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Supporting Information

A Kinetic Study of Ni and NiO Reactions Pertinent to the Earth's Upper Atmosphere

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Table S1. List of second-order rate coefficients for reactions R1 – R7, as a function of temperature and pressure.

Reaction No.	Reaction	Pressure / torr	T / K	Rate coefficient / cm^3 $molecule^{-1}$ s^{-1}
R1	$Ni + O_2 (+ N_2) \rightarrow NiO_2$	3	191	$(5.96 \pm 0.12) \times 10^{-13}$
			218	$(5.33 \pm 0.38) \times 10^{-13}$
			248	$(4.62 \pm 0.12) \times 10^{-13}$
			291	$(3.68 \pm 0.19) \times 10^{-13}$
		6	293	$(3.45 \pm 0.18) \times 10^{-13}$
				$(6.76 \pm 0.17) \times 10^{-13}$
		10		$(11.5 \pm 0.26) \times 10^{-13}$
		3	346	$(2.96 \pm 0.14) \times 10^{-13}$
			343	$(2.88 \pm 0.12) \times 10^{-13}$
			373	$(2.43 \pm 0.13) \times 10^{-13}$
			404	$(1.98 \pm 0.06) \times 10^{-13}$
			406	$(2.02 \pm 0.07) \times 10^{-13}$
			455	$(1.55 \pm 0.06) \times 10^{-13}$
R2	$Ni + O_3 \rightarrow NiO + O_2$	3	293	$(6.5 \pm 0.7) \times 10^{-10}$
R3a	$NiO + O_3 \rightarrow Ni + 2O_2$	3	293	$(1.4 \pm 0.5) \times 10^{-10}$
R3b	$NiO + O_3 \rightarrow NiO_2 + O_2$	3	293	$(2.5 \pm 0.7) \times 10^{-10}$
R4	$NiO + CO \rightarrow Ni + CO_2$	3	190	$(3.24 \pm 0.65) \times 10^{-11}$
			295	$(3.02 \pm 0.53) \times 10^{-11}$
			377	$(2.83 \pm 0.51) \times 10^{-11}$
R5	$NiO + O_2 (+ N_2) \rightarrow ONiO_2$	3	293	$(1.13 \pm 0.27) \times 10^{-13}$
			380	$(0.79 \pm 0.29) \times 10^{-13}$
R6	$NiO + H_2O (+ N_2) \rightarrow Ni(OH)_2$	3	293	$(1.38 \pm 0.25) \times 10^{-11}$
		6		$(2.32 \pm 0.42) \times 10^{-11}$
		10		$(3.35 \pm 0.83) \times 10^{-11}$
		3	348	$(8.65 \pm 0.45) \times 10^{-12}$
			383	$(7.01 \pm 0.12) \times 10^{-12}$
R7	$NiO + CO_2 (+ N_2) \rightarrow NiCO_3$	3	191	$(4.24 \pm 0.76) \times 10^{-13}$
			293	$(1.69 \pm 0.30) \times 10^{-13}$
		6		$(3.31 \pm 0.60) \times 10^{-13}$
		10		$(5.24 \pm 0.94) \times 10^{-13}$
		3	375	$(0.93 \pm 0.17) \times 10^{-13}$

Table S2. Molecular properties and heats of formation (at 0 K) of NiO, $ONiO_2$, $NiCO_3$ and $Ni(OH)_2$, and the stationary points on the NiO + CO, Ni + O_2, $NiCO_3$ + H_2O and $ONiO_2$ + H_2O potential energy surfaces.

