Thermal Instability and Associated Potential Safety Hazards of [Rh(ethylene)2Cl]2 Catalyst

Daniel Valco, Reactive Chemicals SME

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Approved for External Release

Presentation Outline

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  - Rhodium (I) Precatalysts
- Goal of Study
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  - Storage conditions
  - Calorimetry Testing and Results
  - Gas Chromatography & Mass Spectroscopy Testing and Results
  - Thermokinetic Modelling Results
- Conclusions & Recommendations
- Questions

Presenter Introduction: Daniel Valco

Hometown:

Bay Village, OH

- Suburb on the shore of Lake Erie west of Cleveland, OH

2011:

B.S. in Chemical Engineering at The Ohio State University (Columbus, OH)

- Honors Thesis “Study of Higher Non-Precious Metal Loadings in Oxygen Reduction Catalysts for Use in Proton Exchange Membrane Fuel Cell”

2011 - 2013 :

Ph.D. candidate in Chemical Engineering at Michigan State University (East Lansing, MI)

- Transferred to UIUC; followed research advisor to continue studies

2013 - 2017 :

Ph.D. in Chemical Engineering at University of Illinois (Urbana-Champaign, IL)

- Autoignition and combustion chemistry of conventional and bio-derived kerosene type fuels and components

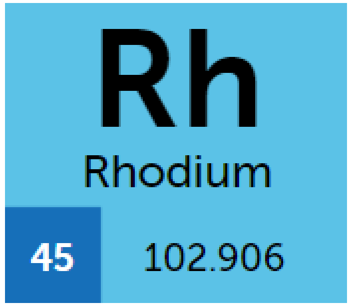
2018 - Present:

Reactive Chemicals Subject Matter Expert

- Focus on Flammability, Dust Explosions, and Calorimetry (hDow)

Rhodium Catalysis

- Rhodium is a critical transition metal in catalyzing chemical transformations in both academia and industry.
  - Major use is in catalytic converters in cars (estimated 80% of current Rh[1])
- Versatile for many different chemical transformations
  - Multiple oxidation states of Rh and a number of ligands can "tailor-make" for high selectivity
- Rhodium(I) "Precatalysts"
  - Rhodium(I) Catalysts with labile ligands
  - Many are commercially available
- Safety Concerns with Rh(I) precatalysts
  - Explosions upon heating of certain Rh(I) precatalyst complexes during microanalytical combustion have been reported[2]
  - No root causes or universally recognized understanding of the hazards



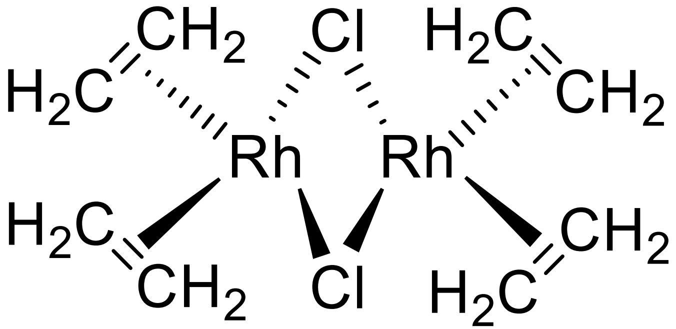
Goal: Promote awareness of possible hazards within the scientific community

CORTEVA agriscience

[1]Royal Society of Chemistry (https://www.rsc.org/periodic-table/element/45/rhodium)
[2]Usón, R. et al (a) J. Organomet. Chem. 1981, 217, 251−257. (b) J. Organomet Chem. 1981, 220, 103−113. (c) J. Organomet. Chem. 1982, 240, 429−439..

[Rh(ethylene)2Cl]2 Catalyst

Basic Information and Storage Conditions



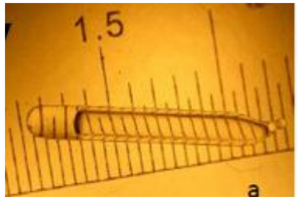
- Chlorobis(ethylene)rhodium dimer (Di-μ-chlorotetraethylene dirhodium(I))
  - Popular and representative of Rh(I) precatalyst complexes with weakly coordinated olefin ligands
  - Focus of this study
- Storage Conditions
  - Recommended: -20C and under an inert atmosphere (varies depending on SDS consulted)
  - Typical Use Setting: Almost impossible to maintain a fully inert storage condition after container is opened and used unless in a glovebox setting.
- Stability
  - Scientists' observations indicate that it loses its catalyst strength overtime (presumably from decomposition)

