Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Surface Chemistry and Stability of Metastable Corundum-Type In_2O_3

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A FT-IR experiments in flowing He

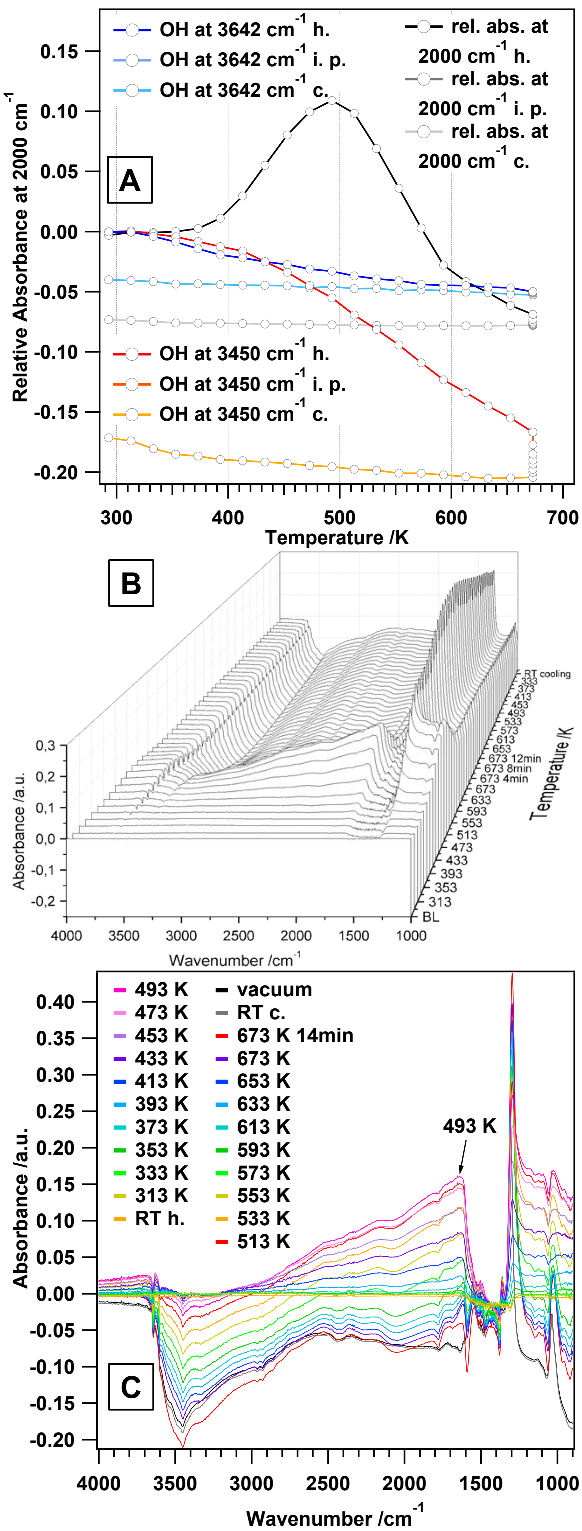

Figure S1. Panel A: development of OH species and the absorbance as a function of heating and cooling. Panel B: *in situ* FT-IR data of rh-In_2O_3 in flowing He (1 mL s^{-1}). Panel C: selected FT-IR spectra used for analysis of Panel A. A heating-cooling cycle (10 K min^{-1})

from room temperature to 700 K and back was applied. h = heating, c = cooling, i. p. = isothermal period.

