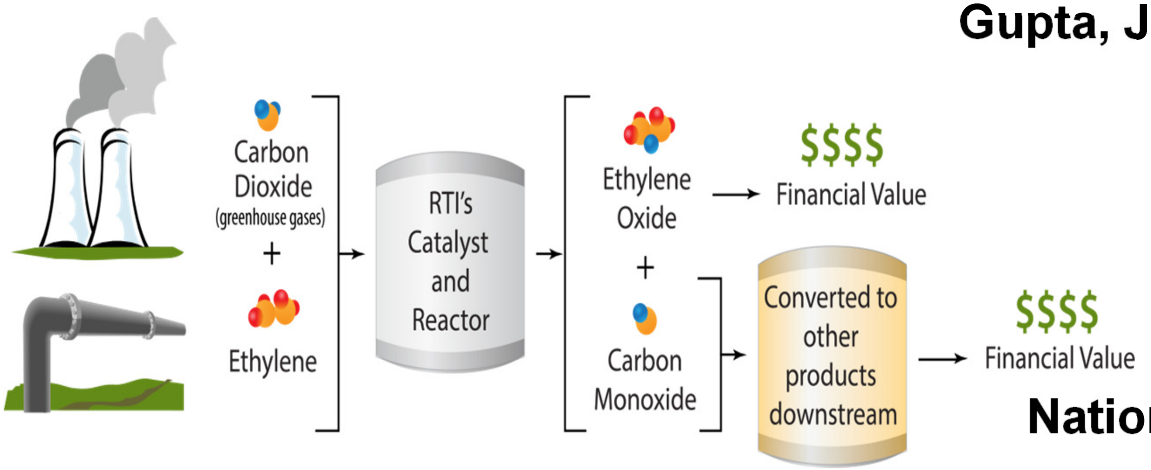
Novel Catalytic Process Technology for Utilization of CO_2 for Ethylene Oxide and Propylene Oxide Production

DE-FE0030678

Marty Lail, Paul Mobley, Jonathan Peters, Angela Zheng, Vijay Gupta, Jak Tanthana, and Jim Zhou

RTI International

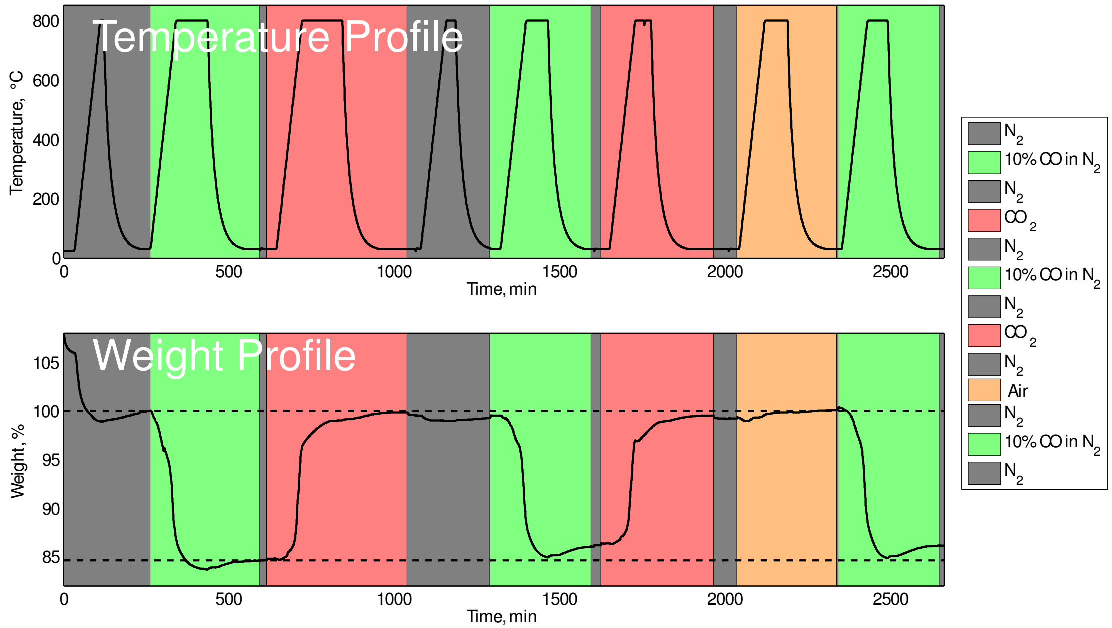


Steve Mascaro
US Department of Energy
National Energy Technology Lab

Presented August 17th, 2018
2018 NETL CO_2 Capture Technology Project Review Meeting
Pittsburgh, PA

Materials Background

Previous Work (NETL, DE-FE00004329)

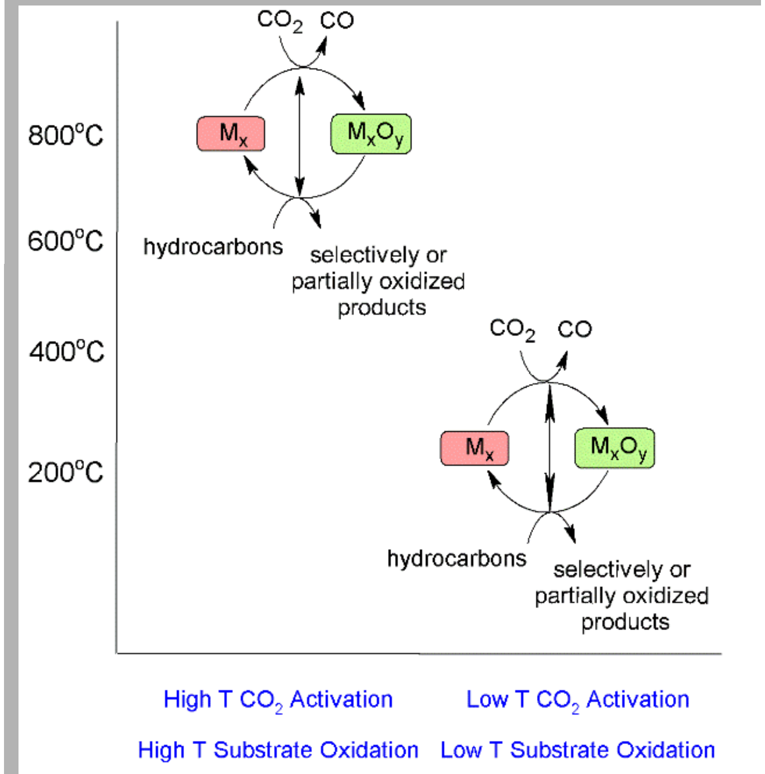


- Mixed metal oxide (MMO) developed
- $(Fe_2O_3)(SnO_2)_{1.41}(Al_2O_3)_{1.82}$
- Utilization of CO_2 for char gasification

Shen, J. P.; Mobley, P. D.; Douglas, L. M.; Peters, J. E.; Lail, M.; Norman, J. S.; Turk, B. *RSC Advances* **2014**, *4*, 45198

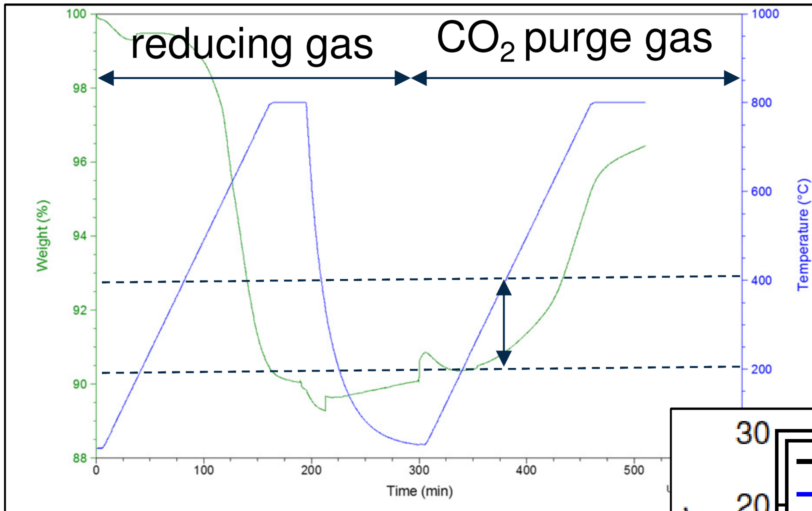
Shen, J.-P.; Lail, M.; Turk, B.; Mobley, P. D.; Norman, J. S.; Douglas, L.; Peters, J. Mixed Metal Oxides and Uses Thereof. 9,884,313, July 31, 2014.