Molecule (electronic state)	Geometry (Cartesian co-ordinates in Å) [a]	Rotational constants (GHz) [a]	Vibrational frequencies (cm^{-1}) [a]	$\Delta_f H^o$(0 K) (kJ mol^{-1}) [b]
NiO ($^3\Sigma^-$)	Ni, 0.0, 0.0, 0.0 O, 1.631, 0.0, 0.0 [c]	15.1470	861 [c]	301.9 [d]
$ONiO_2$ ($^3B_2$)	Ni, 0.0, 0.0, -0.280 O, 0.0, 0.0, -1.917 O, 0.0, -0.649, 1.448 O, 0.0, 0.649, 1.448	37.5506 3.8750 3.5125	79, 182, 495, 543, 801, 1240	157.0 [e]
NiO_3 ($^3A_2$)	Ni, 0.0, 0.0, 0.837 O, 0.0, 0.0, -1.528 O, -1.103, 0.0, -0.700 O, 1.103, 0.0, -0.700	12.9810 5.4015 3.8144	251, 364, 373, 740, 821, 919	280.6
$NiCO_3$ ($^3B_1$)	Ni, 0.0, -1.668, 0.0 O, -1.096, -0.194, 0.0 C, -0.0, 0.615, 0.0 O, -0.0, 1.810, 0.0 O, 1.096, -0.194, 0.0	13.1403 2.7796 2.2943	152, 426, 437, 658, 764, 799, 916, 1089, 1802	-174.1 [e]
$Ni(OH)_2$ (^3B_g)	Ni, 0., 0., 0. O, -1.737, 0.103, 0. H, -2.389, -0.601, 0. O, 1.737, -0.103, 0. H, 2.389, 0.601, 0.	508.0441 4.6756 4.6329	120, 174, 355, 476, 594, 652, 802, 3893, 3895	-215.1 [e]
OCNiO	Ni, 0.473, 0.196, -0. O, 1.431, 1.560, 0. C, -1.271, -0.416, -0. O, -2.385, -0.608, -0.	51.5479 2.6501 2.5205	93, 328, 369, 411, 745, 2163	84.2 [e]
OCNiO → Ni + CO_2 transition state	Ni, -0.956, -0.359, -0.253 O, -0.698, 1.278, 0.230 C, 0.840, 0.182, -0.028 O, 1.899, 0.581, 0.126	15.9956 3.8640 3.1122	-363i, 256, 318, 416, 757, 2077	162.3 [e]
NiO_2 ($^1A_1$)	Ni, 0.017, 0.0, 0.047 O, -0.087, 0.0, 1.805 O, 1.227, 0.0, 1.327	32.2939 [b] 9.3788 7.2680	591, 648, 1023 [b]	319.0 [f]
ONiO ($^1\Sigma_g^+$)	Ni, 0.0, 0.0, 0.0 O, 0.0, 0.0, 1.578 O, 0.0, 0.0, -1.578	6.3420 [b]	82 (×2), 902, 1150 [b]	172.0 [f]

