Effect of impurities on hydrogenation of CO_2 Master's thesis

NEO CARBON ENERGY

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Neo-Carbon Energy seminar

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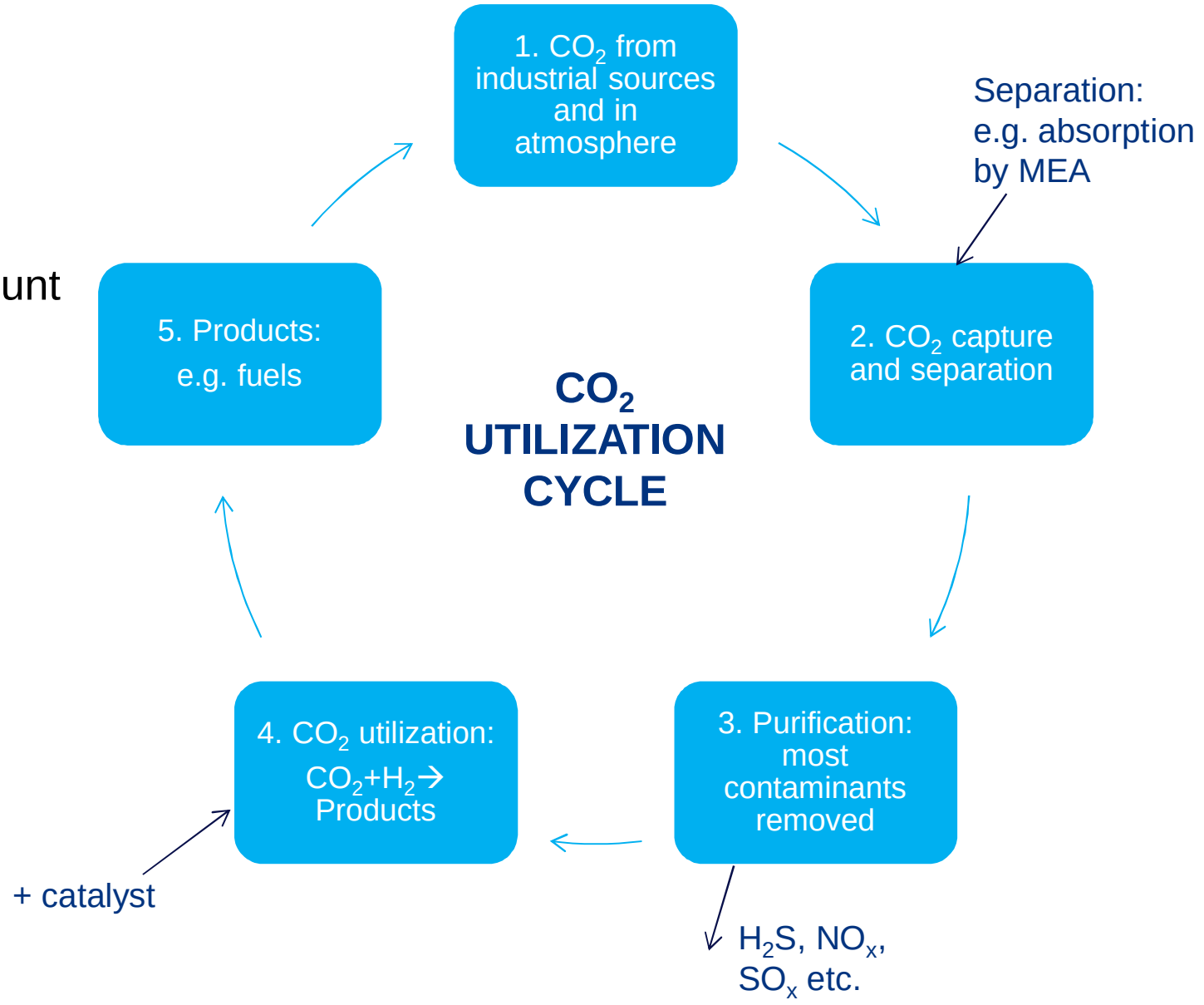
Structure

