UNIVERSITY OF CAMBRIDGE

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MoVNbTeO for Chemical Looping – Oxidative Dehydrogenation of Ethane

Samuel Gabra[1], Herme G. Baldoví[1], Gareth Williams[2], Stephen Poulston[2], John Dennis[1]

[1] Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge, UK

[2] Johnson Matthey Technology Centre, Blounts Court Road, Sonning Common, Reading RG4 9NH, UK

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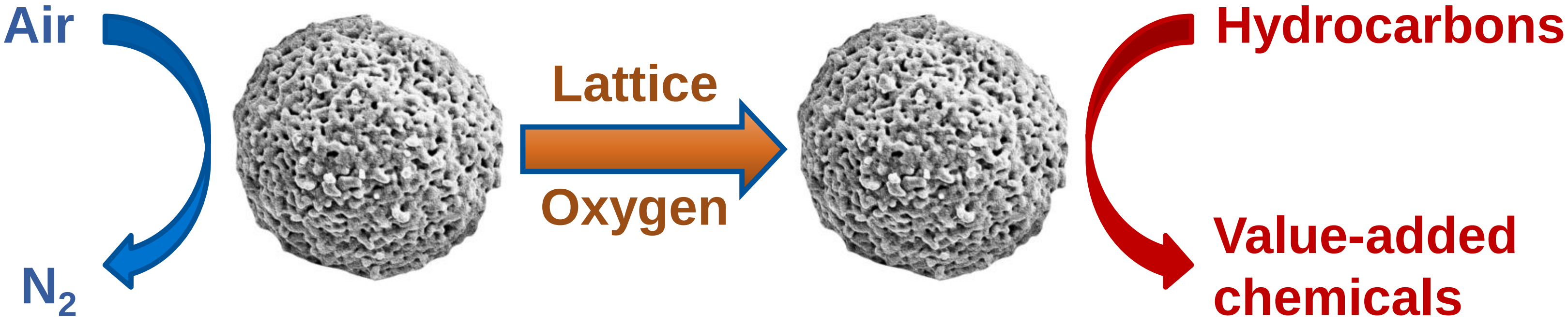
Introduction: What is chemical looping ?

- Chemical looping is based on the redox cycling of oxygen carriers to **convey lattice oxygen to a reaction**.
- The concept was originally intended to enable inherent separation of CO_2 and N_2 in **carbon capture from combustion systems**.
- Chemical looping can be exploited to produce value-added chemicals to potentially render the reaction **safer**, **more selective** and **more intensive**.



Oxidative dehydrogenation (ODH) of ethane

- Ethylene is an important intermediate with a global annual production of **180 Mte** in 2017 and forecast to exceed **270 Mte** by 2026.

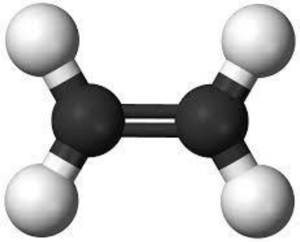
- It is made conventionally through the high temperature **pyrolysis** of hydrocarbon feedstocks in the presence of steam (**steam cracking**).

$$C_2H_6 \rightarrow C_2H_4 + H_2 \qquad \Delta H^{\circ}_{298} = +136\ \text{kJ/mol}$$

- The reaction is a highly **endothermic** and limited by **thermodynamic equilibrium**.

- An alternative method is the **oxidative dehydrogenation of ethane (ODH) to ethylene**.

$$C_2H_6 + \frac{1}{2}O_2 \rightarrow C_2H_4 + H_2O \qquad \Delta H^{\circ}_{298} = -106\ \text{kJ/mol}$$



Oxidative dehydrogenation (ODH) of ethane

- Conventional ODH imposes critical **safety hazards** and increased **costs** as it involves feeding a mixed stream of **ethane** and **oxygen** to the reactor.
- Chemical looping ODH (**CL-ODH**) has been proposed as an alternative.
- Different catalysts have been investigated for CL-ODH, including VO_x[1], MoO_x[2], LaSrFeO[3] and Mg_6MnO_8[4].
- However, all of these catalysts are **active** at temperatures **≥ 600°C**.

[1] Al-Ghamdi *et al.*, 2013, [2] Khadzhiev *et al.*, 2015, [3] Gao *et al.*, 2016, [4] Yusuf *et al.*, 2018

Oxidative dehydrogenation (ODH) of ethane

Motivation

- Develop a CL-ODH catalyst that is active at low temperatures (< 500°C).

