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Neutral Noble-Metal-Free $VCoO_2$ and $CrCoO_2$ Cluster Catalysts for CO Oxidation by O_2

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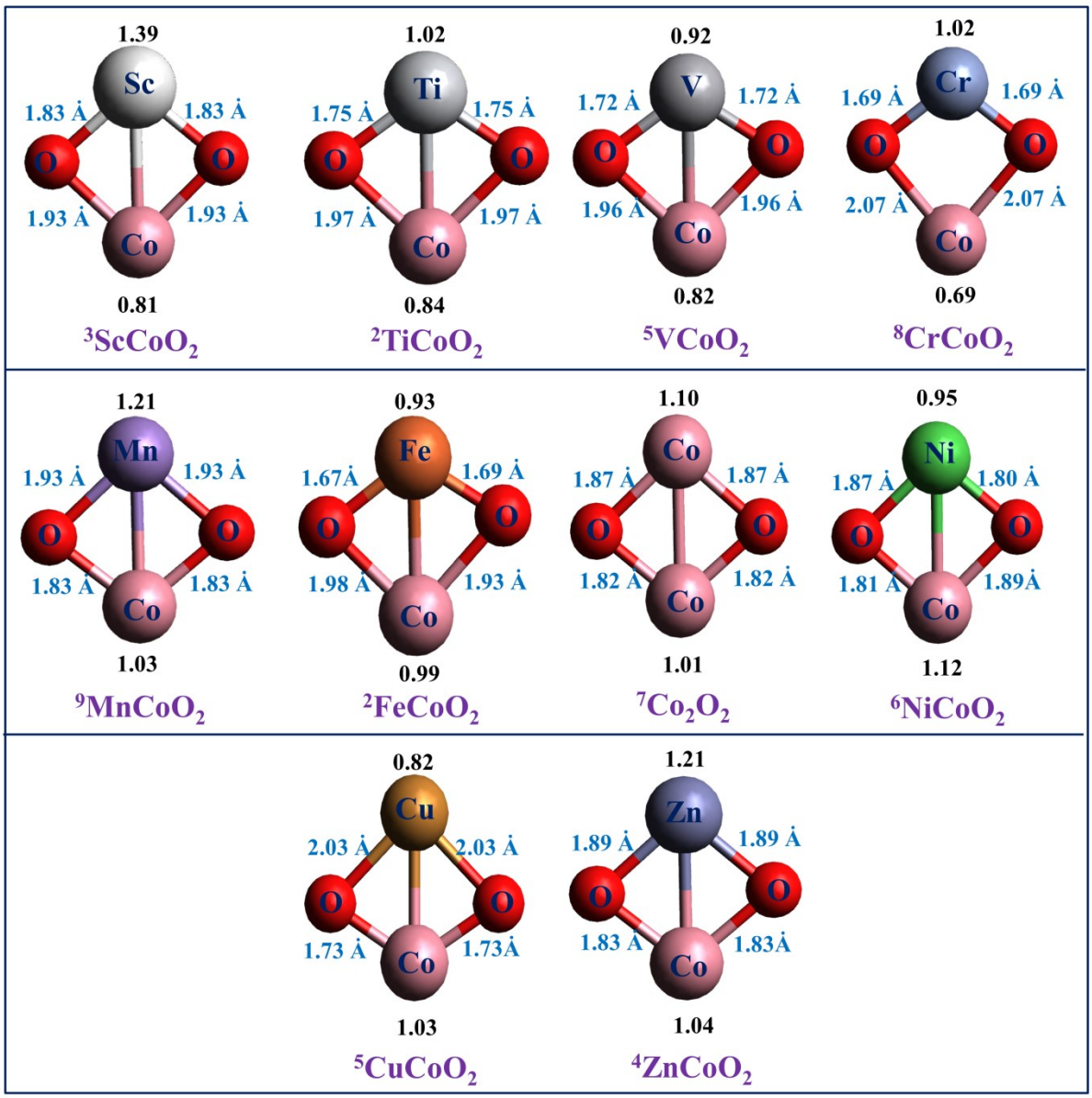

Figure S1. Optimized $TMCoO_2$ (TM=Sc–Zn) clusters at B3LYP/TZVP method. (Superscript value corresponds to ground electronic state of the cluster, blue colour values represent bond distance values (in Å) and black colour values represent natural charge values respectively)

