Electronic Supporting Information

In-situ observation of highly oxidized Ru species in Ru/CeO_2 catalyst under propane oxidation

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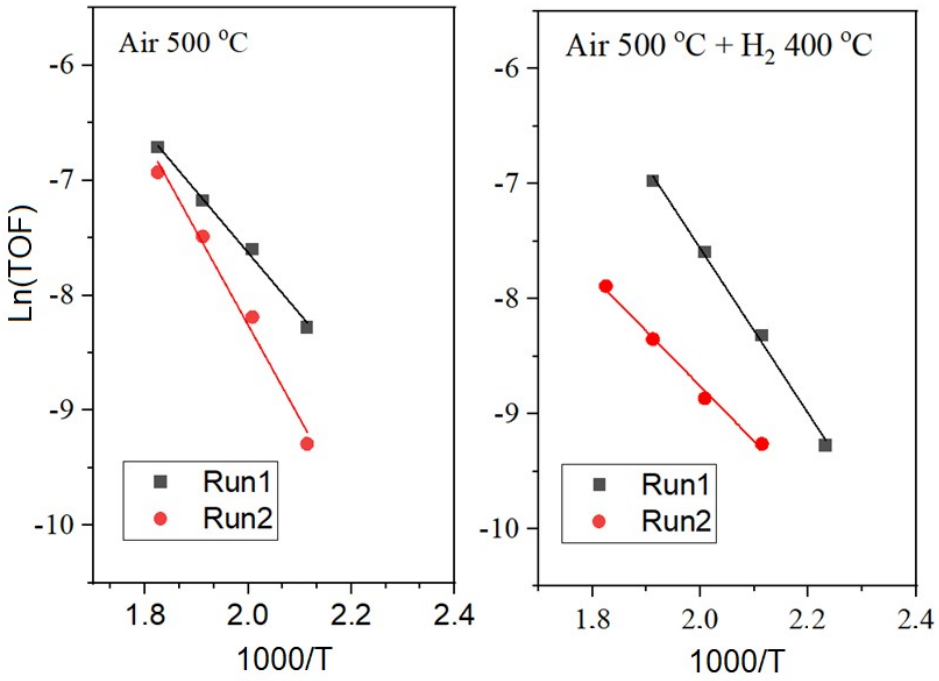

Figure S1. The Arrhenius plots for the oxidized (pre-treated in air at 500 ºC) and reduced (pre-treated in air at 500 ºC, then in H_2 at 400 ºC) Ru/CeO_2 samples.

