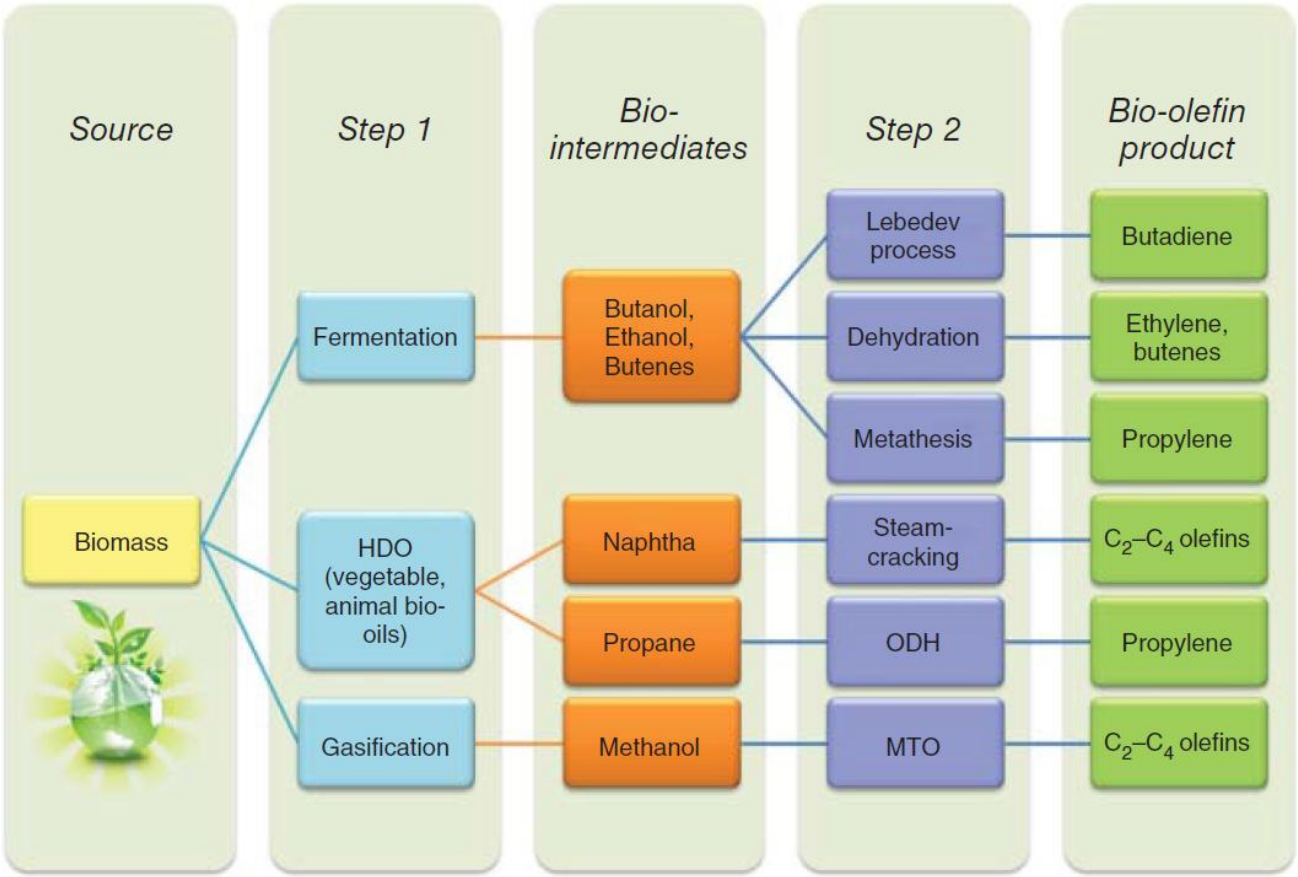
3ο Πανελλήνιο Συνέδριο Βιοκαυσίμων & Εναλλακτικών Καυσίμων
15 & 16 Μαΐου 2025, Λίμνη Πλαστήρα

Αξιοποίηση Βιογλυκερόλης προς Παραγωγή Προπυλενίου μέσω Καταλυτικής Υδροαποξυγόνωσης

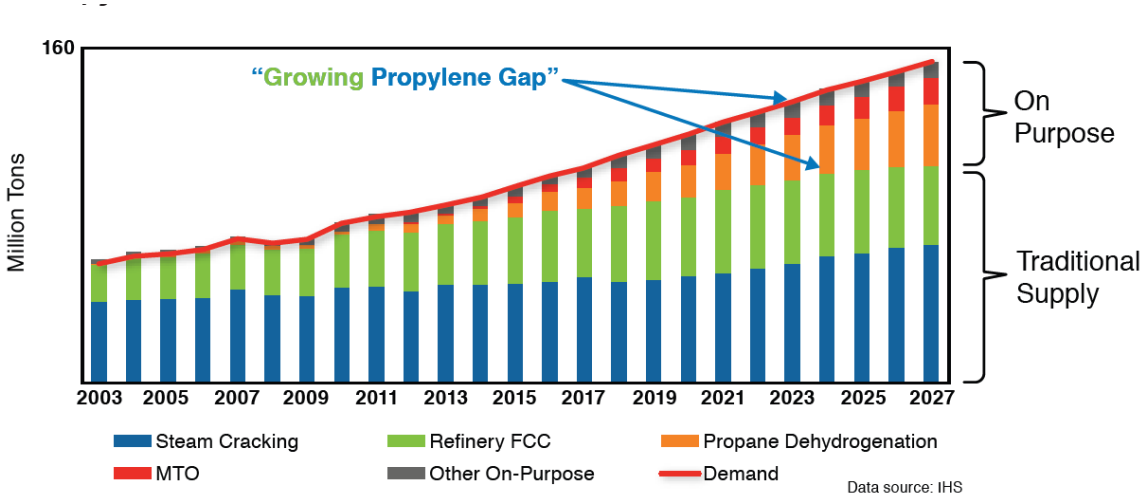
Γεωργία Ιωαννίδου, Αγγελική Α. Λεμονίδου

