Supporting Information

Inserted Hydrogen Promotes Oxidation Catalysis of Mixed $Ru_{0.3}Ti_{0.7}O_2$ as Exemplified with Total Propane Oxidation and HCl Oxidation Reaction

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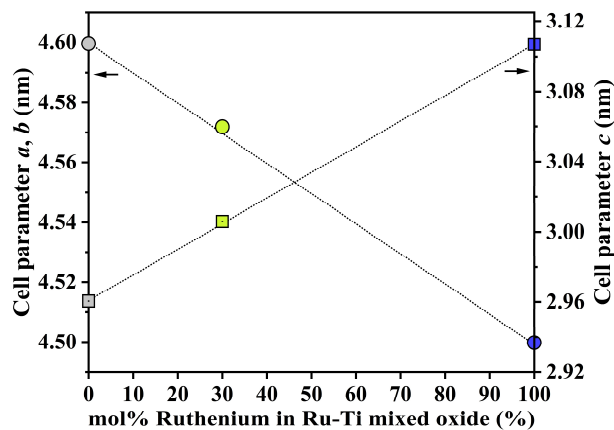Bernd.Smarsly@phys.Chemie.uni-giessen.de; yunguo@ecust.edu.cn

Figure S1: Lattice parameters of rutile TiO_2, RuO_2 and $Ru_xTi_{1-x}O_2$ of Ru_30, as derived from the peak deconvolution of rutile (110) and rutile (101). Assuming the validity of Vegard's rule, the composition x of $Ru_xTi_{1-x}O_2$ in Ru_30 is determined to be x=30 ± 3%.
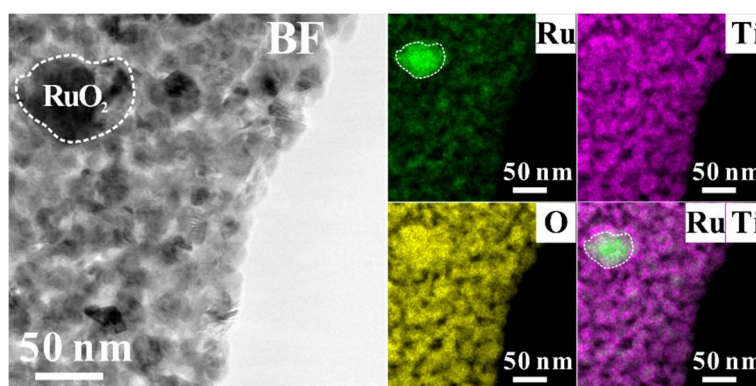

Figure S2: High resolution bright field (BF) images of Ru_30. EDS mapping images are also presented on the right: green = Ru; magenta = Ti; yellow = O, indicating the presence of big RuO_2 particles supported on an otherwise mixed $Ru_xTi_{1-x}O_2$; x = 26 ± 4 mol%.
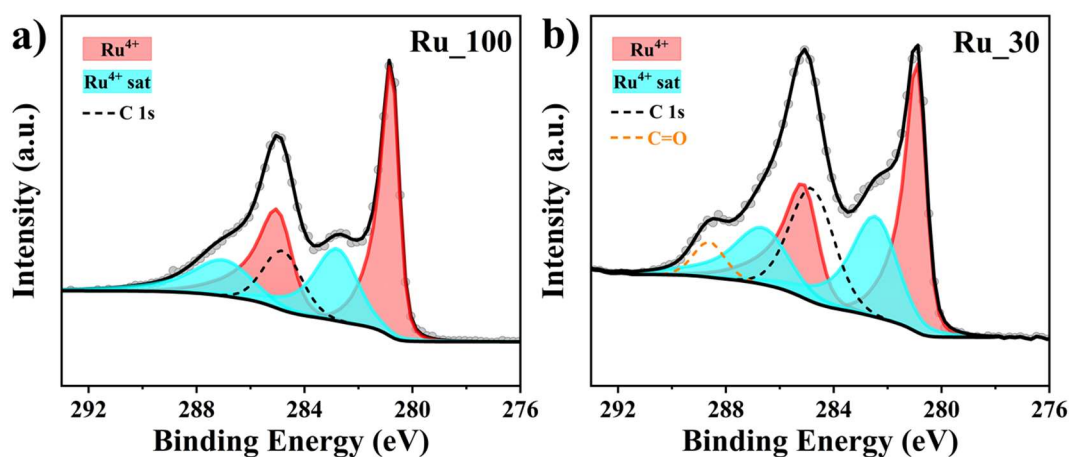