Experimental Methods

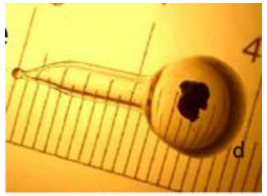
Calorimetry and Modelling

- Differential Scanning Calorimeter (DSC)
  - TA Instruments Discovery DSC 2500
  - N2 and Air environment testing conducted in custom glass containers
- Thermal Activity Monitor (TAM)
  - TA Instruments Thermal Activity Monitor IV
  - N2, Air, and Air Purge environment testing conducted for 2 week isothermal at 25C
- Gas Chromatography & Mass Spectroscopy (GC/MS)
  - Agilent 6890 Gas Chromatograph with Agilent 5973N Mass Selective Detector
- Advanced Kinetics and Technology Solutions (AKTS) Modelling
  - Isoconversion kinetic method

DSC 2500



Glass Capillary (Cap)



Glass Ampoule (Amp)

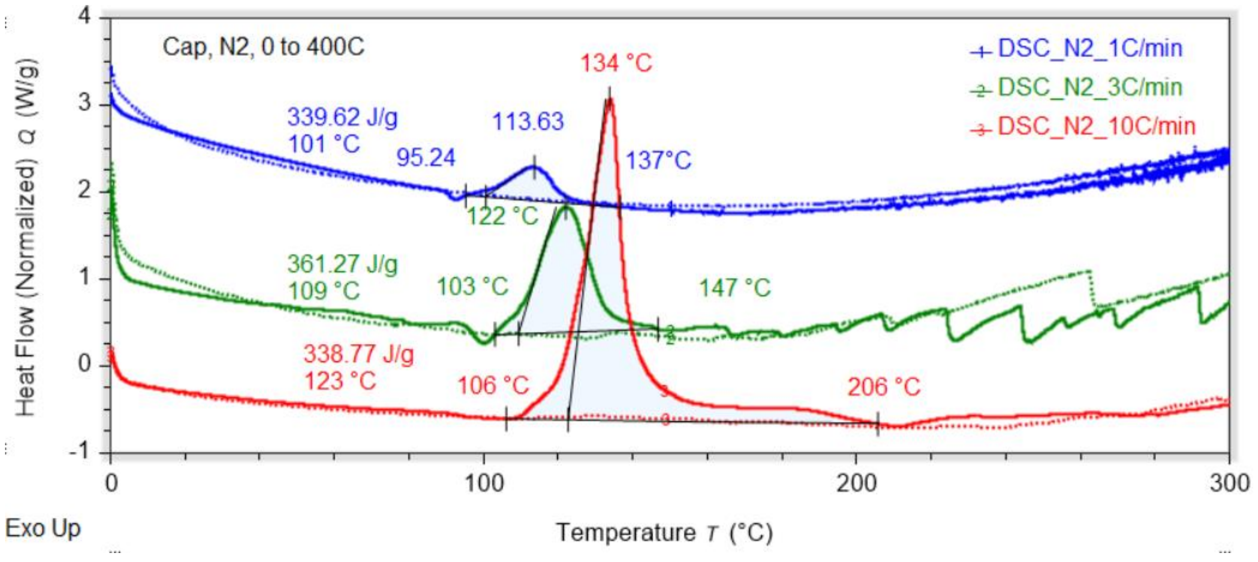
TAM IV

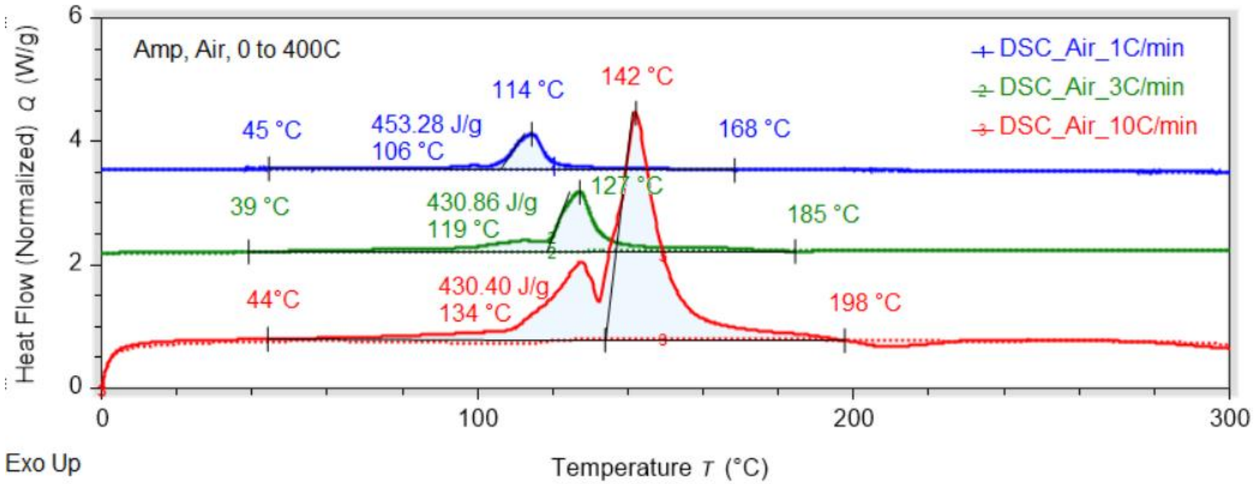
Agilent GC/MS

Calorimetry Testing

Differential Scanning Calorimetry (DSC)

- DSC Results
  - N2 Atmosphere: onset temperature of ~100 °C and a total heat of -346.6±12.8 J/g
  - Air Atmosphere: onset temperature of ~43 °C and an additional -91.6 J/g produced from oxidation
  - Scan rates indicate shift in peak temp, typically indicative of autocatalytic behavior (time/heat dependance)
- Safety Concerns
  - Low onset temperatures, easily obtainable
  - Decomposition of this chemical will produce significant amount of highly flammable gases
    - 1 molecule can release up to 4 molecules of ethylene!



