Supplementary Information

The effect of polarization and reaction mixture on the Rh/YSZ oxidation state during ethylene oxidation studied by Near Ambient Pressure XPS

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Supplementary information 1

The repeatability/reproducibility of the lower Rh oxidation state under polarization was verified by another two independent experiments. First reduced Rh was exposed gradually to more oxidative conditions (R was decreasing) at 350°C. Please note that in the experiments showed in the manuscript Rh was initially oxidized and R was increasing stepwise. As shown in the characteristic spectra presented in figure S1a relatively higher oxide component is observed under OC as compared to CC conditions, similar to the observations discussed in the main text. In a similar experiment performed at 250 °C the comparison of Rh 3d spectra at OC and CC conditions indicate the same trend. In particular as shown in figure S1b the contribution of the RhO_x component is enhanced under OC conditions. Overall, by taking into account that the expressed Rh spectra differences under OC and CC conditions are above the measurement error, as well as that the same evidences were found in 3 independent experiments, we believe that the reduction of RhO_x under CC conditions is a solid experimental evidence of this work.



Figure S1. Rh $3d_{5/2}$ NAP-XPS spectra recorded in various $p_{(C2H4)}/p_{(O2)}$ reaction mixtures under open and close (U_{WC} = 1.5 V) circuit conditions a) at 350 °C and b) at 350 °C. The spectra are normalized in height to facilitate the comparison.



Figure S2. Comparison of the O 1s spectra recorded at OC and 1.5 V at 350 °C, for R=0.33 and 0.4 mixture compositions. The blue line is the mathematical difference between the two spectra.