Figure S3: Deconvolution of Ru 3d XP spectra of freshly prepared Ru_100 and Ru_30.
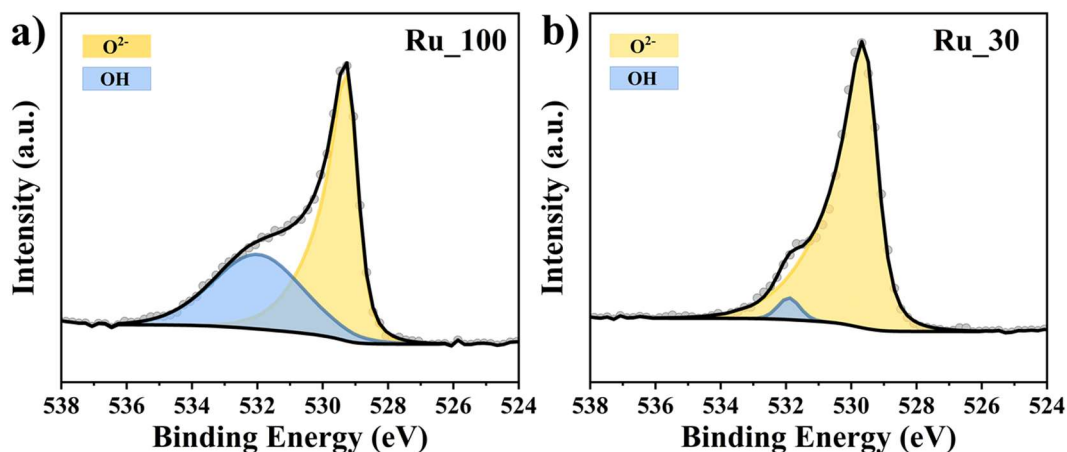
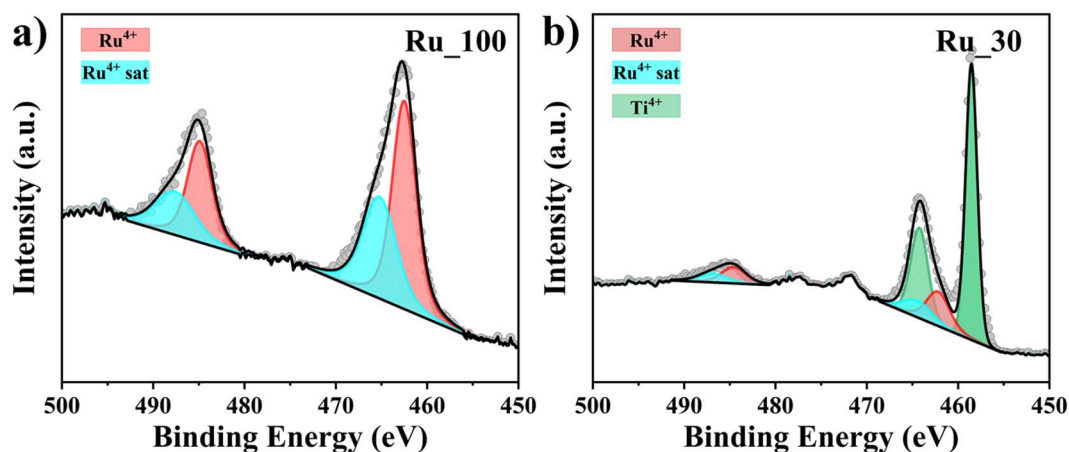**Figure S4:** Deconvolution of O 1s spectra of freshly prepared Ru_100 and Ru_30.

Figure S5: Deconvolution of Ru 3p and Ti 2p XP spectra of Ru_100 and Ru_30.

Table S1: Optimized fitting parameters for the deconvolution of Ru 3d, Ru 3p, Ti 2p and O 1s of used in our study.

	Ru_100	Ru_30	Ru_30_250R	Ru_30_250R_300O
BE (eV) Ru3d-5/2	280.7	280.8	280.8	281.0
FWHM	0.71	0.82	0.85	0.85
Line shape	LF (0.4, 1, 45, 280)			
BE (eV) Ru3d-3/2	284.9	285.0	284.9	285.2
FWHM	1.32	1.30	1.12	1.31
Line shape	LF (0.4, 1, 45, 280)			
BE (eV) Ru3d-5/2 sat	282.7	282.3	281.6	282.5
FWHM	1.81	1.89	1.51	1.88
Line shape	LF (0.6, 1, 45, 280)			
BE (eV) Ru3d-3/2 sat	286.9	286.5	285.8	286.7
FWHM	2.43	2.26	2.34	2.28
Line shape	LF (0.6, 1, 45, 280)			
BE (eV) Ru3d-5/2 metal	-	-	280.2	280.3
FWHM	-	-	0.60	0.71
Line shape	LF (1.2, 1, 400; 280)			
BE (eV) Ru3d-3/2 metal	-	-	284.4	284.5

		Ru_100		Ru_30
FWHM	-	-	0.80	0.89
Line shape	LF (1.01, 1.25, 500, 50)			