Τμήμα Χημικών Μηχανικών
Αριστοτέλειο Πανεπιστήμιο Θεσσαλονίκης

Conversion of biomass intermediates to light olefins

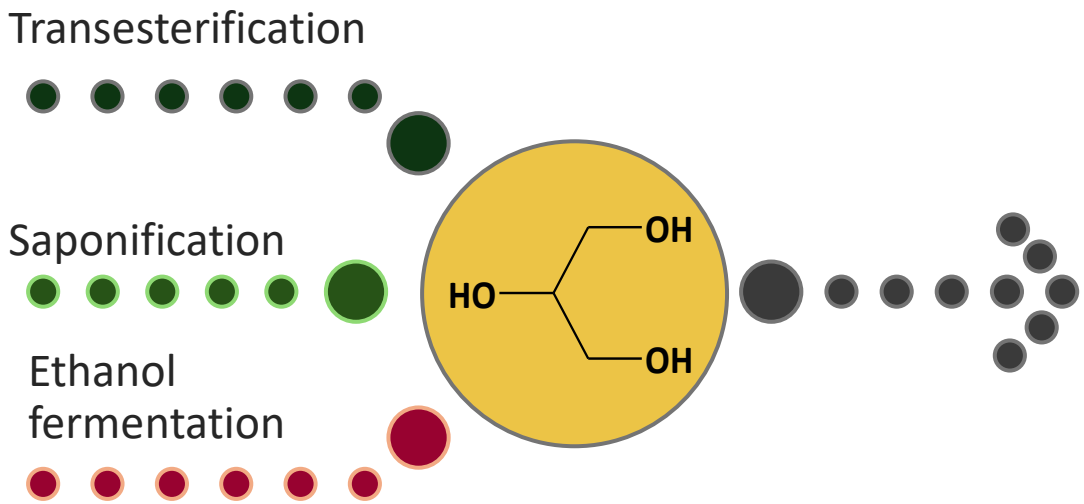


Cavani et al, Chemicals and Fuels from biobased building blocks, Chapter 1, 2016, Wiley



Propylene: 150 Mmtons in 2023

Glycerol conversion to propylene



Hydrodeoxygenation, HDO

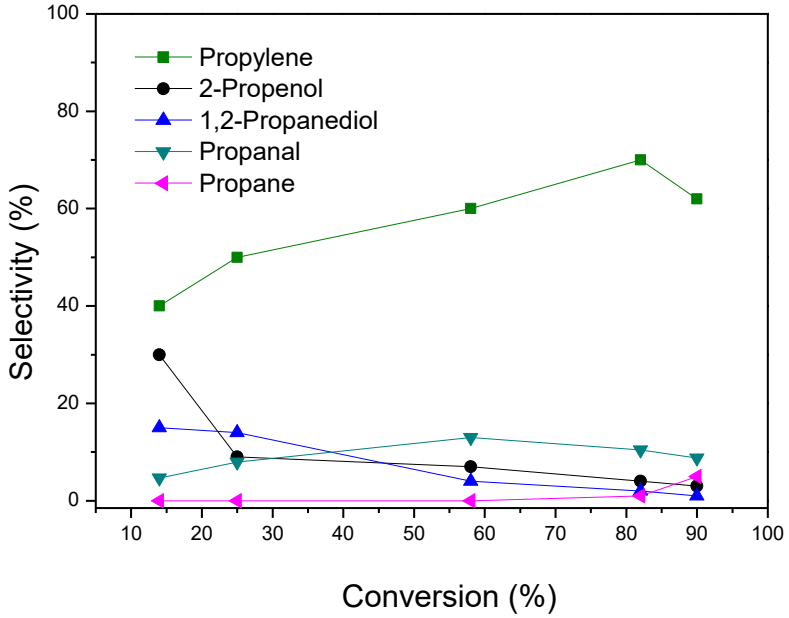
$$C_3H_8O_3 \xrightarrow{-3H_2O/+2H_2} C_3H_6 \xrightarrow{} C_3H_8$$

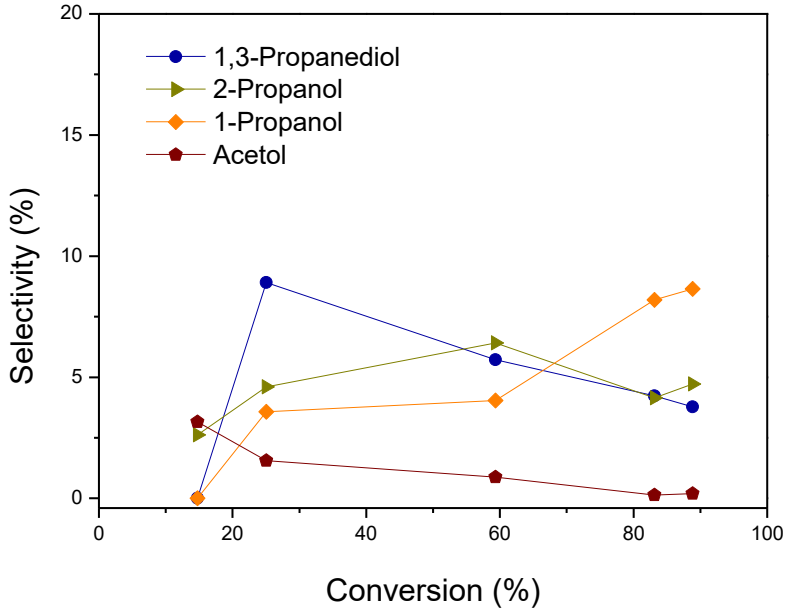
Catalyst characteristics

- ✓ Active in C – O bond scission
- ✓ Inactive in C – C bond cleavage
- ✓ Mild hydrogenation activity