- Examine the performance in chemical looping *vs.* cofeeding.

- Investigate the variation of activity with respect to structural changes.

Catalyst preparation

- Multi-metallic **$MoV_{0.24}Te_{0.24}Nb_{0.19}$ (M1)** was prepared by the slurry method[1].

- **Oxalic acid** was used as a reductant.

- Metal ratios and the oxidation state of the metals were varied through **calcination regimes** and **oxalic acid ratio**.

Sample name	Molar ratio of oxalate:Mo used in method of preparation*
M1 batch 1	Oxalate/Mo = high, regime 1
M1 batch 2	Oxalate/Mo = high, regime 2
M1 batch 3	Oxalate/Mo = low, regime 1
M1 batch 4	Oxalate/Mo = low, regime 2

*** Calcination regime 1:** Inert atmosphere
Calcination regime 2: Successive steps of inert atmosphere and air

[1] Valente *et al.*, 2018

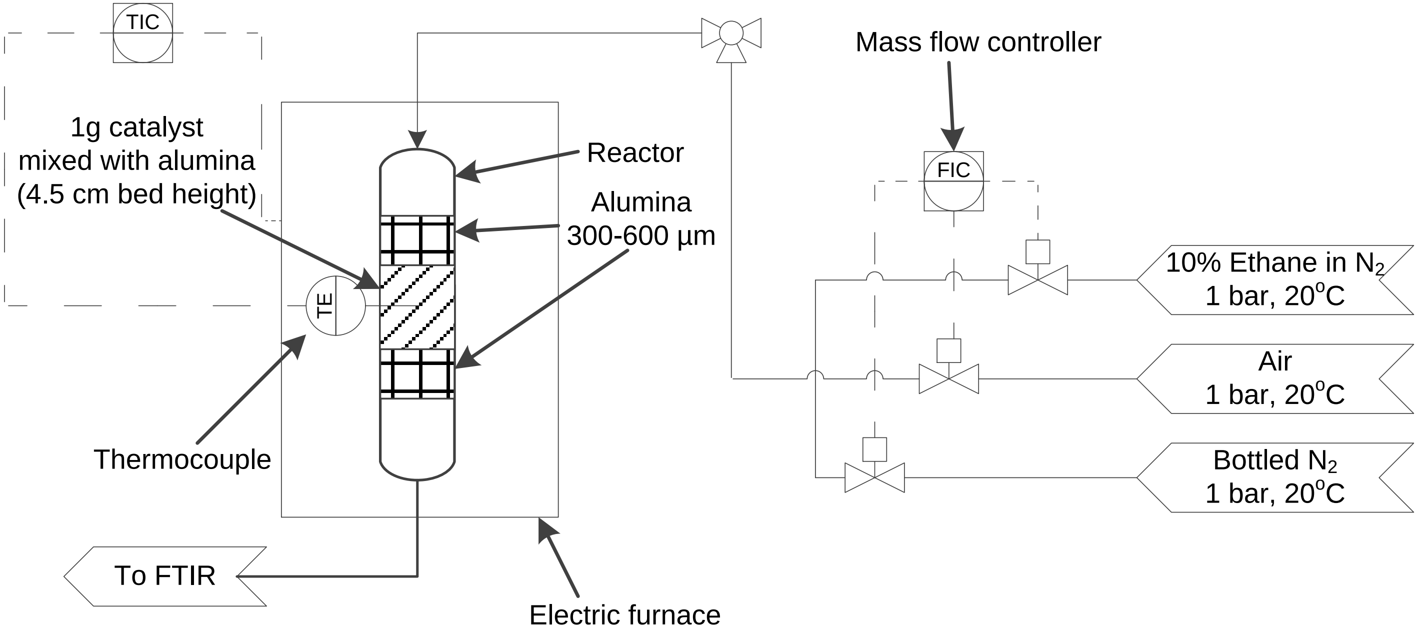
Catalyst preparation

- Many metal phases are produced during preparation, including M1, M2, $TeMo_5O_{16}$ and $Mo_x(V/Nb)_{5-x}O_{14}$.
- The **M1 phase** has an orthorhombic crystalline structure of $Te_2M_{20}O_{57}$ (where M=Mo, V, Nb).
- The M1 phase **possesses the only active sites** for alkane activation[1].
- **Other phases**, including the M2 phase, **cannot activate alkanes**.
- Hence, it is desirable to **maximise the ratio of the M1 phase** in the catalyst, while at the same time **optimising oxygen kinetic properties**.

