

Supporting Information

Activation of Surface ReO_x Sites on Al_2O_3 Catalysts for Olefin Metathesis

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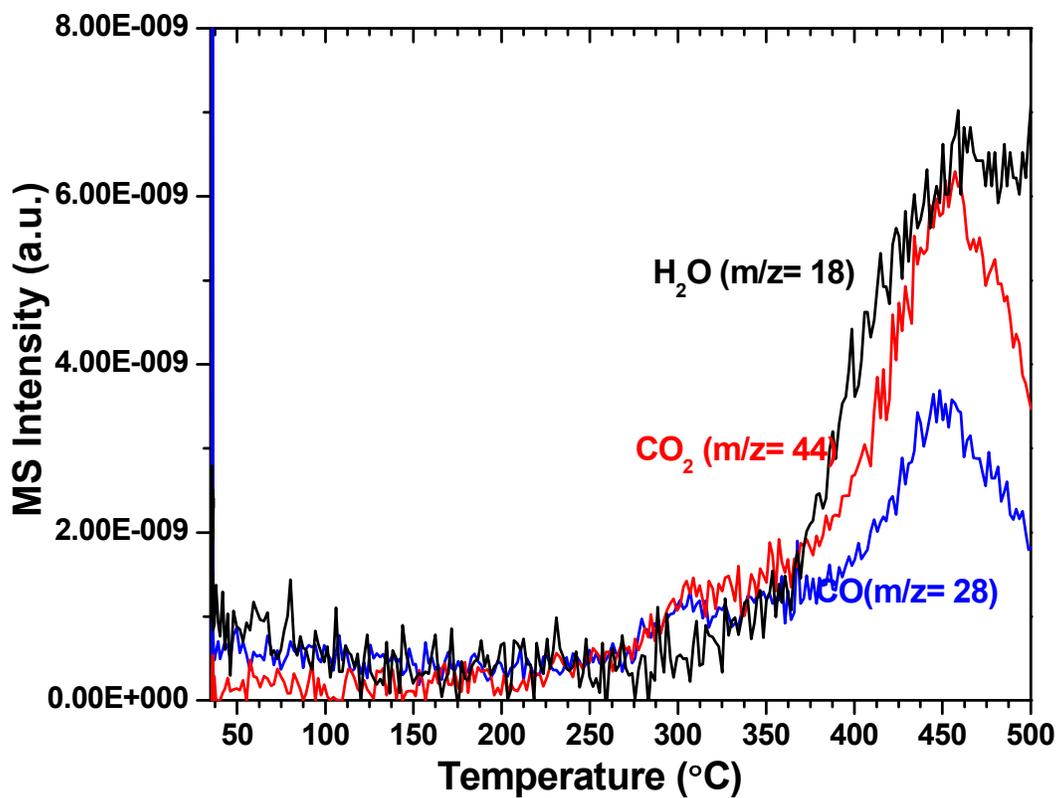


Figure S1. Oxidation products during TPO (2% O₂/Ar) after C₃⁻ adsorption at 30°C for 60 minutes, flushing with Ar at 30°C for 60 minutes, heating in flowing Ar to 200°C and cooling down to 30°C to begin the TPO experiment. The CO MS m/z=28 signal was corrected for contributions from CO₂ cracking in the MS.