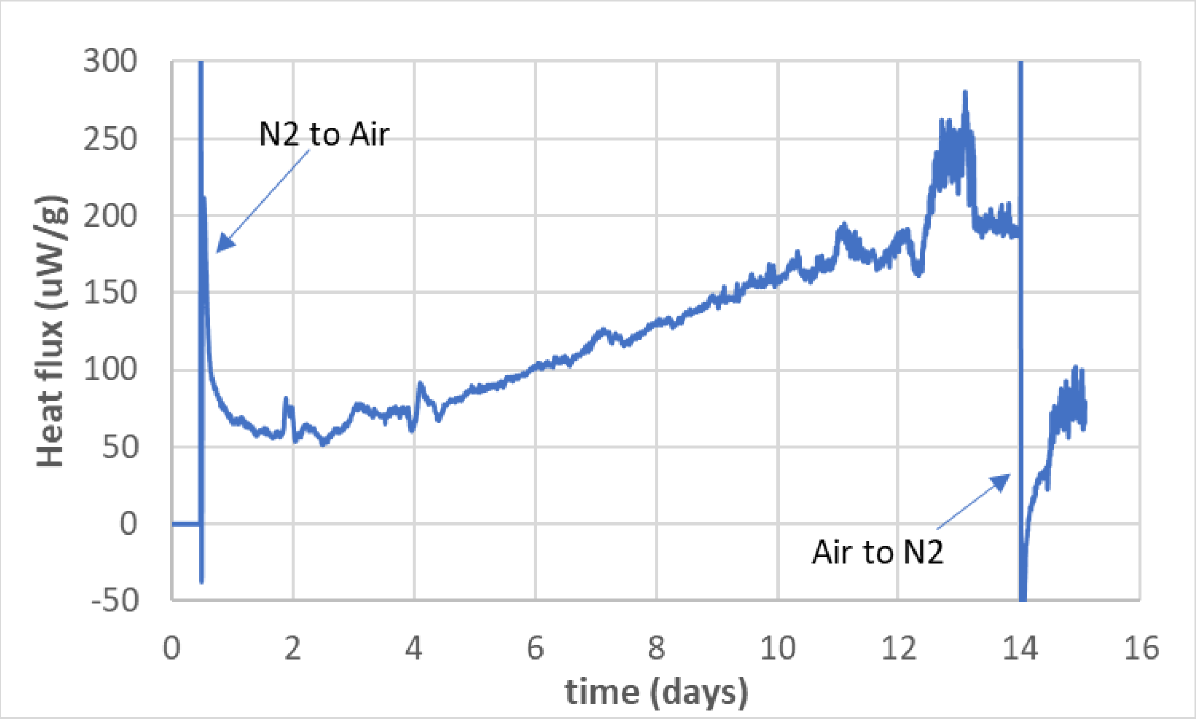


Calorimetry Testing

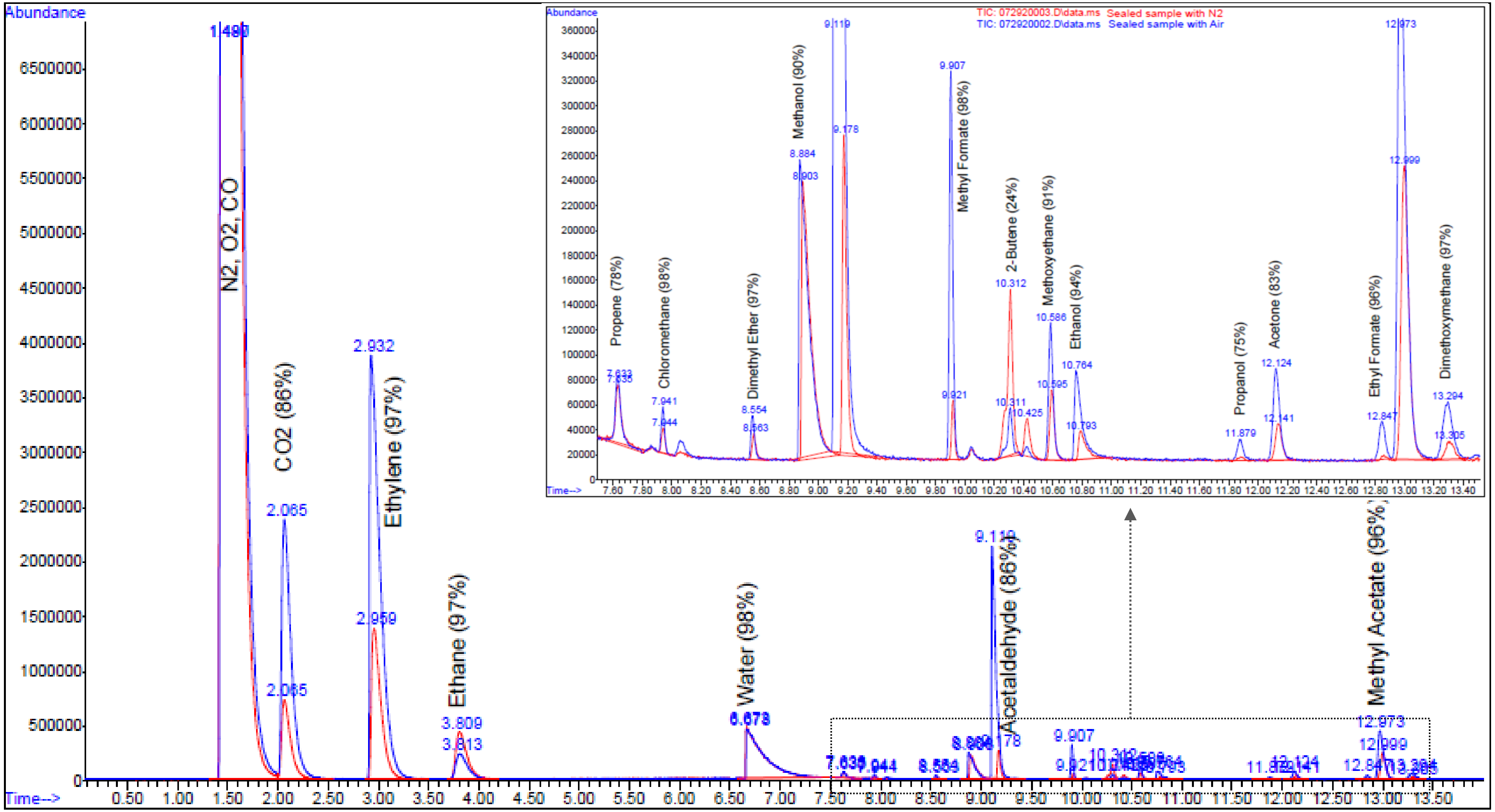
Thermal Activity Monitor (TAM)

Entry	Conditions	Mass (mg)	Heat (J/g)	Heat flux[1] (μW/g)
1	Sample sealed with a N_2 headspace	108.5	–0.69	0.30
2	Sample sealed with an air headspace	128.6	–14.91	9.62
3	Sample with a 200 mL/h air flow	109.1	–150.13	172

- TAM Results
  - Isotherm scan at 25C for 2 weeks
  - Comparison between N2 and Air indicates sample is sensitive to oxygen present
  - Sealed Air versus Flowed Air indicates sample will continue to react based on available O2
- Safety Concerns
  - Importance of an inert atmosphere for stability
  - Significantly higher reaction rates when exposed to air (order of magnitude)
- What gas is being generated from the reaction?