- Required high temperature for removal of oxygen from CO_2 (~800° C)
- High temperature difficult for selective oxidations
- Needed to develop new material

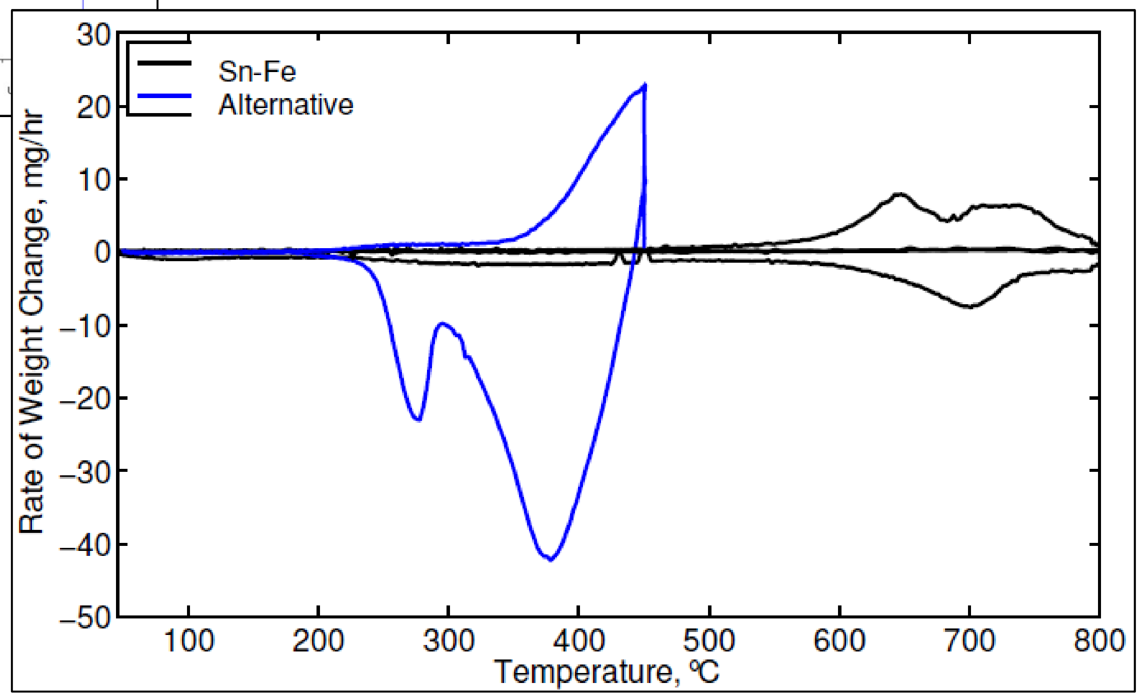


New Materials Working at Lower Temperature

Low temperature oxygen abstraction



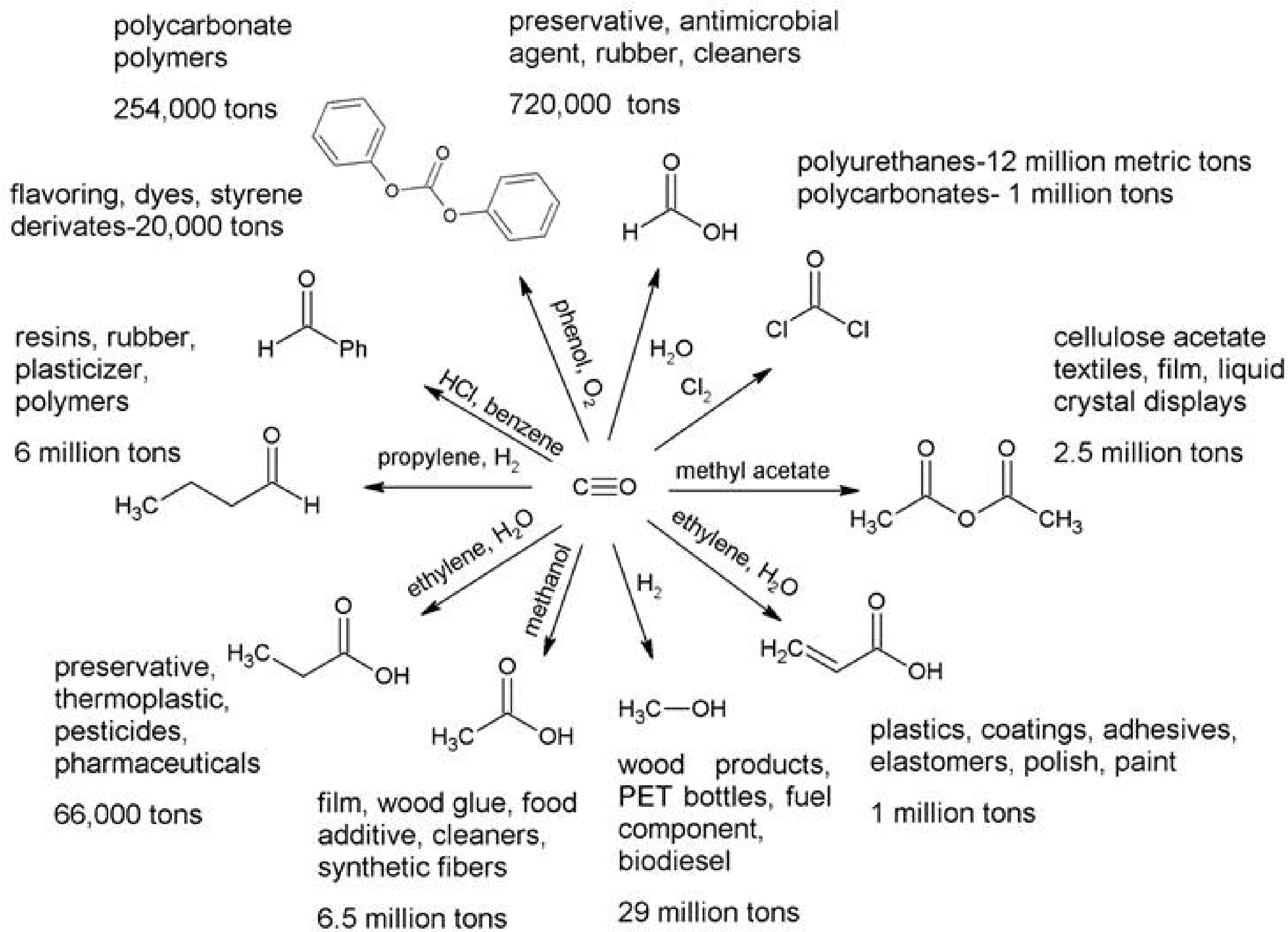
- Screened and discovered new compositions
- Have comparable overall capacity for oxygen from CO_2



- Remove oxygen at lower temperatures compared to the earlier materials
- Work funded in 2015 by CCEMC, Alberta, CAN K130115

Mobley, P. D.; Peters, J. E.; Akunuri, N.; Hlebak, J.; Gupta, V.; Zheng, Q.; Zhou, S. J.; Lail, M., Utilization of CO_2 for Ethylene Oxide. *Energy Procedia* **2017,** *114*, 7154-7161

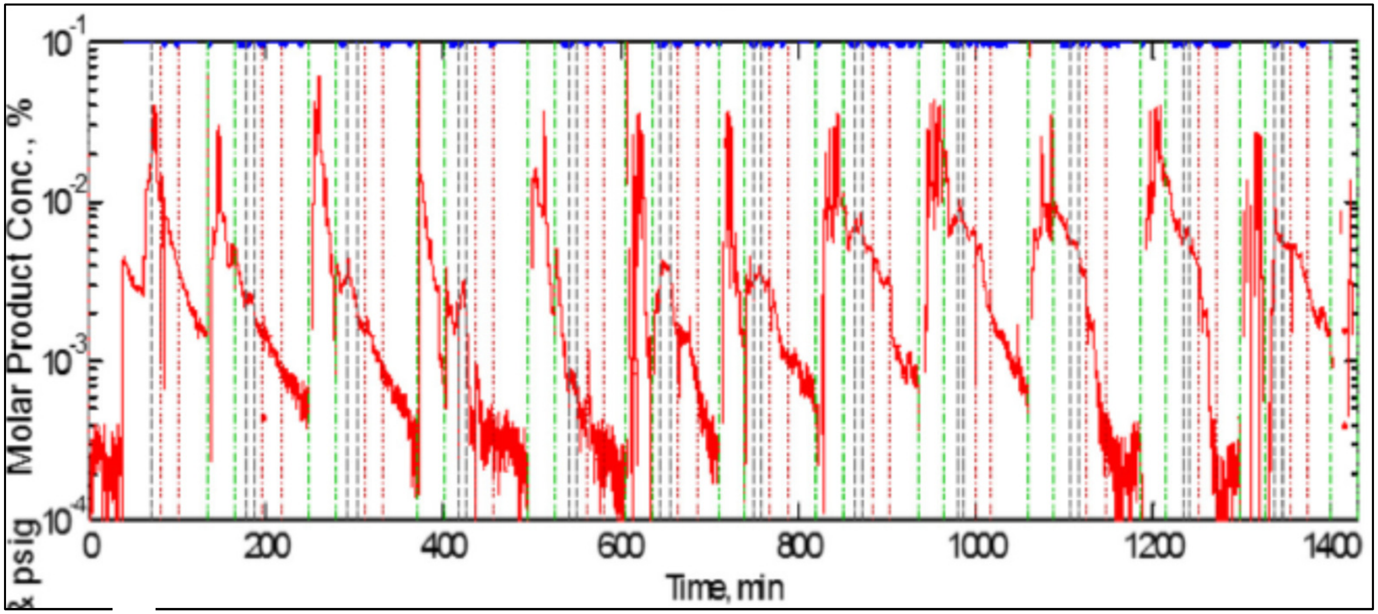
Market Potential: Carbon Monoxide



- CO produced has numerous applications
  - More than 59 Mt of CO are used annually
- Large and growing market for CO globally ($23 billion, 5.7% expected annual growth)
- Industrial CO source could drive new economic activity
- Significant CO stream

Evaluation of Material for EtO Selectivity

- Evaluated new materials in automated fixed-bed micro-reactor
- MKS FTIR multi-gas analyzer
- GC-MS
- Probed optimal reaction conditions using DOE
- Identified relatively low temperature region for operation
- Higher temperature than conventional EtO process
    - *300° C*
    - *20 bar total pressure*
    - *1 C_2H_4: 2 CO_2*

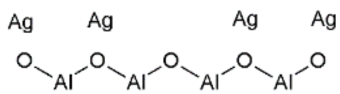


- FTIR Multi-gas analyzer results for EtO
- Result shown for many cycles

Comparison to Conventional EtO Production

- Ethylene epoxidation has been practiced for many years with single pass conversions and overall yield being low
- FTIR showed similar yield as O_2-based catalysts but uses CO_2