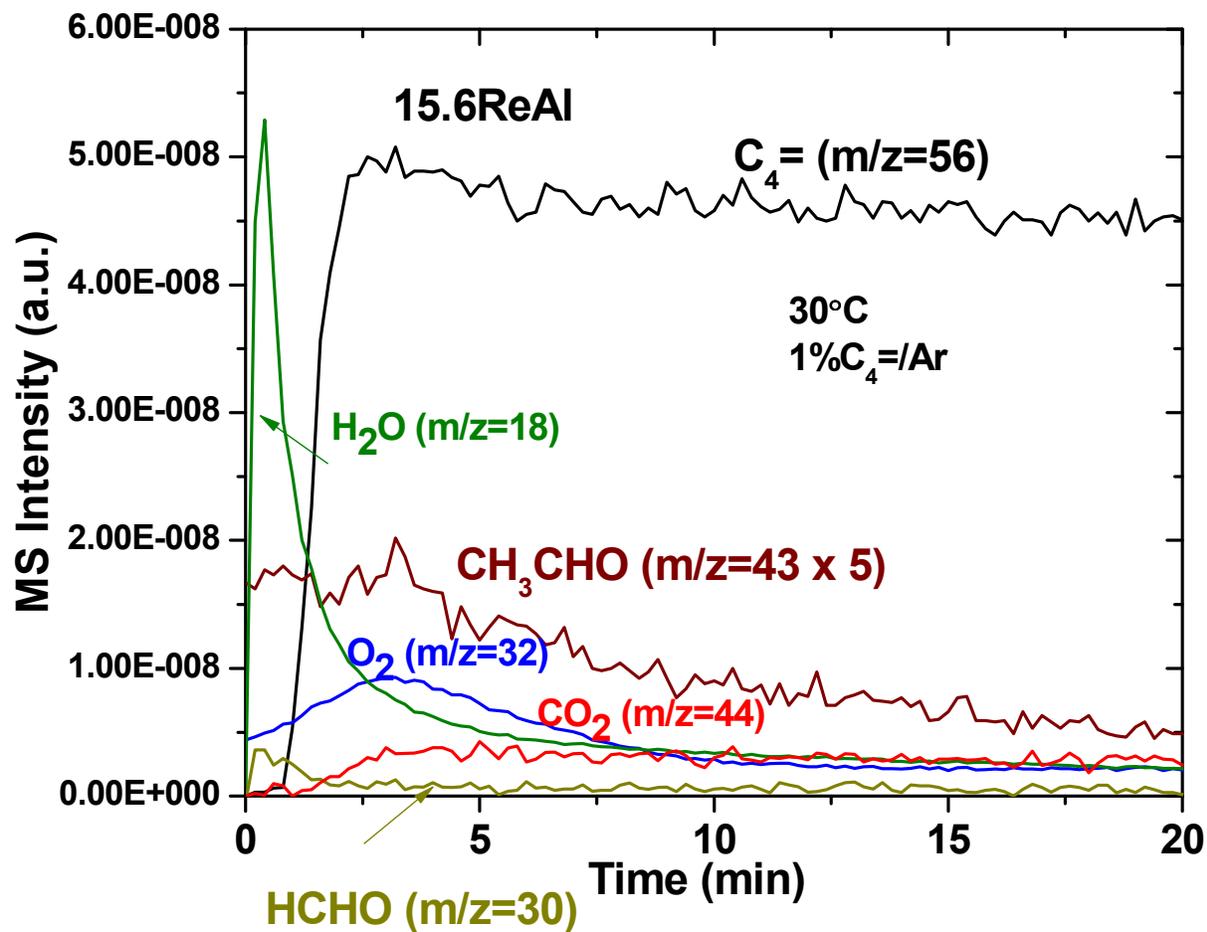


Figure S2. Time-resolved evolution of products during activation of supported $\text{ReO}_4/\text{Al}_2\text{O}_3$ catalyst with C_4^- at 30°C

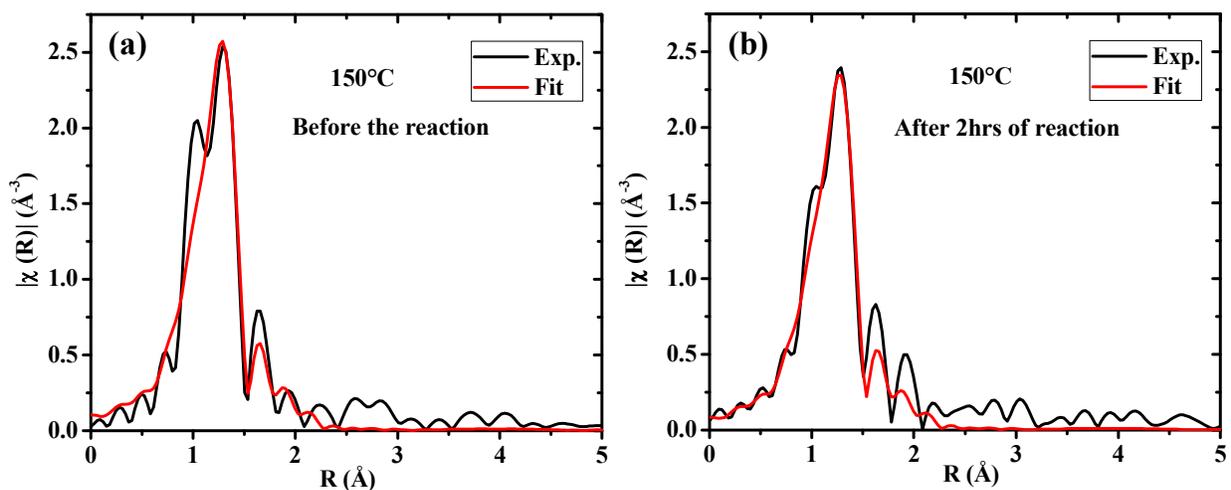


Figure S3. Experimental Re L_1 -edge EXAFS spectrum in R space and corresponding fit for 15.6% $\text{ReO}_x/\text{Al}_2\text{O}_3$ catalyst (a) before and (b) after propylene metathesis at 150°C .