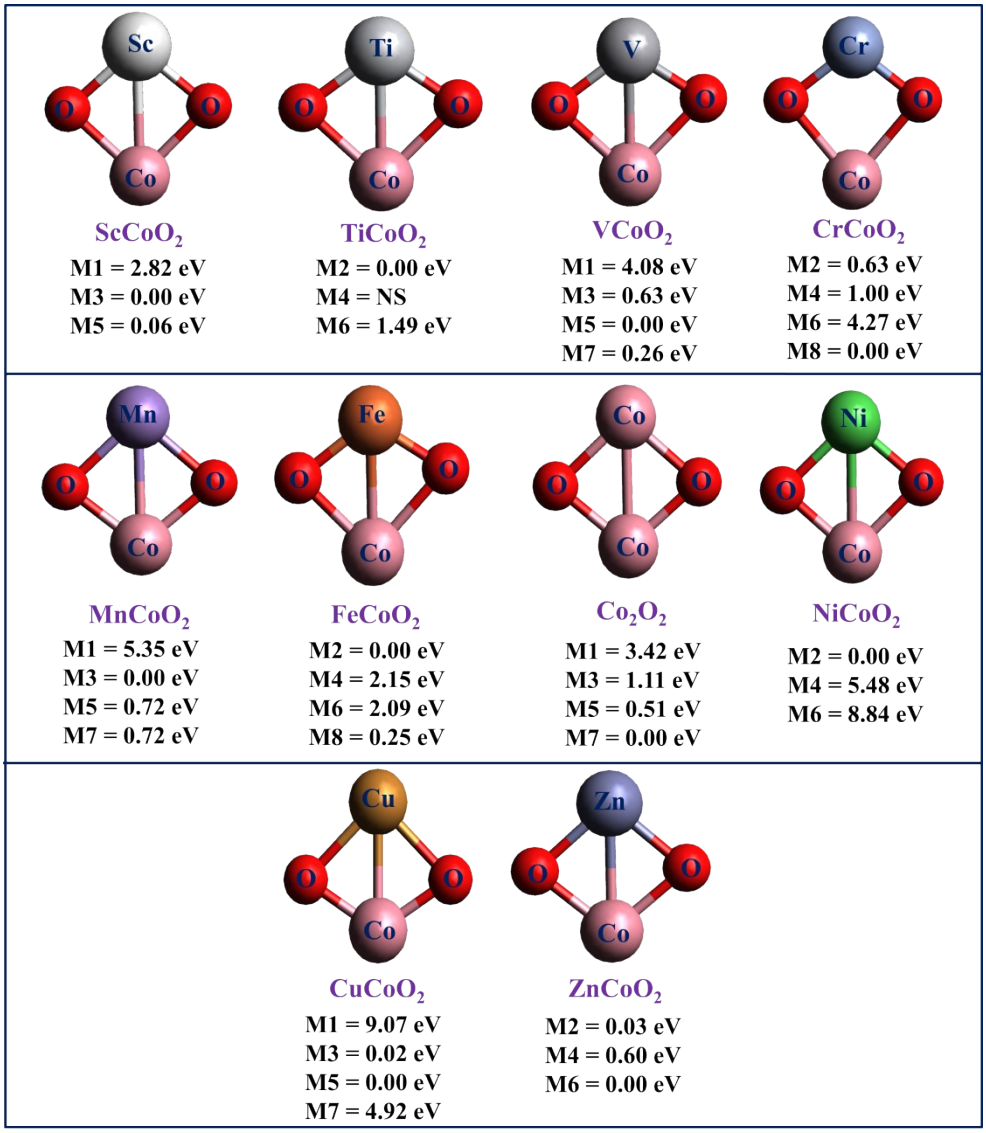

Figure S2. Optimized $TMCoO_2$ (TM=Sc–Zn) clusters with various spin multiplicities at PBE0/def2-TZVPP method in NWChem 6.0 program. (M denotes the spin multiplicity (2S+1), NS=Not Stable)