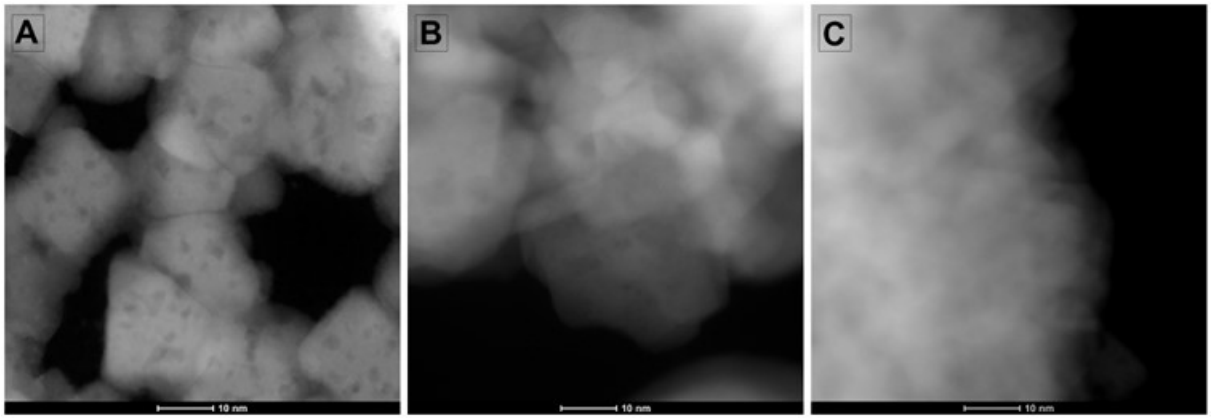

Figure S2. High-resolution HAADF-STEM images of the oxidized Ru/CeO_2 catalyst (calcined in air at 500 ºC) before (a) and after (b) the C_3H_8 oxidation test and the reduced in H_2 at 400 ºC Ru/CeO_2 catalyst after the C_3H_8 oxidation test (c).