Table S1. Calculated activation energies from the Arrhenius plots of the temperature-dependent impedance experiments for the rh-In_2O_3 sample treated in different gas atmospheres.

gas	T-range /K	E_A heating /kJmol^{-1}	T-range /K	E_A cooling /kJmol^{-1}
He	617 – 700	105	615 – 702	97
	584 – 617	23	477 – 615	68
	544 – 584	49	378 – 477	93
	497 – 544	33		
	374 – 497	59		
	337 – 374	25		
H_2 (673 K) light blue trace Fig. 5	425 – 493	250	–	–
	358 – 425	65		
	300 – 358	26		
H_2 (523 K) grey trace Fig. 5	433 – 486	216	–	–
	297 – 313	226		
H_2 (498 K) light red trace Fig. 5	447 – 499	135	–	–
	302 – 313	454		
CO	512 – 559	73	–	–
	303 – 414	136		
CO_2	620 – 698	85	615 – 698	106
	485 – 620	40	483 – 615	45
	360 – 485	74	376 – 483	81
			338 – 376	46

Note that for H_2 and CO the E_A's upon re-cooling were not calculated due to the presence of metallic conductivity over the whole temperature range.

Table S2. Equivalent circuit parameters obtained from the simulation of the impedance spectra of Figure 3A for the sample treated in dry He.

Temperature /K	R_{gi} /Ω	C_{gi} /F	R_{gb} /Ω	C_{gb} /F
423	$1.06\cdot10^{7}$	$1.44\cdot10^{-11}$	$2.46\cdot10^{7}$	$1.94\cdot10^{-9}$
473	$8.85\cdot10^{5}$	$2.11\cdot10^{-11}$	$1.45\cdot10^{7}$	$1.70\cdot10^{-9}$
493	$3.05\cdot10^{5}$	$2.42\cdot10^{-11}$	$1.30\cdot10^{7}$	$1.68\cdot10^{-9}$
523	$1.36\cdot10^{5}$	$2.55\cdot10^{-11}$	$1.00\cdot10^{7}$	$1.49\cdot10^{-9}$

Table S3. Equivalent circuit parameters obtained from the simulation of the impedance spectra of Figure 3B for the sample treated in dry He.

Temperature /K	R_{gi} /Ω	C_{gi} /F	R_{gb} /Ω	C_{gb} /F
473	$3.21\cdot10^{6}$	$2.25\cdot10^{-11}$	$3.84\cdot10^{7}$	$1.01\cdot10^{-10}$
523	$3.15\cdot10^{5}$	$2.27\cdot10^{-11}$	$1.83\cdot10^{7}$	$3.34\cdot10^{-9}$
573	$4.78\cdot10^{4}$	$2.25\cdot10^{-11}$	$3.41\cdot10^{6}$	$1.53\cdot10^{-9}$
623	$2.77\cdot10^{4}$	$2.14\cdot10^{-11}$	$6.49\cdot10^{5}$	$6.30\cdot10^{-10}$

B FT-IR experiments in flowing H_2

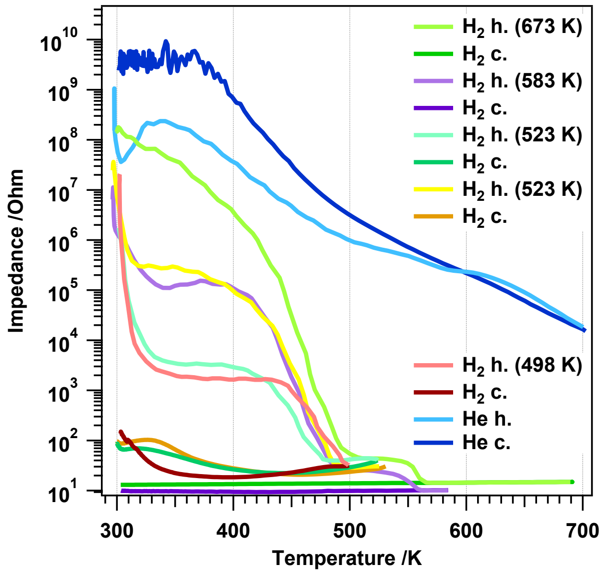

Figure S2. *In situ* electrochemical impedance measurements on rh-In_2O_3 in flowing H_2 (1 mL s^{-1}). Heating-cooling cycles from room temperature to different maximum temperatures and back, as well as applied heating and cooling rates (10 K min^{-1}), are identical in all experiments. h = heating, c = cooling.