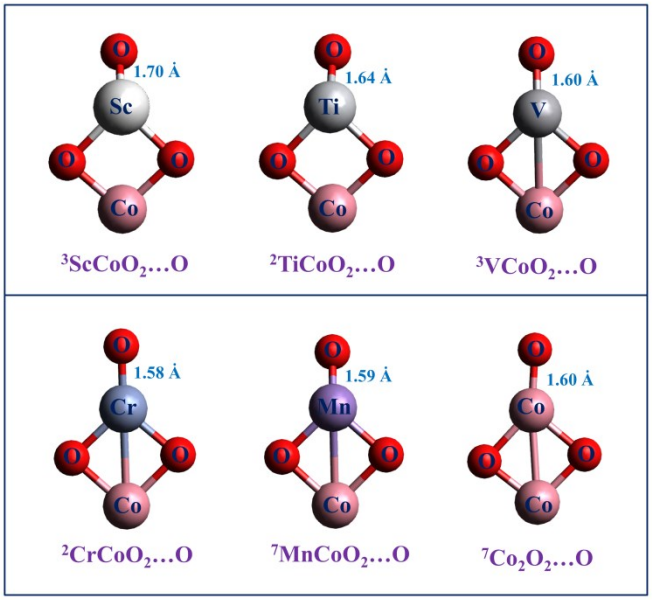

Figure S3. The optimized structures of interaction between $TMCoO_2$ (TM= Sc–Mn, Co) clusters with O atom at B3LYP/TZVP method. (Superscript value corresponds to ground electronic state of the clusters and blue colour values represent bond distance values (in Å))

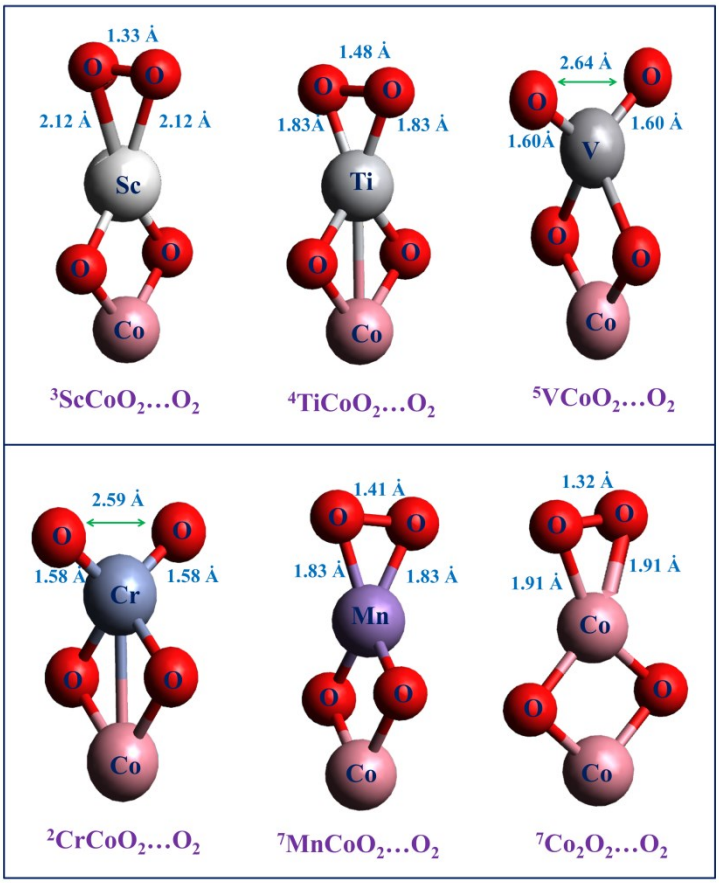

Figure S4. The optimized structures of interaction between $TMCoO_2$ (TM=Sc–Mn, Co) clusters with O_2 molecule at B3LYP/TZVP method. (Superscript value corresponds to ground electronic state of the clusters and blue colour values represent bond distance values (in Å))