	Ru_100	Ru_30
BE (eV) Ru3p-3/2	462.5	462.2
FWHM	3.11	3.00
Line shape	LF(1, 1, 45, 280)	
BE (eV) Ru3p-1/2	484.9	484.5
FWHM	3.2	3.00
Line shape	LF(1, 1, 45, 280)	
BE (eV) Ru3p-3/2 sat	465.3	464.5
FWHM	4.34	3.81
Line shape	LF(1, 1, 45, 280)	
BE (eV) Ru3p-1/2 sat	487.6	486.9
FWHM	5.07	4.08
Line shape	LF(1, 1, 45, 280)	
BE (eV) Ti2p-3/2	-	458.5
FWHM	-	1.46
Line shape	GL(30)	
BE (eV) Ti2p-1/2	-	464.2
FWHM	-	2.24
Line shape	GL(30)	

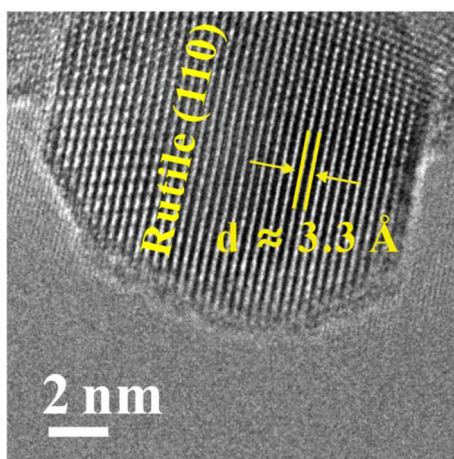|	Ru_100	Ru_30
BE (eV) O-1s	529.2	529.5
FWHM	0.86	1.07
Line shape	LF(0.37, 1.2, 25, 110)	
BE (eV) O-1s sat	532.0	531.9
FWHM	3.22	0.80
Line shape	GL(30)	

Figure S6: HR-TEM images of Ru_30, showing the plane distance d ≈ 3.3 Å, which is shorter than the d-spacing of Ru_30_250R shown in Fig 3c, indicating a lattice expansion along (110) direction after hydrogen treatment at 250 °C.
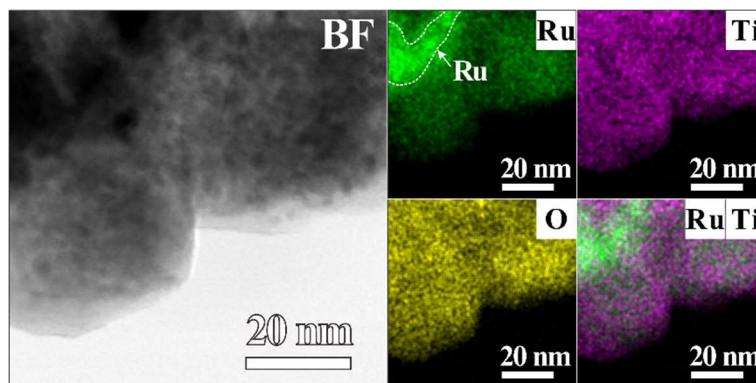
Figure S7: High resolution bright field (BF) images of Ru_30_250R with metallic Ru particles. EDS mapping images are also presented on the right: green = Ru; magenta = Ti; yellow = O.
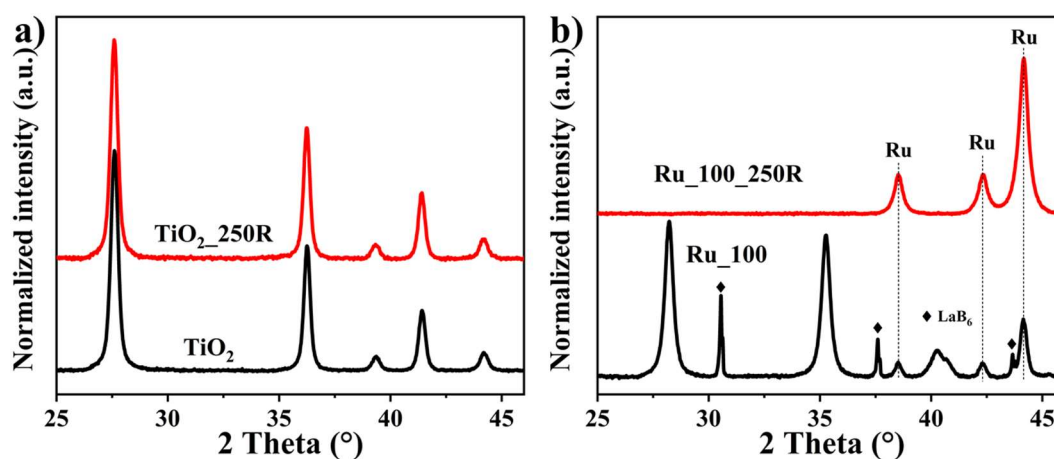

Figure S8: XRD diffraction from Ru_100 (a) and pure rutile TiO_2 (b) before and after reduction treatment with $4\%H_2/N_2$ at 250 °C.

