.69	-4.30	-1.94
VO_2	-717.6 [e]	-713.59	0.00	0.0
Cr_2O_3	-1139.7	-703.06	-1.55	4.47
Cr_3O_4	-1531.0	-703.06	2.17	6.60
CrO_2	-598.0	-703.06	-3.30	-1.94
MnO	-385.2	-697.91	4.84	10.88
MnO_2	-520.0	-697.91	-3.58	-1.94
FeO	-272.0	-695.42	9.43	10.88
Fe_3O_4	-1118.4	-695.42	3.13	6.60
Fe_2O_3	-824.2	-695.42	0.67	4.47
CoO	-237.9	-692.61	8.75	10.88
Co_3O_4	-891.0	-692.61	5.06	6.60
Ni_2O_3	-489.5	-687.47	3.18	4.47
Cu_2O	-168.6	-685.57	11.32	17.29
CuO	-157.3	-685.57	6.75	10.88

ZnO	-350.5	-695.44	4.55	10.88
Y_2O_3	-1905.3	-723.10	-5.43	4.47
ZrO_2	-1100.1	-727.10	-10.65	-1.94
NbO	-405.8	-719.03	24.68	10.88
NbO_2	-796.2	-719.03	0.28	-1.94
Nb_2O_5	-1899.5	-719.03	-9.32	-8.35
MoO_2	-588.9	-706.98	1.18	-1.94
RuO_2	-305.0	-692.33	4.28	-1.94
RuO_4	-239.3	-692.33	8.38	-27.59
Rh_2O_3	-343.0	-689.56	9.85	4.47
PdO	-85.4	-679.54	5.21	10.88
Ag_2O	-31.1	-674.92	4.96	17.29
CdO	-258.4	-685.63	0.49	10.88
La_2O_3	-1793.7	-713.49	-11.55	4.47
HfO_2	-1144.7	-731.83	-8.70	-1.94
Ta_2O_5	-2046.0	-725.60	-7.32	-8.35
WO_2	-589.7	-711.60	5.75	-1.94
WO_3	-842.9	-711.60	-10.07	-14.77
Re_2O_7	-1240.1	-699.41	-8.34	-21.18
OsO_4	-394.1	-690.27	-3.35	-27.59
IrO_2	-274.1	-688.57	2.45	-1.94
HgO	-90.8	-671.51	-3.16	10.88

[a] Formation enthalpies for the oxides adopted from Lide R. D. (ed.), CRC Handbook of Chemistry and Physics, Internet Version, 2005; [b] Formation enthalpies for the metal doped $M_{0.0625}V_{0.9375}O_2$; [c] Decomposition enthalpies for $M_{0.0625}V_{0.9375}O_2$; [d] Decomposition entropies for $M_{0.0625}V_{0.9375}O_2$; (e) adopted from J. Qi, G. Ning, and Y. Lin, Synthesis, Characterization, and Thermodynamic Parameters of Vanadium Dioxide. Mater. Res. Bull. **2008**, 43(8-9): 2300-2307.

Table SI-2 Equilibrium free energies, lattice parameters, and Fermi energies of the $M_{0.0625}V_{0.9375}O_2$ (the DFT calculations are carried without spin-polarization, and the lattice parameters are scaled to four units of $M_{0.0625}V_{0.9375}O_2$)