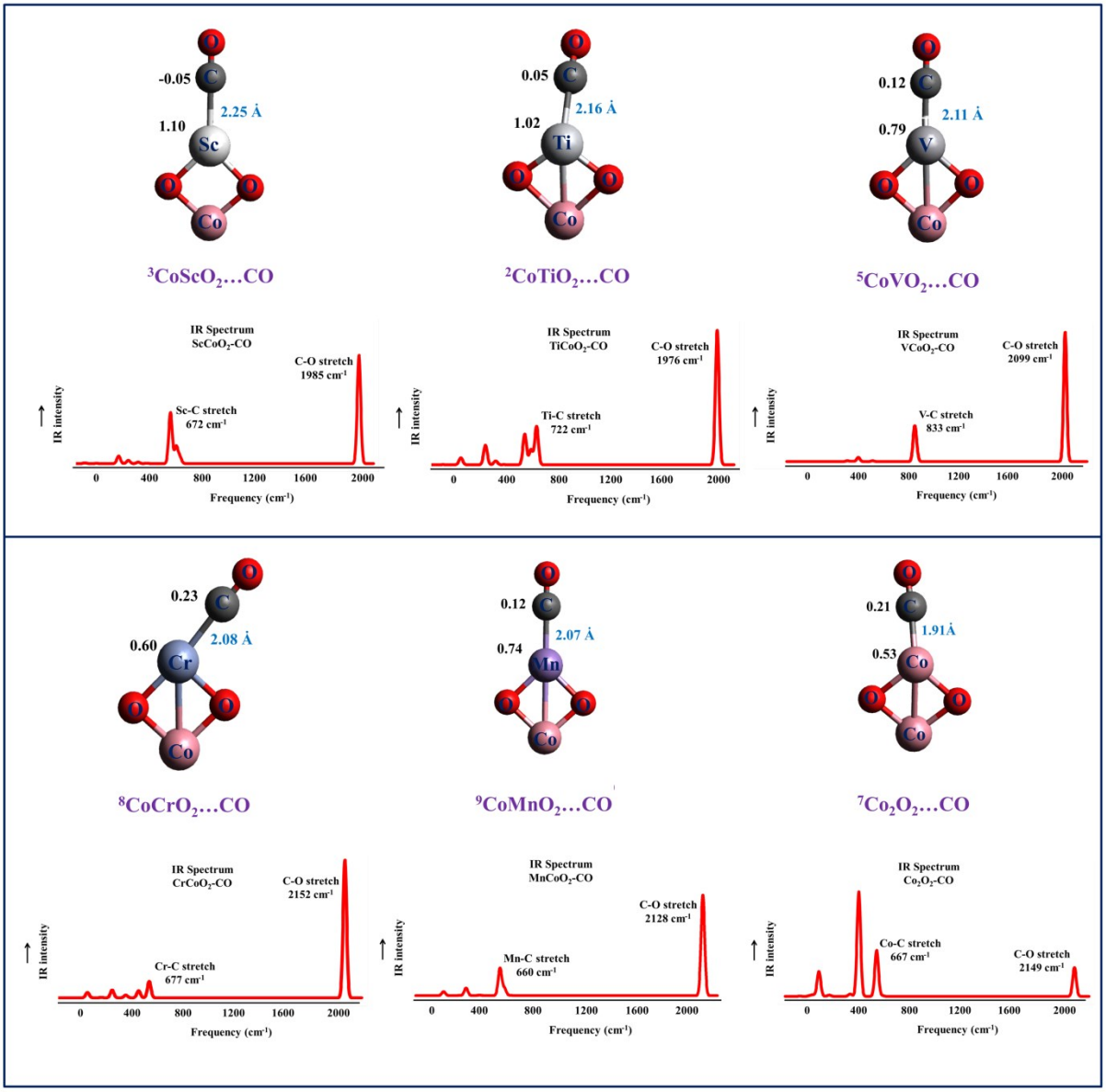

Figure S5. The optimized structures of interaction between $TMCoO_2$ (TM=Sc–Mn, Co) clusters with CO molecule along with its IR spectrum at B3LYP/TZVP method. (Superscript value corresponds to ground electronic state of the clusters and blue colour values represent bond distance values (in Å))

