

Oxidative Dehydrogenation (ODH) of Ethane on V-Mo-Nb-Te-O_x Catalyst:

- Effect of CH₄, CH₃OH, (CH₃S)₂, CO₂ and C₂H₄

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World Scale E/PE complex



- ❑ **Total ethylene production (6.7 bpy)**
 - **Joffre, Alberta – 4.8 bpy from ethane cracking**
 - **Corunna, Ontario – 1.9 bpy from liquid cracking**
- ❑ **Total polyethylene production (3.7 bpy)**

Background

- **Steam Cracking remains as the dominant process for large scale ethylene production**
- **SC processes are known to be intensive in CAPEX/OPEX, energy and emissions**
- **ODH process remains attractive due to significant reduction in process temperature (~400°C), which means less energy consumption and less emission**
- **Current development of V-Mo-Nb-Te-O_x catalysts has pushed ethylene yield close to that of conventional SC process.**
- **Many challenges remain before an ODH process becomes commercially viable**

Research Objectives

Typical laboratory scale tests for ethane ODH are carried out in *pure* gases

Objectives:

To evaluate the stability of V-Mo-Nb-Te-O_x catalysts in presence of typical impurity/recycle products for low temperature ODH process:

- Feed impurities: CH₄, CH₃OH and S-VOC (e.g., (CH₃S)₂).
- ODH products: C₂H₄ and CO₂,

Experimental Conditions

Catalyst:

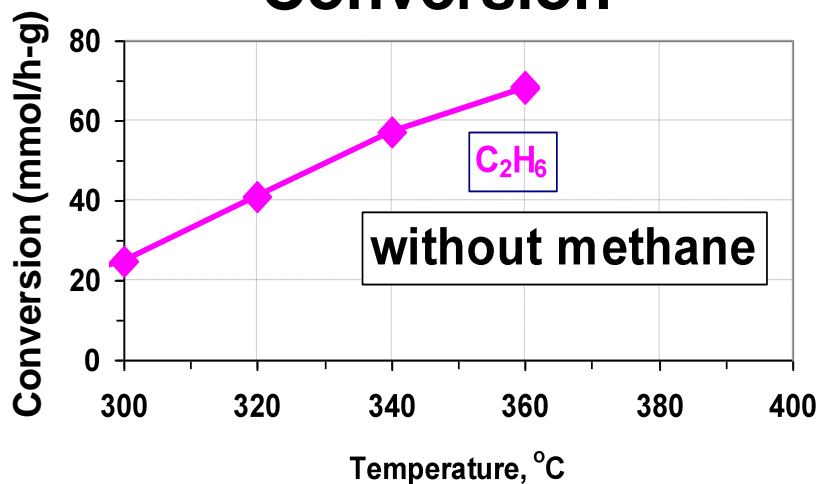
In-house made V-Mo-Nb-Te-O_x Catalyst

Reaction conditions:

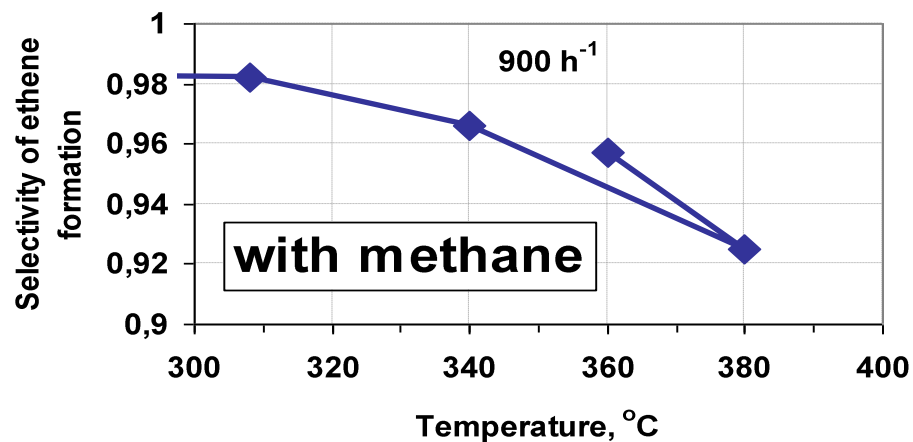
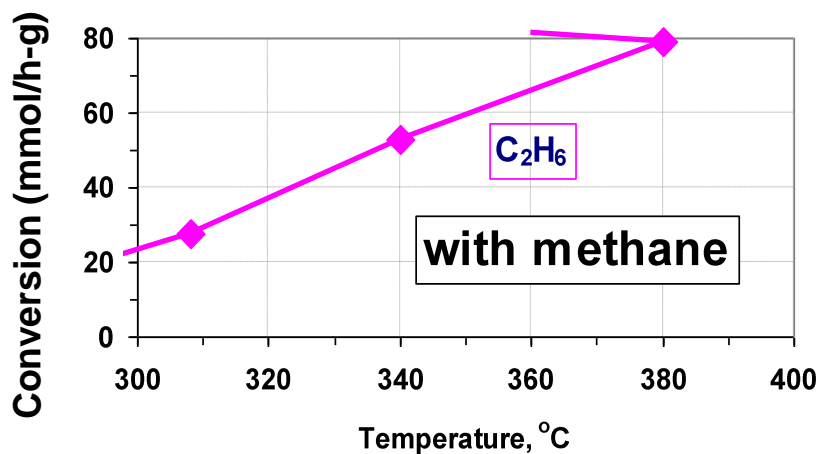
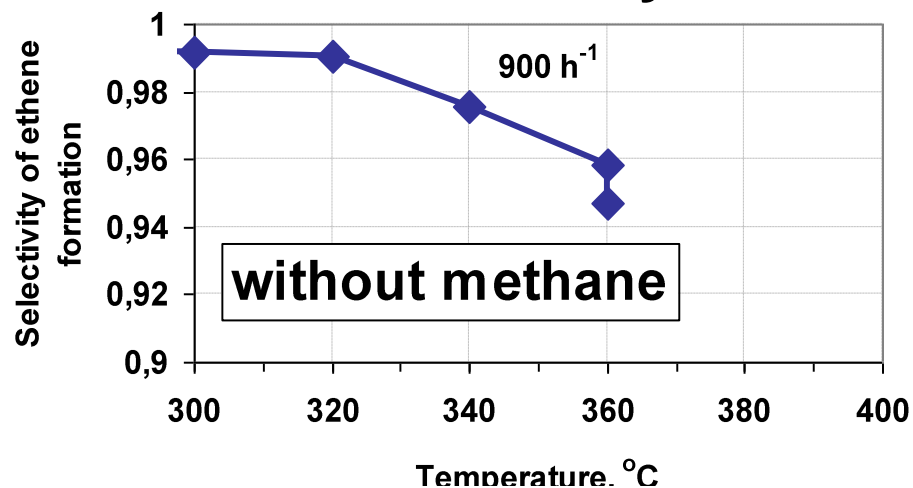
Temperature:	320 – 450°C
Pressure:	atmospheric pressure
Feed Mixture:	~ 75% C₂H₆ + ~ 25% O₂
HGSV:	900 - 18000 h⁻¹