In EXAFS data analysis, the experimental data before and after reaction (150°C) were fitted concurrently. The correction in the threshold energy (ΔE_0) and disorder factor (σ^2) were constrained to be same for data before and after reaction. The bond distance (R) and coordination number (N) of Re-O were allowed to change freely. The fitting k -range is $2\text{-}16 \text{ \AA}$ and R -range is $1\text{-}1.85 \text{ \AA}$. From the quantitative results, the coordination number of Re-O bond before and after reaction is 3.43 ± 0.41 and 3.09 ± 0.45 respectively. Under assumption that no changes in disorder factor, the maximum reduction in coordination after the reaction is: $(3.43 - 3.09) / 3.43 \approx 10\%$.

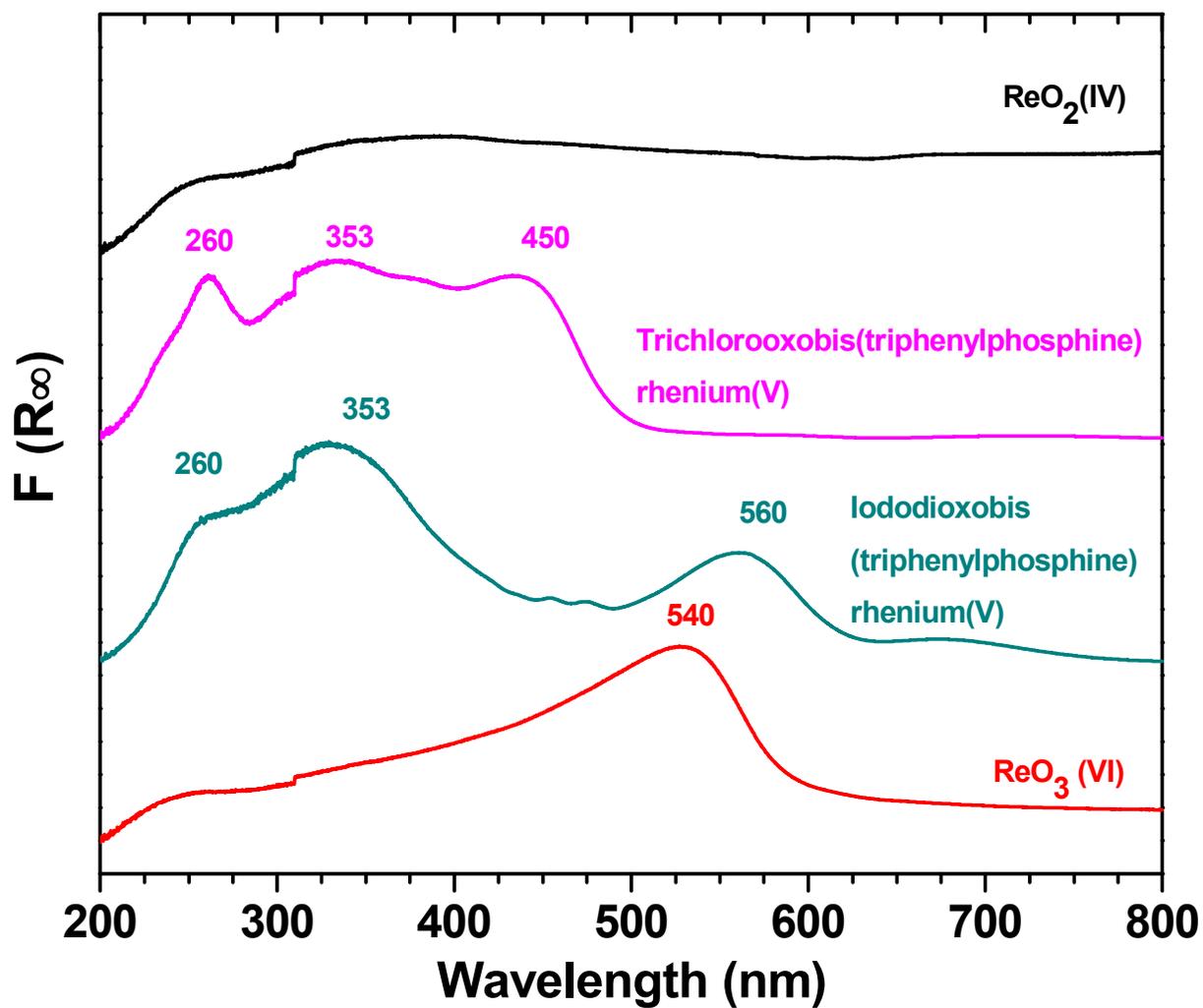


Figure S4. UV-vis spectra of Re^{+4} , Re^{+5} and Re^{+6} reference compounds under ambient conditions.