Table S2: Microstrain and crystallite size of different catalysts determined by Williamson-Hall method.

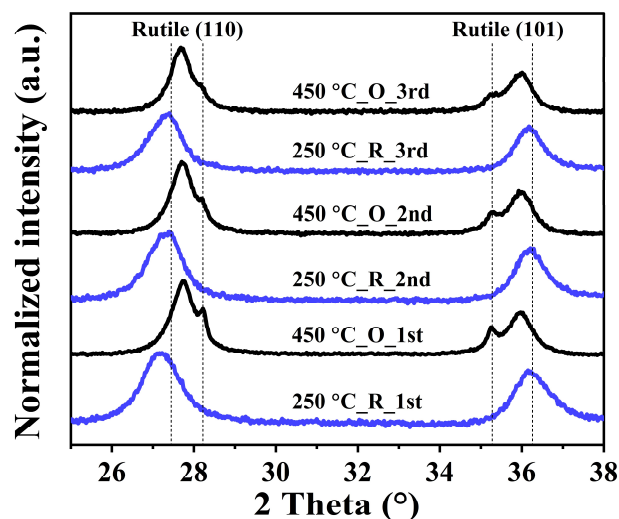| Catalyst	Microstrain	Crystallite size (nm)
Ru_30_250R	0.0120	12.2 ± 3
Ru_30_250R_50O	0.0063	11.5 ± 4
Ru_30_250R_100O	0.0020	12.2 ± 1
Ru_30_250R_200O	0.0013	11.9 ± 1
Ru_30_250R_300O	0.0005	11.2 ± 1
Ru_30_250R_H$_2$_3 cycles	0.0070	13.1 ± 4
Ru_30_250R_C$_3$H$_8$_3 cycles	0.0020	13.8 ± 3

Figure S9: XRD patterns of Ru_30 catalysts after calcination in hydrogen at 250 °C and re-oxidation at 450 °C for three cycles.

Table S3: Optimized peak deconvolution information (cf. **Figure 3**) of Ru_30 catalyst treated in H_2/N_2 at different temperatures.

| Catalyst | Rutile 110 | | | | | | | | |
| | Component (red) | | | Component (green) | | | RuO_2 (blue) | | |
	Pos.	FWHM	Area	Pos.	FWHM	Area	Pos.	FWHM	Area
Ru_30	-	-	-	27.77	0.64	0.80	28.23	0.17	0.12
Ru_30_150R	-	-	-	27.75	0.54	0.73	28.21	0.18	0.10
Ru_30_170R	27.11	0.89	0.31	27.70	0.69	0.73	28.22	0.19	0.09
Ru_30_190R	26.90	0.60	0.28	27.48	0.90	0.97	-	-	-
Ru_30_210R	29.91	0.41	0.14	27.19	1.06	0.99	-	-	-
Ru_30_230R	26.92	0.36	0.06	27.20	1.06	1.04	-	-	-
Ru_30_250R	-	-	-	27.20	1.10	1.22	-	-	-