Effect of CH₄ (+15% to the feed mixture)

Conversion

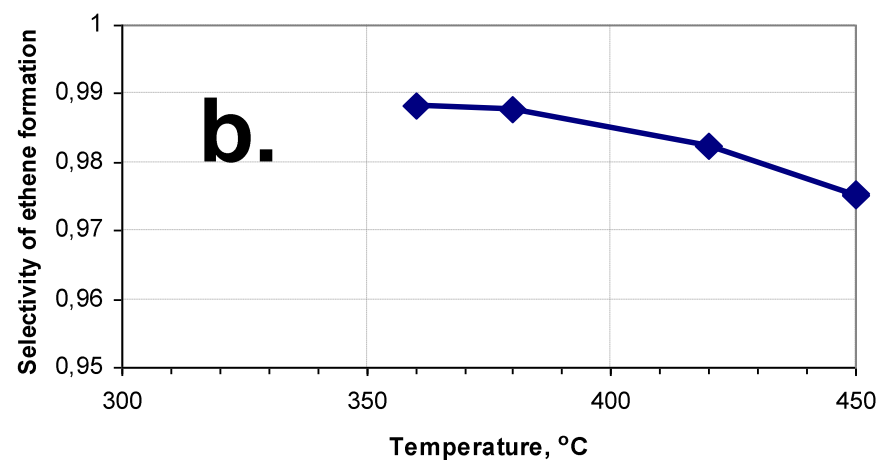
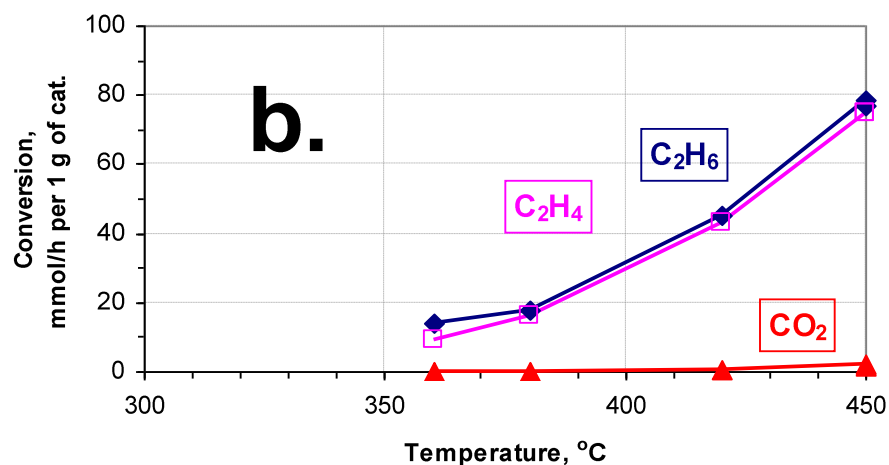
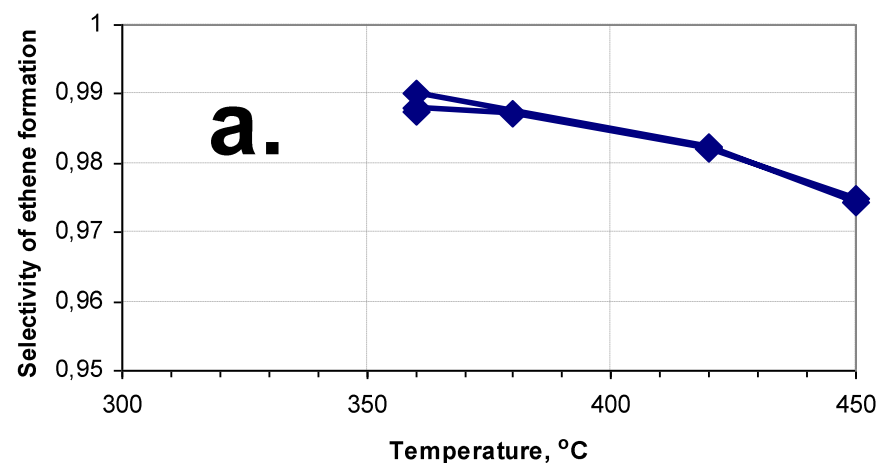
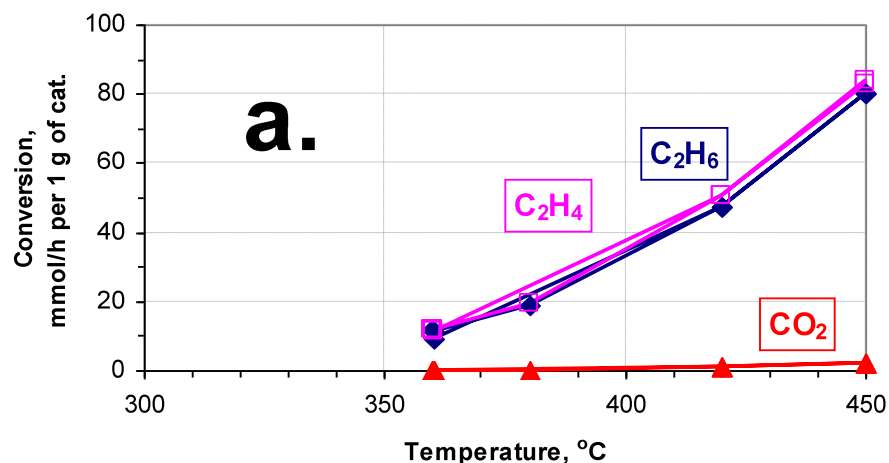