[1] Grasselli *et al.*, 2004

Catalytic performance

- One cycle consisted of: Oxidation with **air** (2.5 mins, 200 ml/min), reduction with **ethane** (1 min, 50-100 ml/min) and purge with **N_2** (2 mins, 200 ml/min) in between.
- Temperature: 325-475°C



Results

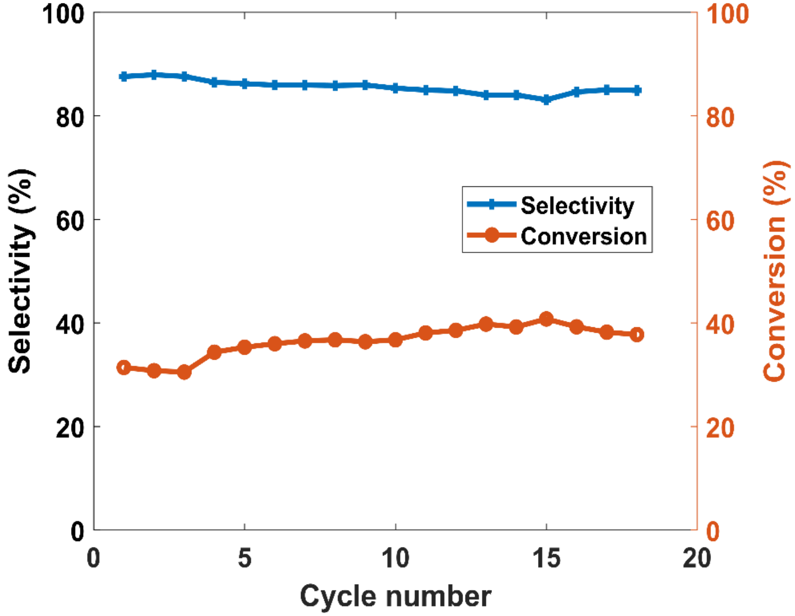
- The different catalyst batches exhibited different performances.
- **M1 batch 4**, with low oxalate ratio and air calcination, performed the best.

Catalyst*	Selectivity	Conversion	Yield
M1 batch 1	89%	6%	**6%**
M1 batch 2	85%	28%	**24%**
M1 batch 3	90%	26%	**24%**
M1 batch 4	81%	62%	**50%**

***Conditions:** 475°C, reduction in ethane (50 ml/min for 1 min), 1 g of catalyst

Results

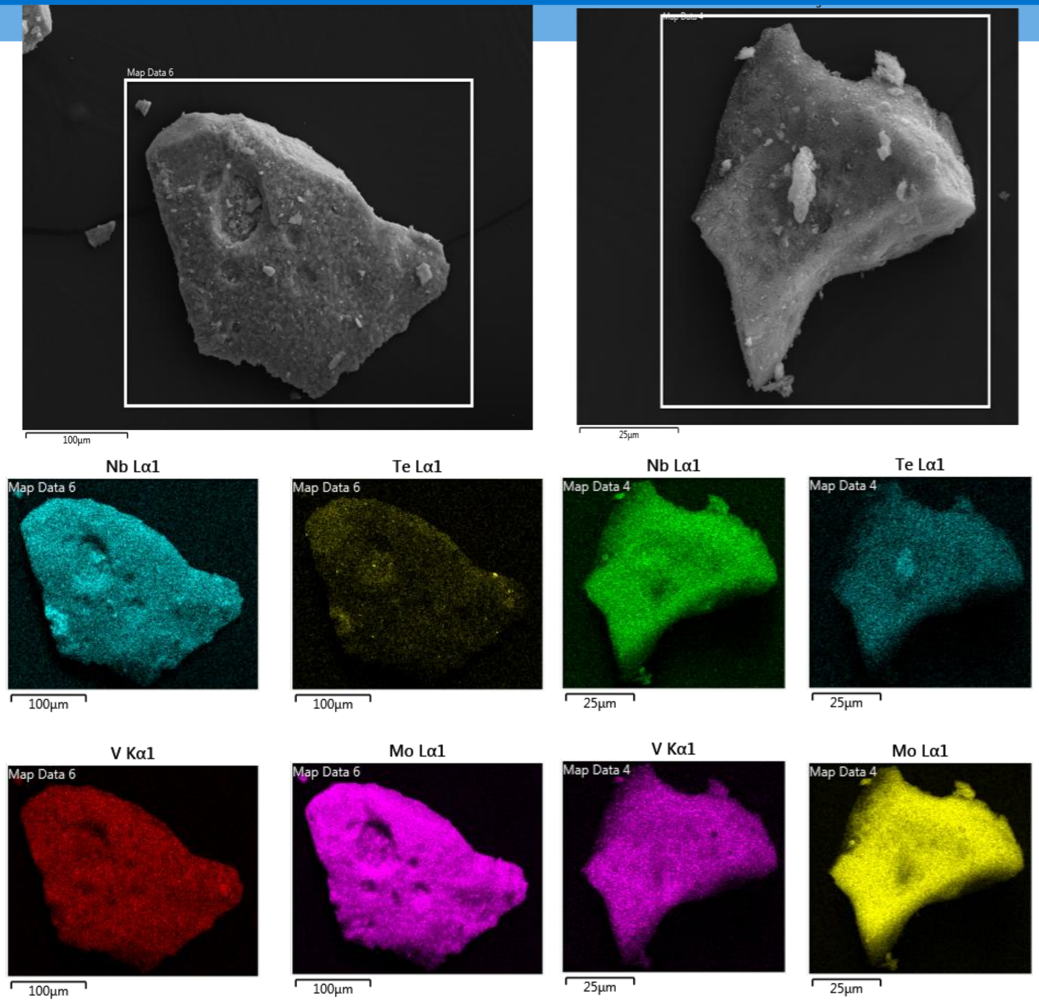
- Around **90% selectivity** and **40% conversion** for **M1 batch 4**.
- The catalyst showed excellent **cyclic stability**.