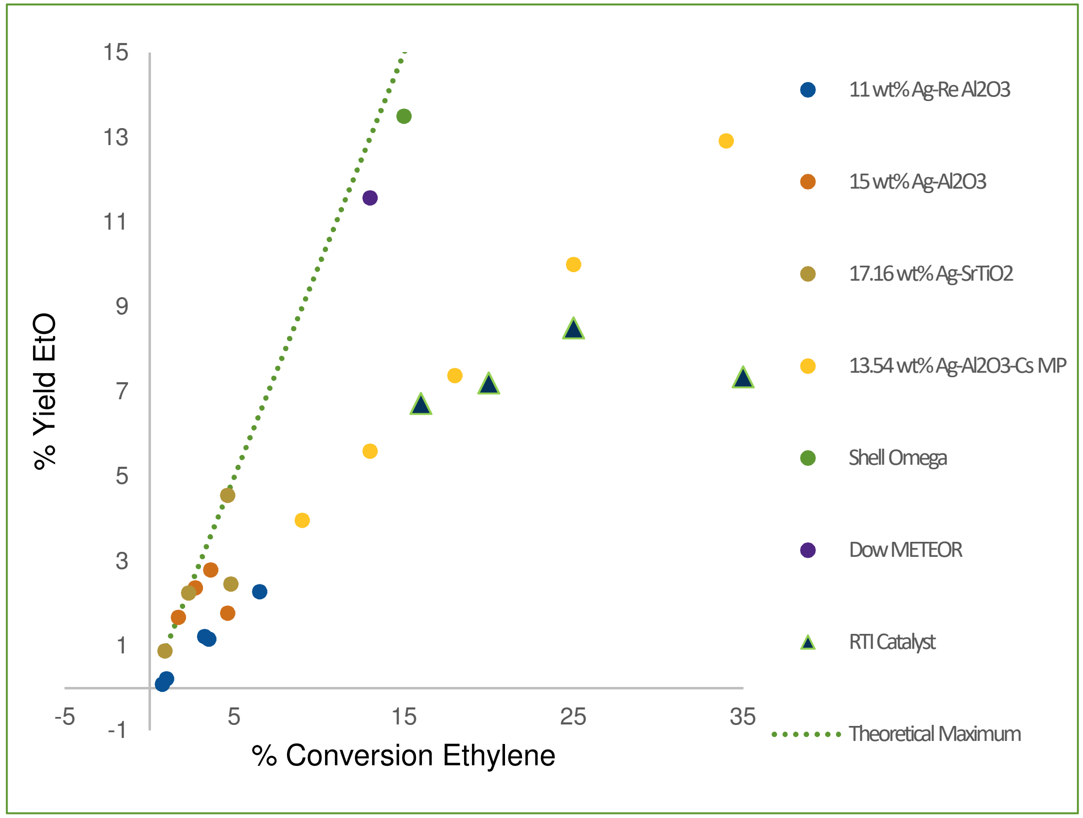
Conventional epoxidation catalyst used with air or oxygen



+ Cl^-, NO_3^-, Cs^+, Na^+, Li^+

silver particles on α-alumina

many promoters investigated to promote selectivity and activity

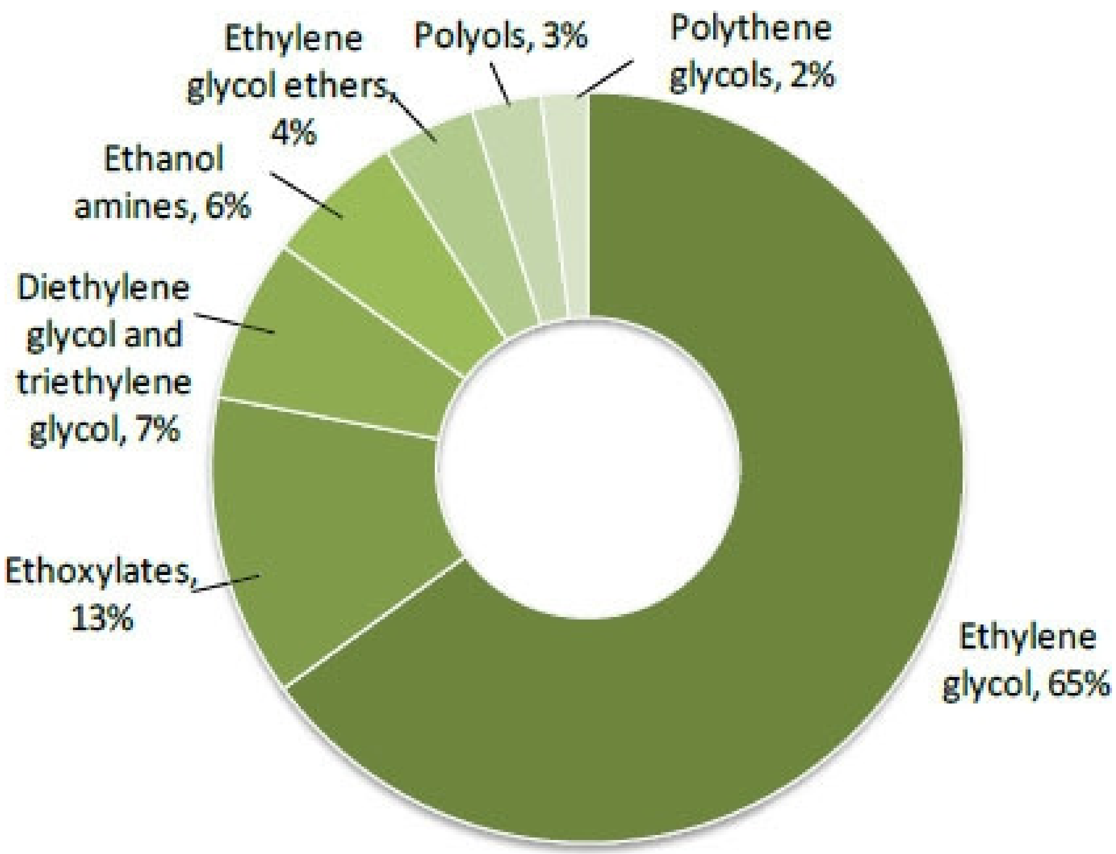


EtO Producers	Current Production Processes
Dow Chemical	METEOR™ EtO/glycol process technology, polyethylene (1,300 kt), ethylene dichloride/vinyl chloride monomer (730 kt)
Shell Global	Shell MASTER Process, Shell OMEGA Process, mono-ethylene glycol (450 kt), styrene monomer (450 kt)
Scientific Design	Couples EO/EG technology with its SynDox® catalysts. Catalysts used at more than 100 EO/EG plants worldwide

Chongterdtoonskul, A.; Schwank, J. W.; Chavadej, S. *J. Mol Cat A* **2013,** *372* (175-182)
Dellamorte, J. C.; Lauterbach, J.; Barteau, M. A. *Catal. Today* **2007,** *120*, 182-185

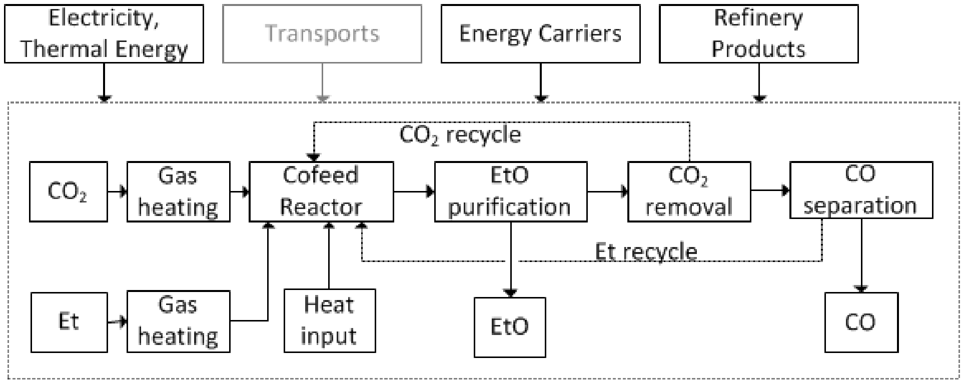
Market Potential: Ethylene Oxide

- Large and growing market for EtO in North America and globally
- Ethylene oxide demand is over 24 Mt globally (~$40 billion USD)
  - 14th most produced organic chemical
  - Global demand expected to grow 6% per annum
  - 4th largest industrial emitter of CO_2 (6.3 Mt per annum globally)



GHG Reductions – Life-cycle Analysis (LCA)

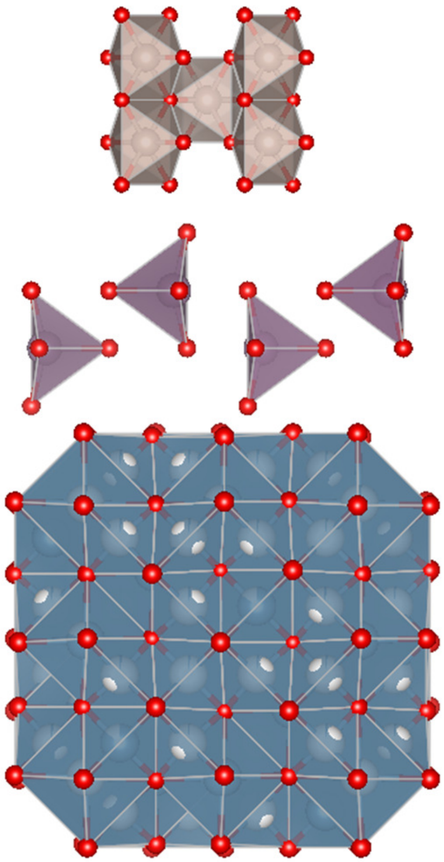
- RTI's technology enables CO_2 from other sources to be utilized to produce ethylene oxide
  - Reduces CO_2 emissions from conventional ethylene oxide process (direct CO_2 emissions of average plant are 150-200 kt-CO_2/yr)
  - Consumes CO_2 as a process feed gas
  - Reduces footprint of CO production (0.67 kg-CO_2/kg-CO)
- A 350 kt production plant could reduce CO_2 emissions by 1 Mt per annum