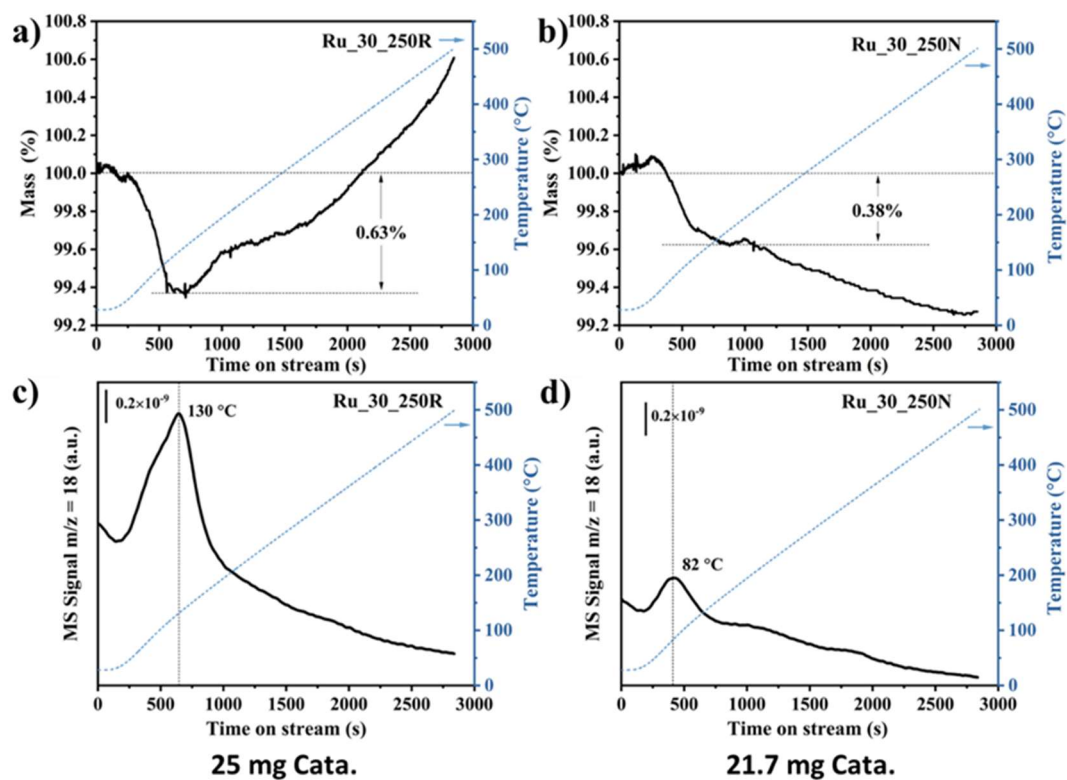| Catalyst | Rutile 101 | | | | | | | | |
| | RuO_2 (blue) | | | Component (green) | | | Component (red) | | |
	Pos.	FWHM	Area	Pos.	FWHM	Area	Pos.	FWHM	Area
Ru_30	35.27	0.22	0.13	35.92	0.70	0.45	-	-	-
Ru_30_150R	35.25	0.23	0.11	35.88	0.63	0.45	-	-	-
Ru_30_170R	35.26	0.23	0.08	35.93	0.64	0.44	36.50	0.85	0.20
Ru_30_190R	-	-	-	36.06	0.79	0.67	36.65	0.83	0.18
Ru_30_210R	-	-	-	36.24	0.90	0.63	36.92	0.66	0.13
Ru_30_230R	-	-	-	36.24	0.89	0.60	36.83	0.50	0.09
Ru_30_250R	-	-	-	36.24	1.04	0.71	-	-	-