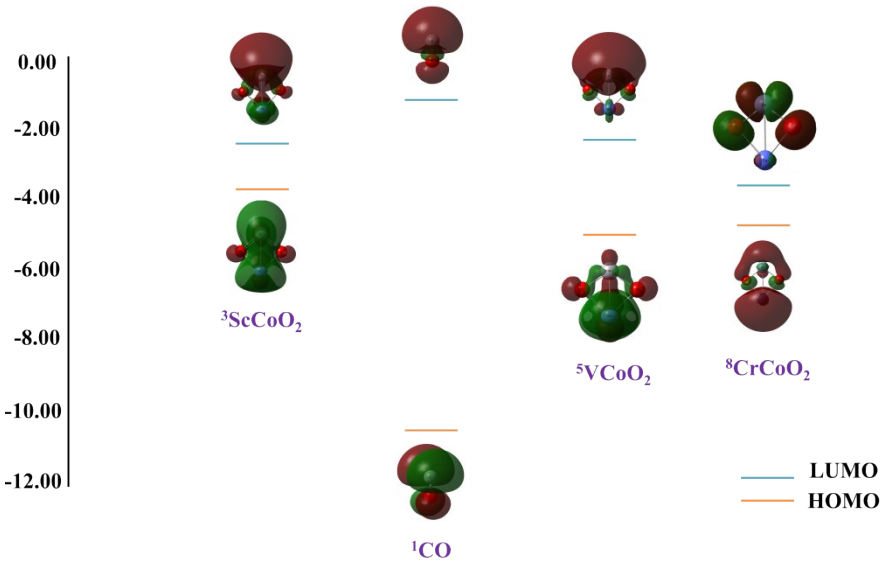

Figure S6. The HOMO and LUMO diagrams of $ScCoO_2$, $VCoO_2$, $CrCoO_2$ clusters and CO molecule.