Selectivity



Methane behaves as a pure diluent

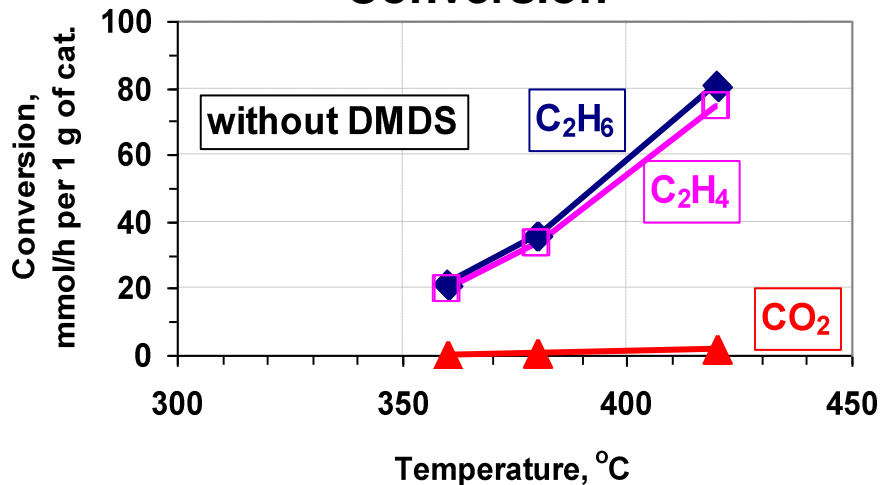
Effect of MeOH (+2000 wppm to the feed mixture)



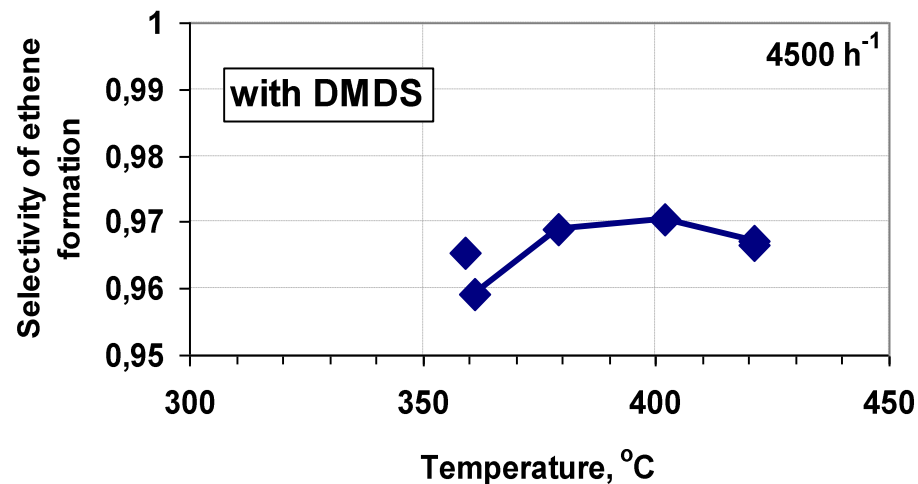
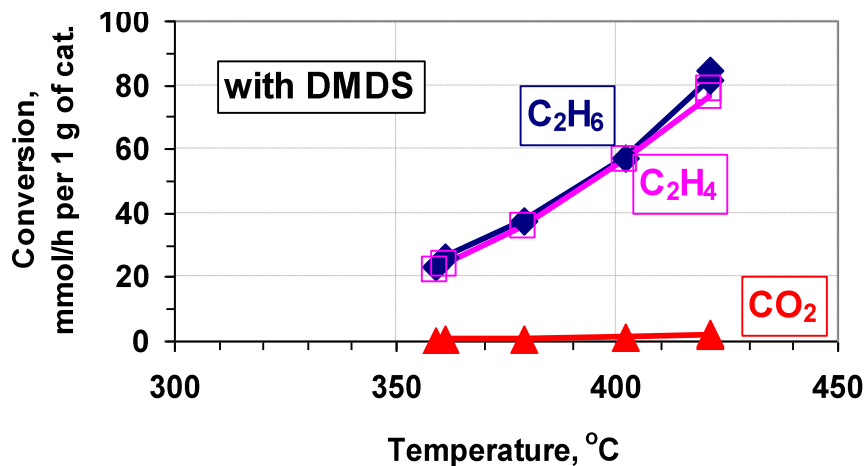
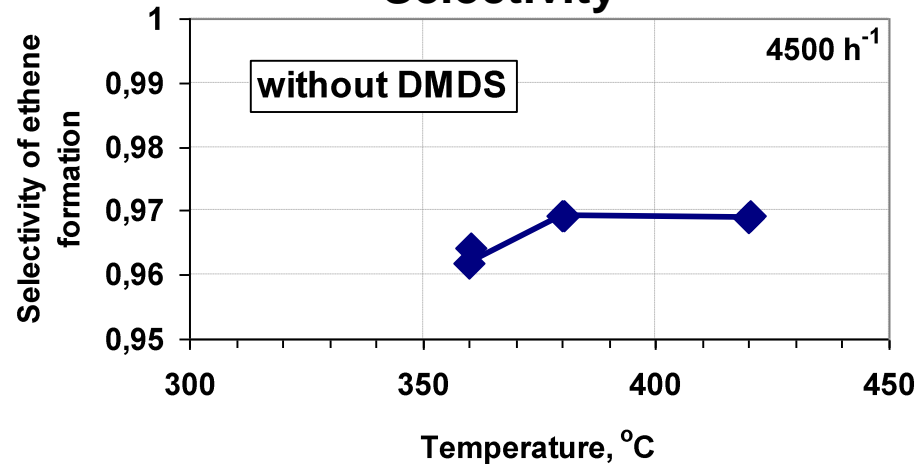
MeOH (0.2wt%) causes negligible change in ethane ODH