	Conventional Production (tonne $CO_{2\text{-}e}$/tonne EtO)	CO_2-EtO Production (tonne $CO_{2\text{-}e}$/tonne EtO)	CO_2-EtO GHG Benefit (tonne $CO_{2\text{-}e}$/tonne EtO)
Air Separation Unit	0.067	--	0.067
Carbon Dioxide	0.352	-6.270	6.622
Ethylene Input	1.283	3.000	-1.717
Electricity	0.123	0.540	-0.417
Natural Gas	0.390	2.387	-1.997
CO Product	--	-3.810	3.810
CO Purification		3.552	-3.552
Total		-0.601	2.822

Improving the Material

- Addition of promoters to the mixed-metal oxide for increased activity for EtO production
- Optimization of the metal-oxide phases and support for synergistic adsorption and mechanical properties for better EtO selectivity
- Improve metal oxide–support interaction by selection of:
  - support materials
  - particle size
  - porosity
  - ratio of metal-oxide phases on the surface or subsurface of the catalyst
- Changing the fabrication process conditions
  - e.g., calcination temperature



Success Metric	Ideal Target	Minimum Requirement
EtO selectivity	56%	37%
EtO yield	11.5%	5%
CO:EtO mass ratio	4	7
Metal oxide replacement cycle	10 years	3 years
Demonstrated operational time	200 hr	100 hr

Framework for Project

"Novel Catalytic Process Technology for Utilization of CO_2 for Ethylene Oxide and Propylene Oxide Production" (DE-FE0030678)

Characterizing and Refining Metal Oxide Formulation (Tasks 2, 3)

Extension to PO (Task 5)

Key Focus Areas

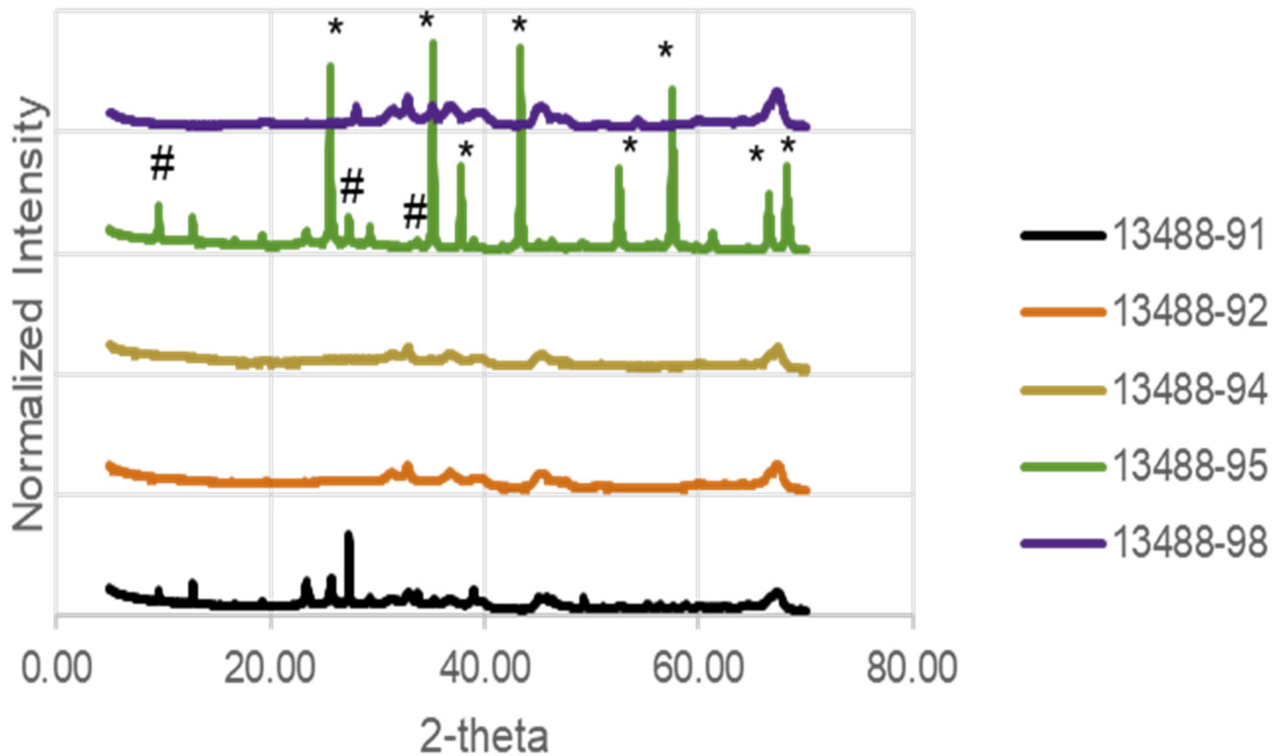
Bench-Scale Evaluation (Task 4, 7)

Process Modeling and Technology Assessments (Task 6, 8, 9)

Timeframe: BP1:10/1/17 to 09/30/18, BP2:10/1/18 to 09/30/19
Budget: BP1 $461,651 (DOE) + $100,000 (cost share)
BP2 $338,349 + $100,000 (cost share)
Total Budget = $1,000,000

RTI International - Dr. S. Jim Zhao, Principle Investigator
US DOE/ NETL – Steve Mascaro, Project Manager