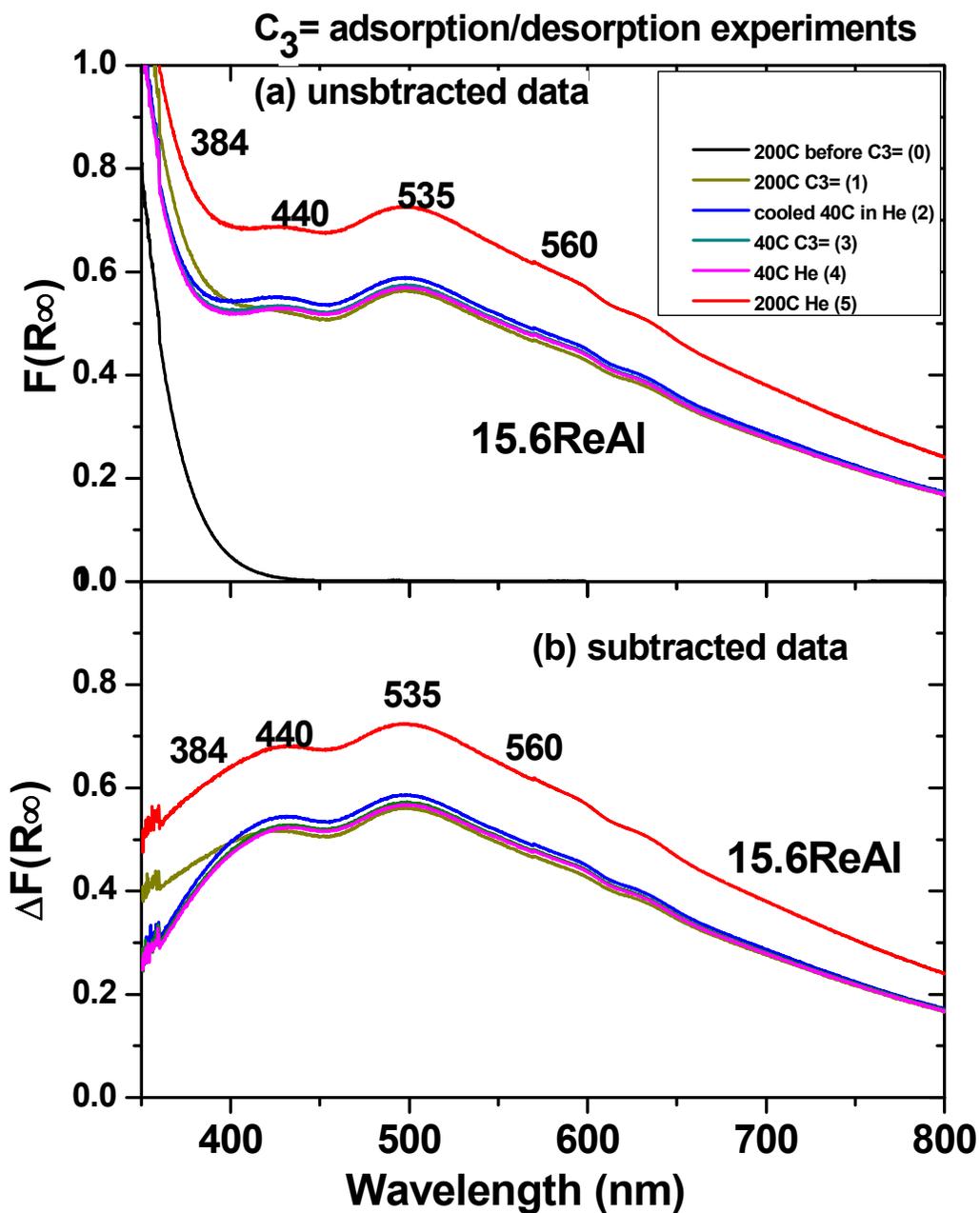


Figure S5. *In situ* UV-vis spectra of the supported 15.6% ReO₄/Al₂O₃ catalyst in the 350-800nm region during several propylene adsorption/reaction/desorption cycles, (a) unsubtractred data and (b) subtractred data. The numbers in parentheses (0-5) indicate the order in which the experiments were performed.