Dopants	U_0 (eV)	V_0 (Å^3)	a (Å)	b (Å)	c (Å)	β (deg)	E_f (eV)
Sc	-22.1171	122.99	5.6911	9.2835	10.969	121.908	4.115
Ti	-22.1701	121.72	5.6452	9.2761	10.9242	121.667	4.4575
V	-21.9166	121.00	5.6452	9.2761	10.9242	121.667	4.4575
Cr	-22.0611	120.46	5.6115	9.2622	10.892	121.669	4.4217
Mn	-21.9714	120.16	5.609	9.2459	10.8875	121.651	4.144
Fe	-21.9017	120.18	5.6055	9.2501	10.8774	121.533	4.4706
Co	-21.7961	120.20	5.6187	9.2417	10.881	121.670	4.1501
Ni	-21.6462	121.01	5.6455	9.2468	10.9066	121.773	4.3391
Cu	-21.5108	122.22	5.6831	9.2582	10.9322	121.802	4.1879
Zn	-21.4601	122.29	5.6798	9.2615	10.9486	121.857	4.301
Y	-22.0716	125.70	5.7402	9.3531	11.0538	122.057	4.1846
Zr	-22.2431	123.83	5.7009	9.3062	10.9876	121.816	4.4171
Nb	-22.2643	122.85	5.6613	9.304	10.9668	121.725	4.0523
Mo	-22.1838	121.99	5.6287	9.299	10.9458	121.604	4.6546
Ru	-21.9285	121.43	5.612	9.3006	10.9144	121.506	4.5708
Rh	-21.7742	121.61	5.6397	9.2811	10.9233	121.702	4.0976
Pd	-21.5397	122.59	5.6714	9.299	10.9405	121.800	4.2852
Ag	-21.3446	124.39	5.7454	9.2964	10.9857	122.007	4.1101
Cd	-21.3358	124.47	5.7383	9.3085	10.9925	122.009	4.1924

La	-21.8759	127.52	5.7891	9.3771	11.0812	122.001	4.2731
Hf	-22.3803	123.41	5.6937	9.3031	10.9685	121.829	4.4862
Ta	-22.4349	122.75	5.6606	9.2985	10.963	121.694	4.2912
W	-22.3619	122.12	5.6306	9.3057	10.9439	121.585	4.8144
Re	-22.1984	121.73	5.6116	9.3022	10.9444	121.540	4.5558
Os	-22.0304	121.47	5.6099	9.2933	10.9382	121.551	4.332
Ir	-21.8630	121.63	5.6277	9.3004	10.9205	121.662	4.156
Pt	-21.5980	122.18	5.6578	9.2884	10.9319	121.713	4.6549
Au	-21.3010	123.63	5.7279	9.2767	11.0277	122.436	4.0549
Hg	-21.1459	125.15	5.7535	9.3194	11.0103	122.007	4.1941

Table SI-3 Free energies calculated from DFT + *U* method, including the transition metal doped VO_2 (M_1) and transition metals

$MV_{15}O_{32}$	U_0 (eV) without spin	U_0 (eV) with spin	Metals[(a)]	U_0 (eV)
$ScV_{15}O_{32}$	-353.8736	-362.5680	Sc_2	-12.4036
$TiV_{15}O_{32}$	-354.7223	-364.1440	Ti_2	-15.8902
$V_{16}O_{32}$	-350.6649	-360.3872	V_2	-11.1264
$CrV_{15}O_{32}$	-352.9780	-362.5872	Cr_2	-19.2462
$MnV_{15}O_{32}$	-351.5424	-360.8544	Mn_{58}	-524.4708
$FeV_{15}O_{32}$	-350.4277	-358.9040	Fe_2	-16.6806
$CoV_{15}O_{32}$	-348.7379	-356.8064	Co_2	-14.2326
$NiV_{15}O_{32}$	-346.3386	-354.8128	Ni_4	-22.2812
$CuV_{15}O_{32}$	-344.1726	-351.8720	Cu_4	-14.8748
$ZnV_{15}O_{32}$	-343.3611	-351.5043	Zn_2	-2.5396
$YV_{15}O_{32}$	-353.1456	-362.2928	Y_2	-12.9322
$ZrV_{15}O_{32}$	-355.8902	-365.6512	Zr_2	-17.0944
$NbV_{15}O_{32}$	-356.2286	-366.0016	Nb_2	-20.4482
$MoV_{15}O_{32}$	-354.9401	-364.4592	Mo_2	-21.8712
$RuV_{15}O_{32}$	-350.8554	-359.8160	Ru_2	-18.5618
$RhV_{15}O_{32}$	-348.3864	-356.9408	Rh_4	-29.0864
$PdV_{15}O_{32}$	-344.6355	-353.9296	Pd_4	-20.7320
$AgV_{15}O_{32}$	-341.5129	-349.2496	Ag_4	-11.3088
$CdV_{15}O_{32}$	-341.3726	-349.9731	Cd_2	-1.8200