Effect of S-VOC (+1000 wppm DMDS as S-VOC)

Conversion

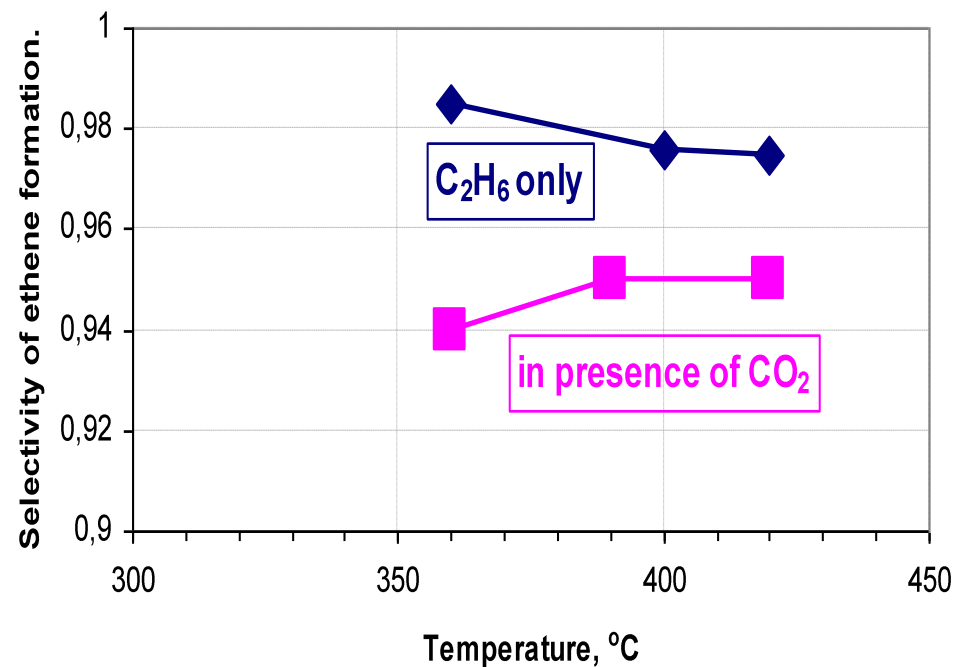
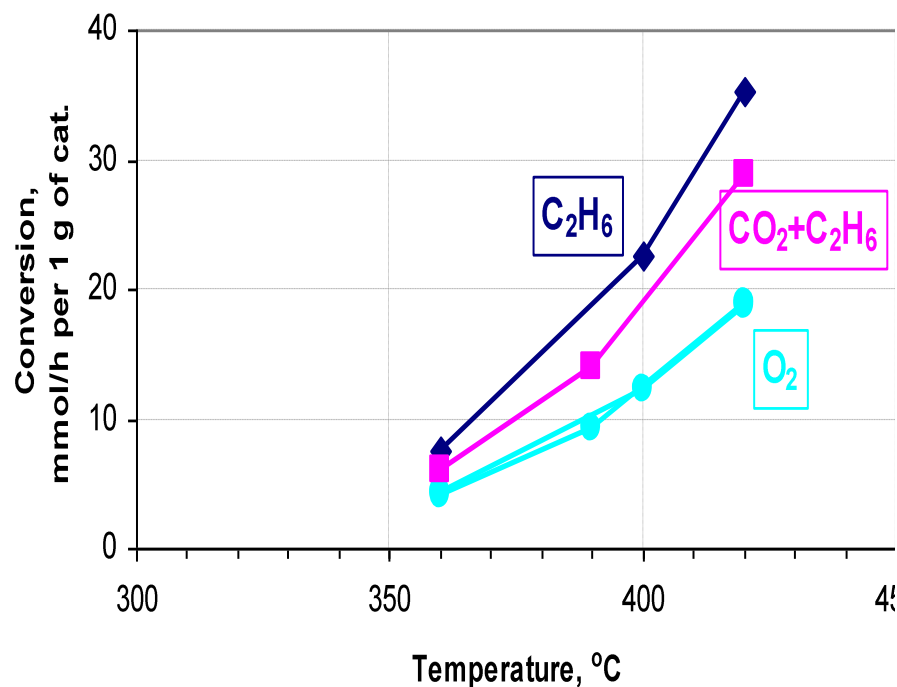