- Motivation and aim
- Experimental part
- Results

Motivation and aim

Motivation

- Reduce CO_2 emissions
  - 1) decrease amount of CO_2 produced
  - 2) CO_2 storage
  - 3) CO_2 utilization



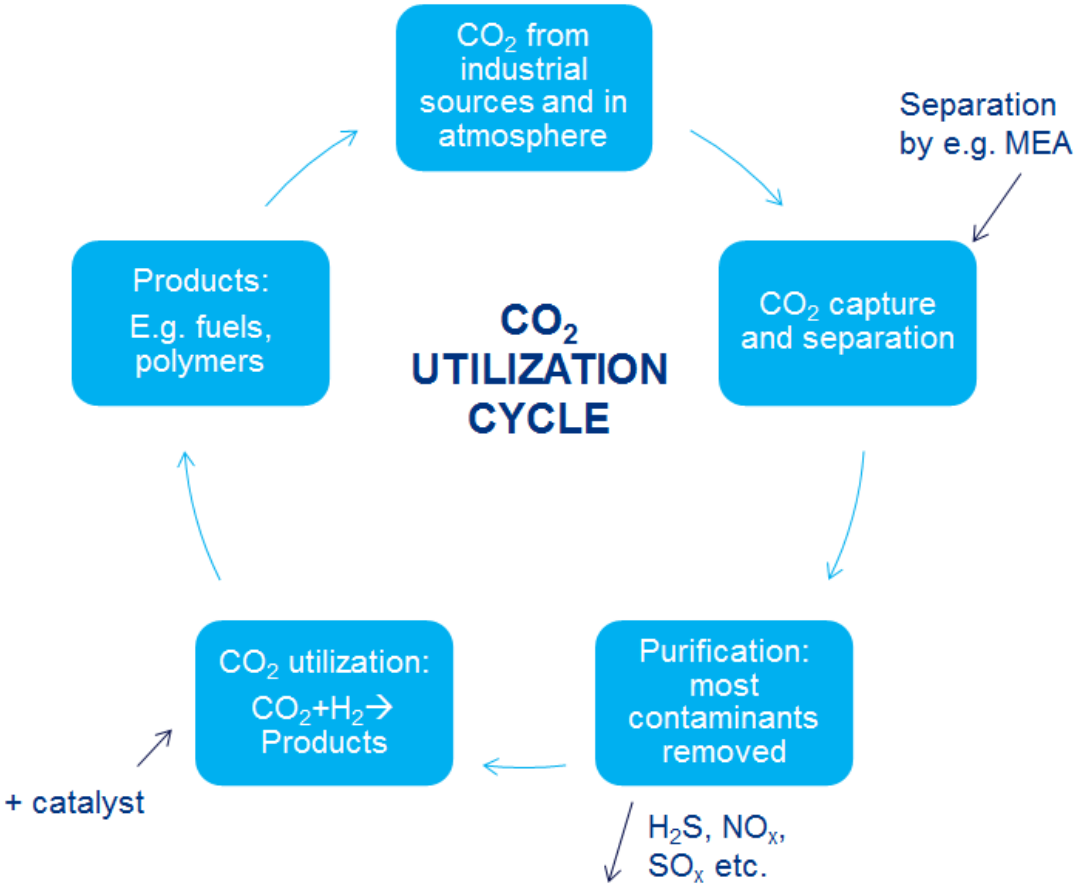
Aim

Aim:

- Find out how impurities in separated CO_2 affect CO_2 hydrogenation and catalyst used

Special emphasis:

- Effect of MEA and H_2S on product formation
- MEA was selected due to lack of earlier studies
- H_2S was selected since it is a typical catalyst poison, common impurity and due to contradictory in earlier studies