$LaV_{15}O_{32}$	-350.0142	-359.7952	La_2	-9.8574
$HfV_{15}O_{32}$	-358.0843	-367.8848	Hf_2	-19.9120
$TaV_{15}O_{32}$	-358.9580	-368.9856	Ta_2	-23.7258
$WV_{15}O_{32}$	-357.7907	-367.9456	W_2	-26.0380
$ReV_{15}O_{32}$	-355.1737	-364.6896	Re_2	-24.8500
$OsV_{15}O_{32}$	-352.4866	-361.7104	Os_2	-22.5066
$IrV_{15}O_{32}$	-349.8075	-358.6480	Ir_4	-35.4260
$PtV_{15}O_{32}$	-345.5677	-355.4384	Pt_4	-24.2320
$AuV_{15}O_{32}$	-340.8163	-350.0016	Au_4	-13.0828
$HgV_{15}O_{32}$	-338.3340	-347.0369	Hg_2	-0.4278

[a] Calculated from the most stable crystal form at 298.15 K and 1 atm.

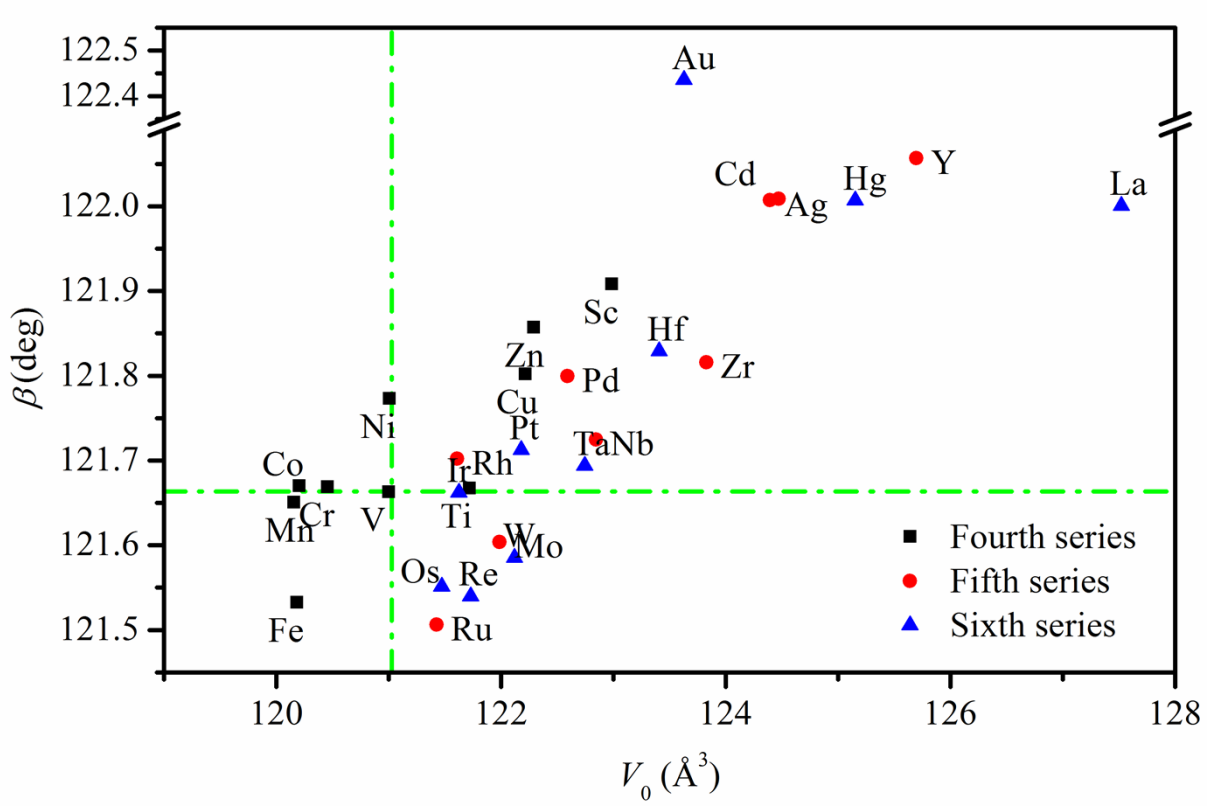

Figure SI-1 Distribution diagram of the transition metal doped VO_2 (M_1) on the β~V_0 plane (the DFT calculations were carried out without spin-polarization)