Selectivity



DMDS shows negligible impact on ethane ODH

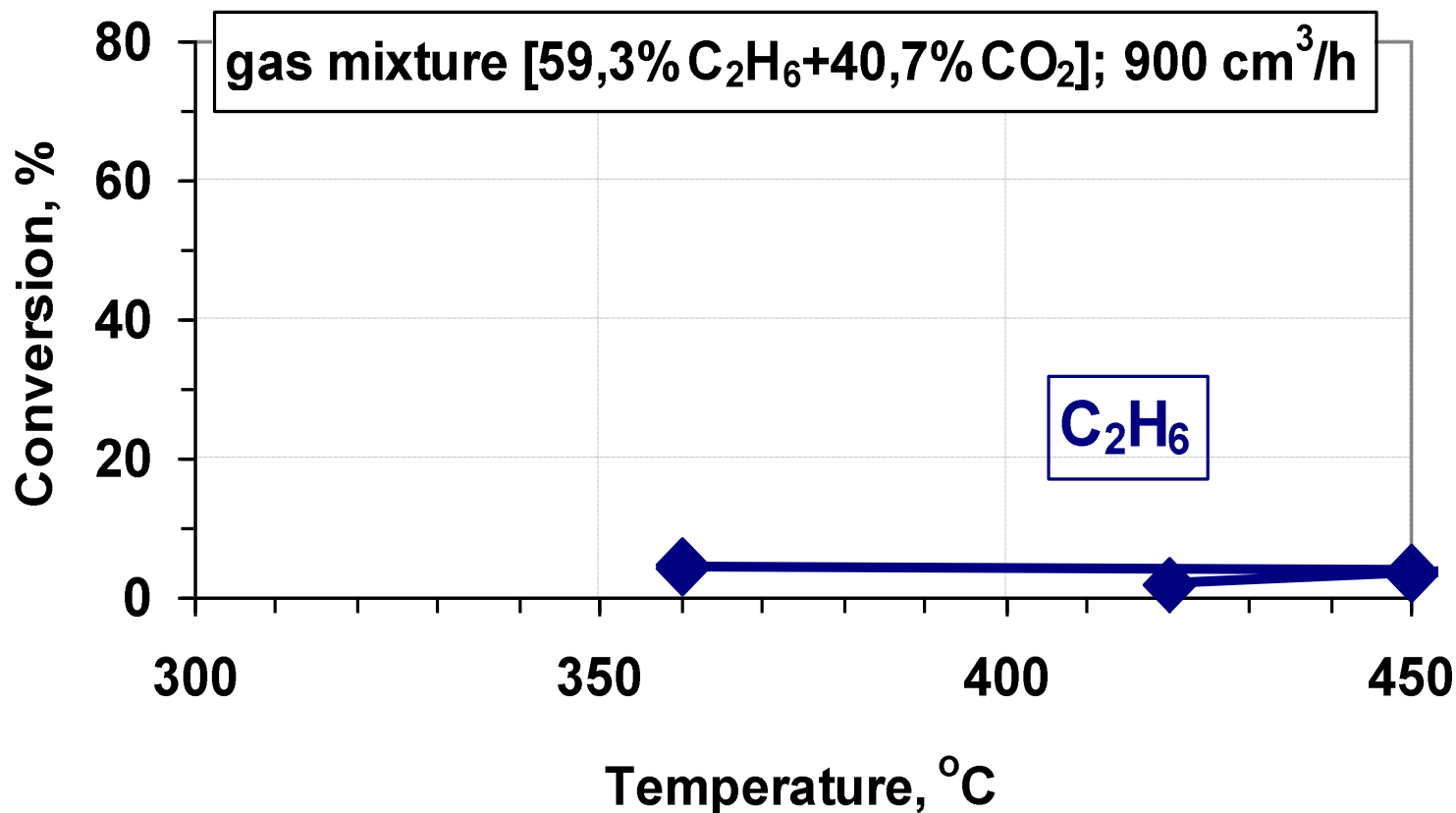
Effect of CO₂ (+32wt% to the feed mixture)