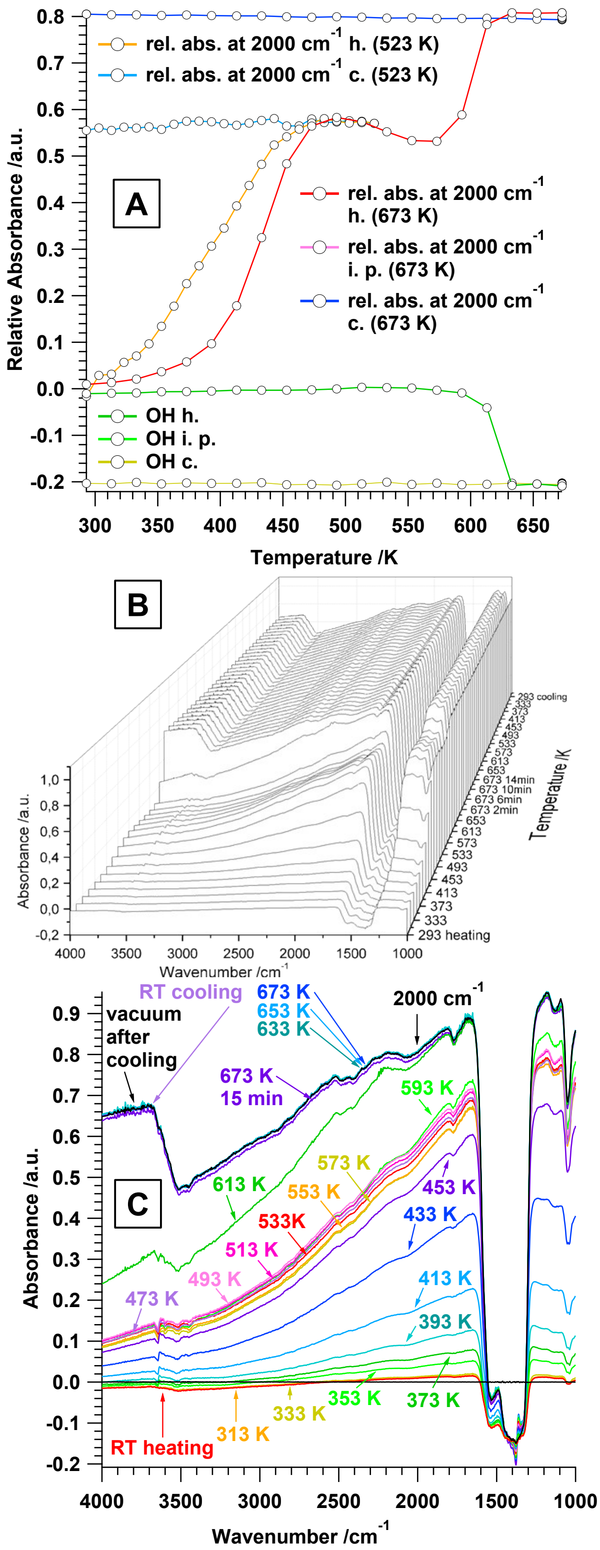

Figure S3. Panel A: Development of OH species and the absorbance as a function of heating and cooling. Panel B: *in situ* FT-IR data of rh-In_2O_3 in flowing H_2 (1 mL s^{-1}). Panel C: selected FT-IR spectra used for analysis of Panel A. A heating-cooling cycle (10 K min^{-1})

from room temperature to 700 K and back was applied. h = heating, c = cooling, i. p. = isothermal period.