Figure S10: TGA-MS raw data of Ru_30_250R and Ru_30_250N. The catalyst is heated from room temperature to 500 °C under 30 mL/min of dry air. Mass spectrometry (c, d) is used to monitor the gas composition during the heating ramp. After peak deconvolution of H_2O signal (m/z = 18) (cf. **Figure 4**), the amount of inserted hydrogen is calculated by the difference of the integral area of H_2O. The amount of inserted hydrogen is also counterchecked by the difference of the weight loss in TG (a, b), the estimated H% is 18.3%, which is very close to the value calculated by the MS data (17.6%).
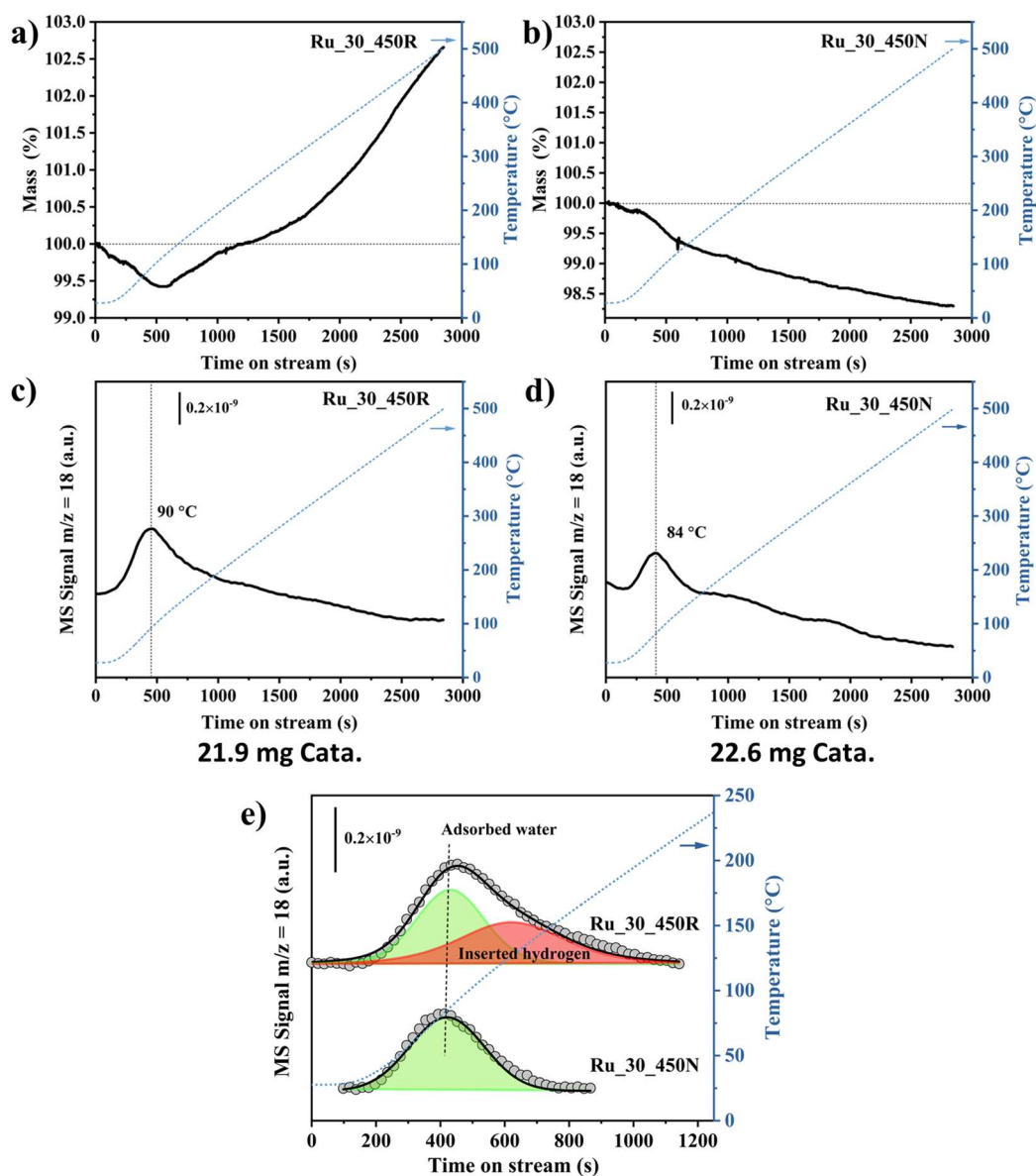
Figure S11: TGA-MS raw data of Ru_30_450R and Ru_30_450N. The catalyst is heated from room temperature to 500 °C under 30 mL/min of dry air. Mass spectrometer (c, d) is used to monitor the gas composition during the heating ramp. e) The amount of inserted hydrogen is calculated by the difference of the integral area of H_2O, indicating lower incorporation of hydrogen into the lattice (6.6 mol%) than for Ru_30_250R (17.6 mol%).
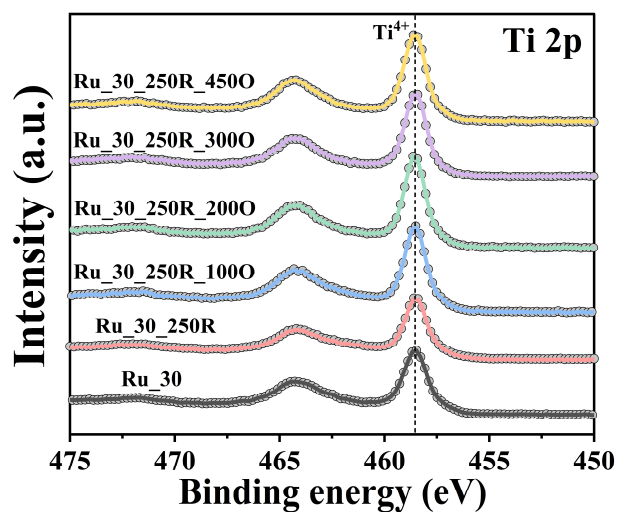
Figure S12: XPS-Ti 2p for fresh Ru_30 in comparison to hydrogen treated sample and the re-oxidized one.
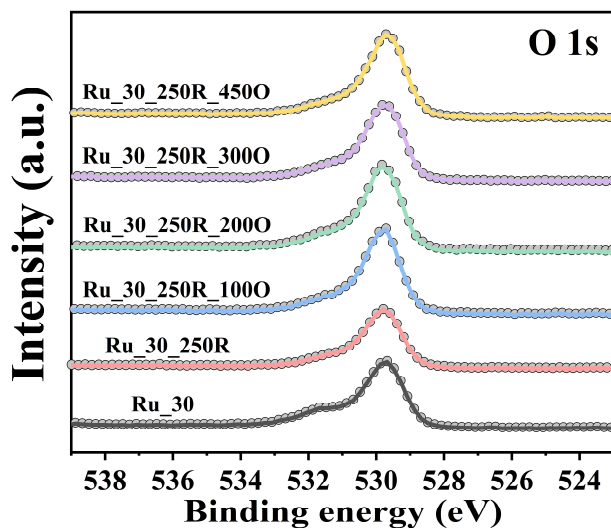