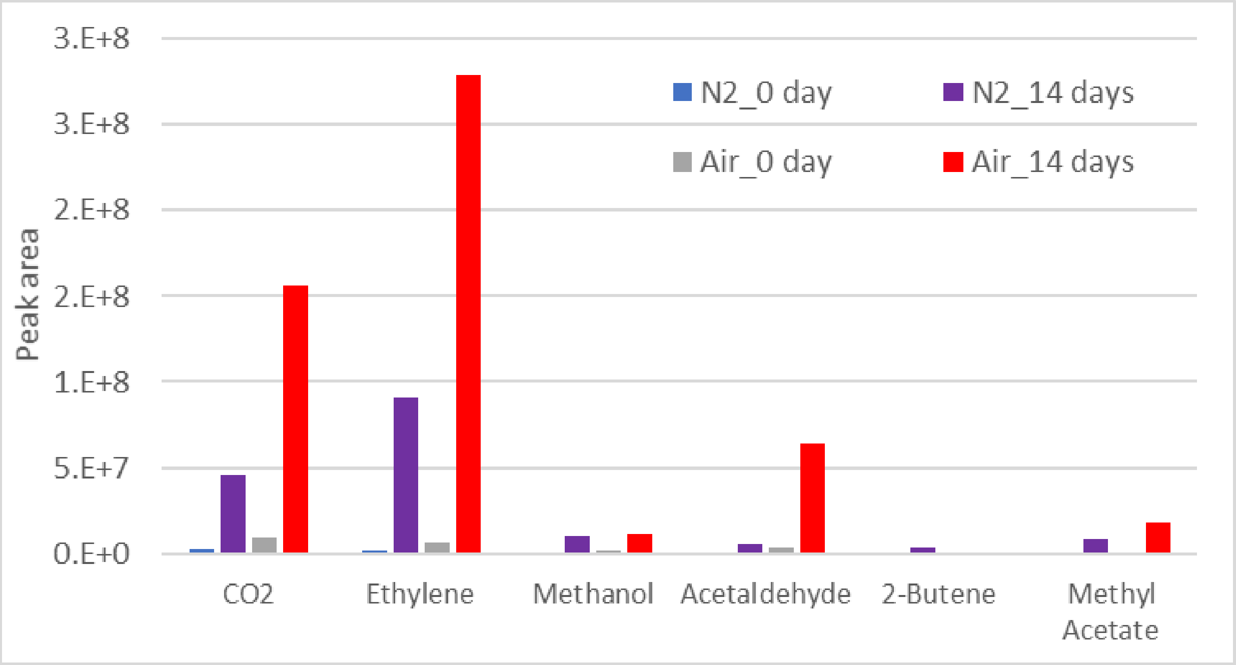
Gas Chromatography and Mass Spectroscopy of Headspace



Calorimetry Testing

Thermal Activity Monitor (TAM)

- Gas Production Comparison
  - Day 0 – Air gas peaks are higher than N2
  - Day 14 – Substantially more gas present with ethylene being the largest peak
- Air Testing
  - These results confirm that the presence of air significantly promoted the decomposition of [Rh(ethylene)2Cl]2
  - Multiple flammable products produced indicate a rather complicated decomposition mechanism
  - High flammability hazard in containers stored and not properly inerted