Glycerol HDO: Product distribution over Mo-based catalyst

Catalyst: 20wt% MoO_3 on carbon black





Conditions:
Batch reactor
Po=80 bar (H_2)
T=300 ^{0}C t=0-6 h

- **Propylene** is the main product with selectivity which increases with glycerol conversion
- **100% propylene selectivity** in gas phase
- Other products → partially deoxygenated compounds with low selectivity

Zacharopoulou et al, Green Chem. 17 (2015) 903

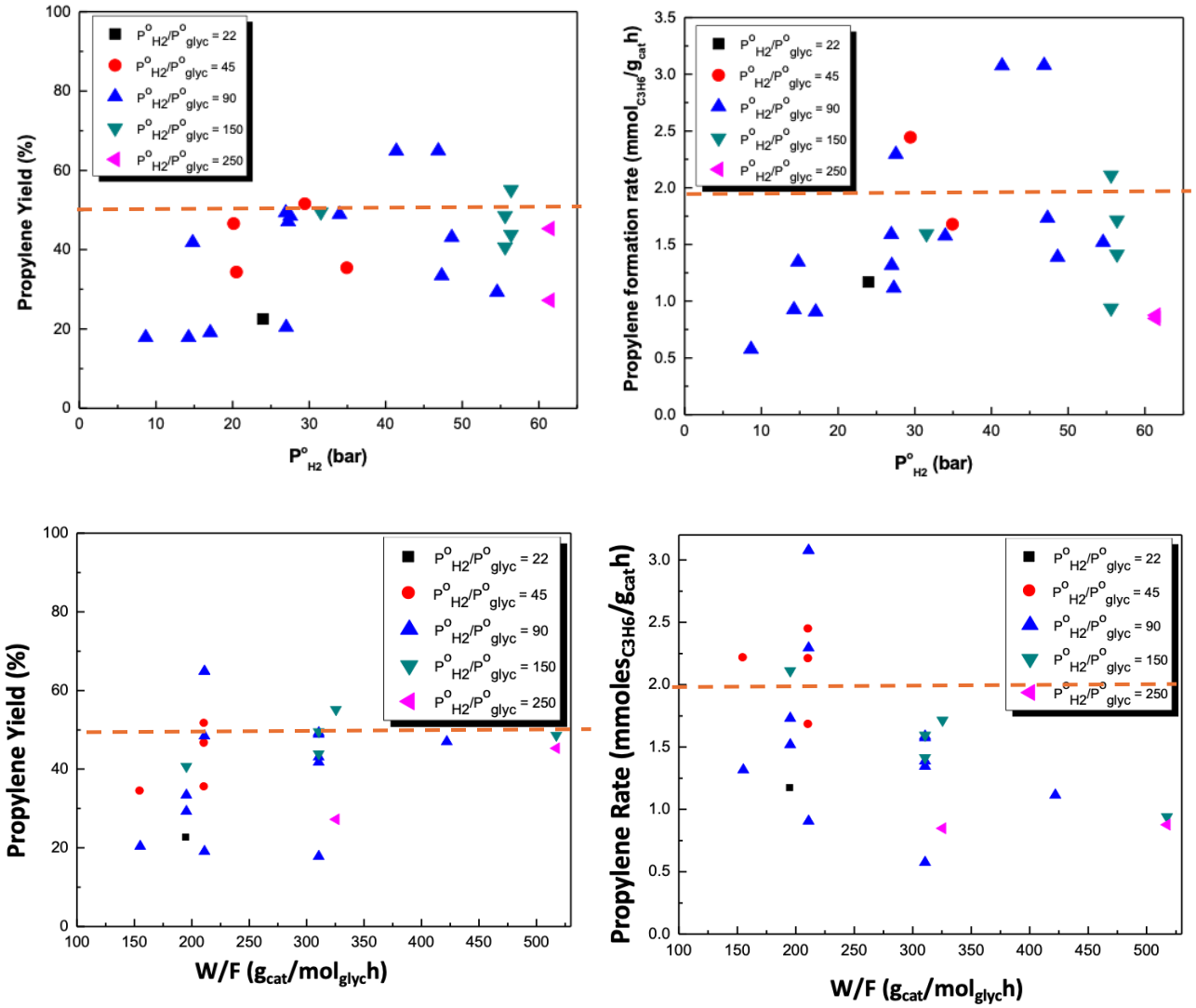
Glycerol HDO under continuous flow: Effect of operating variables

Reactor: fixed bed, operation at 280°C

Catalyst: 8.7 wt% MoO_3 on carbon black

Variable	Range	Units
P^o_{H2}	**8.6 – 61.4**	bar
P^o_{H2}/P^o_{glyc}	**22 – 250**	
W/F	**155 - 517**	g_{cat} h/mol_{glyc}
LHSV	**0.43 – 1.2**	h^{-1}