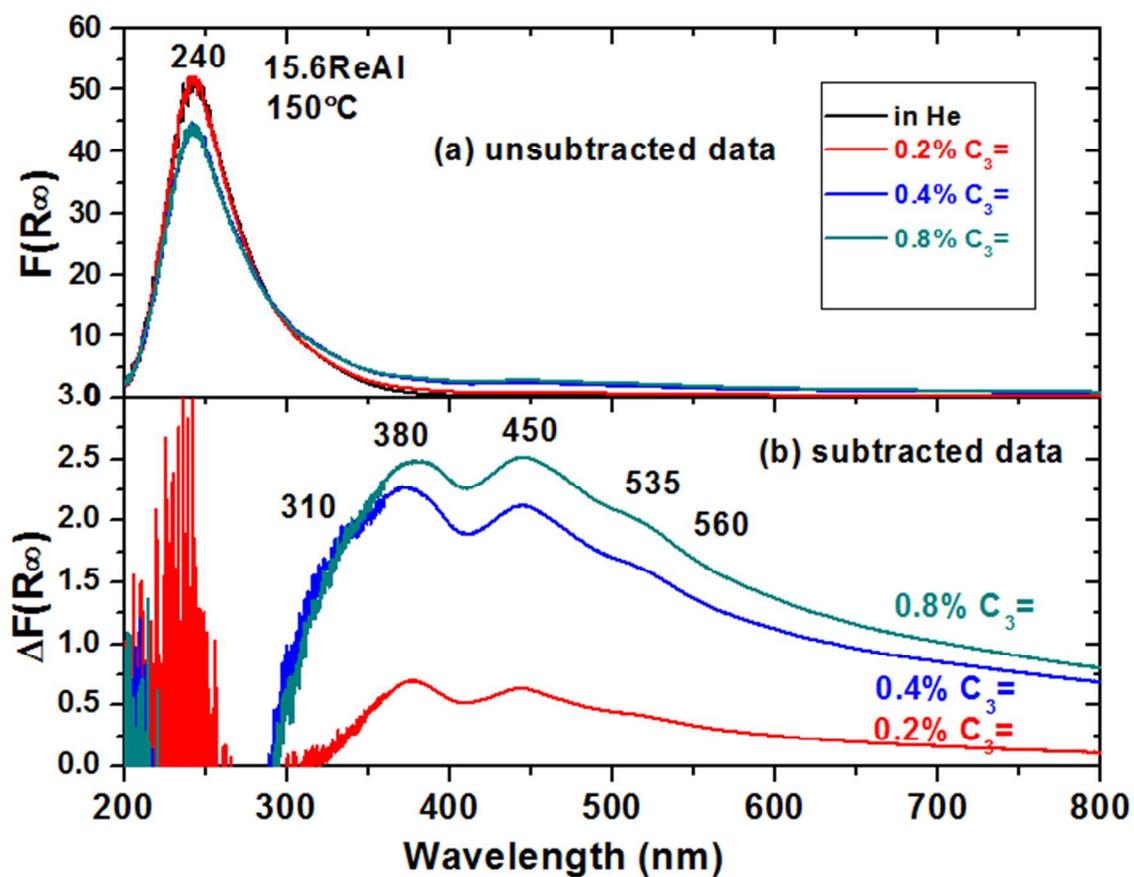


Figure S6. (a) *In situ* UV-vis spectra of the supported 15.6% $\text{ReO}_4/\text{Al}_2\text{O}_3$ catalyst at 150°C as a function of increasing propylene concentration. (b) The *in situ* UV-vis difference spectra are obtained by subtraction of the spectrum in flowing He at 150°C prior to propylene metathesis.