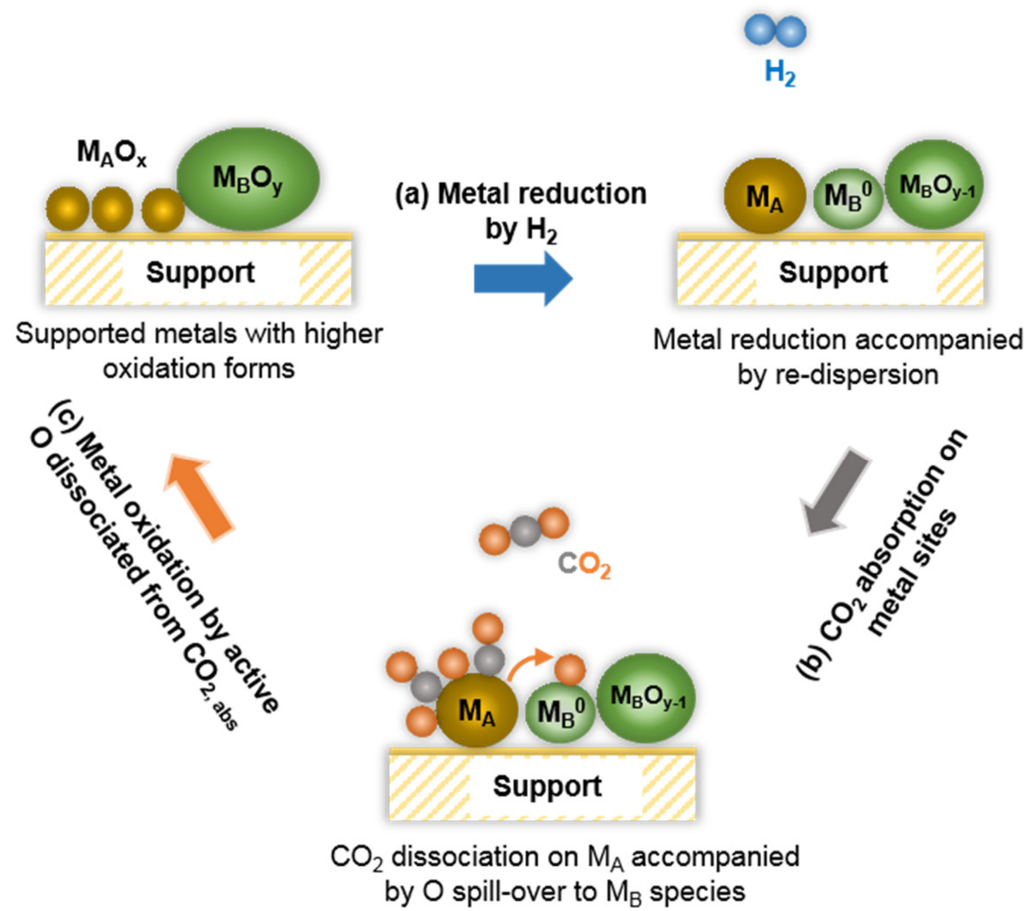
Identifying MMO Phases by XRD

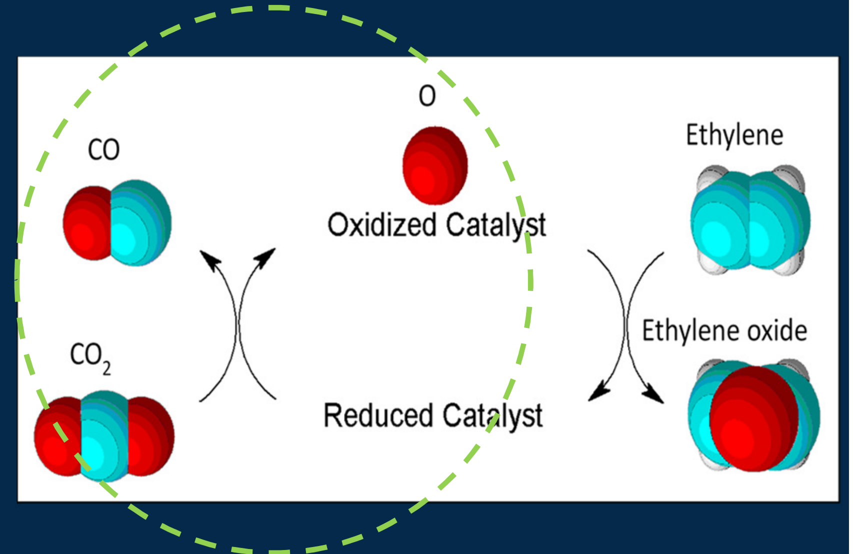


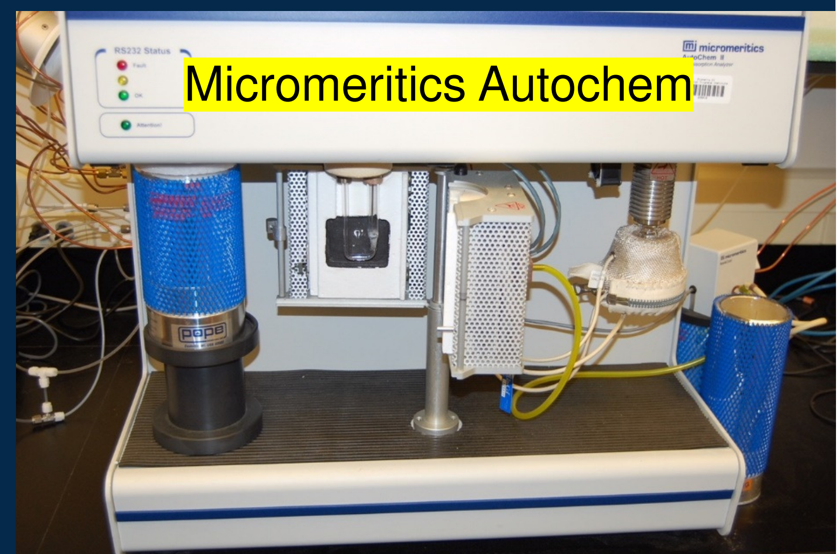
- XRF confirmed quantities of metals anticipated in the MMO's
- Mole ratio of M_1/M_2 varied to elucidate importance in CO_2 reduction
- Mole ratio to support varied to elucidate metal-support interactions
- XRD confirmed common metal oxide phases
- Small nanoparticle size of metal oxides
- Low crystallinity of support phase in primary samples

Characterizing the MMO using pulsed CO_2- Chemisorption

Experimental demonstration of CO_2 reduction

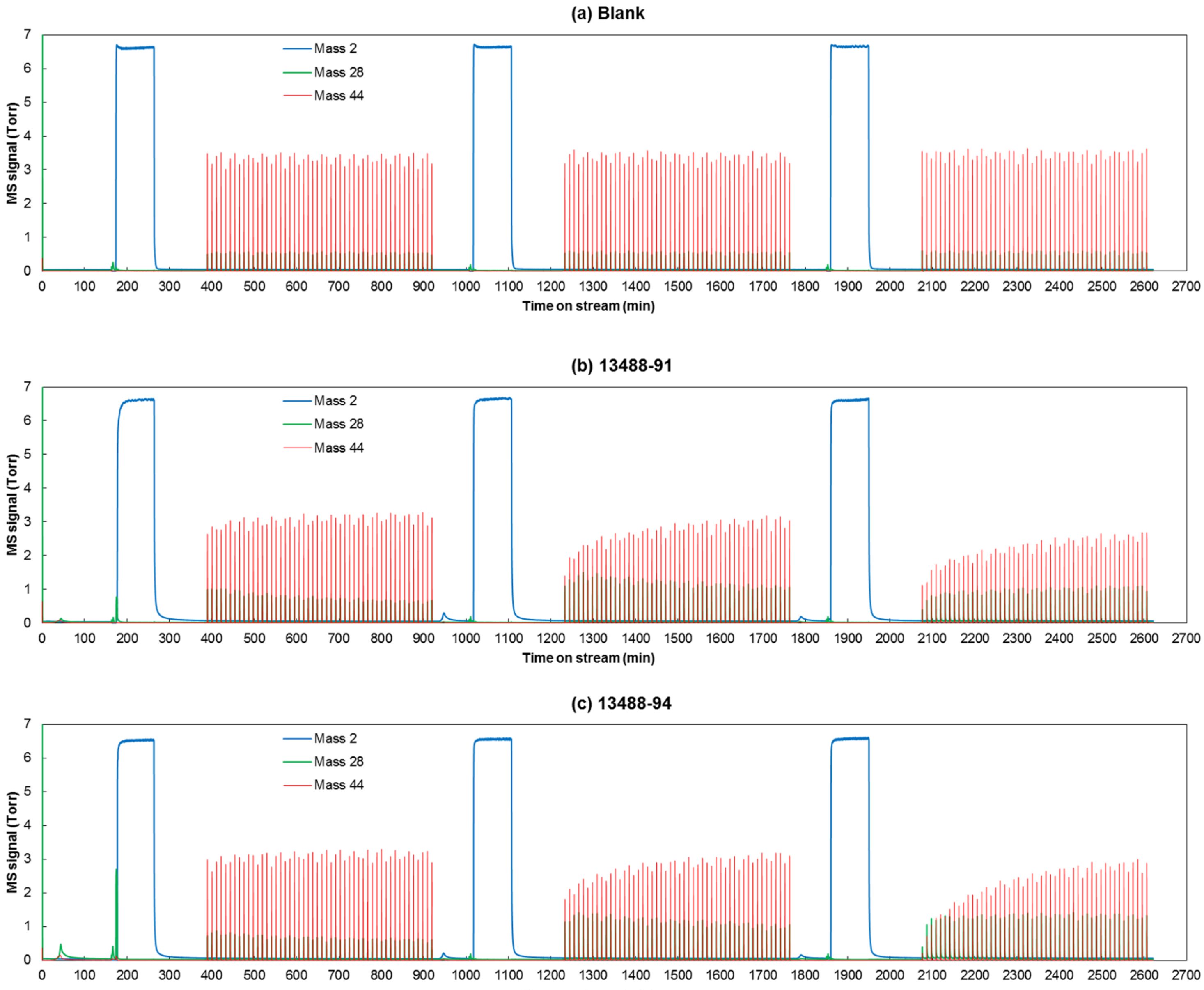






Catalytic CO_2-to-CO conversion < 600 °C

H_2 reduction @400 oC | CO2 pulse oxidation @400 oC | H_2 reduction @500 oC | CO2 pulse oxidation @500 oC | H_2 reduction @600 oC | CO2 pulse oxidation @600 oC

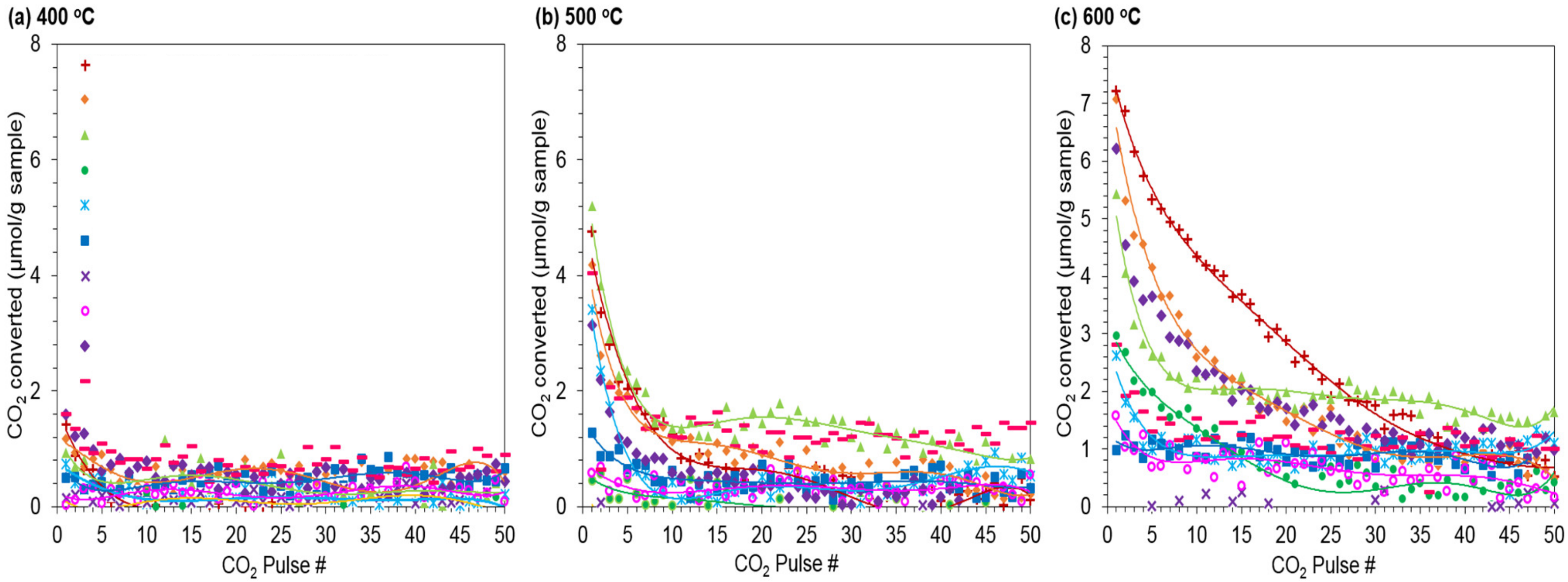


Test conditions:

- 400-600° C
- 1 atm CO_2
- 5% H_2 at 400° C reduction step

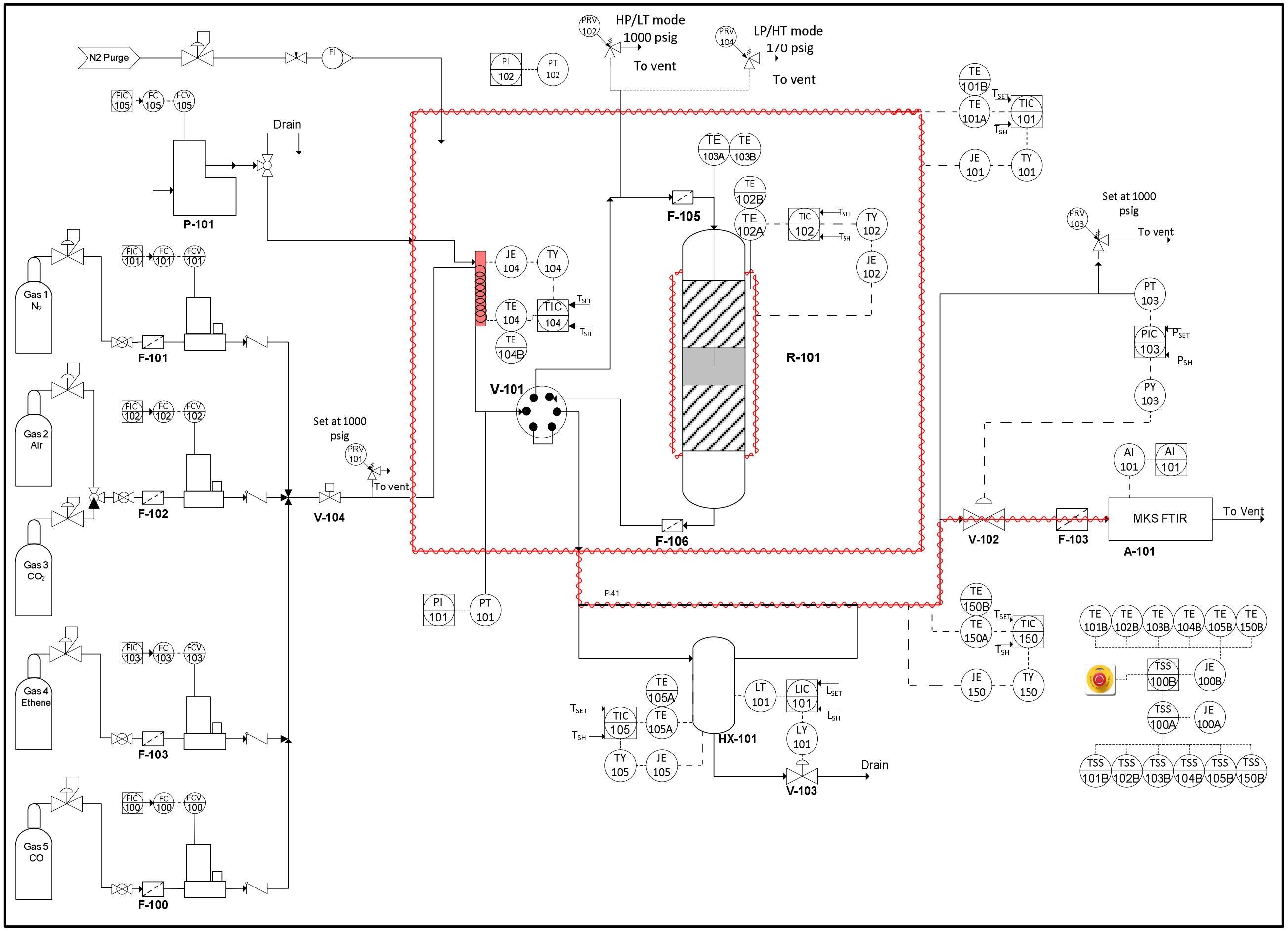
- Confirms CO_2 reduction
- 400° C low level of activity
- 500 -600° C higher activity
- ~2 wt% CO_2 reduction capacity shown in these experiments

Summary of CO_2 Reduction Findings



- A metal/support interaction is conducive to oxygen abstraction from CO
- The optimum metal oxide mole ratio for CO_2 reduction is approximately 0.25
- Increasing the crystal size from ~30 to ~50 nm does not appear to have a significant impact on CO_2 reduction
- Chloride is neither a poison nor a promoter to CO_2 reduction
- For this type of MMO, CO_2 reduction can be achieved at temperatures 500-600° C

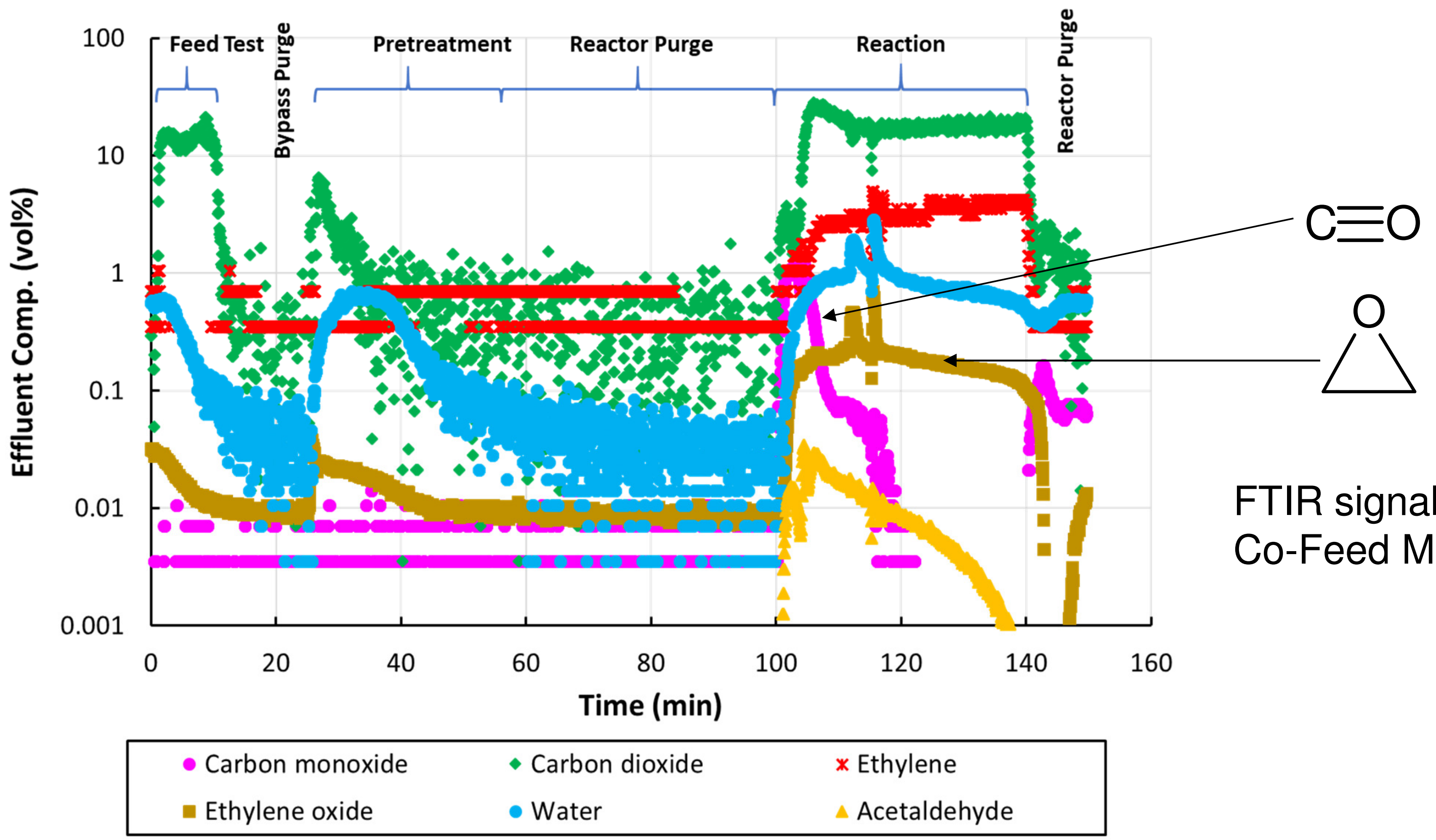
Testing MMO's for Ethylene Epoxidation



- Used a microreactor
- Fixed bed
- Micro-GC and FTIR gas analysis
- Carbon trap on product stream to further verify products
- Started with a baseline material to reproduce earlier results

	Pretreatment	Reaction	Oxidation
Gas Composition (vol%)	Reduction - CO: 5 Oxidation - CO_2: 5 N_2: balance	CO_2: 17.5 - 32.5 C_2H_2: 5 - 12.5 N_2: balance	O_2: 5 N_2: balance
Temperature (℃)	500-600	325-350	500-600
Pressure (bar)	20	20	20