- Glycerol conversion almost complete (~100%)
- **Propylene yield >50% & rate >2 mmol/g h**
  25 < P^O_{H2} < 45 bar and
  90 < P^o_{H2}/P^o_{GLY} < 150
  at LHSV = 1.2 h^{-1} , W/F = 211 $g_{cat}h/mol_{glyc}$



Ioannidou et al, Catal. Today 423 (2023) 113902

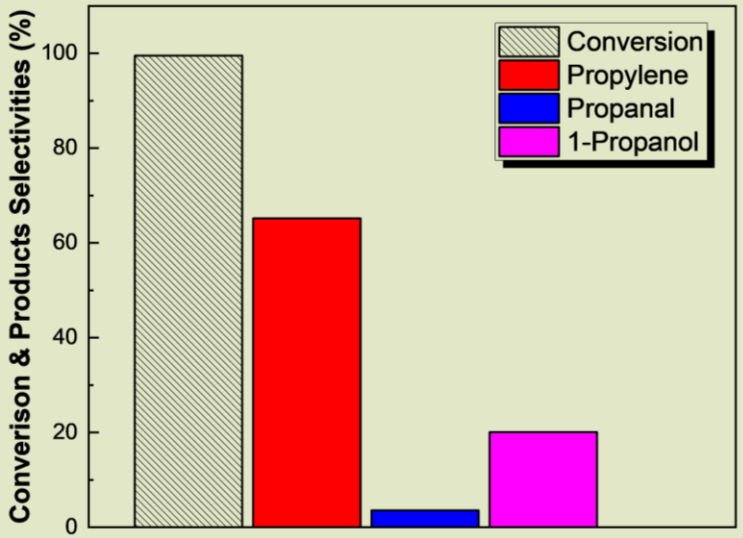
Glycerol HDO under continuous flow: Effect of operating variables