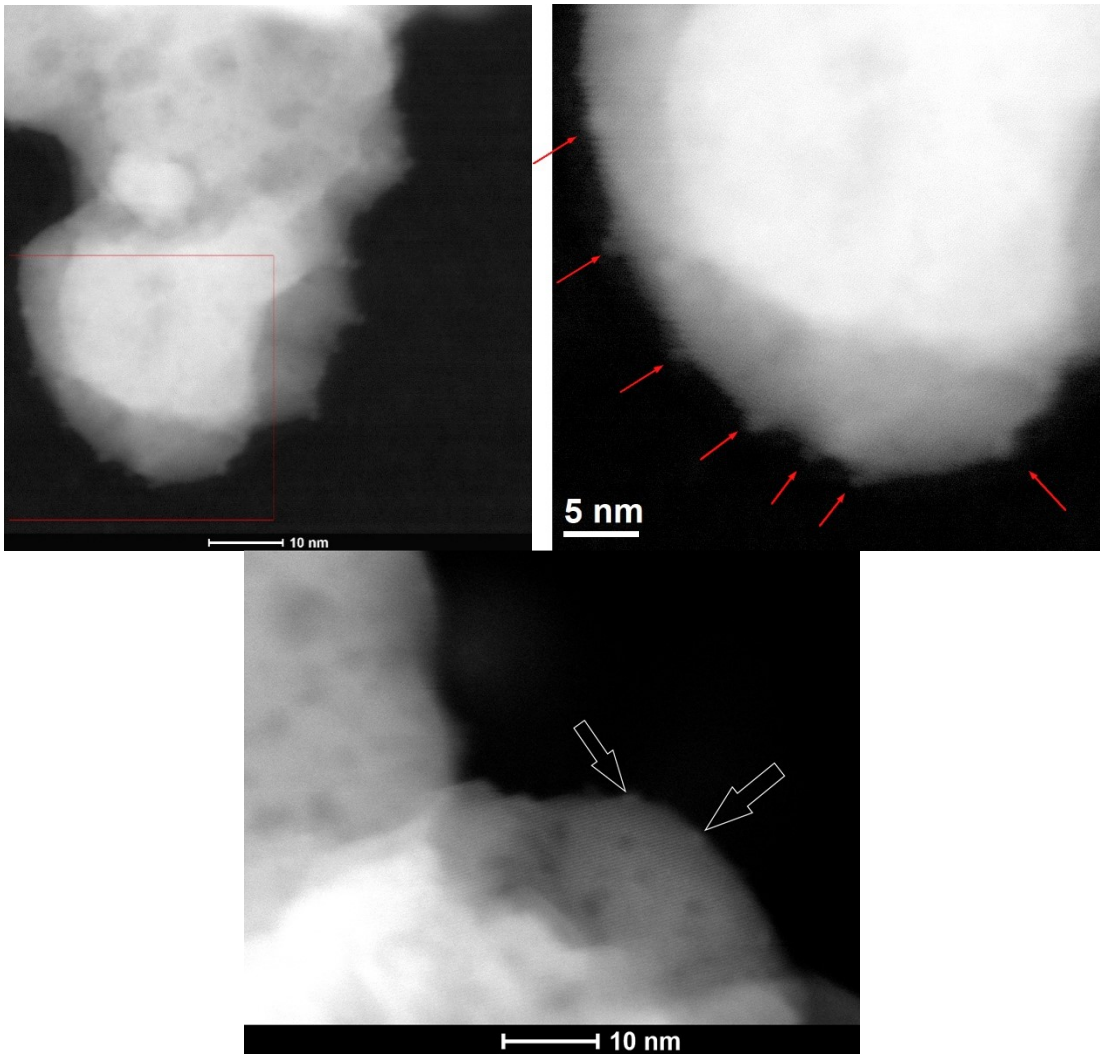

Figure S3. High-resolution HAADF-STEM images of the reduced in H_2 at 400 ºC Ru/CeO_2 catalyst.

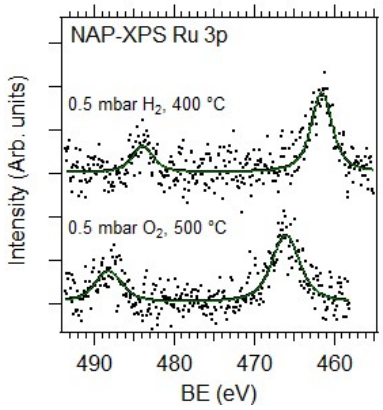

Figure S4. NAP-XPS Ru 3p spectra collected while exposing the oxidized Ru/CeO_2 catalyst to 0.5 mbar oxygen at 500 °C and hydrogen at 400 °C.

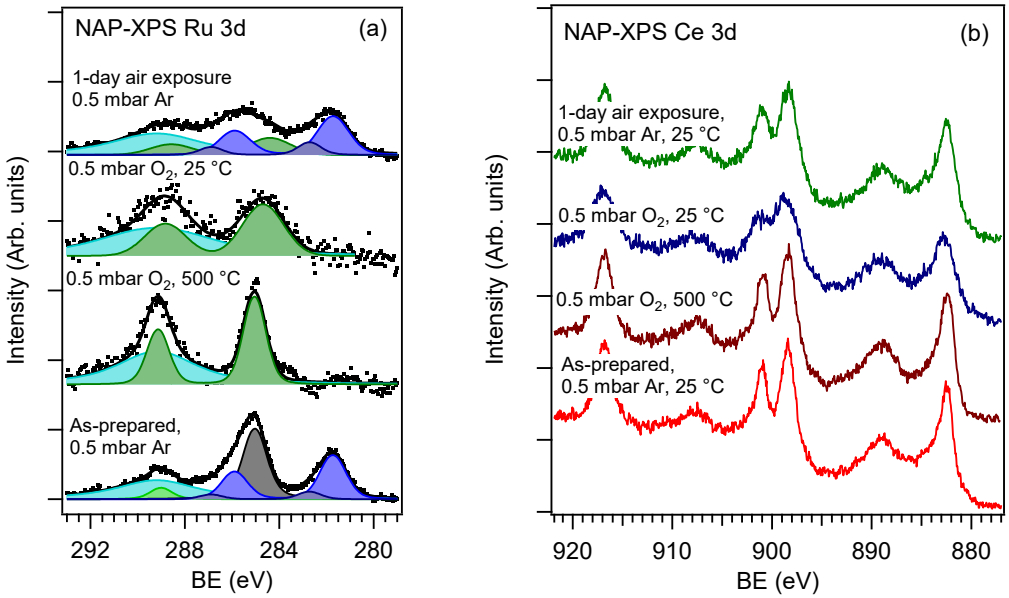

Figure S5. NAP-XPS Ru 3d (a) and Ce 3d (b) regions collected while subsequently exposing the oxidized Ru/CeO_2 catalyst to 0.5 mbar argon at 25 °C, 0.5 mbar oxygen at 500 °C, 0.5 mbar oxygen at 25 °C (after cooling in oxygen), and 0.5 mbar argon at 25 °C after exposing to air for 24 hours. The air-exposed catalyst was mechanically stirred and pressed into the In foil before the measurement.

