Electronic Supplementary Information for:

Trends in C-O and N-O bond scission on rutile oxides described by oxygen vacancy formation energies

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Table S1. Comparison between DFT-calculated and experimental (EXP) lattice constants (in Å) of 3*d* rutile oxides.

Rutile	DFT	EXP
TiO_2	2.97,4.67	2.96,4.59
VO_2	2.84,4.59	2.85,4.56
CrO_2	2.93,4.45	2.92,4.54
MnO_2	2.89,4.45	2.88,4.40
FeO_2	2.80,4.44	
CoO_2	2.88,4.31	
NiO_2	2.93,4.35	

Table S2. Adsorption energies (ΔE_{Ads} in eV) of CO_2 with or without dispersion corrections[1] on the 3*d* rutile (110) surfaces.

Rutile	No dispersion	Dispersion
TiO_2	-0.25	-0.51
VO_2	-0.20	-0.42
CrO_2	-0.17	-0.38
MnO_2	-0.06	-0.23
FeO_2	0.00	-0.16
CoO_2	-0.06	-0.23
NiO_2	-0.04	-0.20

Table S3. Calculated activation energies (ΔE_{Act} in eV), reaction energies (ΔE_{Diss} in eV) and C(N)-O distance (d in Å) at the TSs for C-O and N-O bond scission on 3d rutile (110) surfaces.

Rutile	$CO_2 \rightarrow CO+O$			$N_2O \rightarrow N_2+O$		
	ΔE_{Act}	ΔE_{Diss}	d	ΔE_{Act}	ΔE_{Diss}	d
TiO_2	0.62	-0.51	1.28	0.13	-3.80	1.27
VO_2	1.29	0.29	1.59	0.43	-3.01	1.35
CrO_2	1.65	1.22	1.73	0.57	-2.03	1.44
MnO_2	1.85	1.49	2.05	0.67	-1.46	1.36
FeO_2	2.24	1.81	1.91	0.83	-1.27	1.42
CoO_2	2.36	2.22	2.12	0.89	-0.53	1.49
NiO_2	3.23	3.19	2.42	1.25	0.23	1.55

Rutile	$CH_3OH \rightarrow CH_3+OH$			$NH_2OH \rightarrow NH_2+OH$		
	ΔE_{Act}	ΔE_{Diss}	d	ΔE_{Act}	ΔE_{Diss}	d
TiO_2	1.03	-0.44	2.05	0.18	-2.67	1.46
VO_2	1.25	0.55	2.55	0.17	-1.65	1.45
CrO_2	1.56	0.76	2.85	0.49	-1.52	1.85
MnO_2	1.49	0.54	2.81	0.50	-1.48	1.89
FeO_2	1.83	0.95	2.75	0.59	-0.59	1.99
CoO_2	2.00	1.03	2.75	0.65	-0.78	2.55
NiO_2	2.21	1.40	2.55	0.94	-0.03	2.65

Table S4. Adsorption energies (ΔE_{Ads} in eV) of the intermediates on the 3*d* rutile (110) surfaces.

Rutile	ΔE_{CO2}	ΔE_{CO}	ΔE_{O}	ΔE_{N2O}	ΔE_{N2}
TiO_2	-0.25	-0.13	-3.95	-0.20	-0.04
VO_2	-0.20	-0.07	-3.17	-0.14	-0.03
CrO_2	-0.17	-0.21	-2.06	-0.12	-0.03
MnO_2	-0.06	-0.01	-1.52	-0.04	-0.03
FeO_2	0.00	-0.16	-1.29	0.02	-0.02
CoO_2	-0.06	-0.37	-0.61	-0.03	-0.03
NiO_2	-0.04	-0.02	0.15	-0.03	-0.01

Rutile	ΔE_{CH3OH}	ΔE_{CH3}	ΔE_{OH}	ΔE_{NH2OH}	ΔE_{NH2}
TiO_2	-1.00	-1.04	-4.66	-0.86	-2.19
VO_2	-0.90	-0.51	-4.06	-0.73	-1.58
CrO_2	-0.91	-0.67	-3.67	-0.74	-1.54
MnO_2	-0.76	-0.82	-3.61	-0.58	-1.18
FeO_2	-0.68	-0.88	-3.21	-0.44	-1.11
CoO_2	-0.83	-0.98	-3.10	-0.64	-1.17
NiO_2	-0.65	-1.03	-2.68	-0.52	-0.94

Table S5. Vacancy formation energies (ΔE_{Vac} in eV) for the 3*d* rutile (110) surfaces.