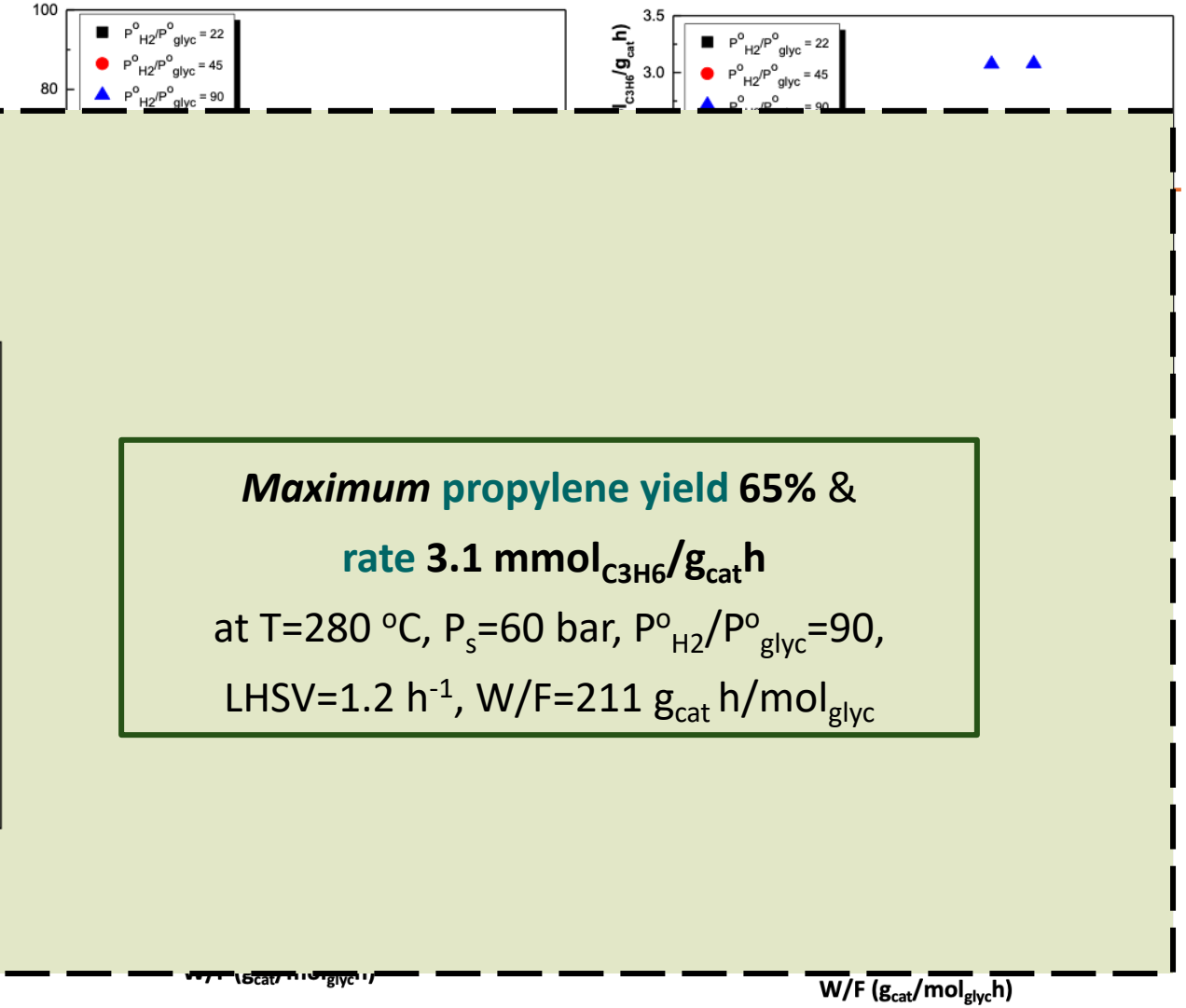
Reactor: fixed bed, operation at 280°C

Catalyst: 8.7 wt% MoO_3 on carbon black

Variable
P^o_{H2}
P^o_{H2}/P^o_{glyc}
W/F
LHSV

- Glycerol co
- **Propylene**
  25 < P^O_{H2} <
  90 < P^o_{H2}/
  at LHSV =





***Maximum* propylene yield 65%** &

rate 3.1 $mmol_{C3H6}/g_{cat}h$

at T=280 °C, P_s=60 bar, P^o_{H2}/P^o_{glyc}=90,

LHSV=1.2 h^{-1}, W/F=211 g_{cat} h/mol_{glyc}

Ioannidou et al, Catal. Today 423 (2023) 113902

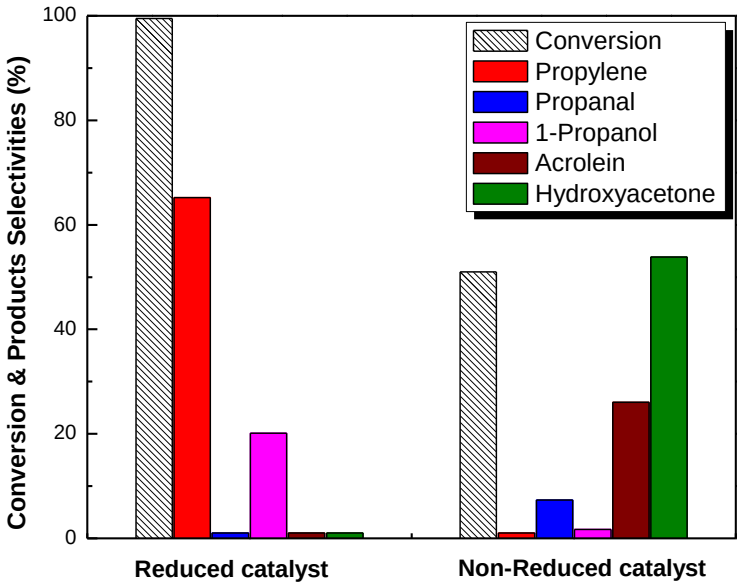
Glycerol HDO: Effect of catalyst pre-reduction

Catalyst: 8.7% Mo/BC (reduction 500°C, 30min)

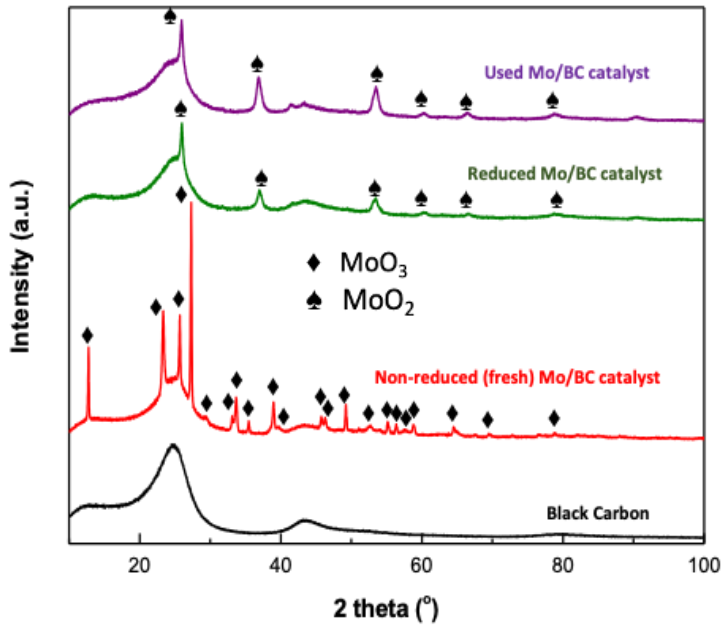
Reaction Conditions: 10wt% aqueous glycerol solution

T=280 °C, P^{o}_{H2} = 60 bar,

LHSV = 1,2 h^{-1}, TOS = 4h



XRD



✓ **65% propylene yield** over reduced catalyst

✓ Non reduced catalyst is less active and totally unselective to propylene

✓ Fresh catalyst consists of MoO_3 while after reduction the crystal phase is MoO_2 indicating reduction of Mo from +6 to +4