CO_2 hydrogenation reactions and catalysts

1. $CO + H_2O$ RWGS
2. $CO + 2\ H_2$ $-(CH_2)-$ $+ H_2O$ Fischer-Tropsch synthesis
3. $CO_2 + 4H_2$ $CH_4 + 2H_2O$ Methanation
4. $CO_2 + 3H_2$ $CH_3OH + H_2O$ Methanol synthesis

- Different catalysts favour different reactions
- Cu-based: Methanol synthesis & RWGS
- Ni-based: Methanation
- Fe-based: RWGS & FT synthesis

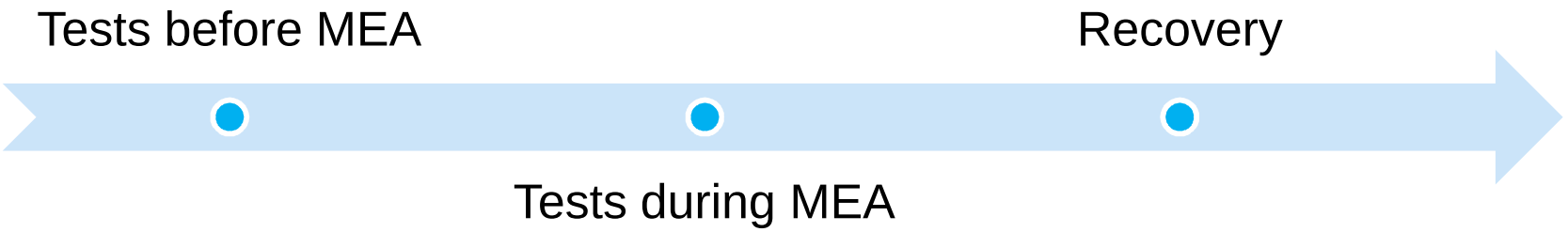
Experimental part

Experiments

- Temperature programmed desorption (TPD) experiments
  - Effect of MEA studied
  - Gas analyzed by MS
  - Catalyst characterization and formation of CH_4 studied
- Reaction tests in a plug flow reactor(PFR)
  - Effect of H_2S studied
  - Gas analyzed by GC
  - Detailed information about type and amount of product formed