***Conditions:** 475°C, reduction in ethane (100 ml/min for 1 min), 1 g of catalyst

Effect of calcination regime

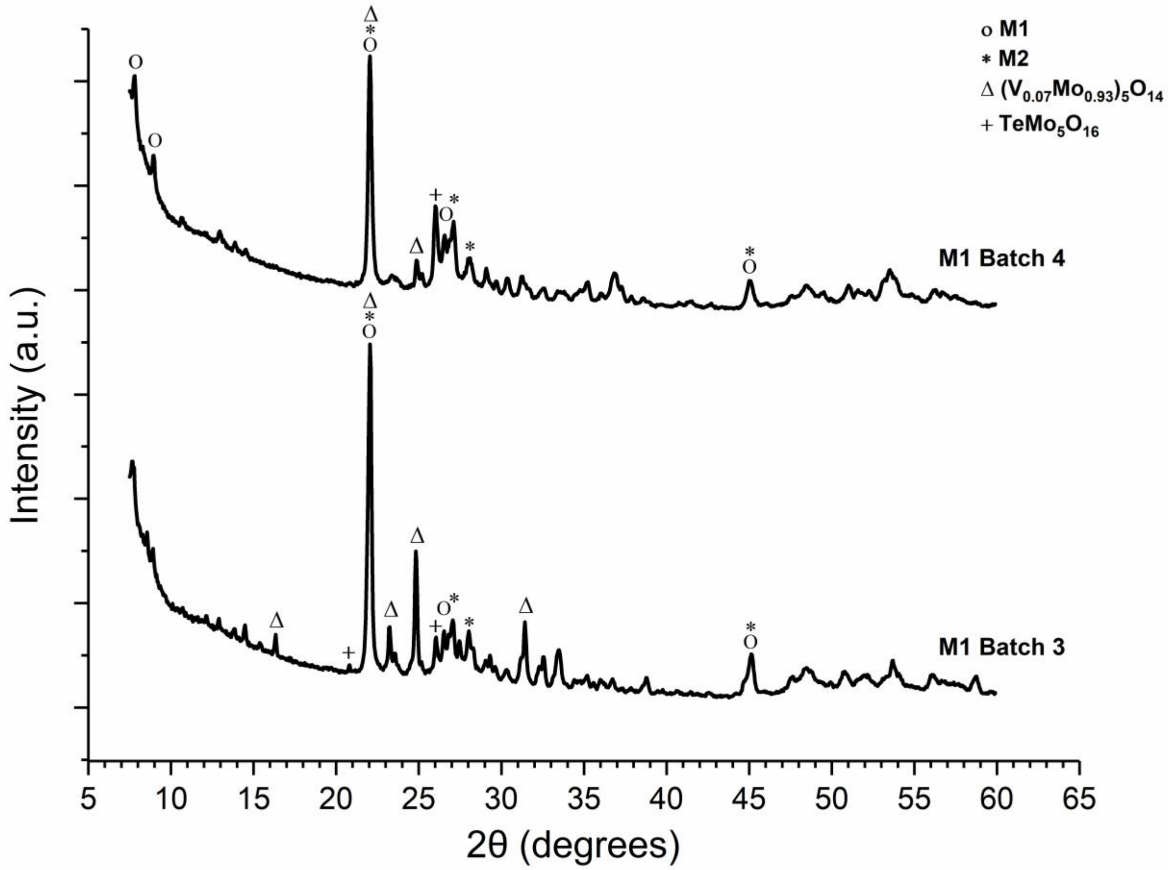
- Te sublimation is evident in batch 3 (calcined only in inert atmosphere).
- Te^{4+} cations are essential for the formation of M1 phase, which is active for ethane ODH
- Air calcination helps in the stabilization of Te^{4+} and prevents its further reduction and sublimation.