Previous Results

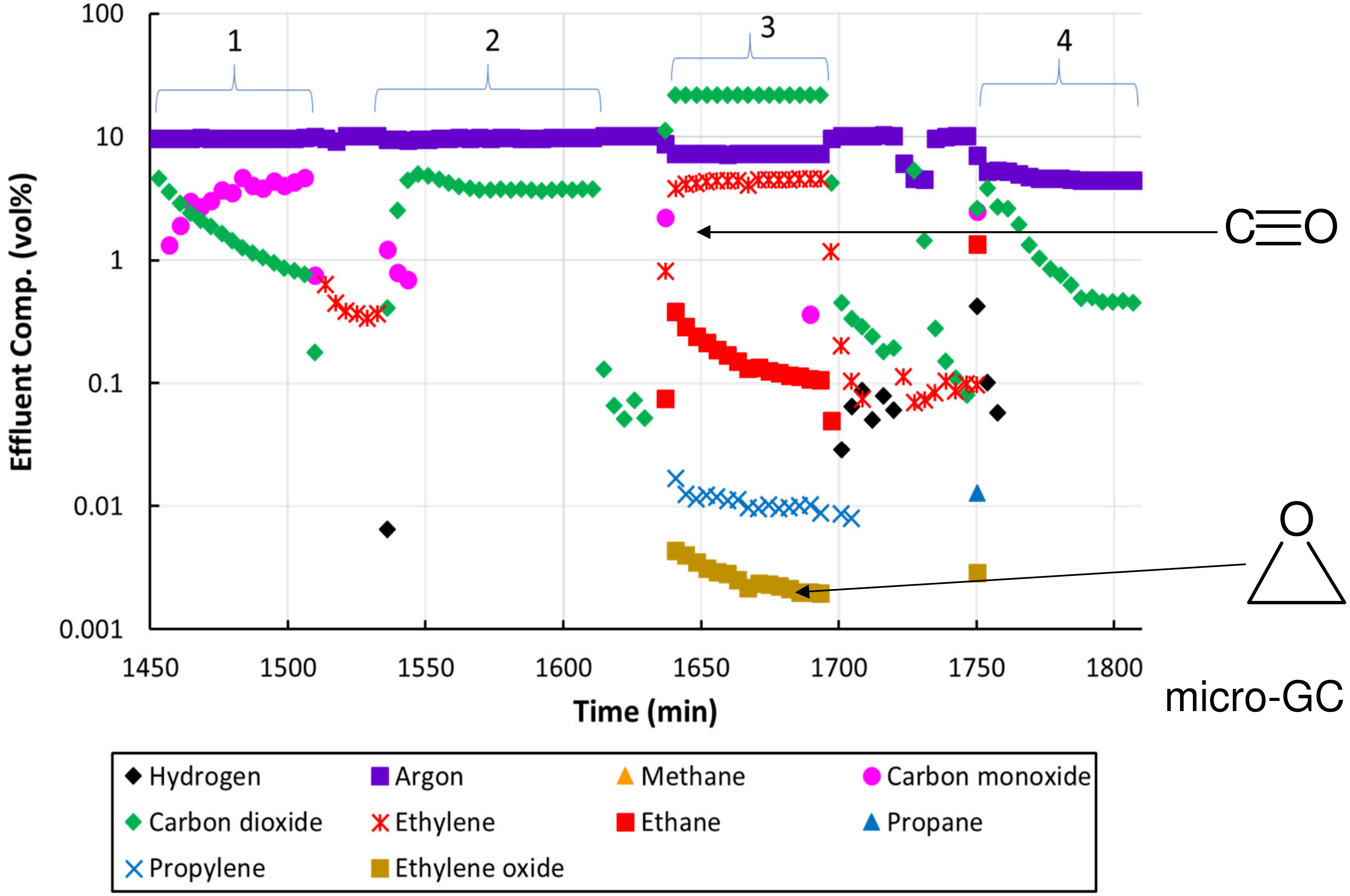


FTIR signals
Co-Feed Mode

- Observed CO and ethylene oxide by FTIR

Task 3 Results with micro-GC detection

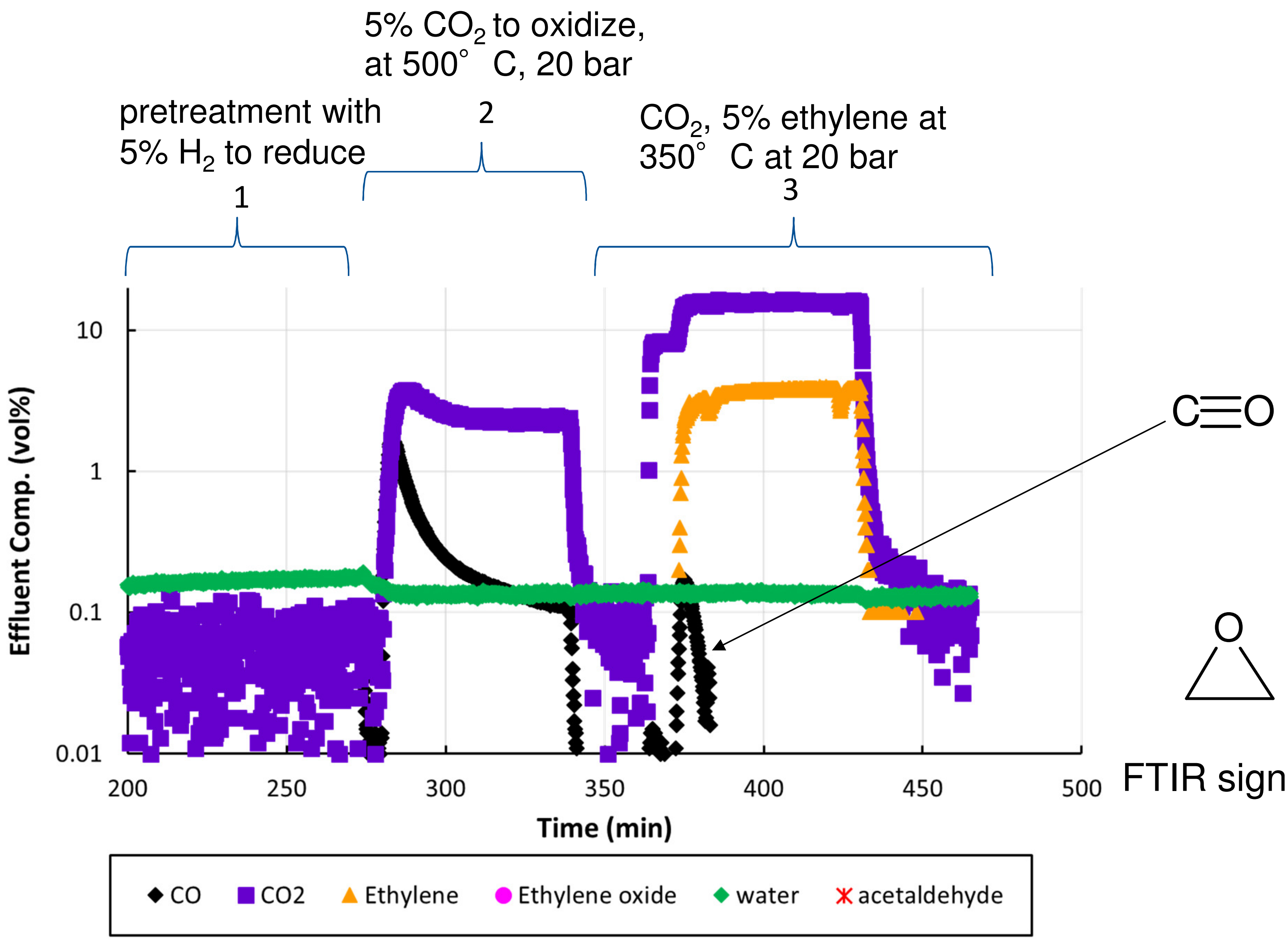
(1) pretreated with 5% CO to reduce, (2) 5% CO_2 to oxidize, at 500°C, 20 bar. (3) Reaction with 25% CO_2, 5% ethylene at 350°C at 20 bar. (4) Oxidation with 5% O_2 at 500°C, 20 bar.



micro-GC signal

- Observed CO , but very little ethylene oxide

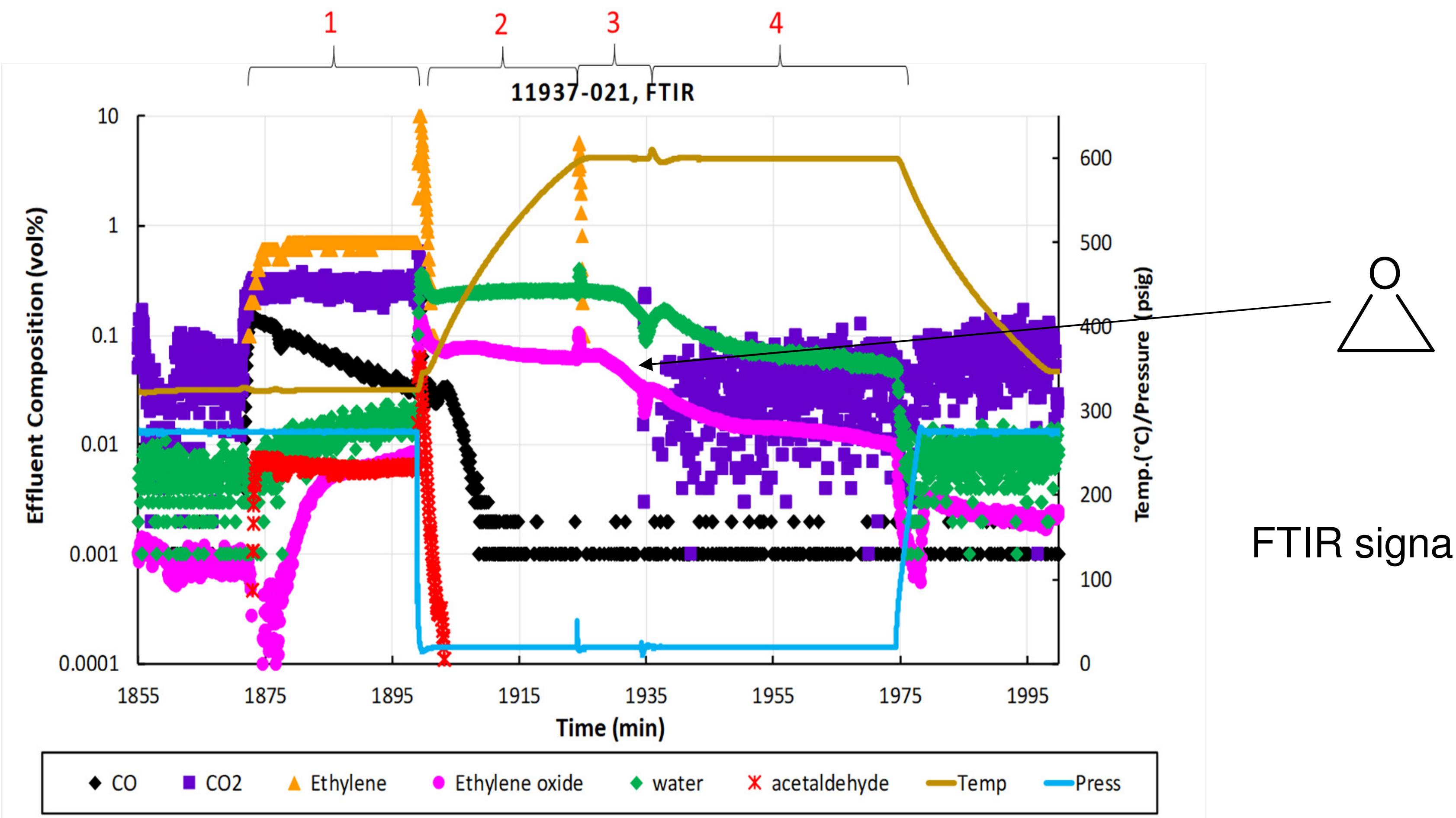
Task 3 Results Repeated with FTIR detection