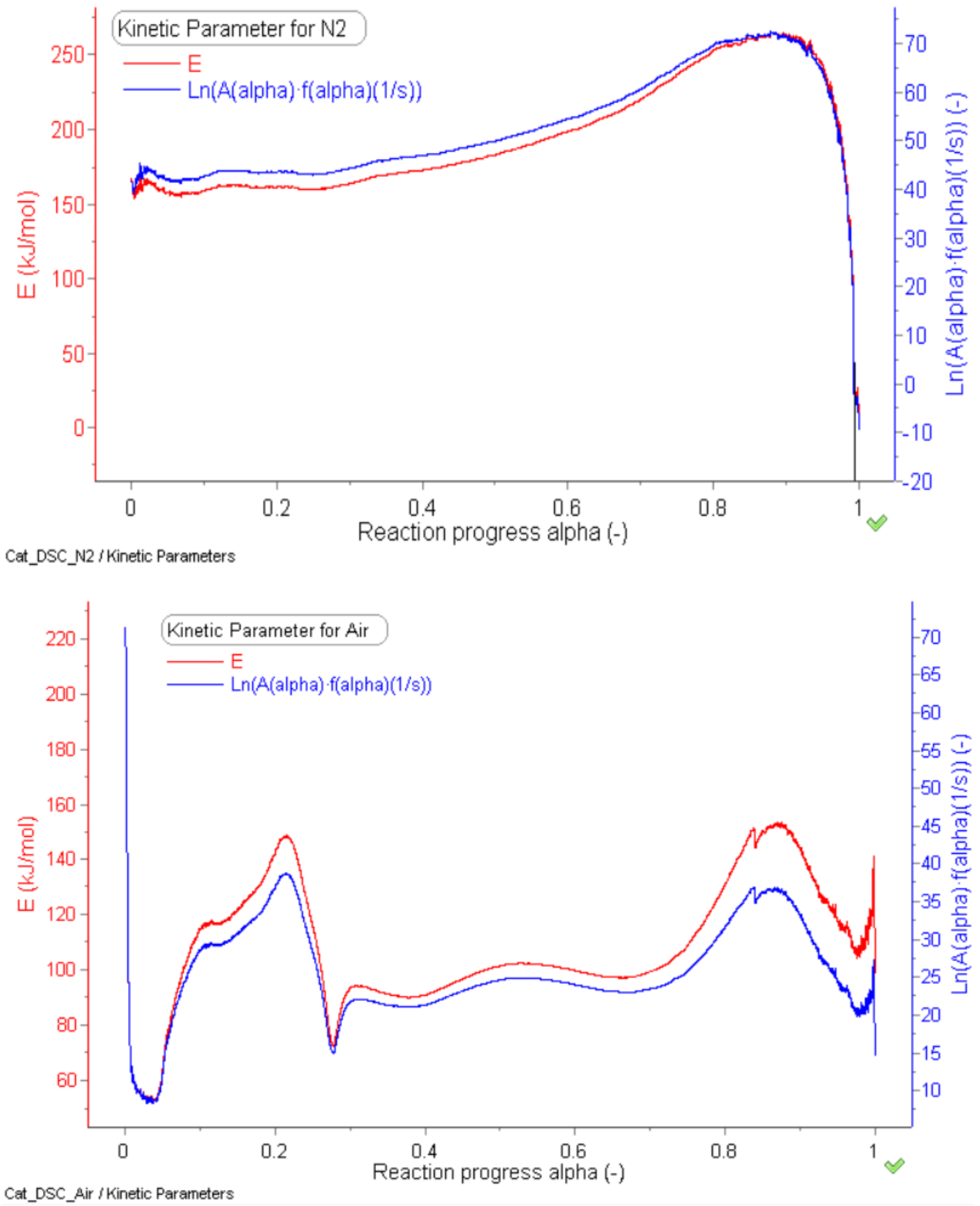
Thermokinetic Model

Model Creation

- Solving the Arrhenius equation based on reaction progress/conversion (α) of the reaction

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha} = \ln\left(A(\alpha)\cdot f(\alpha)\right) - \frac{E(\alpha)}{RT(t_{\alpha})}$$

- Determine these kinetic parameters by fitting the heat flux of DSC tests
- Model fit
  - Indicates complicated decomposition mechanism; more so in Air compared to N2
  - Very good fit/prediction of DSC data



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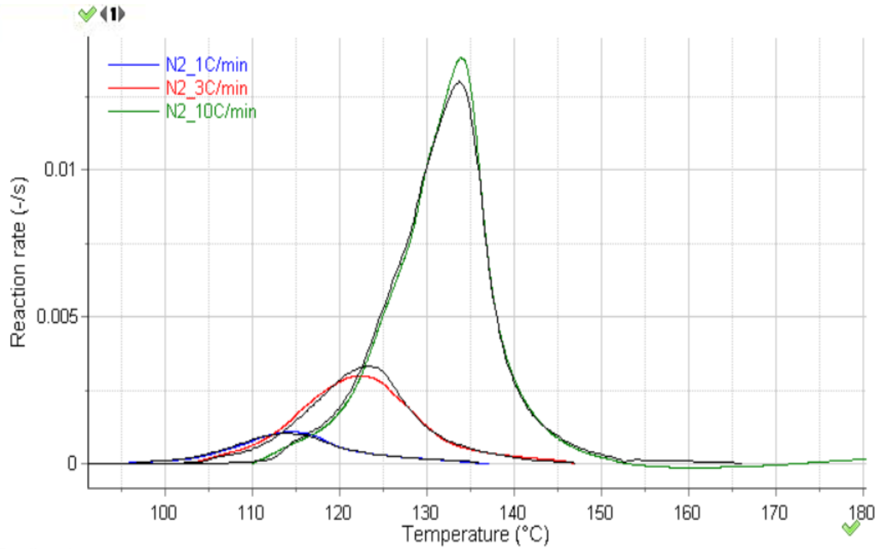
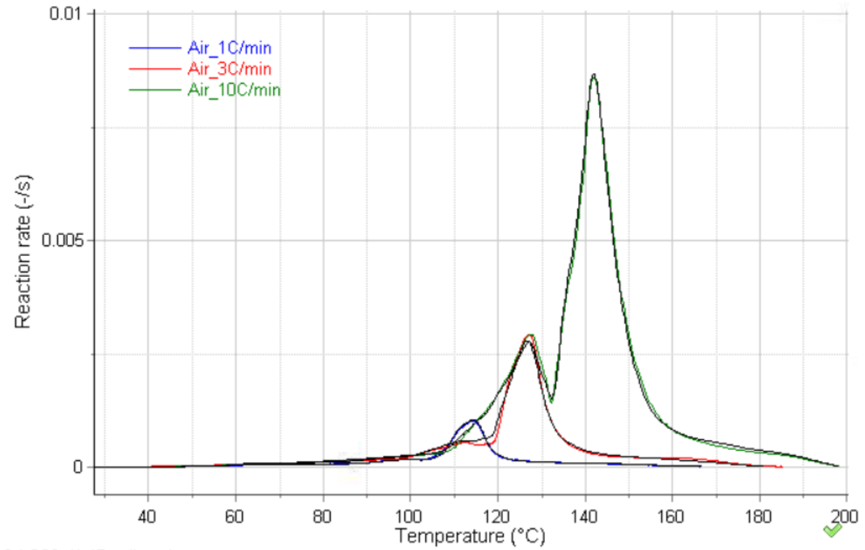