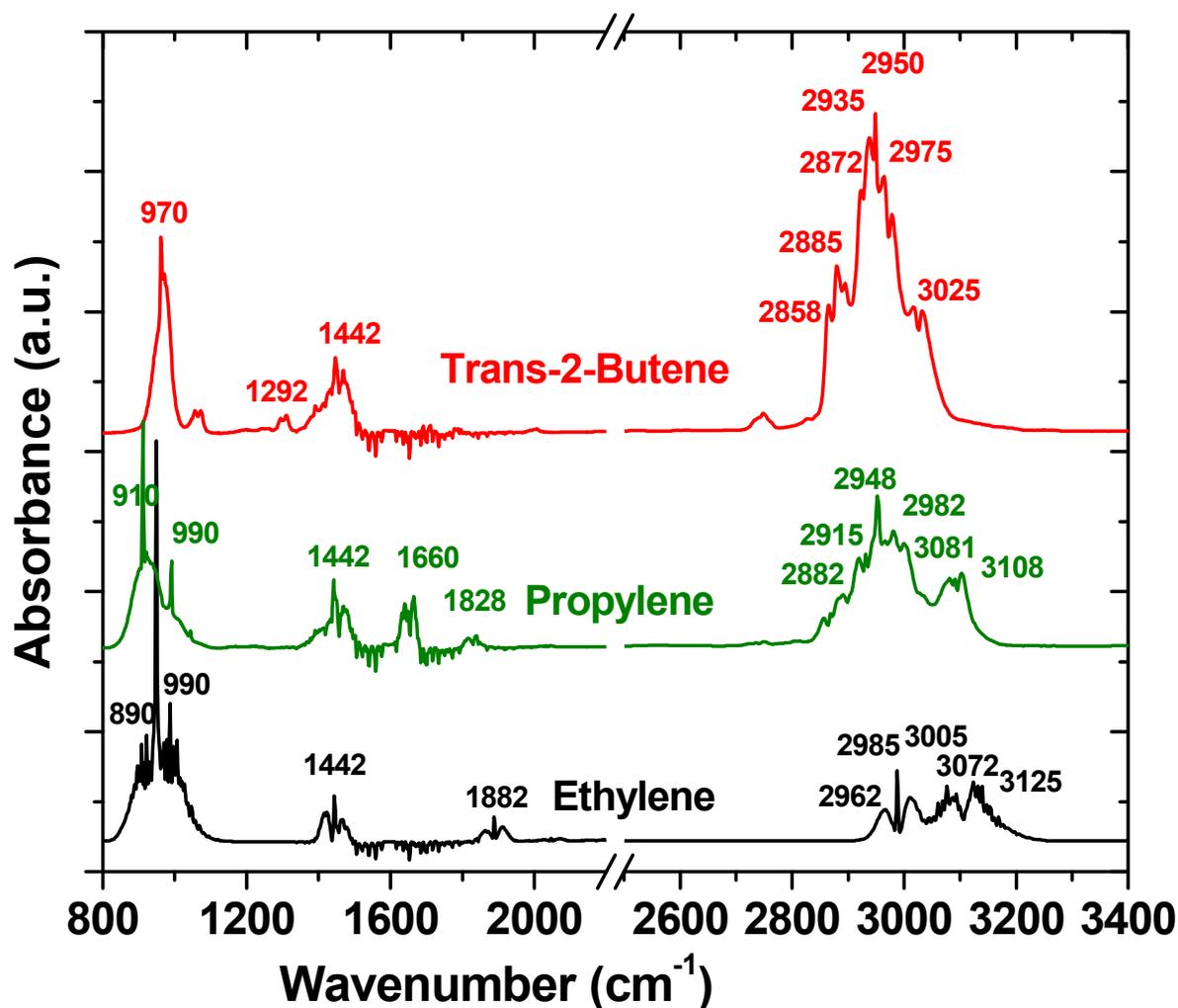


Figure S7. IR spectra of gas phase ethylene, propylene and 2-butene. IR bands were not present in the 1800-2800 cm^{-1} range.

S1. *In situ* IR spectroscopy

The difference IR spectra of the adsorption of trans-2-butene on the supported 15.6% $\text{ReO}_x/\text{Al}_2\text{O}_3$ catalyst, followed by titration of the surface intermediates by ethylene, are given in Figure S8. After 60 mins of trans-2-butene adsorption, bands appear from gas phase trans-2-butene (875, 2945, 3015, and 3035 cm^{-1}) and adsorbed species $\delta_s(\text{CH}_3)$ [1375 and 1390 cm^{-1}],

$\delta_s(\text{CH}_2)$ of vinyl group ($-\text{CH}=\text{CH}_2$) [1415 cm^{-1}], $\delta_{\text{as}}(\text{CH}_3)$ [1445 cm^{-1}], $\delta_s(\text{CH}_2)$ [1470 cm^{-1}], $\nu(\text{C}=\text{C})$ [1650 cm^{-1}], $\nu_s(\text{CH}_2)$ [2865 cm^{-1}], $\nu_s(\text{CH}_3)$ [2890 cm^{-1}], $\nu_{\text{as}}(\text{CH}_2)$ [2925 and 2935 cm^{-1}], and $\nu_{\text{as}}(\text{CH}_3)$ [2960 and 2980 cm^{-1}].^{1,2} Upon introduction of ethylene, new bands from gas phase ethylene appear at 2990 , 3080 , and 3125 cm^{-1} .^{1,2} Oddly, IR bands from the vinyl group and $\text{C}=\text{C}$ still exist, but no bands at $>3000 \text{ cm}^{-1}$ are detected for their corresponding $=\text{C}-\text{H}$ stretching vibrations. The IR spectra do not change with increasing contact time with ethylene and no noticeable change is observed when increasing the temperature to 50°C under ethylene. Increasing the temperature to 100°C under ethylene causes a large decrease in bands at 1390 , 1415 , 1470 , 1650 , 2890 , 2935 , and 2980 cm^{-1} . This suggests that two adsorbed surface olefinic species exist: Species I (the decrease bands) that desorbs at $\sim 100^\circ\text{C}$ and Species II (remaining bands: 1375 , 1390 , 1445 , ~ 1680 , 1470 , 2870 , 2935 , and 2960 cm^{-1}) that is stable up to 150°C . The exact identity of the adsorbed surface olefinic species cannot be determined, but the presence of $\nu(\text{C}=\text{C})$ bands indicates that both surface intermediates have olefinic bonds.