Rutile	ΔE_{Vac}
TiO_2	3.95
VO_2	3.17
CrO_2	2.06
MnO_2	1.52
FeO_2	1.29
CoO_2	0.61
NiO_2	-0.15

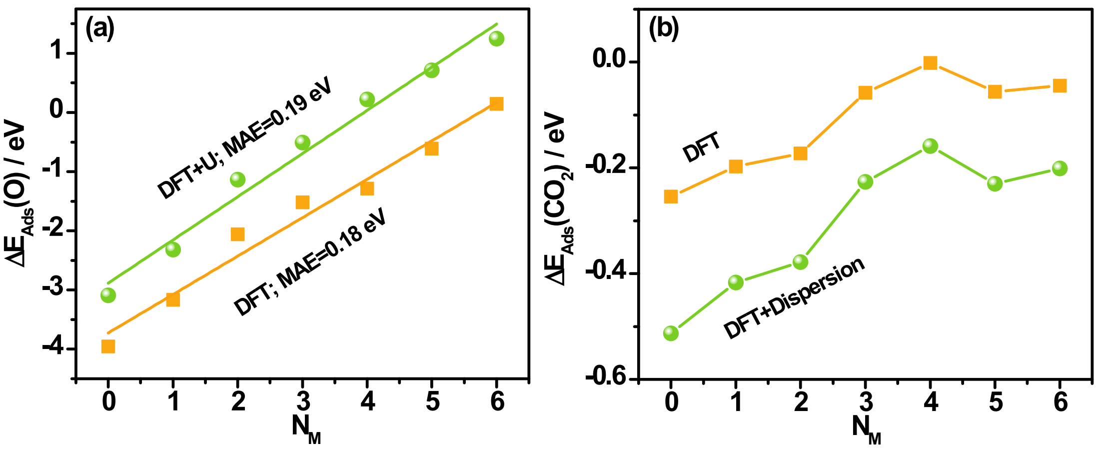

Figure S1. (a) Effect of +U on the adsorption energy of oxygen ($\Delta E_{Ads}(O)$) using ½O_2 as a reference. (b) Effect of dispersion on the adsorption energy of CO_2, $\Delta E_{Ads}(CO_2)$, at the bridge oxygen vacancy on rutile-type (110) surfaces. N_M is the number of outer electrons of 3*d* metals in the rutile oxides, which are calculated based on the periodic table and the oxidation state of the oxide.[2] For instance, Mn cations in MnO_2 have 3 outer electrons, as Mn's electronic distribution ends at $3s^24d^5$ and its oxidation state is +4. The U values of 5.5, 3.32, 2.1, 3, 4.9, 5.37 and 6.37 are used for Ti to Ni, taken from refs 3-7.