Ioannidou et al, Catal. Today 423 (2023) 113902

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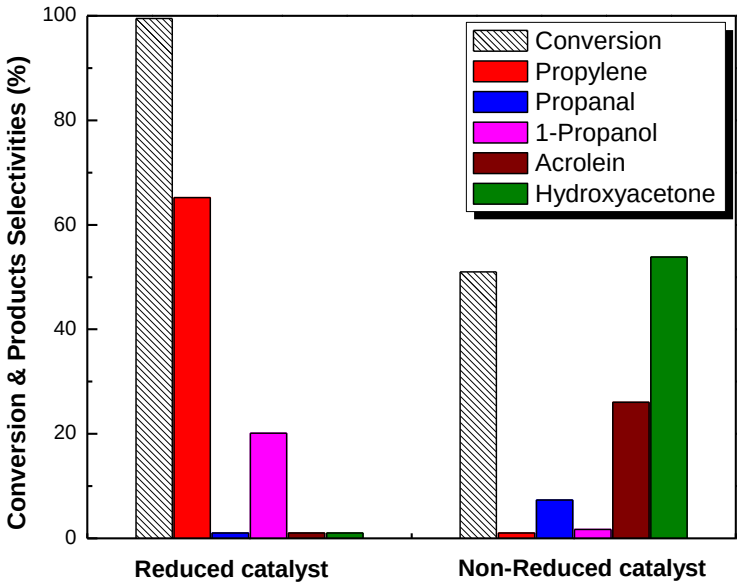
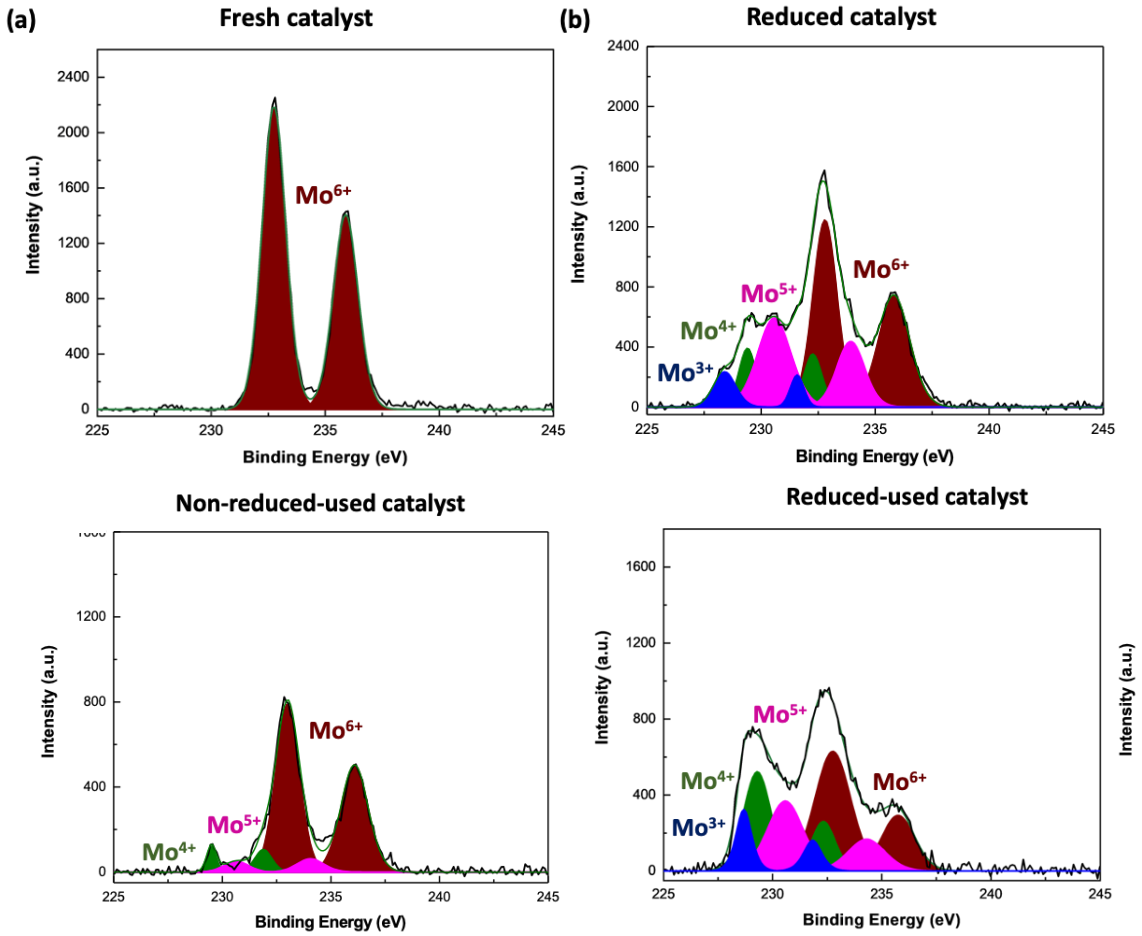


XPS spectra



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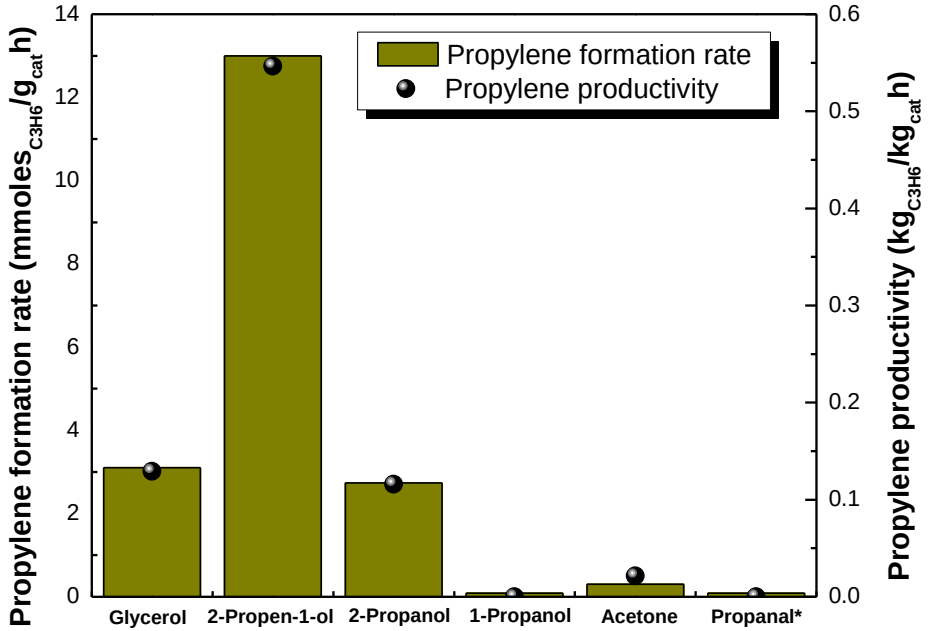
- ✓ Non reduced catalyst is less active and totally unselective to propylene