Reaction rate

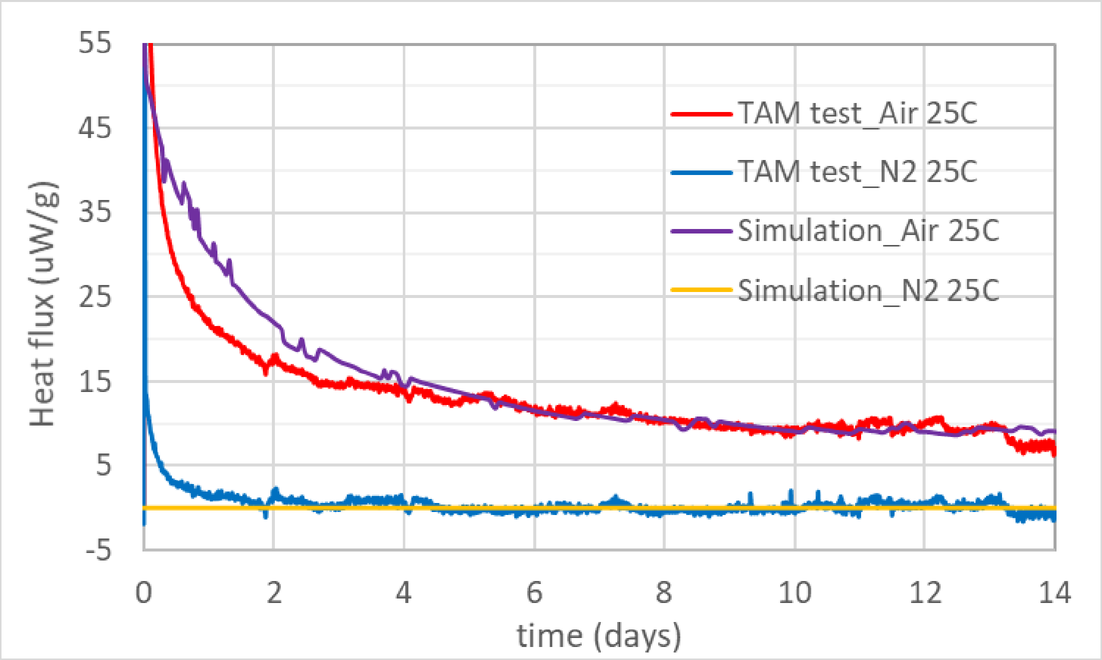


Cat_DSC_Air / Reaction rate

Thermokinetic Model

Confirmation of Model and Predictions

- Model was used to predict 25C isothermal and compared with TAM data
  - Model prediction aligns well with low temperature data despite not using TAM data to build the model
  - Verifies predictive capability to allow for further simulations
- Model Predictions
  - Adiabatic induction time to maximum rate simulation for inert (N2) and air
  - Drastic reductions in thermal stability under and air atmosphere