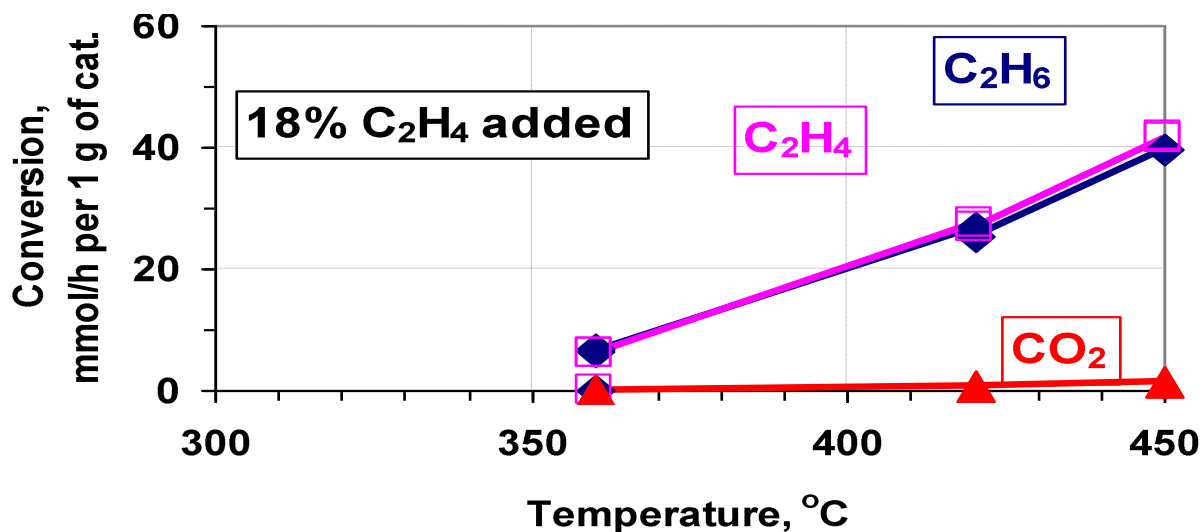
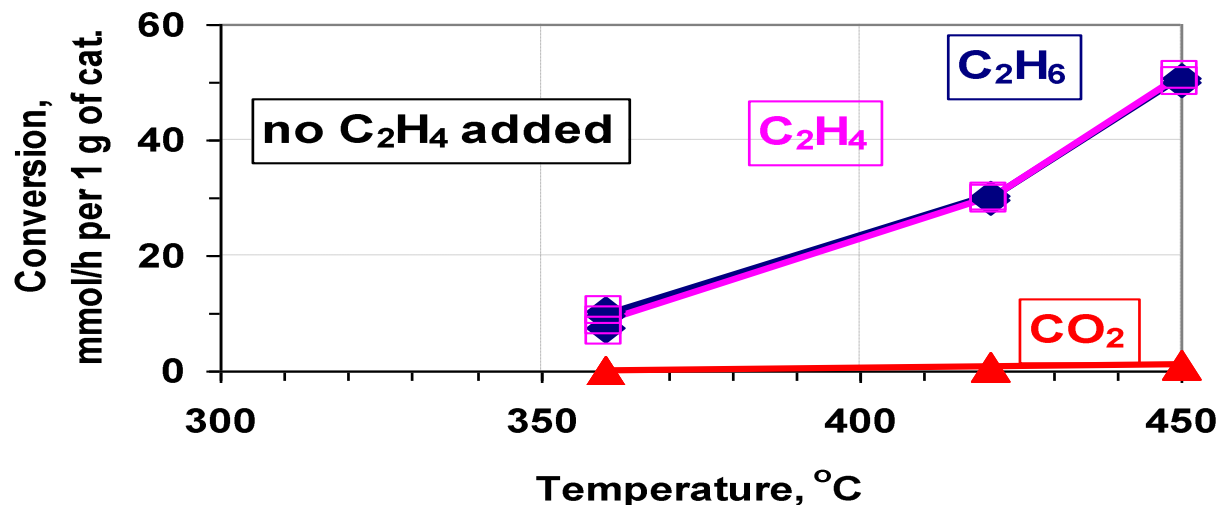
The presence of CO₂ shows detectable influence on both conversion and selectivity

Effect of CO₂ (addition of CO₂ to Ethane ONLY)

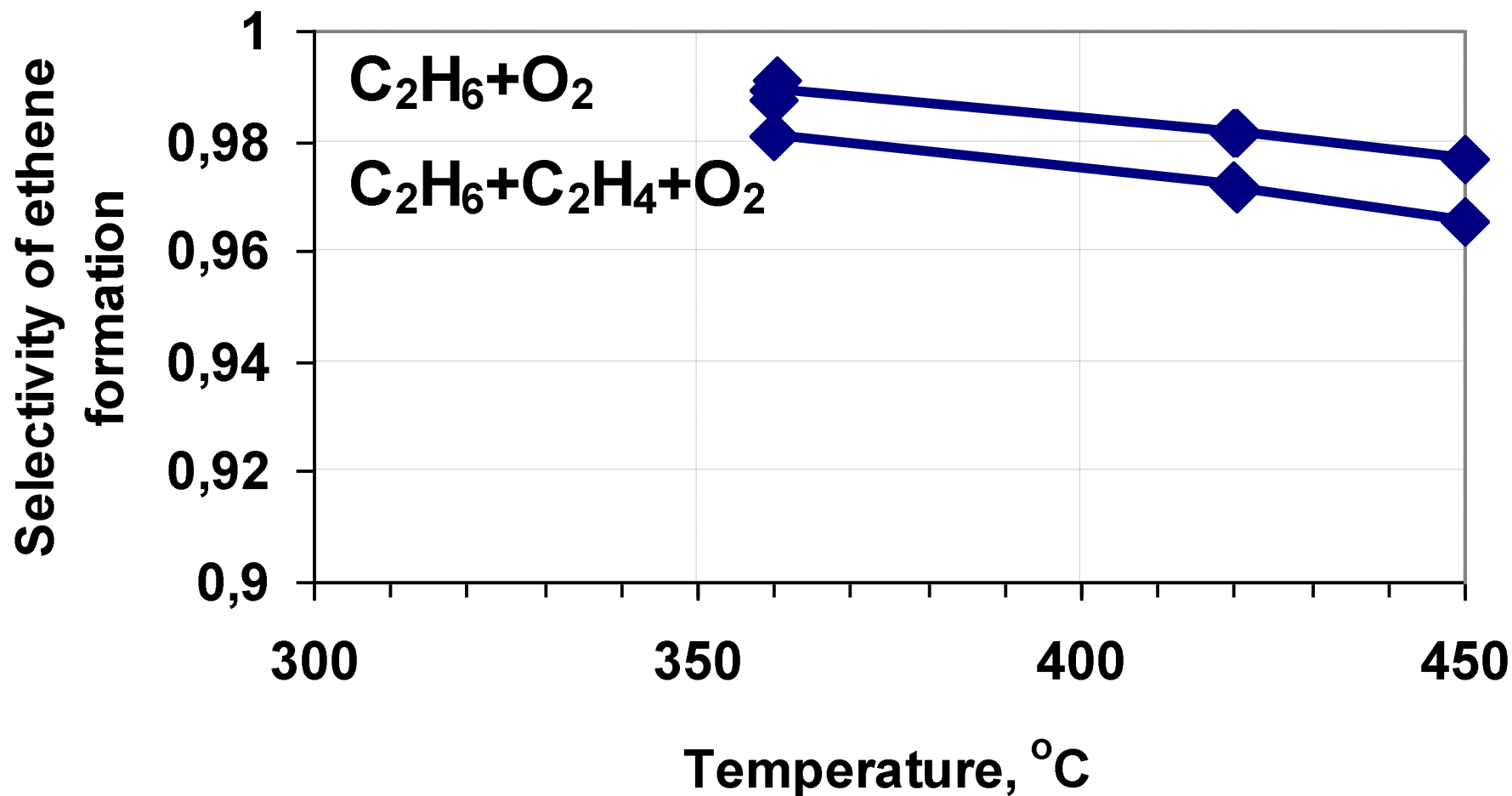
CO₂ (pure CO₂, no oxygen in the reaction mixture)



