

To date, IR evidence of metathesis metal carbene intermediates has not been reported due to experimental difficulties with detecting small population of active sites and intermediate species [2, 4]. ME-DRIFTS on Mo-TUD at 410 °C during propylene (101 kPa) metathesis allowed us to isolate species that respond to

periodic (0.011 Hz) propylene modulation (from 90 to 101 kPa). The obtained spectra showed significant propylene gas phase contributions that overlapped with expected metal carbene IR signatures (**Figure 3A**). They were removed in the phase domain (PD) by subtraction of spectra at identical reaction conditions on an inert low surface area SiO₂ (**Figure 3B**), allowing us to obtain reproducible spectra at 380 and 410 °C with bands due to Mo ethylidene (2855, 2882, 2921, and 2933 cm⁻¹) and molybdacyclobutane (2973, 3010, 3077, 3092, and 3106 cm⁻¹) [5]. To the best of our knowledge, this is the first experimental evidence at reaction conditions of metal carbenes formation and possible involvement as true reaction intermediates (**Scheme 1B**). The evolution of a broad band at 3600 cm⁻¹ due to H-bonded OH and the decrease of a band at 3736 cm⁻¹ due to silanols [6] also suggests their possible interactions with active sites during reaction (**Scheme 1A**).

Over the next year, we will continue our in situ characterization of active sites and intermediates species on various supported SiO₂, TiO₂, and TiO₂/SiO₂ catalysts via in situ MES-DRIFTS, ME-UV-visible, and Raman spectroscopies while trying to prove their true catalytic relevance via concomitant kinetic measurements.

Impact on Career and Participating Students

A Ph.D. student is funded through this award. She has been instrumental in the development of novel in situ spectroscopic techniques for detection of surface intermediates with high sensitivity. The research has been transformative in allowing her to explore and lead efforts in methods development impactful to catalysis. Two chemical engineering undergraduates also joined our research efforts. Under the PI and graduate student guidance, they have been mastering the techniques, supporting modelling calculations, and participating in the results interpretation. The research has provided them with opportunities to be exposed to advanced spectroscopic techniques and chemistries relevant to industry while participating in the development of advanced methods and tools in heterogeneous catalysis. The ACS-PRF funding has allowed the PI to establish and further develop leading in situ/operando techniques while exploring new applications of relevance to catalysis. A manuscript is in preparation to describe the design, modelling, and application of the new in situ cell.

References

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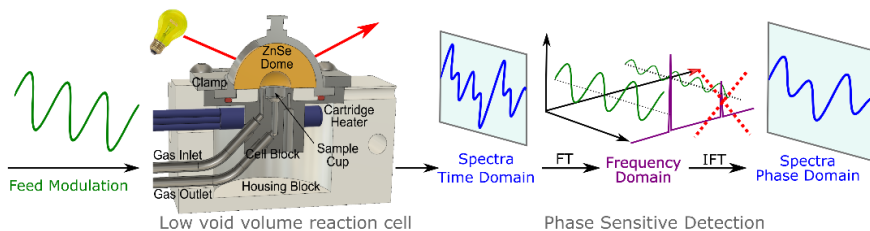


Figure 2. Schematics of ME-DRIFTS and PSD procedure. The in situ cell ($\tau \sim 1$ s) allows IR experiments of matching sampling time (~ 1 s/averaged spectra)

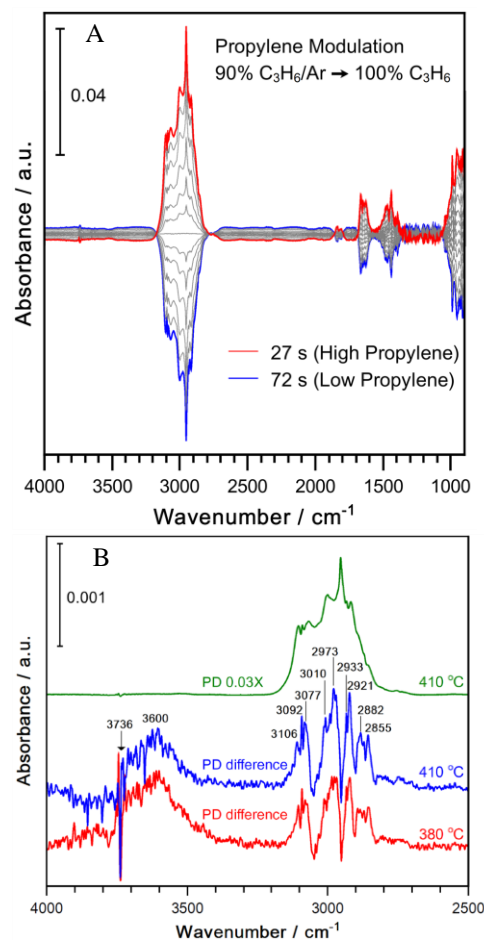


Figure 3. A) ME-DRIFTS in PD of ~ 7 Mo-TUD during propylene metathesis at 410 °C, 700 cm³/min/g_{cat}, olefin modulation of 1 cycle/90 s. B) PD spectra of Mo-TUD (top trace) and PD difference spectra at 27 s of Mo-TUD from same spectra on SiO₂ sand