Both experiments focus on CO_2 + H_2 → products

TPD experiments

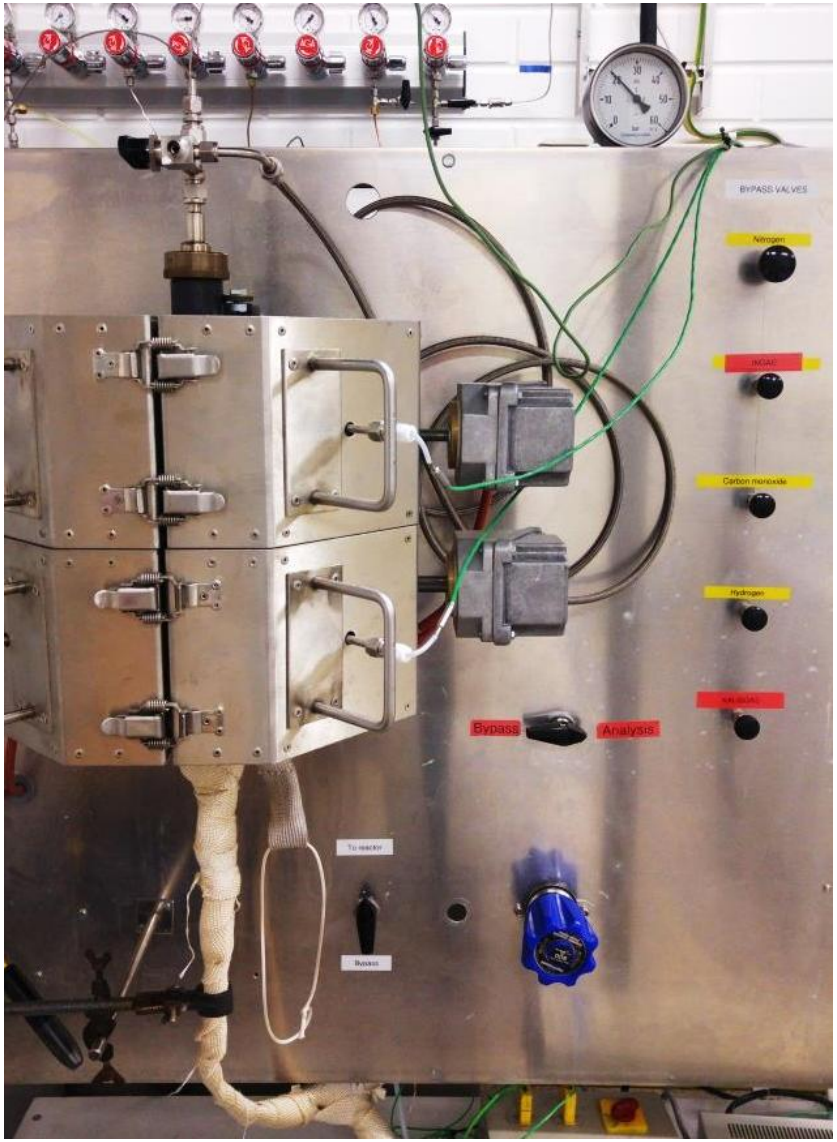


Reaction tests in 300 ^{o}C in atmospheric pressure:

- Effect of MEA studied
  - MEA (573 ppm) connected to carrier gas
- Formation of CH_4 followed
- Constant H_2 flow, to which CO_2 is pulsed

Reaction tests in PFR

- Effect of H_2S studied
- Pre-mixed reactant gas → continuous reaction
- Five phases for each catalyst
    1. Initial reaction
    2. 1st poisoning
    3. 1st recovery
    4. 2nd poisoning
    5. 2nd recovery



Catalysts

- Four different catalysts studied
  - 2xFe-based → FT products
  - Cu: → CH_3OH
  - Ni: → CH_4

Name	Components	Pellet size (mm)	Density (g/cm3)	BET surface area (m2/g)	Producer	Experiments
FeMn	5Fe:5Mn:Al2O3	~7x1.2	0.42	200	in-house	TPD & PFR
low α -Fe	100Fe:4.6Si:2Cu:1.4K	pulverized	Unknown	Unknown	in-house	TPD & PFR
Cu	Unknown*	1.5x1.5	1.8	64.8	BASF	TPD & PFR
Ni	Unknown**	0.2-0.3	Unknown	Unknown	BASF	TPD