Figure S13: XPS-O1s for fresh Ru_30 in comparison to hydrogen treated sample and the re-oxidized one.
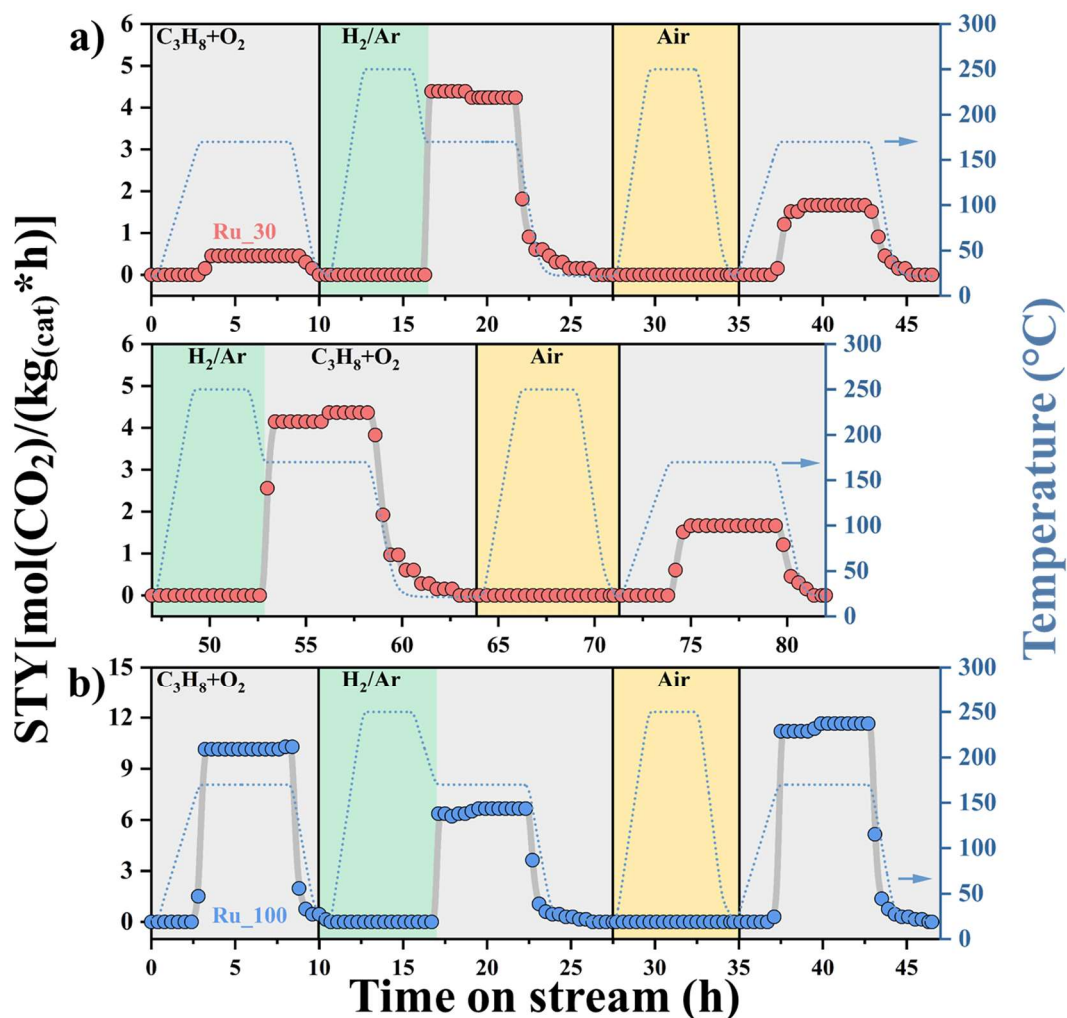
Figure S14: STY as a function of reaction time on catalytic propane combustion over a) Ru_30 and b) Ru_100 when measured for 3 cycles at 170 °C (blue dotted line). Before switched to the reaction mixture the catalyst is exposed to different gas atmosphere during the heat ramping: first under reaction mixture, followed by reduction under 4% H_2/Ar for 3 hours, and last pretreated under air for 3 hours. The grey background represents total C_3H_8 oxidation reaction conditions: 1 vol% C_3H_8, 5 vol% O_2, balanced by N_2; total volume flow: 100 sccm/min, temperature ramp: 1 K/min. The green background represents the gas mixture during heating and cooling stage: 4% H_2/Ar, total volume flow: 50 sccm/min. The yellow background represents the gas mixture during the heating and cooling stage: Air, 50 sccm/min.
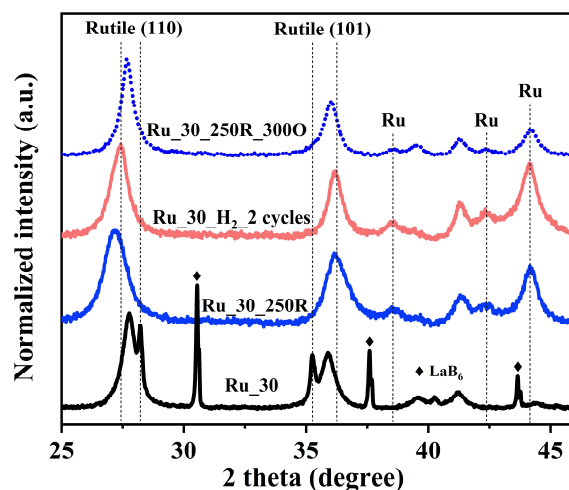
Figure S15: XRD data before and after cyclic experiments at 250 °C for Ru_30. HCl oxidation reaction conditions: 3 sccm HCl, 1.5 sccm O_2, balanced by Ar; total volume flow: 15 sccm/min. The XRD patterns of fresh Ru_30, Ru_30_250R and Ru_30_250R_300O are also presented as reference; the dotted lines are guiding lines to follow the shift in 2θ. Here Ru_30_H$_2$_2 cycles means the catalyst after 2 cycles (2 in-situ treatments under hydrogen and then switched to reaction mixture) of Deacon tests and finally cooled down under 4% H_2/Ar.
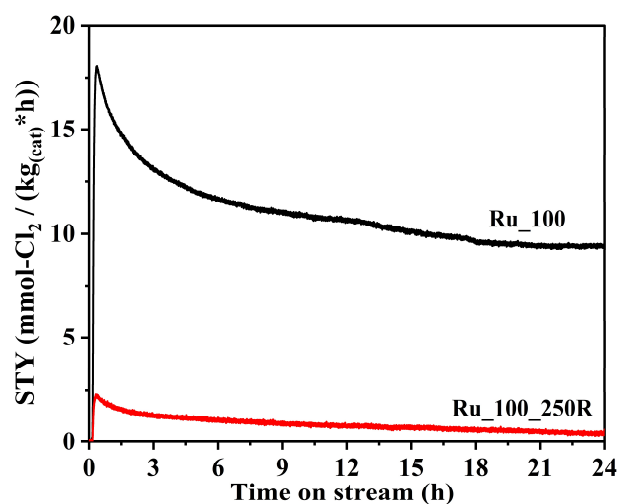