M1 batch 3 **M1 batch 4**

Effect of calcination regime

- M1 and M2 were the main phases in batch 4.
- Batch 3 contained high amount of $(V_{0.07}Mo_{0.93})_5O_{14}$ in addition to M1 and M2 phases.

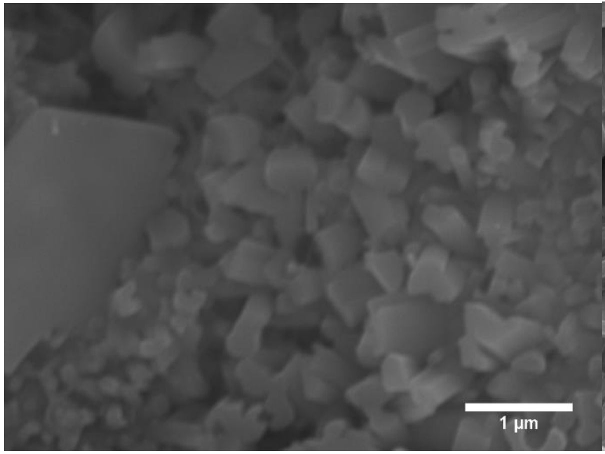


Effect of oxalate ratio

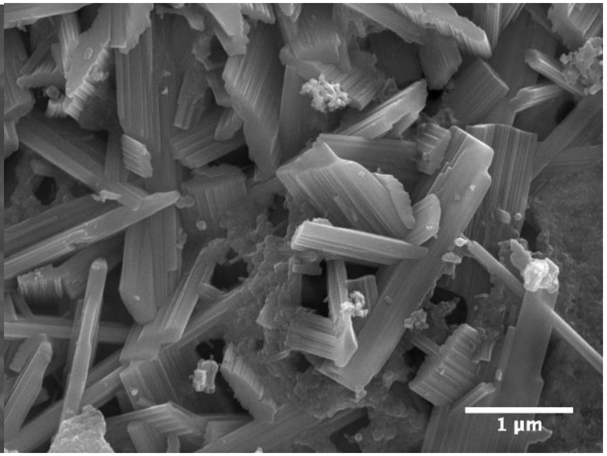
- The image of batch 4 indicates the presence of needle-like crystallites with striated edges, which is a typical structure of M1 phase.

- Batch 2, which contained a higher oxalate ratio, possessed much smaller crystallites than batch 4.

- The excessive presence of oxalic acid hinders the long-range ordering of the material in the [0 0 1] direction.