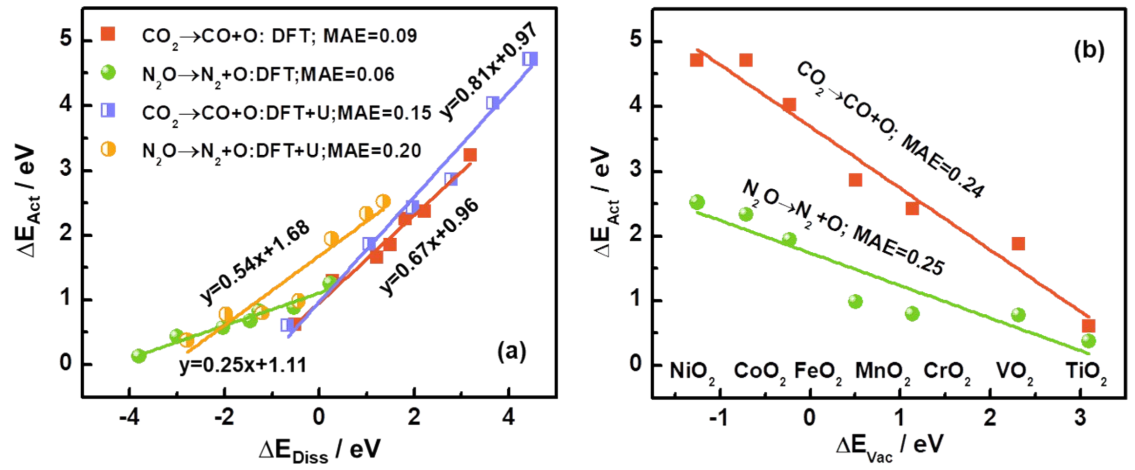

Figure S2. (a) BEP Relations for CO_2 and N_2O scission at the (110) surface of rutile oxides. Data are provided for fully converged PBE calculations and single-point PBE+U calculations. (b) Correlation between the activation energies for CO_2 and N_2O scission (single-point PBE+U calculations) with the formation energies of oxygen vacancies (fully relaxed PBE+U calculations). The mean absolute errors (MAEs, in eV) are provided in each case.

Note: In line with the trends for oxygen adsorption energies in Fig. S1(a), the slopes are steeper upon including U in the calculations. The larger MAEs with respect to PBE are presumably due to the use of single-point calculations to assess the reaction energies and barriers, instead of fully relaxed data.

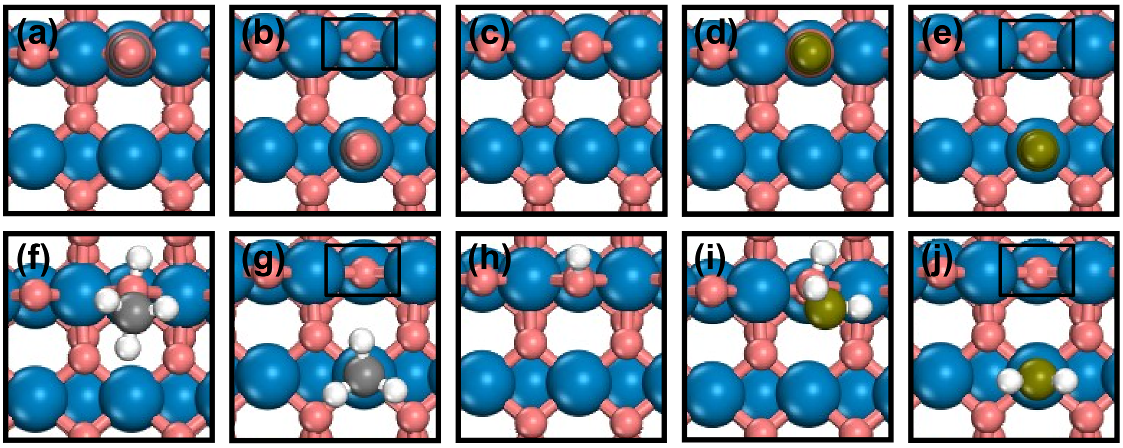

Figure S3. Optimized configurations for (a) CO_2, (b) CO, (c) O, (d) N_2O, (e) N_2, (f) CH_3OH, (g) CH_3, (h) OH, (i) NH_2OH, and (j) NH_2 adsorption on 3*d* rutile (110) surfaces. The blue, vermilion, grey, ochre and white balls represent 3d metals (Ti-Ni), O, C, N and H atoms, respectively. The bridge O vacancy is denoted by the rectangle on the reduced surfaces.

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