Figure S16: Catalytic HCl oxidation test of fresh Ru_100 sample in comparison to that of Ru_100_250R at 250 °C. Ru_100_250R is about one order of magnitude less active in HCl oxidation than Ru_100. Reaction conditions: 3 sccm HCl, 1.5 sccm O_2, balanced by Ar; total volume flow: 15 sccm/min.
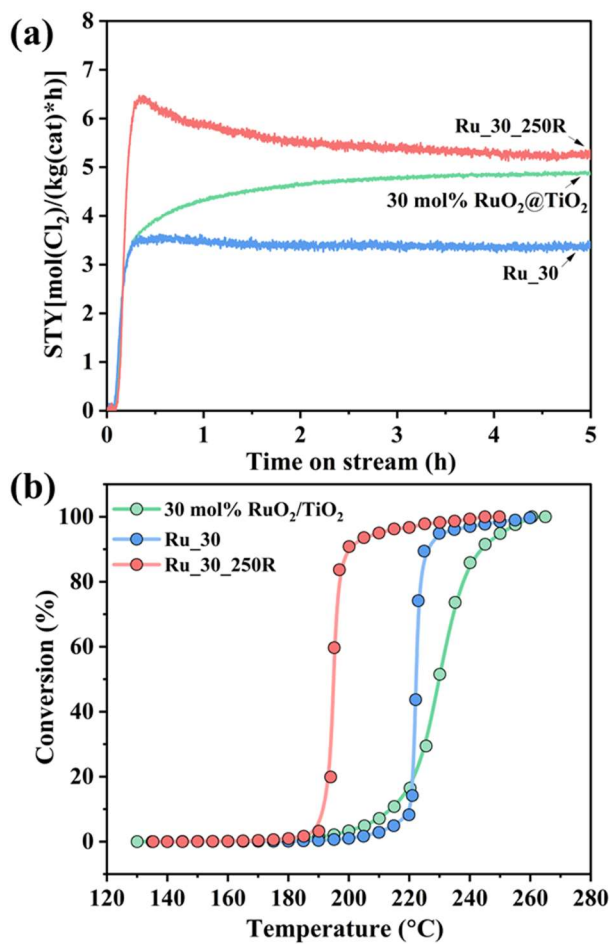
Figure S17: Catalytic HCl oxidation test at 250 °C (a) and propane oxidation test (b) of 30 mol% RuO$_2$/TiO$_2$_rutile catalyst, the benchmark catalyst, however with similar Ru loading as Ru_30 in comparison with catalytic tests of Ru_30 and Ru_30_250R. Reaction conditions for HCl oxidation: 3 sccm HCl, 1.5 sccm O$_2$, balanced by Ar; total volume flow: 15 sccm/min; Reaction conditions for propane oxidation: 1 vol% C$_3$H$_8$, 5 vol% O$_2$, balanced by N$_2$; total volume flow: 100 sccm/min, temperature ramp: 1 K/min. 30 mol% RuO$_2$/TiO$_2$_rutile catalyst is prepared by incipient wetness impregnation method and calcined at 450 °C for 4 h.