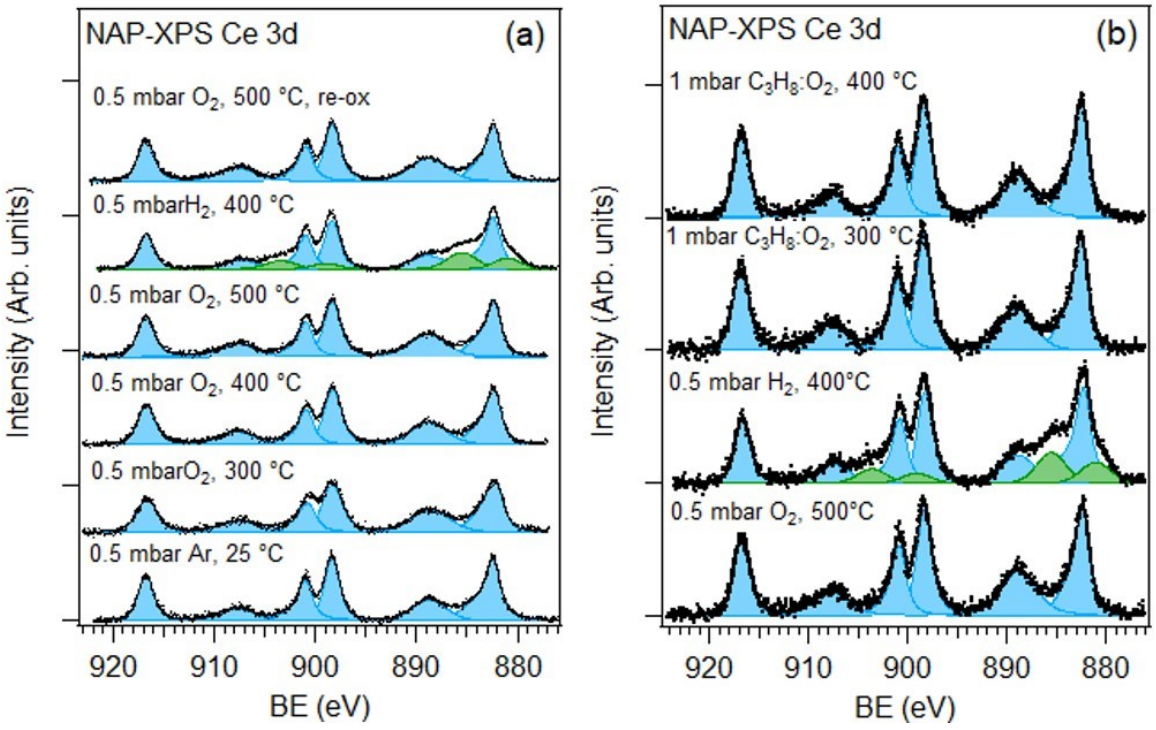

Figure S6. NAP-XPS Ce 3d spectra collected: (a) while pre-treating the oxidized Ru/CeO_2 catalyst in different environments (neutral (Ar), oxidative (O_2), and reducing (H_2) gas atmospheres) at different temperatures; (b) during propane oxidation (C_3H_8+O_2 (1:10)) on the reduced Ru/CeO_2 catalyst at 300 and 400 ºC.