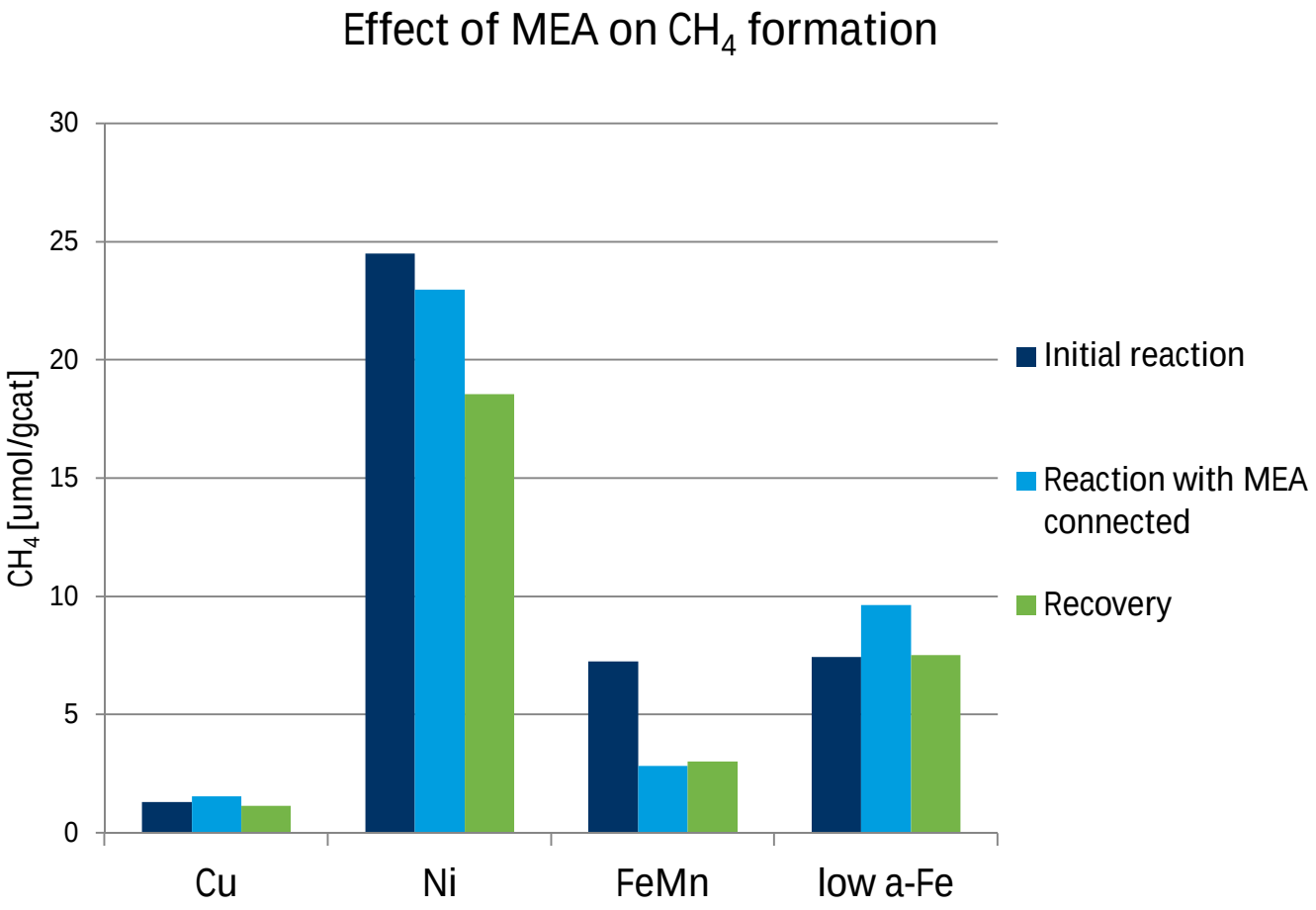
* CuO: 50<wt%<75, ZnO 15<wt%<20

**NiO: 15 wt%

Results

TPD – Effect of MEA

- MEA has an
  - increasing effect on CH_4 formation for Cu and low a-Fe catalysts
  - decreasing effect on CH_4 formation for Ni and FeMn catalysts, from which the catalyst does not recover