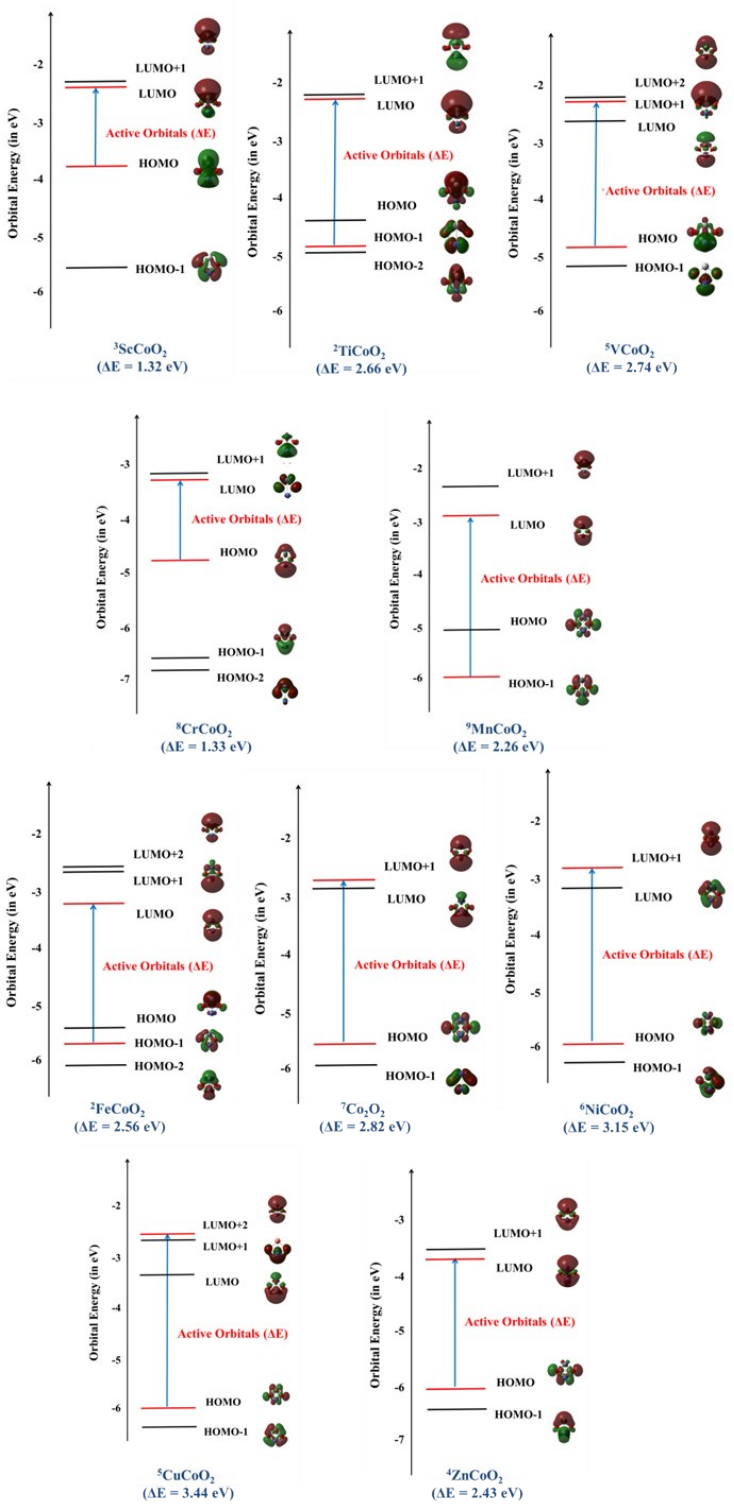

Figure S7. The frontier molecular orbital diagram of $TMCoO_2$ (TM=Sc–Zn) clusters (Pair of active orbitals for HOMO-LUMO calculation).

Table S1. Calculated dissociation energies to remove an oxygen atom DE(O), molecular oxygen DE(O_2), doped TM atom (TM=Sc–Zn) and Co atom (energies in eV) in $TMCoO_2$ (TM=Sc–Zn) clusters.

$TMCoO_2$	DE(O)	DE(O_2)	DE(TM)	DE(Co)
$^{3}ScCoO_2$	5.08	7.12	6.89	2.55
$^{2}TiCoO_2$	6.32	8.11	7.95	2.11
$^{5}VCoO_2$	6.12	7.13	7.93	2.31
$^{8}CrCoO_2$	4.97	4.91	6.17	2.35
$^{9}MnCoO_2$	5.11	5.33	4.62	5.01
$^{2}FeCoO_2$	3.79	3.74	3.47	1.99
$^{7}Co_2O_2$	4.68	5.25	-	4.41
$^{6}NiCoO_2$	5.07	4.15	4.56	4.91
$^{5}CuCoO_2$	4.23	3.32	3.58	6.35
$^{4}ZnCoO_2$	4.20	3.38	2.37	5.37

Table S2. The HOMO-LUMO gap (pair of active orbitals) values (in eV) of $TMCoO_2$ (TM=Sc–Zn) clusters.

$TMCoO_2$	H-L Gap
$^{3}ScCoO_2$	1.32
$^{2}TiCoO_2$	2.66
$^{5}VCoO_2$	2.74
$^{8}CrCoO_2$	1.33
$^{9}MnCoO_2$	2.26
$^{2}FeCoO_2$	2.56
$^{7}Co_2O_2$	2.82
$^{6}NiCoO_2$	3.15
$^{5}CuCoO_2$	3.44
$^{4}ZnCoO_2$	2.43

Table S3. Calculated dissociation energies to remove an oxygen atom DE(O), molecular oxygen DE(O_2), doped TM atom (TM=Sc–Zn) and Co atom (energies in eV) and vertical ionization energy (VIE) of $TMCoO_{3-4}$ (TM=V, Cr) clusters.

$TMCoO_{3-4}$	**DE(O)**	**DE(O_2)**	**DE(TM)**	**DE(Co)**	**VIE**
$^3VCoO_3$	5.89	6.90	10.59	4.90	9.06
$^5VCoO_4$	3.70	4.48	10.56	6.16	9.72
$^2CrCoO_3$	5.90	5.76	7.96	5.22	11.12
$^2CrCoO_4$	3.26	4.04	7.49	4.91	10.40

Table S4. Relative Energy (ΔE), Enthalpy of Reaction (ΔH) and Gibbs Free Energy (ΔG) changes during the CO oxidation reaction process with $VCoO_2$ and $CrCoO_2$ cluster (energies in eV).