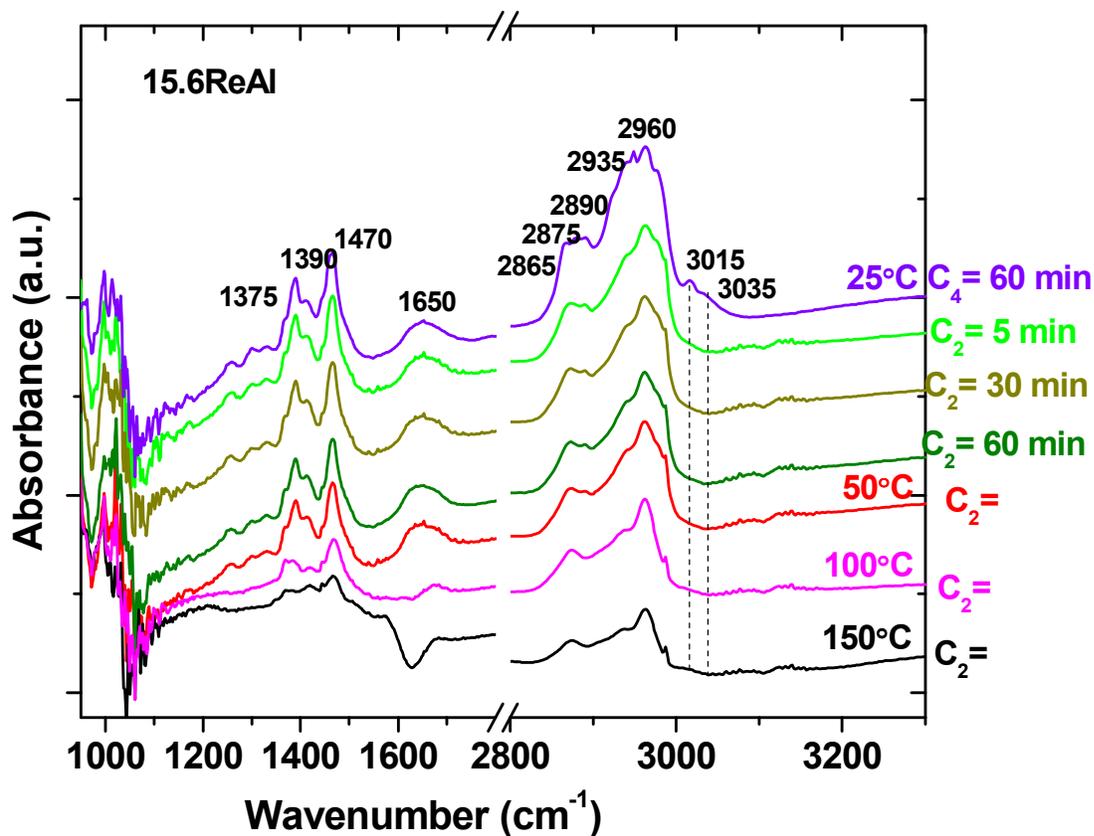


Figure S8. *In situ* difference IR spectra of the 15.6ReAl catalyst during C_4^- adsorption and titration with C_2^- . IR bands were not present in the 1800-2800 cm^{-1} range.

The *in situ* difference IR spectra of the 15.6 ReAl catalyst in Ar after adsorption of C_4^- , C_3^- and C_2^- are shown in Figure S9. For IR band assignments after C_3^- and C_4^- adsorption, please see the main article. Upon 45 minutes of flowing Ar after C_2^- adsorption, bands from complexes of C_2^- remain on the surface. 1370, 1455, 2960 and 2989 cm^{-1} bands can be assigned to δ_s (CH_2), and ν_s (CH_2) vibrations of the adsorbed C_2^- complexes.² The higher $\nu(C=C)$ band position at 1650 cm^{-1} indicates these complexes are not of allylic nature.