Reaction tests – Effect of H_2S on Cu catalyst

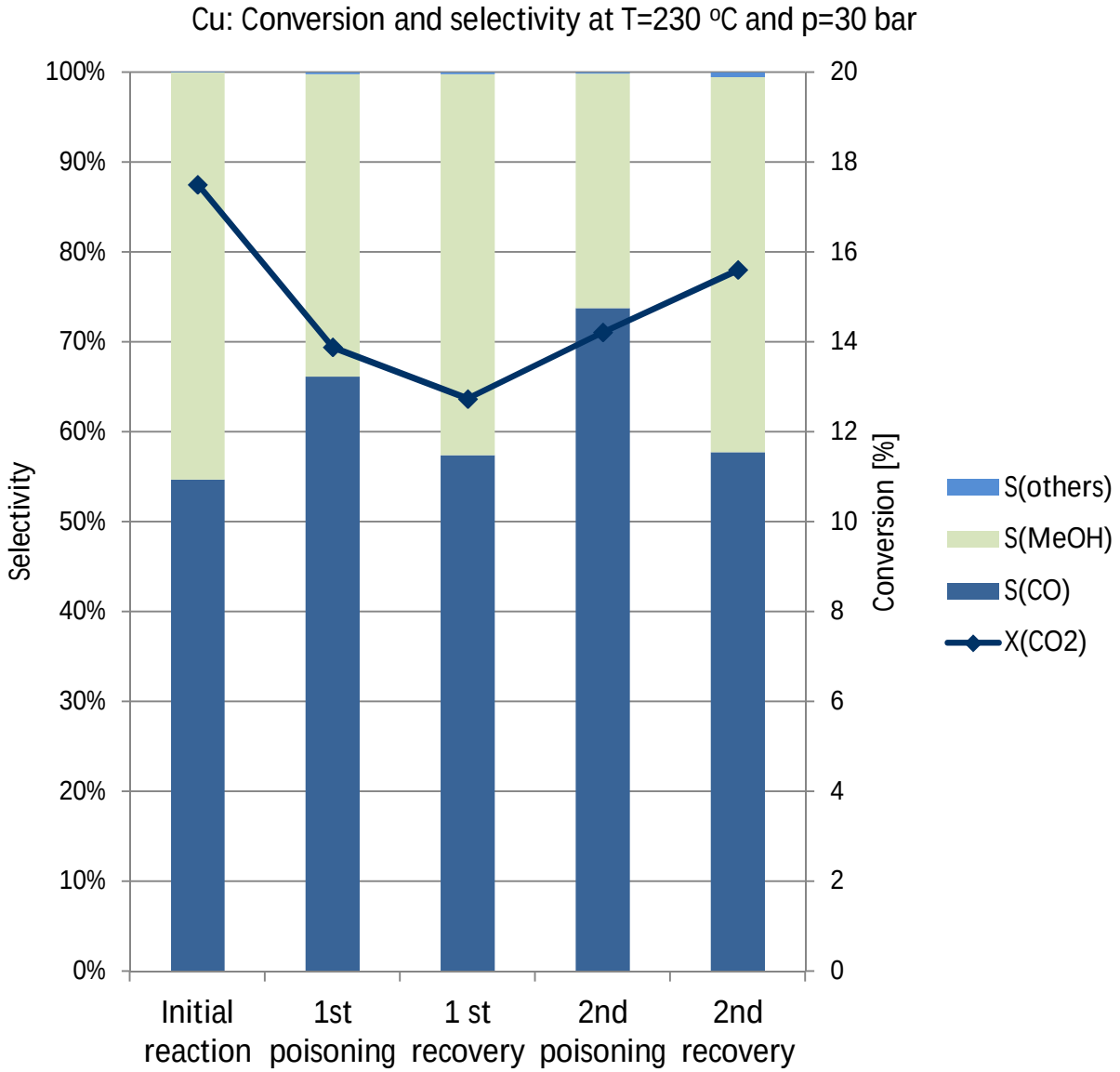
- 1st poisoning: 33.2 ppm
- 2nd poisoning: 60 ppm

- Conversion drops slightly, but recovers
- Methanol selectivity decreases during poisoning

→Surprisingly good resistance against H_2S

→Selectivity change due to:

- →RWGS being more spontaneous than the methanol synthesis
- →lower WHSV during poisoning→decomposition of methanol to CO