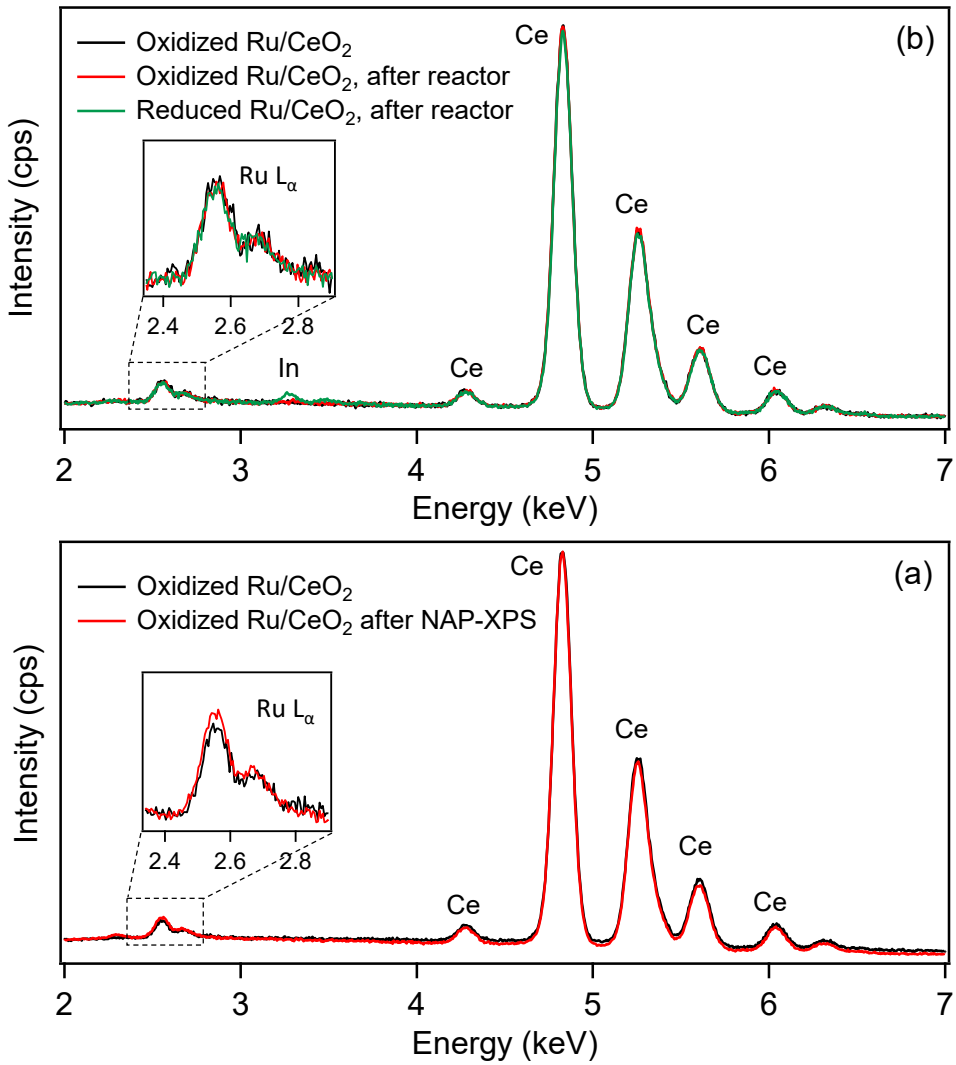

Figure S7. (a) EDS analysis of the oxidized Ru/CeO_2 sample before and after the reducing-oxidizing cycle in the NAP cell (the reduction in 0.5 mbar H_2 at 400 °C followed by the subsequent re-oxidation in 0.5 mbar O_2 at 500 °C); (b) EDX analysis of the oxidized Ru/CeO_2 sample before and after the propane oxidation test in catalytic reactor, and EDX analysis of the reduced Ru/CeO_2 sample after propane oxidation in the reactor (the visible signal of In originates from the In foil used as a support for the catalyst).