Effect of Ethylene (+18wt% to the feed mixture)

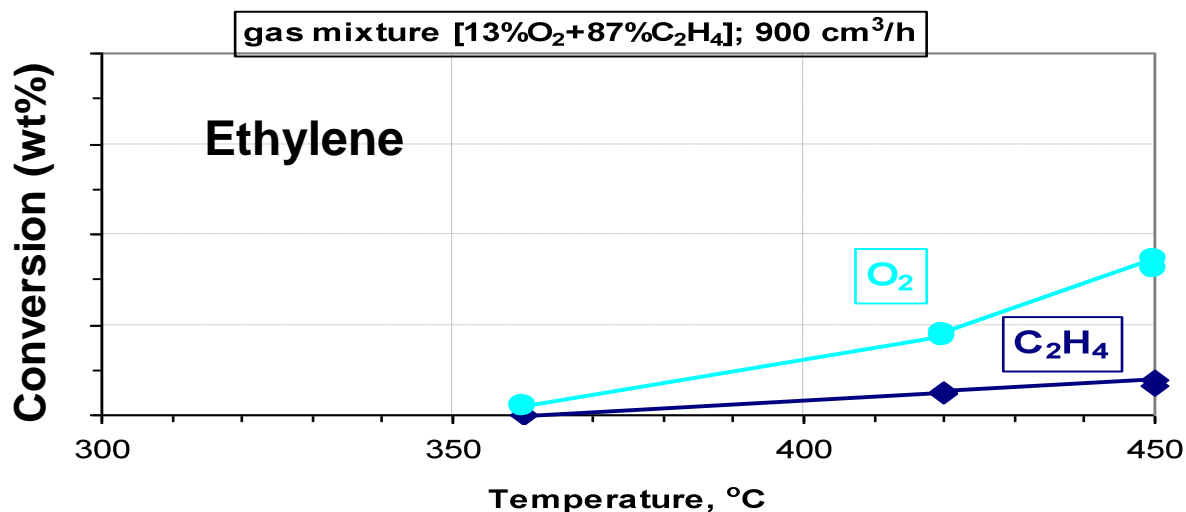
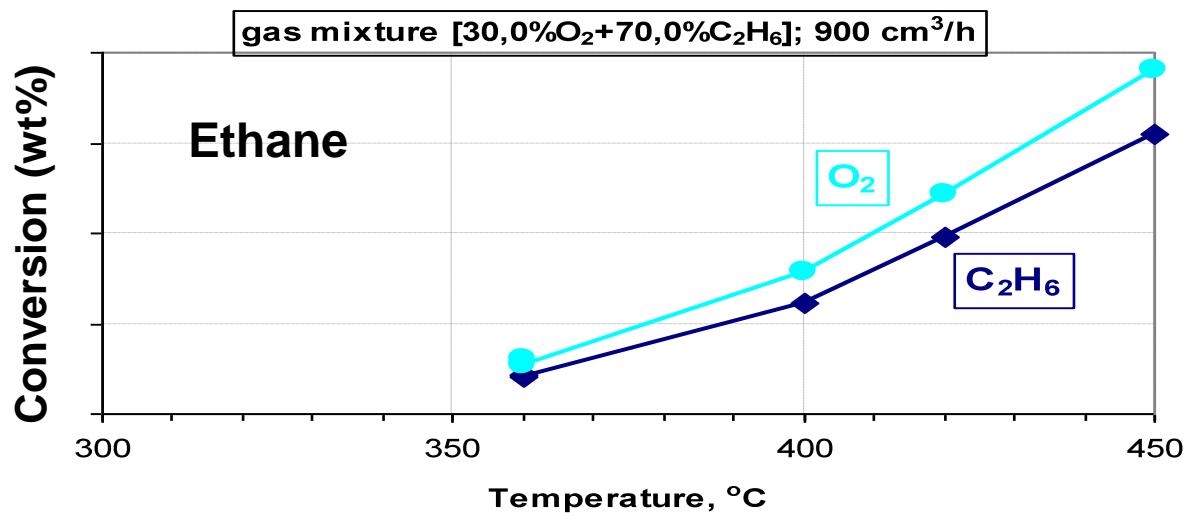