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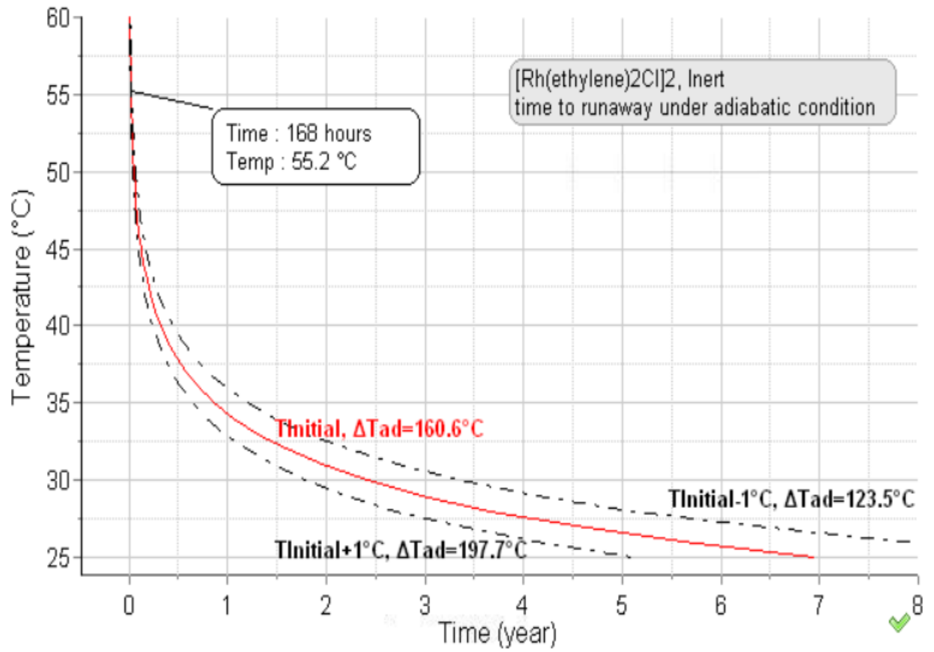

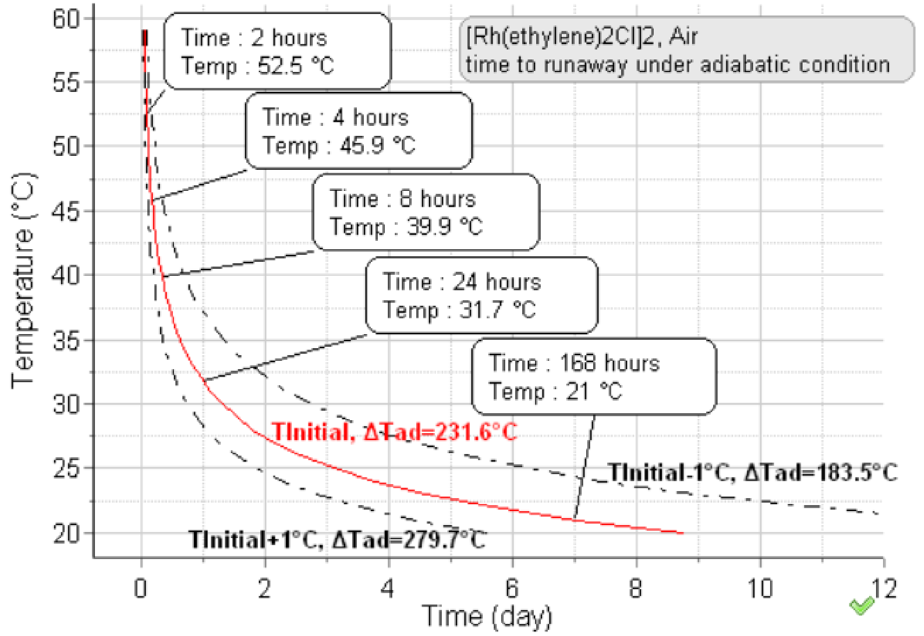

Conclusions

- Properties of the [Rh(ethylene)2Cl]2 catalyst, while inherently useful to prevent reassociation for their intended use in chemical transformations, present potential hazards because of their thermal instability

- Air plays a major role in the instability of these chemicals, accelerating the decomposition rate substantially

- Decomposition of the [Rh(ethylene)2Cl]2 catalyst is complex, as seen in the modelling work and gaseous products produced

- Encourage scientists to employ safer measures, e.g., inert atmosphere and safe temperature windows, to prevent potential incidents relating to these thermal instability hazards when using the Rh(I) precatalyst complexes with weakly coordinated ligands

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Ming Sheng,* Qiang Yang,* Darren Huff, Andrew G. Schafer, Craig Tucker, and Daniel Valco

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