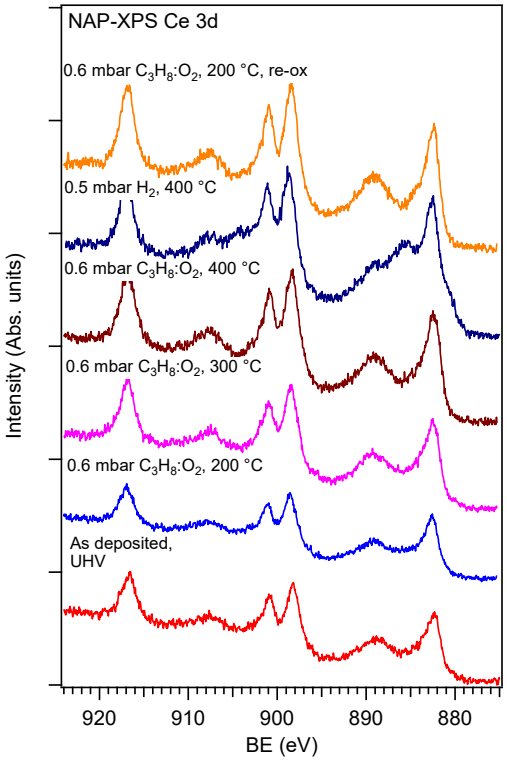

Figure S8. NAP-XPS Ce 3d spectra collected from the as-deposited planar Ru/CeO_2 catalyst in UHV and during exposure to 0.6 mbar C_3H_8+O_2 (1:10) at 200-400 ºC, 0.5 mbar H_2, and again 0.6 mbar C_3H_8+O_2 (1:10) at 400 ºC.

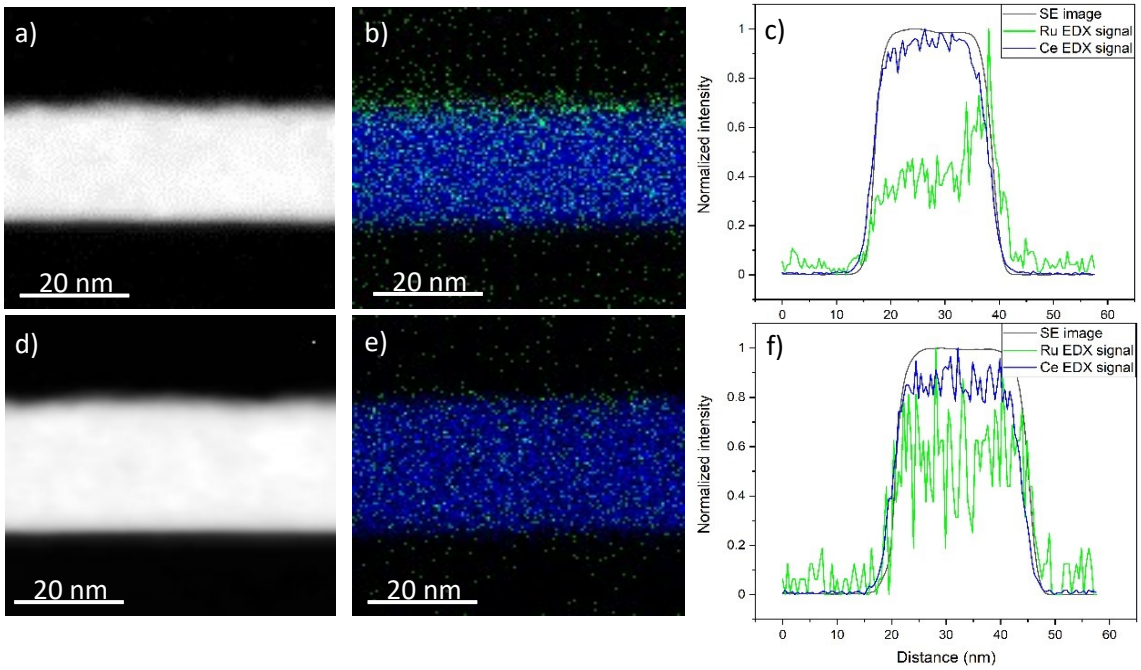

Figure S9. STEM-EDX analysis of the planar Ru/CeO_2 sample before (a-c) and after (d-f) the the NAP-XPS experiment. Intensities are normalized to maximum [0, 1].