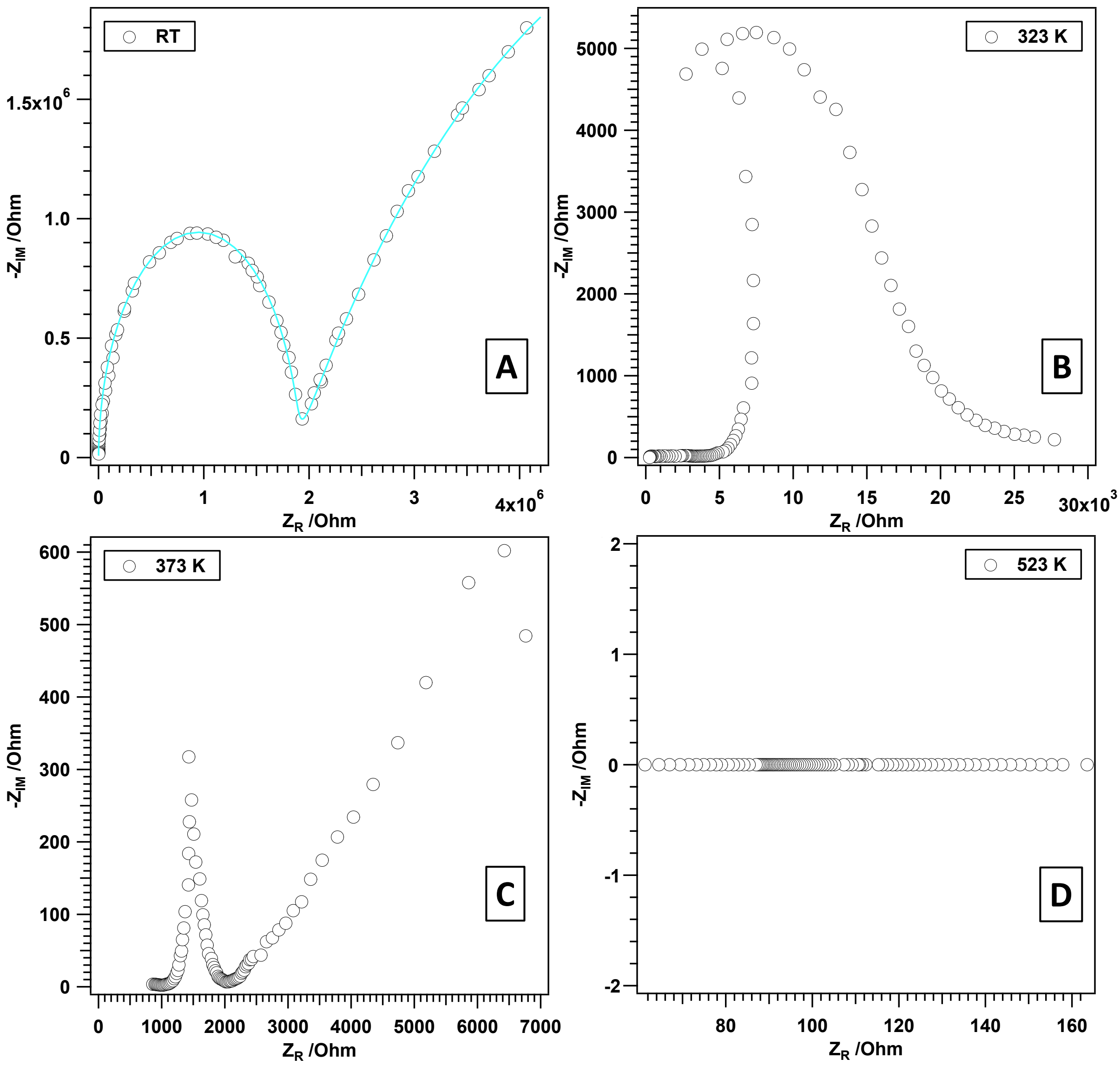

Figure S4. Nyquist plots (data points) and simulated spectra (continuous lines) of rh-In_2O_3 treated in dry H_2 at selected temperatures between RT and 523 K.

Table S4. Equivalent circuit parameters obtained from the simulation of the impedance spectrum of Figure 6 and S3A for the sample treated in dry H_2.