	B3LYP/TZVP			**M06/TZVP**		**B3LYP/TZVP**			**M06/TZVP**
species	ΔE	ΔH	ΔG	ΔE	species	ΔE	ΔH	ΔG	ΔE
$VCoO_4$ + CO → $VCoO_3$ + CO_2					**$CrCoO_4$ + CO → $CrCoO_3$ + CO_2**				
RC1	0.00	0.00	0.00	0.00	RC4	0.00	0.00	0.00	0.00
IM1	-2.12	-2.18	-1.67	-2.32	IM9	-2.35	-2.39	-1.92	-2.70
TS1	-1.11	-1.03	-0.51	-1.05	TS5	-0.73	-0.75	0.03	-1.53
IM2	-2.22	-2.33	-1.93	-2.23	IM10	-1.89	-1.92	-1.18	-2.28
PC1	-1.74	-1.76	-1.73	-1.80	PC4	-2.18	-2.19	-2.21	-2.31
$VCoO_3$ + 2CO → $VCoO_2$(CO) + CO_2					**$CrCoO_3$ + 2CO → $CrCoO_2$(CO) + CO_2**				
RC2	0.00	0.00	0.00	0.00	RC5	0.00	0.00	0.00	0.00
IM3	-0.82	-0.83	-0.41	-0.53	IM11	-0.38	-0.40	-0.01	-0.92
TS2	-0.01	-0.05	0.43	0.16	TS6	0.30	0.25	0.35	0.06
IM4	-0.44	-0.48	-0.01	-1.08	IM12	-0.26	-0.41	-0.09	-1.02
PC21	0.45	0.43	0.46	-0.16	PC51	0.46	0.43	0.44	0.38
IM5	-0.87	-0.89	-0.07	-0.38	IM13	-0.83	-0.92	-0.02	-1.35
TS3	-0.30	-0.31	0.23	-0.18	TS7	-0.02	-0.08	0.96	-0.32
IM6	-1.39	-1.53	-0.88	-0.89	IM14	-0.83	-0.87	0.19	-1.39
PC2	-0.67	-0.70	-0.27	-0.33	PC5	-1.07	-1.11	-0.71	-2.00
$VCoO_2$(CO) + O_2 → $VCoO_4$ + CO					**$CrCoO_2$(CO) + O_2 → $CrCoO_4$ + CO**				
RC3	0.00	0.00	0.00	0.00	RC6	0.00	0.00	0.00	0.00
IM7	-2.31	-2.36	-1.94	-2.36	IM15	-1.06	-1.12	-0.39	-0.11
TS4	-0.82	-0.86	-0.15	-0.87	TS8	0.40	0.24	1.02	0.51
IM8	-4.35	-4.40	-3.93	-4.81	IM16	-1.50	-1.51	-1.07	-0.72
PC3	-3.36	-3.38	-3.31	-3.60	PC6	-2.52	-2.55	-2.39	-2.50
					RC6	0.00	0.00	0.00	0.00
					IM17	-1.72	-1.74	-1.27	-2.54
					TS9	-1.21	-1.26	-0.43	-1.97
					IM18	-3.83	-3.86	-3.36	-4.71
					PC6	-3.07	-3.10	-2.94	-3.79

Table S5. The scaled rate constant values for the CO oxidation reaction with $VCoO_2$ and $CrCoO_2$ cluster.

$VCoO_2$			**$CrCoO_2$**		
reaction	**k**	**Value**	**reaction**	**k**	**Value**
(ii)	k1	2.56×10^{-19}	(vii)	k5	1.39×10^{-30}
(iii)	k2	1.42×10^{-23}	(viii)	k6	9.73×10^{-10}
(iv)	k3	1.01×10^{-20}	(ix)	k7	6.68×10^{-10}
(v)	k4	4.97×10^{-22}	(x)	k8	2.50×10^{-18}

Table S6. Calculated free energy span (δE) values for the CO oxidation reaction with $VCoO_2$ and $CrCoO_2$ cluster (energies in kcal/mol).

Reaction	**δE**
$VCoO_4 + CO \rightarrow VCoO_3 + CO_2$	26.48
$VCoO_3 + 2CO \rightarrow VCoO_2(CO) + CO_2$	31.59
$VCoO_2(CO) + O_2 \rightarrow VCoO_4 + CO$	34.51
$CrCoO_4 + CO \rightarrow CrCoO_3 + CO_2$	37.98
$CrCoO_3 + 2CO \rightarrow CrCoO_2(CO) + CO_2$	25.10
$CrCoO_2(CO) + O_2 \rightarrow CrCoO_4 + CO$	32.95