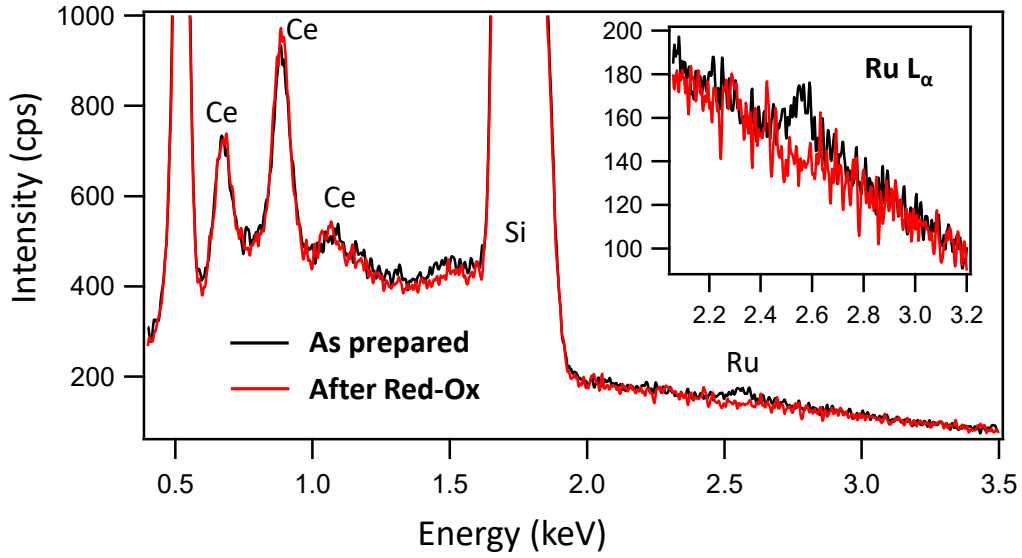

Figure S10. EDS analysis of the as-deposted planar Ru/CeO_2 sample before and after the reducing-oxidizing cycle in NAP cell (the reduction in 0.5 mbar H_2 at 400 °C followed by the subsequent re-oxidation in 0.5 mbar O_2 at 500 °C).

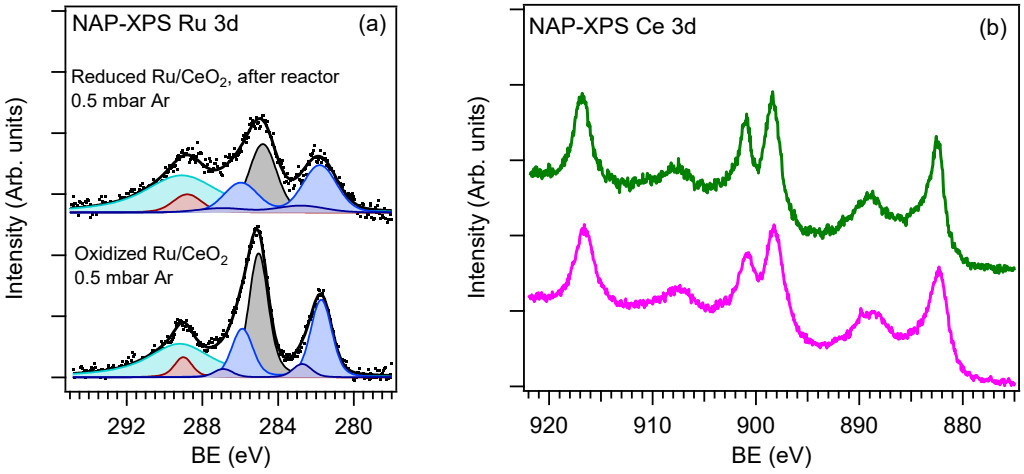

Figure S11. NAP-XPS Ru 3d (a) and Ce 3d (b) spectra collected from the oxidized Ru/CeO_2 catalyst before and after the propane oxidation test in catalytic reactor. The catalytic test included H_2 pre-treatment at 400 ˚C.