FTIR signals

- Confirmed ethylene oxide not being produced

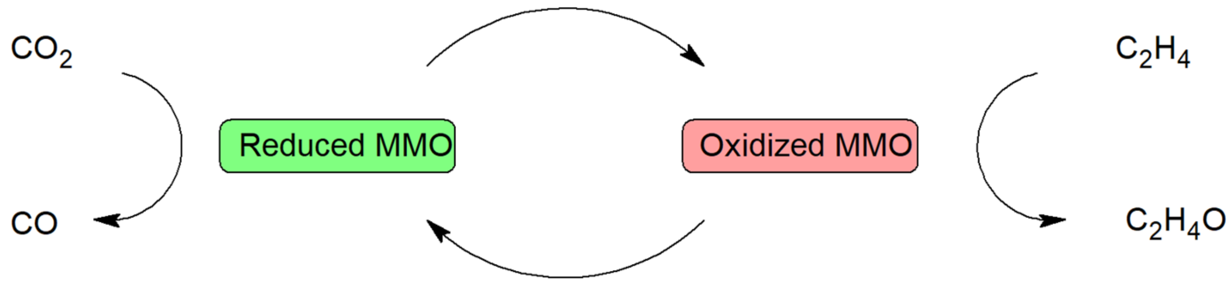
Possibility of Oxygen in the Reactor

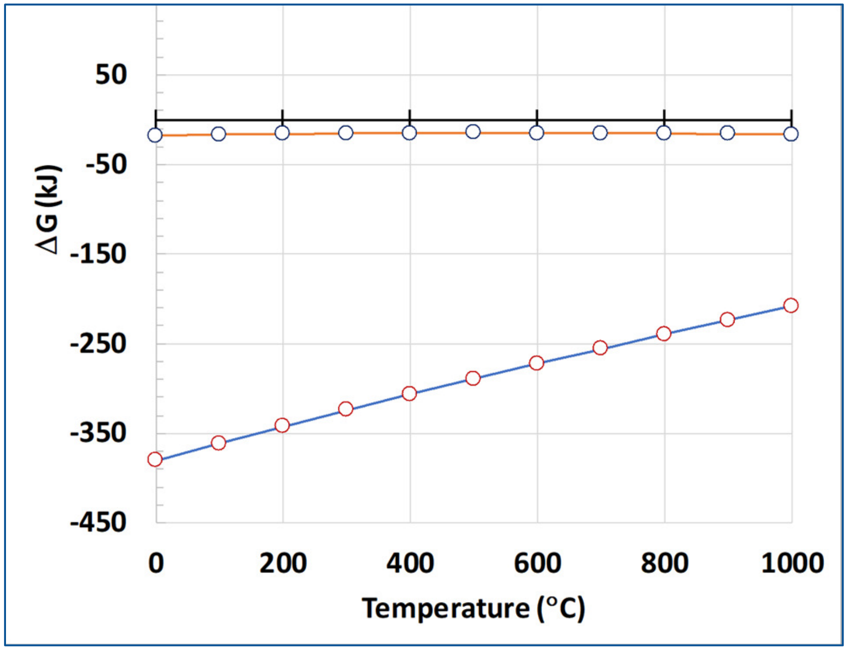


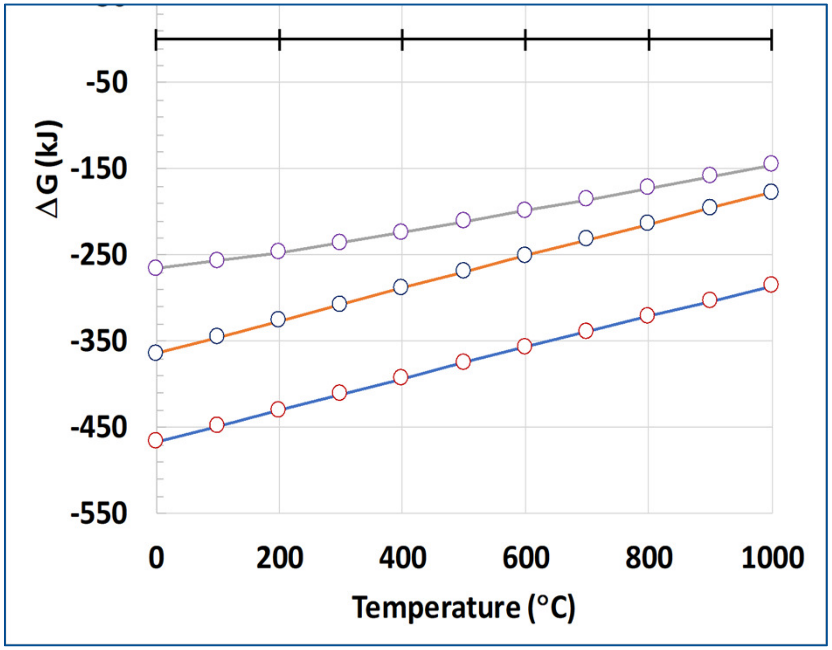
FTIR signals

- Simulating the leak of oxygen into the reactor produces ethylene oxide

Thermodynamics of CO_2 Reduction/ Ethylene Epoxidation



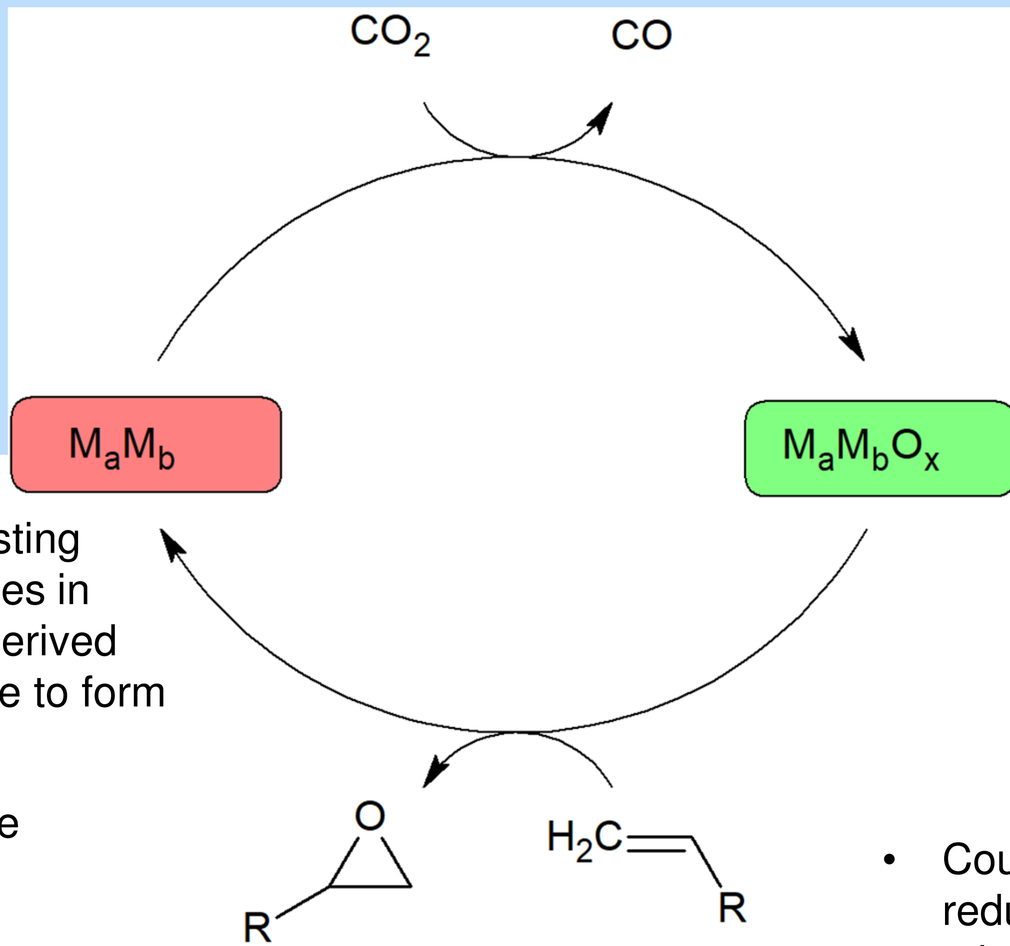




- Thermodynamically favorable reactions can be postulated for both redox steps
- The cycle is not closed, probably why ethylene oxidation is not being observed

Conclusions and Future Directions

- Characterized mixed metal oxides for thermochemical CO_2 reduction
- Identified formulation for CO_2 reduction between 500-600° C
- Confirmed the production of CO in microreactor testing under process conditions



- Met BP1 milestones for characterization
- Baseline catalyst testing shows inconsistencies in transfer of oxygen derived from CO_2 to ethylene to form ethylene oxide
- Need to refine phase selection to meet thermodynamic requirements
- Have not yet met BP1 milestone for refinement of MMO to show higher EtO yield
- Could apply existing CO_2 reducing formulation to other MT market chemicals as alternative to epoxides

Acknowledgements

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