M1 batch 2



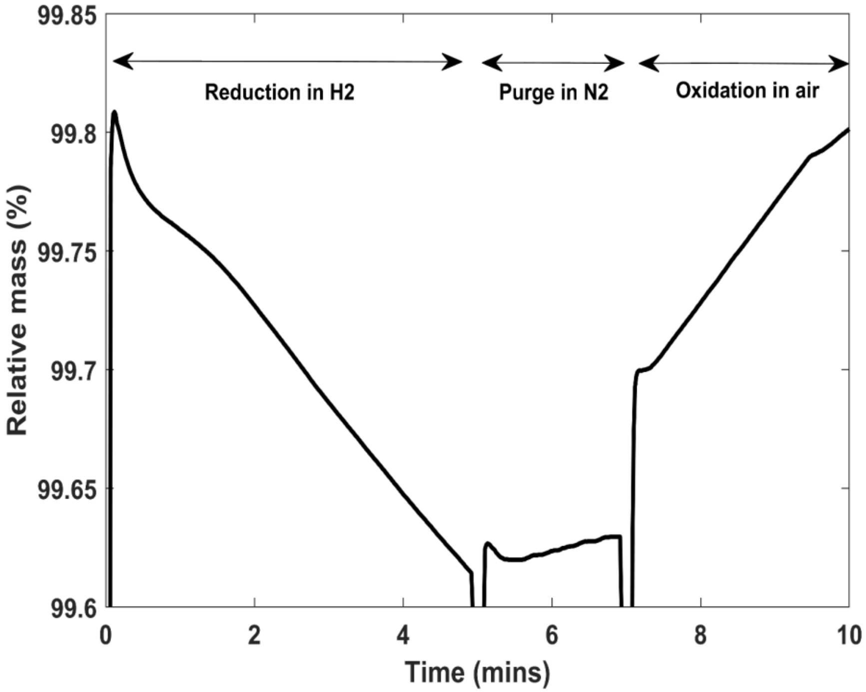
M1 batch 4

Oxygen transport properties of the catalyst

- Quick reoxidation, making it suitable for chemical looping.
- Preparation conditions did not affect oxygen transport properties.

Rate of oxygen release

Temperature (°C)	M1 batch 3 (μmol of $O_2/g_{catalyst}$.min)	M1 batch 4 (μmol of $O_2/g_{catalyst}$.min)
325	0.09	0.06
375	0.13	0.13
425	0.25	0.25
475	0.94	0.94



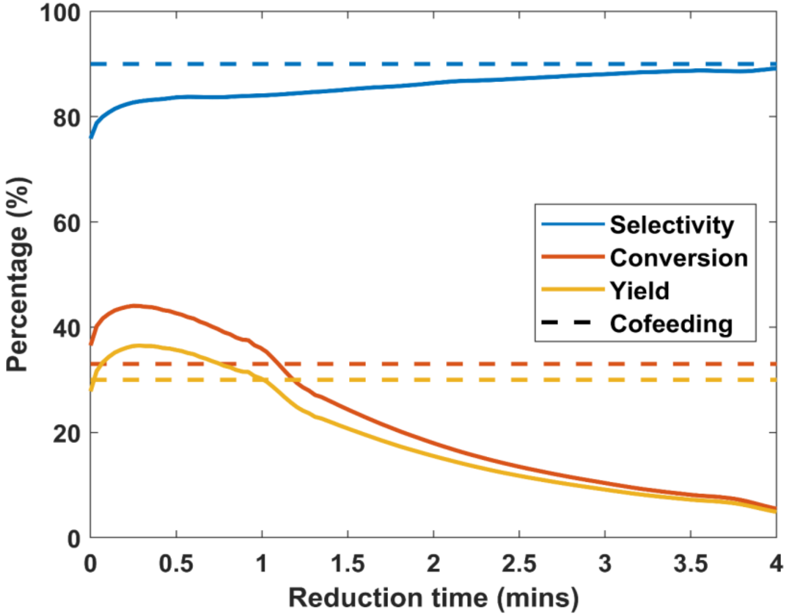
Chemical looping vs cofeeding

	Cofeeding			CL		
Temperature (°C)	Selectivity	Conversion	**Yield**	Selectivity	Conversion	**Yield**
325	97%	2%	**2%**	97%	1.8%	**2%**
375	96%	6.7%	**6%**	96%	8.4%	**8%**
425	94%	15%	**14%**	92%	23%	**21%**
475	90%	33%	**30%**	86%	37%	**32%**

- Chemical looping resulted in slightly lower selectivities, but higher conversion.
- Overall, chemical looping led to higher yields.

Chemical looping vs. cofeeding

- Selectivity increases as the catalyst is more reduced.
- Conversion and yield are higher for CL in the first minute of reduction.
- The superior performance in the CL mode is probably due to flushing weakly-bound oxygen which contributes in total oxidation.



- At the start of the reduction, the catalyst possessed high oxidation state, which helped in supplying reactants with high pO_2 and hence, facilitating higher conversion and lower selectivity.

Conclusion

- **Chemical looping** is feasible for the **oxidative dehydrogenation of ethane.**
- The catalyst, in chemical looping mode, can achieve **50% ethylene yield** at **475°C**, with **selectivity** and **conversion** around **80%** and **61%** respectively.
- Up to **97% selectivity** was achieved **at low temperatures (~325°C).**
- Chemical looping can result in **higher ethylene yields** compared to cofeeding.

Acknowledgments

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Pioneering research and skills

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Thank You

Any questions ?