Pre-treatment	T_{50} [ºC]		r_{275} [μmol·g^{-1}·s^{-1}]		$TOF_{275}\cdot10^3$ [s^{-1}]		E_a [kJ/mol]	
	Run1	Run2	Run1	Run2	Run1	Run2	Run1	Run2
Air 500 ºC	312	320	12.0	9.7	1.21	0.98	44	67
Air 500 ºC + H_2 400º C	302	400	14.3	3.7	1.45	0.37	60	40

Table S1. Results of the analysis of the C_3H_8 conversion curves for Ru/CeO_2 catalyst, where r_{275} presents a specific reaction rate at 275 °C [μmol·g^{-1}·s^{-1}], TOF_{275} - turnover frequency (TOF) at 275 °C [s^{-1}], E_a – activation energy, [kJ/mol]. The r_{275}, TOF_{275}, E_a values were calculated by the procedure described in detail by Ledwa et al. in [2].

Catalyst	The feed gas	Reaction temperautre [ºC]	E_a [kJ/mol]	$rC_3H_8 \times 10^6$ [mol·g^{-1}·s^{-1}]	TOF $\times 10^3$ [s^{-1}]	Ref.
(1.5 wt.%)Ru/CeO_2	0.2 vol.% C_3H_8, 2 vol.% O_2, 97.8 vol.% Ar, 30 000 mL·h^{-1}·g_{cat}^{-1}	200	58.6	35.2	6.14	[1]
$Ru_{0.05}Ce_{0.95}O_{2-y}/Al_2O_3$	mixture 250 vppm of propane in the air, 120000 mL h^{-1} gcat^{-1}	275	40	0.68	3.33	[2]
(2 wt.%) Ru/CeO_2(rods)	0.2% C_3H_8 + 2% O_2/Ar, 120000 mL h-1 gcat -1	155	28.6	21.26	344	[3]
(2 wt.%) Ru/CeO_2(cubes)		155	58.5	7.81	781	
(2 wt.%) Ru/CeO_2(octahedra)		155	74.7	1.25	261	
Oxidized (1 wt%Ru)Ru/CeO_2	mixture 250 vppm of propane in the air, 120000 mL h-1 gcat -1	275				This work
Run1			44	12.0	1.21	
Run2			67	9.7	0.98	
Reduced (1 wt%Ru)Ru/CeO_2						
Run1			60	14.3	1.45	
Run2			40	3.7	0.37	

Table S2. Ru/CeO_2 activity in C_3H_8 oxidation. Literature data.

References

[1] Hu, Z., Wang, Z., Guo, Y., Wang, L., Guo, Y., Zhang, J., & Zhan, W. (2018). Total Oxidation of Propane over a Ru/CeO2 Catalyst at Low Temperature. *Environmental Science and Technology*, *52*(16), 9531–9541. https://doi.org/10.1021/acs.est.8b03448

[2] Ledwa, K. A., Kępiński, L., Ptak, M., & Szukiewicz, R. (2020). Ru0.05Ce0.95O2-y deposited on functionalized alumina as a smart catalyst for propane oxidation. *Applied Catalysis B: Environmental*, *274*. https://doi.org/10.1016/j.apcatb.2020.119090.

[3] Wang, Z., Huang, Z., Brosnahan, J. T., Zhang, S., Guo, Y., Guo, Y., Wang, L., Wang, Y., & Zhan, W. (2019). Ru/CeO2 Catalyst with Optimized CeO2 Support Morphology and Surface Facets for Propane Combustion. *Environmental Science and Technology*, *53*(9), 5349–5358. https://doi.org/10.1021/acs.est.9b01929.