$NiO_2 \rightarrow ONiO$ singlet transition state	Ni, 0.0, 0.0, 0.497 O, 0.0, 1.010, -0.870 O, 0.0, -1.010, -0.870	15.4863 [b] 13.1135 7.1007	286i, 590, 869 [b]	431.8 [f]
$NiCO_3$-H_2O triplet complex	Ni, 1.105, 0.425, 0.409 O, -0.487, 1.477, 0.099 C, -1.202, 0.382, 0.337 O, -2.396, 0.261, 0.327 O, -0.322, -0.649, 0.611 O, 2.594, 1.623, -0.116 H, 2.272, 2.427, -0.547 H, 3.446, 1.386, -0.502	9.1864 1.6303 1.3915	50, 82, 152, 217, 341, 354 387, 475, 598, 653, 767, 808, 907, 1101, 1633, 1784, 3771, 3869	-534.2 [e]
$NiCO_3$-H_2O to $Ni(OH)_2 + CO_2$ transition state	Ni, 0.763,-0.700, 0.542 O, -0.453, 0.909, 0.664 C, -1.354, 0.169, -0.109 O, -2.397, 0.599, -0.495 O, -0.854, -1.050, -0.297 O, 1.788, 0.807, -0.015 H, 0.612, 1.200, 0.150 H, 2.140, 0.876, -0.909	5.7043 2.0436 1.6633	-1310i, 121, 147, 308, 391, 463, 533, 581, 696, 720, 754, 835, 911, 1120, 1429, 1679, 1821, 3844	-494.9 [e]
$ONiO_2$-H_2O triplet complex	Ni, -0.004, 0.056, -0.005 O, 1.100, 1.391, 0.011 O, -1.761, 0.541, 0.013 O, -1.712, -0.764, 0.016 O, 1.639, -0.985, -0.093 H, 2.098, -0.098, -0.035 H, 1.867, -1.502, 0.690	7.9706 3.0259 2.2049	167, 176, 199, 278, 388, 394, 478, 551, 629, 661, 821, 1219, 1562, 3216, 3813	-117.3 [e]
$ONiO_2$-H_2O to $Ni(OH)_2 + O_2$ transition state	Ni, 0.076, 0.148, -0.031 O, -1.354, -0.833, -0.051 O, 1.688, -0.726, -0.132 O, 1.922, 0.551, -0.007 O, -1.310, 1.449, 0.020 H, -1.808, 0.412, 0.022 H, -1.416, 1.894, 0.871	8.7688 2.9797 2.2369	1126i, 166, 172, 198, 411, 492, 549, 569, 616, 732, 757, 1224, 1362, 1859, 3813	-112.6 [e]

[a] Calculated at the B3LYP/6-311+g(2d,p) level of theory [1]

[b] Calculated at the CBS-QB3 level of theory [2]

[c] Experimental values: r_e(Ni-O) = 1.627 Å; ω_e = 839 cm^{-1} [3]

[d] Using experimental D_0(NiO) = 373 kJ mol^{-1} [4], $\Delta_f H^o$(Ni) = 428.1 kJ mol^{-1} and $\Delta_f H^o$(O) = 246.8 kJ mol^{-1} at 0 K. [5]

[e] Using $\Delta_f H^o$(CO) = -113.8 kJ mol^{-1}, $\Delta_f H^o(CO_2)$ = -393.2 kJ mol^{-1}, $\Delta_f H^o(H_2O)$ = -238.9 kJ mol^{-1}. [5]

[f] Using a bond energy with respect to Ni + O_2 from a multireference configuration interaction calculation.[6]

Table S3. Parameters used in RRKM fits to the kinetics of reactions R1 and R4 – R7.

Reaction	$\langle \Delta E \rangle_{down}$ cm^{-1}	α	V_0 kJ mol^{-1}	$k_{rec,\infty}$ cm^3 $molecule^{-1}$ s^{-1}	Z(T) [a] cm^3 $molecule^{-1}$ s^{-1}
Ni + O_2	210	0.2	-	5.0×10^{-10} exp(-69/T)	1.9×10^{-11} $T^{1/2}$
NiO + CO	300	0.0	-	8.3×10^{-11} exp(-102/T)	6.4×10^{-12} $T^{1/2}$
NiO + O_2	300	1.0	-	4.8×10^{-10} exp(-352/T)	1.2×10^{-11} $T^{1/2}$
NiO + H_2O	200	0.0	-	6.0×10^{-10} exp(-171/T)	6.0×10^{-12} $T^{1/2}$
NiO + CO_2	240	1.0	14.0	5.2×10^{-10} exp(-305/T)	6.1×10^{-12} $T^{1/2}$