Ioannidou et al, Catal. Today 423 (2023) 113902

Main reaction pathways

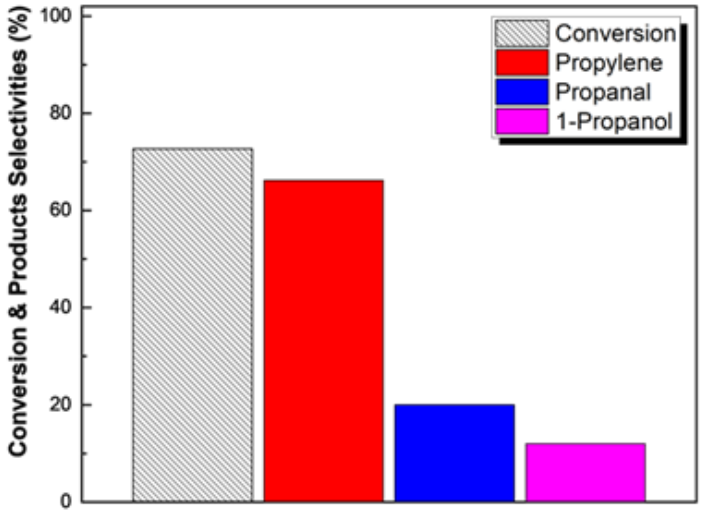
Reaction tests of partially deoxygenated compounds – possible intermediates

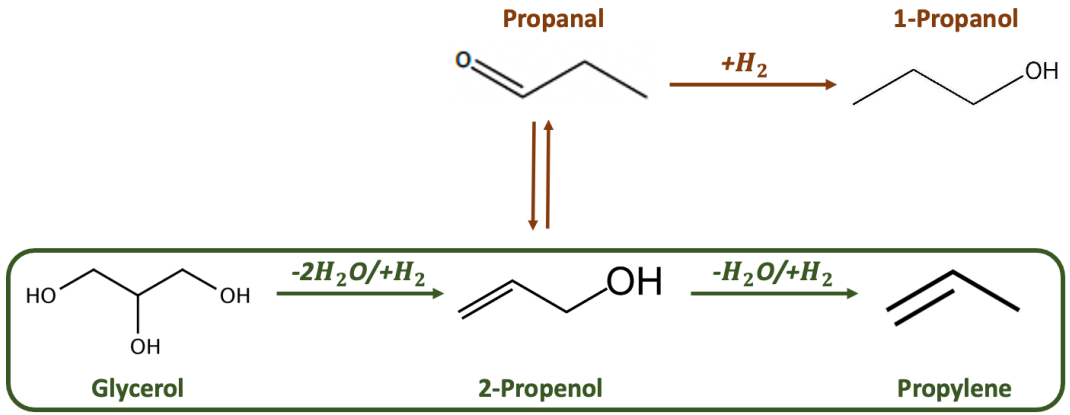
Reaction conditions: *T=280 °C, P_s=60 bar, LHSV=1.2 h^{-1}, TOS=4 h*