Effect of Ethylene (+18wt% to the feed mixture)





Effect of Ethylene (Ethane versus Ethylene)

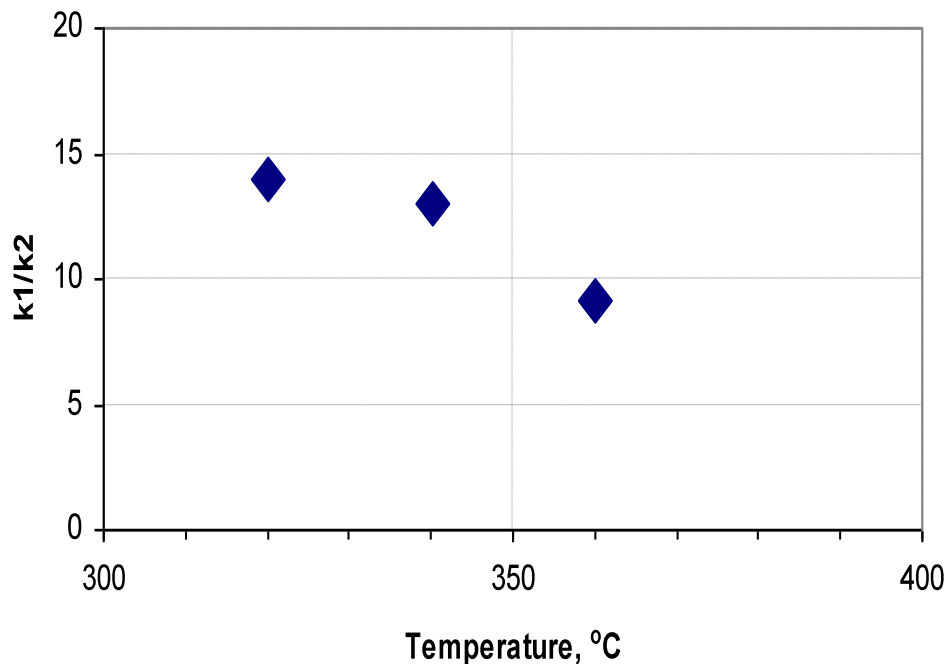


Effect of Ethylene (Ethane vs Ethylene)

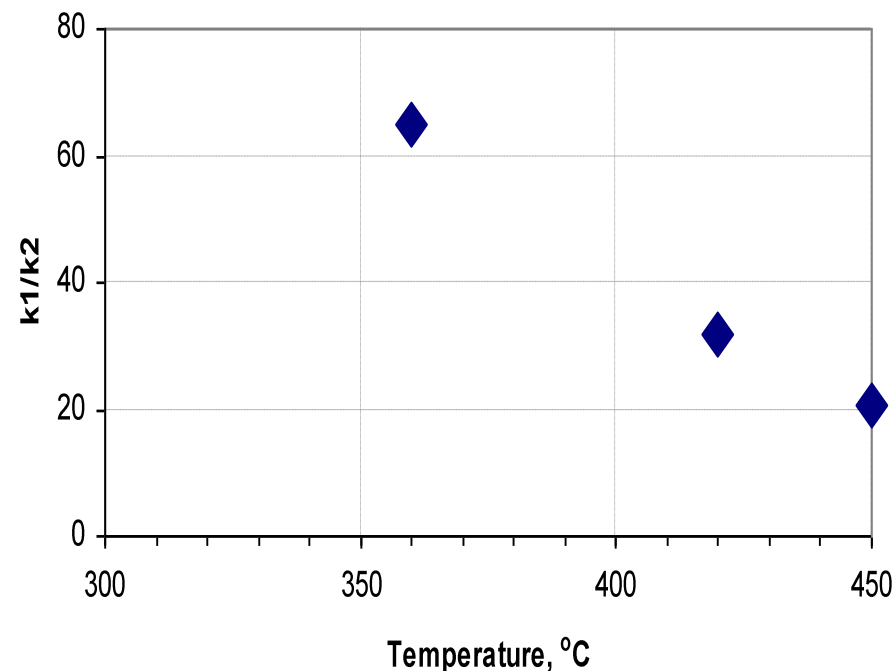
Ratio of Reaction Rates between:

- [ethane oxidation \rightarrow ethylene] (k_1), and
- [ethylene oxidation \rightarrow CO₂] (k_2)

HGSV = 900 h⁻¹



HGSV = 4500 h⁻¹



Concluding Remarks

- As an impurity, **methane did not show any impact** on ethane ODH reactions
- The presence of **MeOH** (2000ppm) and **S-VOC** (DMDS at 1000ppm) had **negligible impact** on selectivity. However, the long term impact of S (e.g., SO_x) remains to be investigated
- The presence of **CO₂** caused a **3-5% reduction** in both ethane conversion and ethylene selectivity (mechanism unknown)
- Competing with ethane ODH, **ethylene converts to CO₂** at about one order of magnitude lower than ethane ODH reaction
- A recycling operation appears to be viable for ethane ODH when the ethane contains expected industrial impurities.
- Low temperature ethane ODH remains to be a promising process, however, many technical challenges remain to be overcome

Acknowledgement ...

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