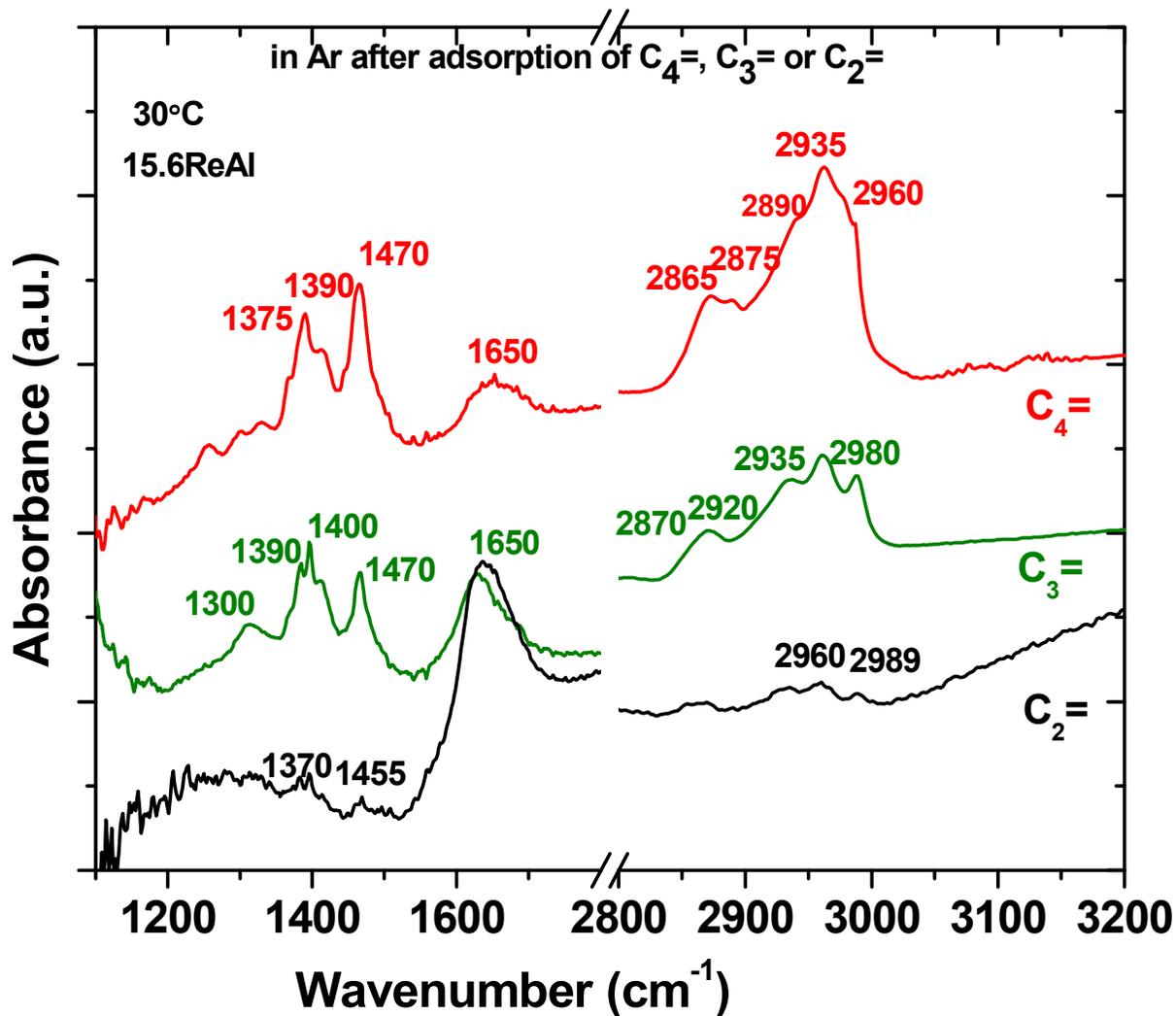


Figure S9. *In situ* difference IR spectra of the 15.6 ReAl catalyst in Ar after adsorption of $C_4=$, $C_3=$ and $C_2=$. IR bands were not present in the 1800-2800 cm^{-1} range.

References

1. Silverstein, M. Webster, F. X.; Kiemle, D. J. Spectrometric Identification of Organic Compounds, Wiley 7th Edition, 2005; pp 85–87.
2. Davydov, A. Molecular Spectroscopy of Oxide Catalyst Surfaces, Wiley 3rd Edition, 2003; pp 332–334.