[a] Collision frequency between the adduct and N_2

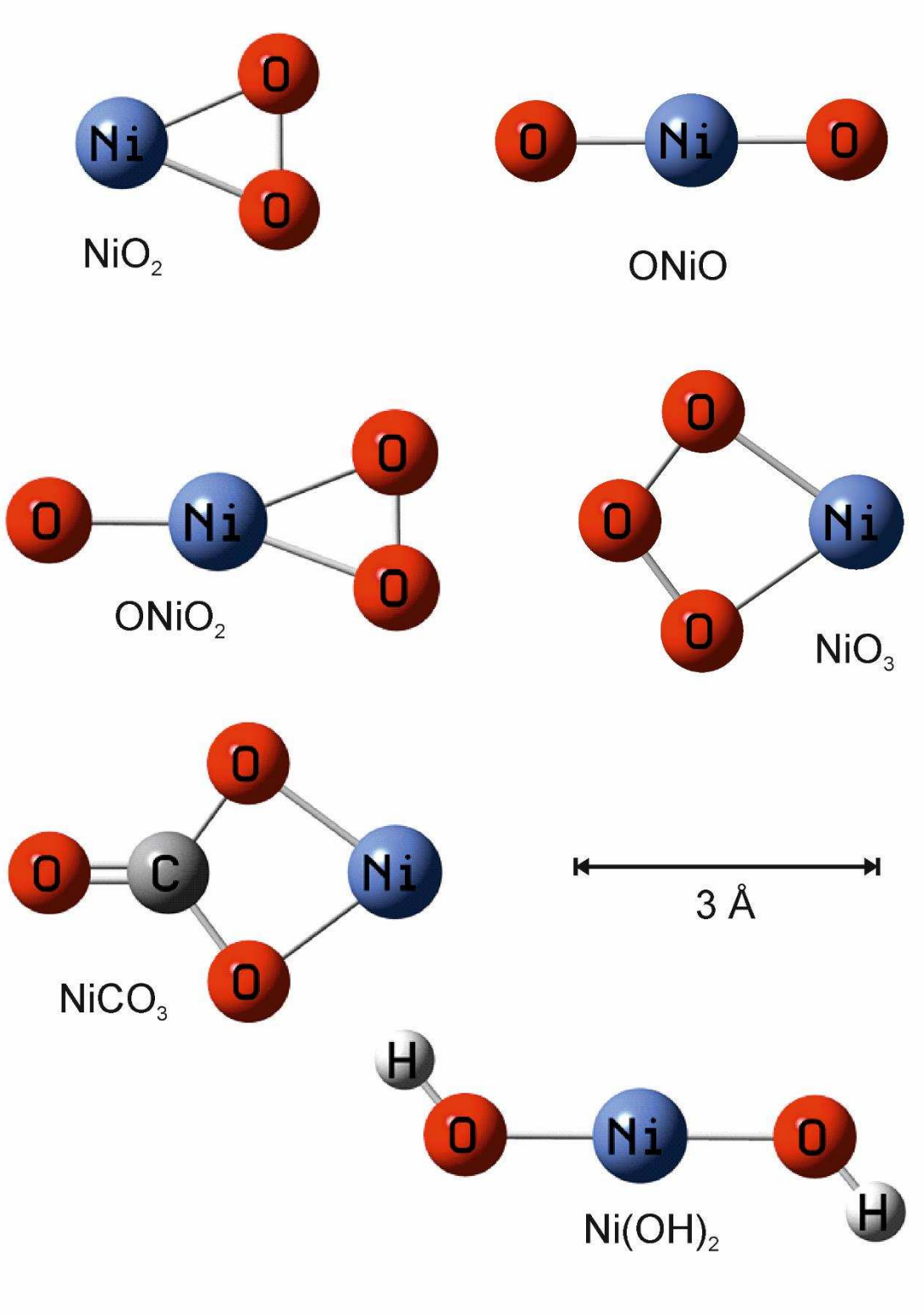

Figure S1. Geometries of the molecules listed in Table S1. See the second column of Table S2 for the Cartesian coordinates of the atoms.