Temperature /K	R_{gi} /Ω	C_{gi} /F	R_{gb} /Ω	C_{gb} /F
RT	$1.86 \cdot 10^{6}$	$2.15 \cdot 10^{-11}$	$9.25 \cdot 10^{6}$	$4.37 \cdot 10^{-10}$

C FT-IR experiments in flowing CO

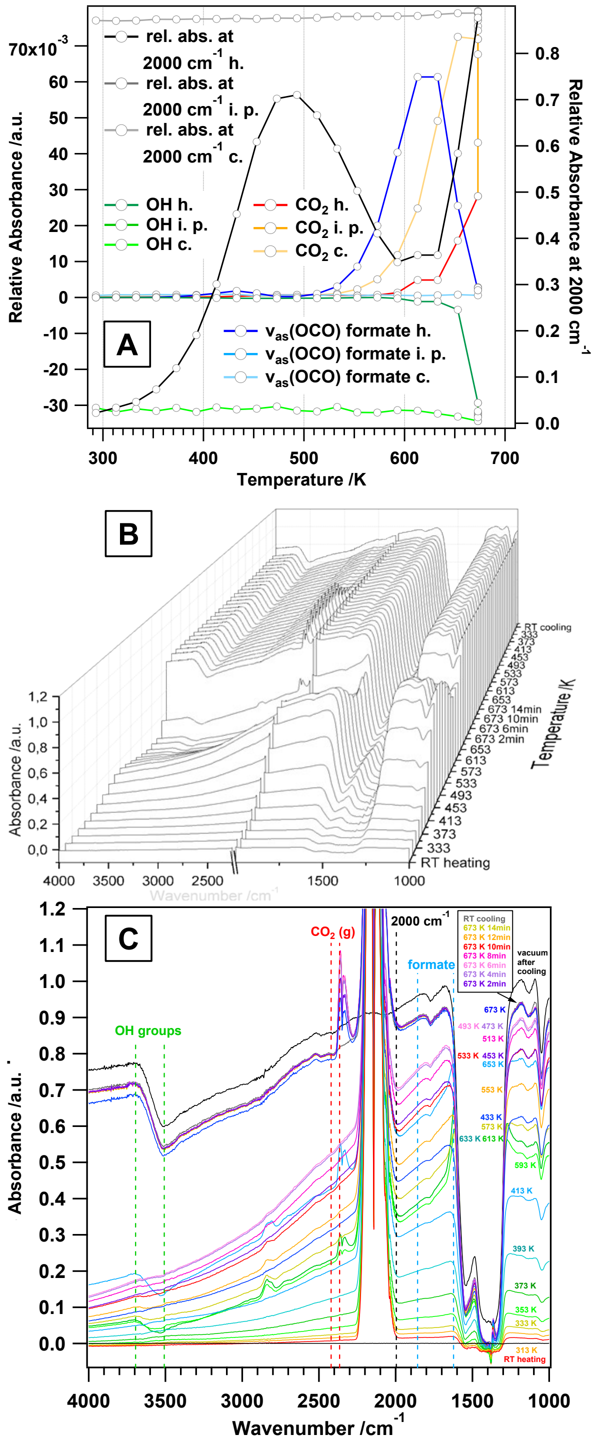

Figure S5. Panel A: development of OH, CO_2, and formate signals and the absorbance as a function of heating and cooling. Panel B: *in situ* FT-IR data of rh-In_2O_3 in flowing CO (1 mL s^{-1}). Panel C: selected FT-IR spectra used for analysis of Panel A. A heating-cooling cycle (10 K min^{-1}) from room temperature to 700 K and back was applied.

Table S5. Equivalent circuit parameters obtained from the simulation of impedance spectra of Figure 8 for the sample treated in dry CO.