✓ **2-propenol** is the main reaction intermediate towards propylene

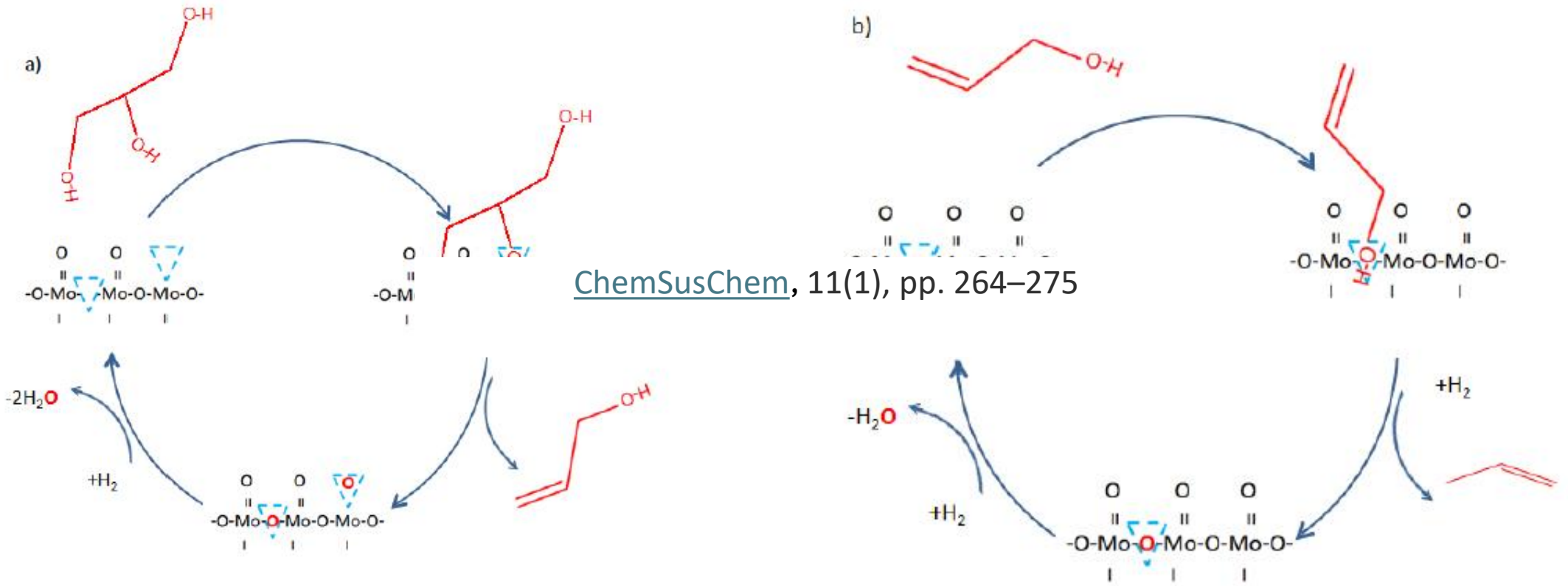
2-Propenol HDO





Ioannidou and Lemonidou, Green Chem., 25 (2023) 10043

Reverse Mars-van Krevelen mechanism



ChemSusChem, 11(1), pp. 264–275

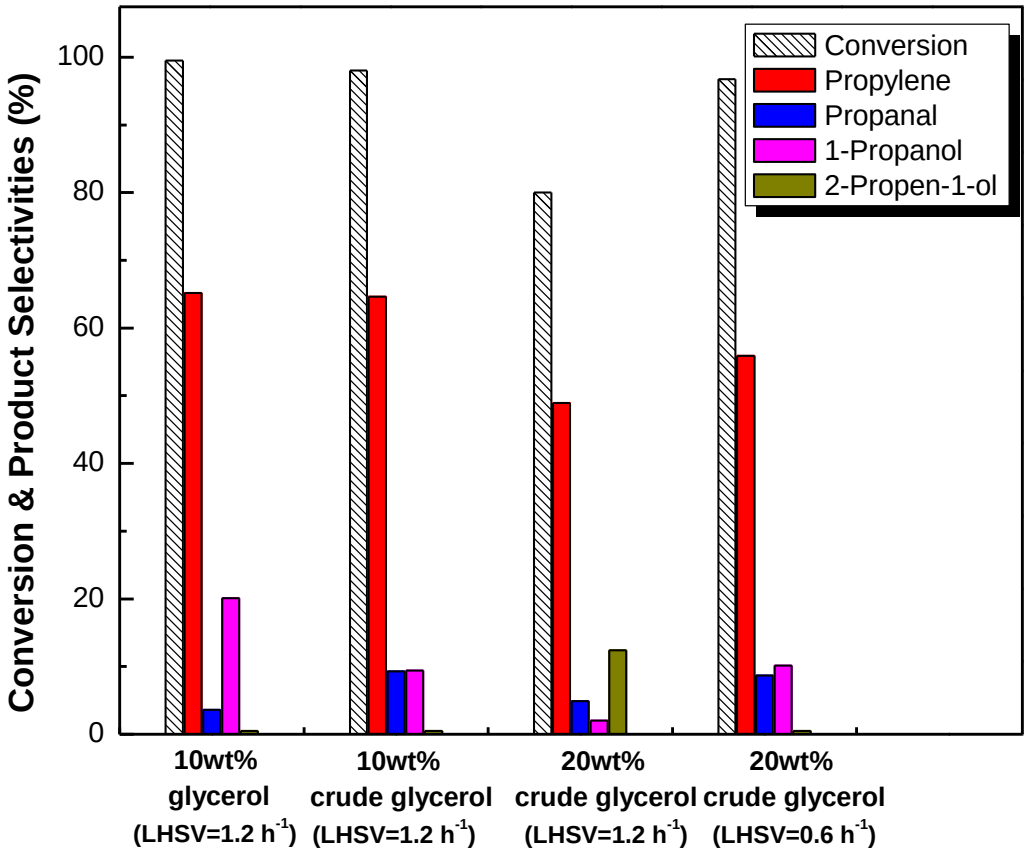
Zacharopoulou et al ChemSusChem, 11(1), (2018) 264–275
Ioannidou and Lemonidou, Green Chem., 25 (2023) 10043

Crude glycerol HDO to propylene

Crude glycerol Composition

91% glycerol, 3.5% H_2O, 3.5% MONG, 2% salts

Reaction conditions: *T=280 °C, P_s=60 bar, P^o_{H2}/ P^o_{glyc}=90, LHSV=1.2 h^{-1}, W/F=211 $g_{cat}/mol_{glyc}h$, TOS=4 h*



✓ Mo-based catalyst proved active and selective towards Propylene using crude glycerol

Concluding remarks

- Molybdena-based catalysts tested under batch and flow conditions showed a promising performance in one step glycerol hydrodeoxygenation yielding propylene (>65% yield)

- Pre-reduction of the catalyst is crucial for the formation of the active MoO_{3-x} species over which the C-O bond is selectively cleaved via the reverse Mars van Krevelen redox mechanism

- Hydrogen availability is the key parameter for the deoxygenation reaction towards propylene

- Preliminary testing with crude glycerol looks promising

Acknowledgments

RESEARCH – CREATE – INNOVATE
Glyco-Biodiesel project, code: T1EDK-02864

HELMHOLTZ
RESEARCH FOR GRAND CHALLENGES

HEPTA Project (collaboration KIT-AUTH)

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