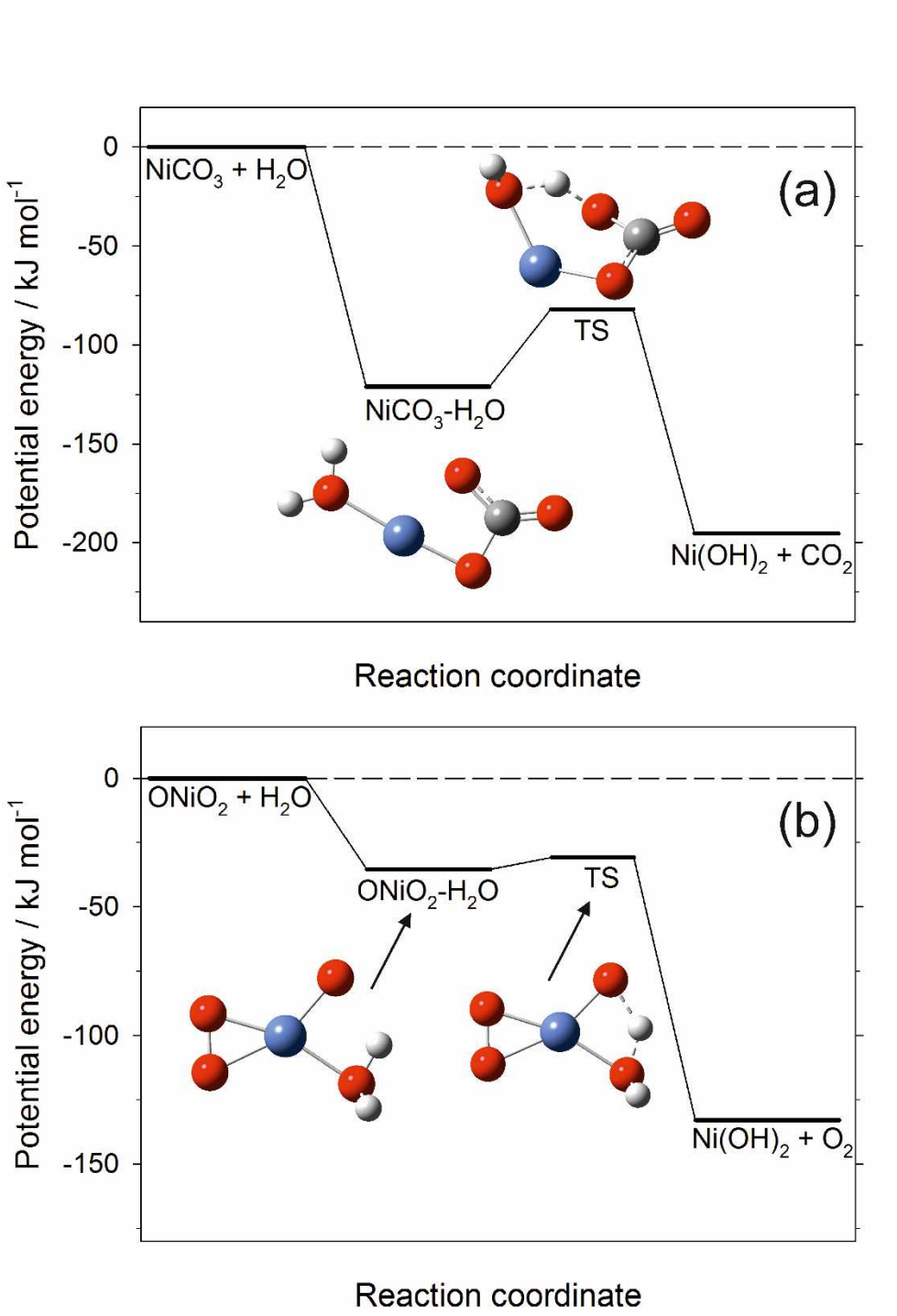

Figure S2. (a) The potential energy surface for the reaction of $NiCO_3$ and H_2O. (b) The potential energy surface for the reaction of $ONiO_2$ and H_2O. Calculated at the CBS-QB3 level of theory. Atom colors: oxygen (red); hydrogen (white); carbon (grey); nickel (blue).

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