Temperature /K	R_{gi} /Ω	C_{gi} /F	R_{gb} /Ω	C_{gb} /F
RT	$2.03 \cdot 10^{6}$	$1.05 \cdot 10^{-11}$	$1.67 \cdot 10^{7}$	$3.80 \cdot 10^{-11}$
323	$1.20 \cdot 10^{6}$	$1.31 \cdot 10^{-11}$	$4.02 \cdot 10^{5}$	$1.60 \cdot 10^{-9}$

D FT-IR experiments in flowing CO_2

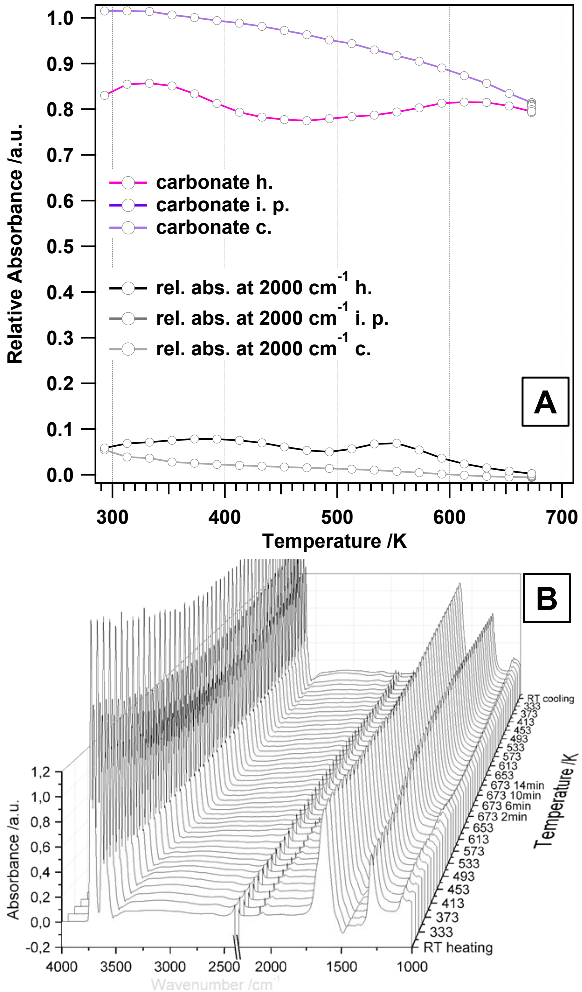

Figure S6. Panel A: development of carbonate species and the absorbance as a function of heating and cooling. Panel B: *in situ* FT-IR data of rh-In_2O_3 in flowing CO_2 (1 mL s^{-1}). A heating-cooling cycle (10 K min^{-1}) from room temperature to 700 K and back was applied.

Table S6. Equivalent circuit parameters obtained from the simulation of the impedance spectra of Figure 10 for the sample treated in dry CO_2.

Temperature /K	R_{gi} /Ω	C_{gi} /F	R_{gb} /Ω	C_{gb} /F
473	$2.27 \cdot 10^{6}$	$2.26 \cdot 10^{-11}$	$3.71 \cdot 10^{6}$	$1.06 \cdot 10^{-10}$
523	$2.90 \cdot 10^{5}$	$2.21 \cdot 10^{-11}$	$2.92 \cdot 10^{6}$	$2.14 \cdot 10^{-10}$
573	$5.10 \cdot 10^{4}$	$2.69 \cdot 10^{-11}$	$1.93 \cdot 10^{6}$	$4.13 \cdot 10^{-10}$
623	$1.50 \cdot 10^{4}$	$1.93 \cdot 10^{-11}$	$5.14 \cdot 10^{5}$	$4.00 \cdot 10^{-10}$

Table S7. Calculated activation energies for the different processes (gi and gb) from the Arrhenius plots for the rh-In_2O_3 sample treated in different gas atmospheres.

gas	T-range /K	E_A (gi) /kJmol^{-1}	E_A (gi) /eV	E_A (gb) /kJmol^{-1}	E_A (gb) /eV
He (Fig. 4A)	423 – 523	82	0.85	16	0.17
He (Fig. 4B)	523 – 623	80	0.83	90	0.94
CO_2	473 – 623	83	0.86	30	0.31