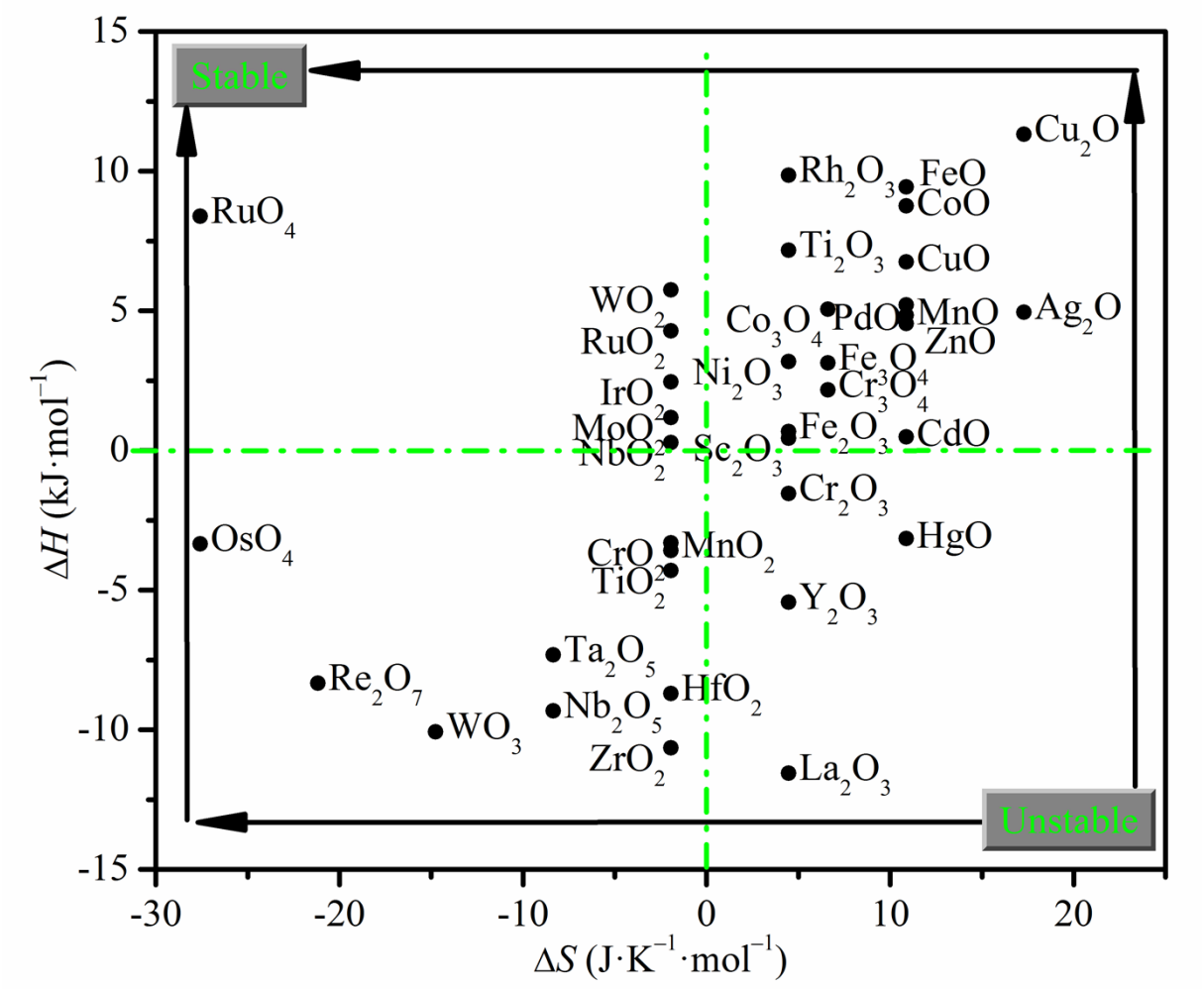

Figure SI-2 Distribution diagram of the transition metal doped VO_2 (M_1) on the plane of their decomposition enthalpies and entropies (the DFT calculations were carried out without spin-polarization)