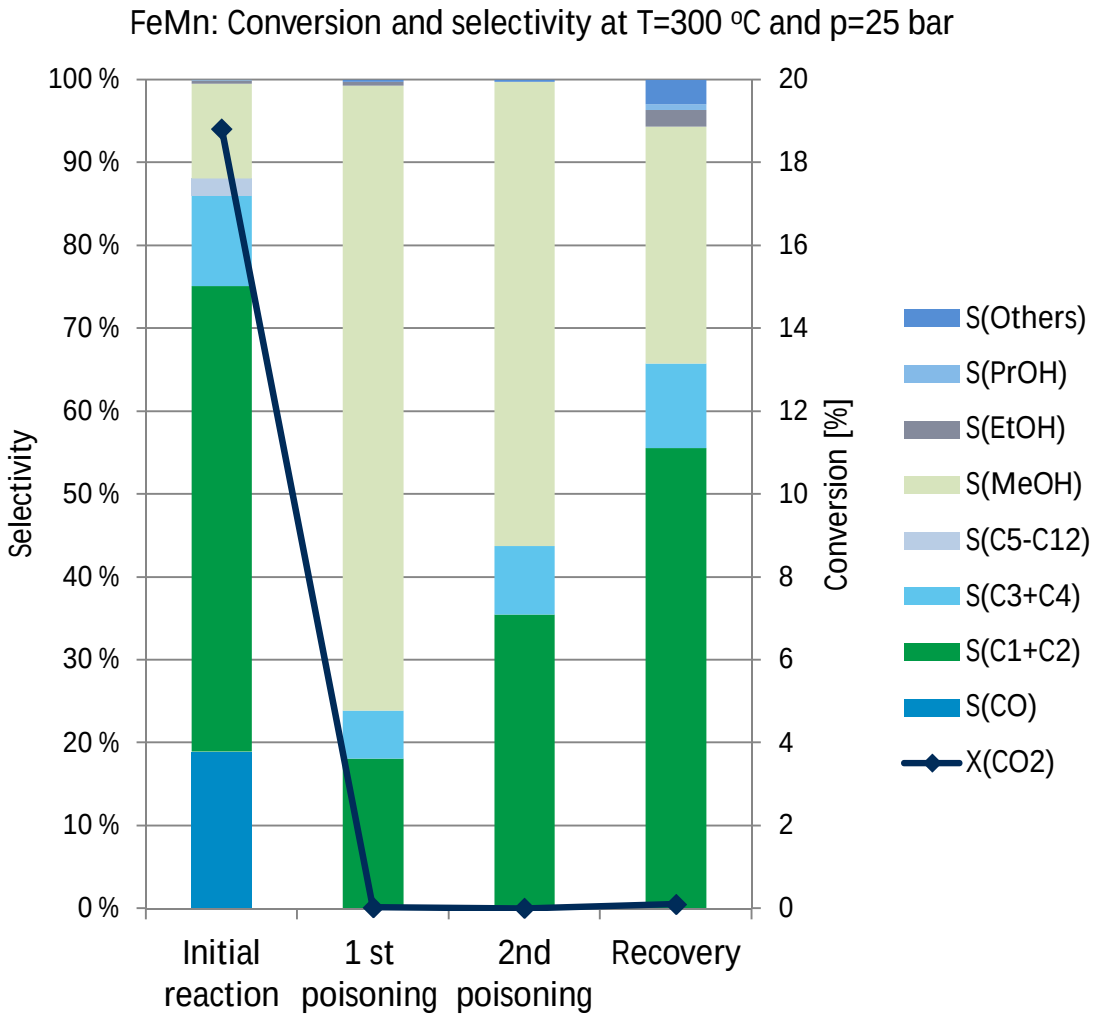


Reaction tests – Effect of H_2S on FeMn catalyst

- 1st poisoning: 33.2 ppm
- 2nd poisoning: 59.8 ppm

- Catalyst deactivates at 1st poisoning
- Catalyst does not recover

→Sensitive to H_2S poisoning

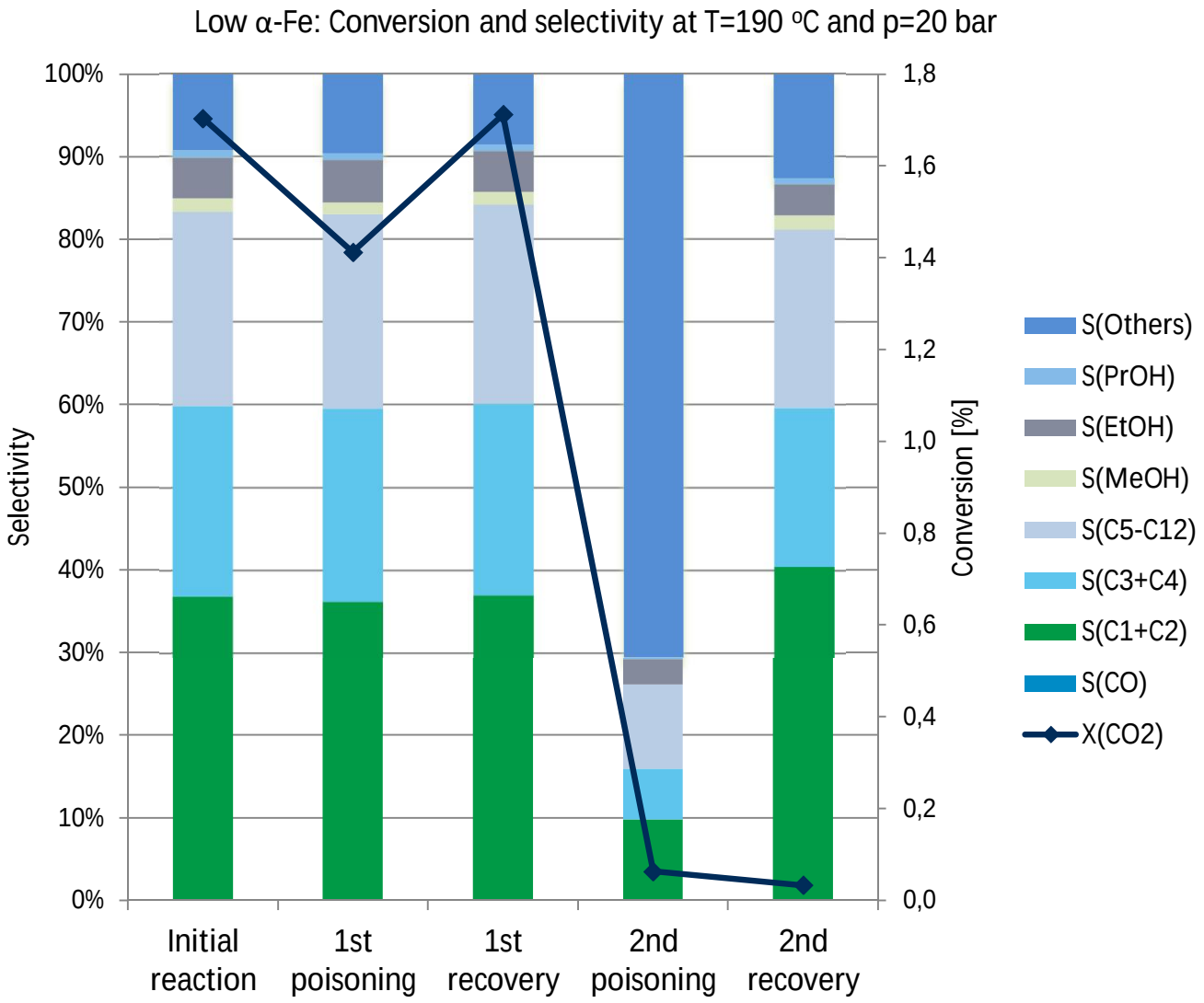


Reaction tests – Effect of H_2S on low a-Fe catalyst

- 1st poisoning: 1.1 ppm
- 2nd poisoning: 63.2 ppm

- Catalyst deactivates during 2nd poisoning and does not recover
- Selectivities remain unaffected

→Some (or most) sites deactivate completely, while others remain unaffected



Conclusion

Effect of MEA

- Cu & low a-Fe catalysts improved their formation of CH_4
- Negative effect on other catalysts

→ Future studies should focus on studying selectivities in detail to confirm whether MEA actually has an increasing effect on CH_4 formation

Effect of H_2S

- Cu catalyst: Surprisingly resistant to H_2S, but selectivity was modified
- Fe-based catalysts: Deactivated and did not recover

→ The effect of lower concentrations of H_2S could be studied for Fe-based catalysts

References

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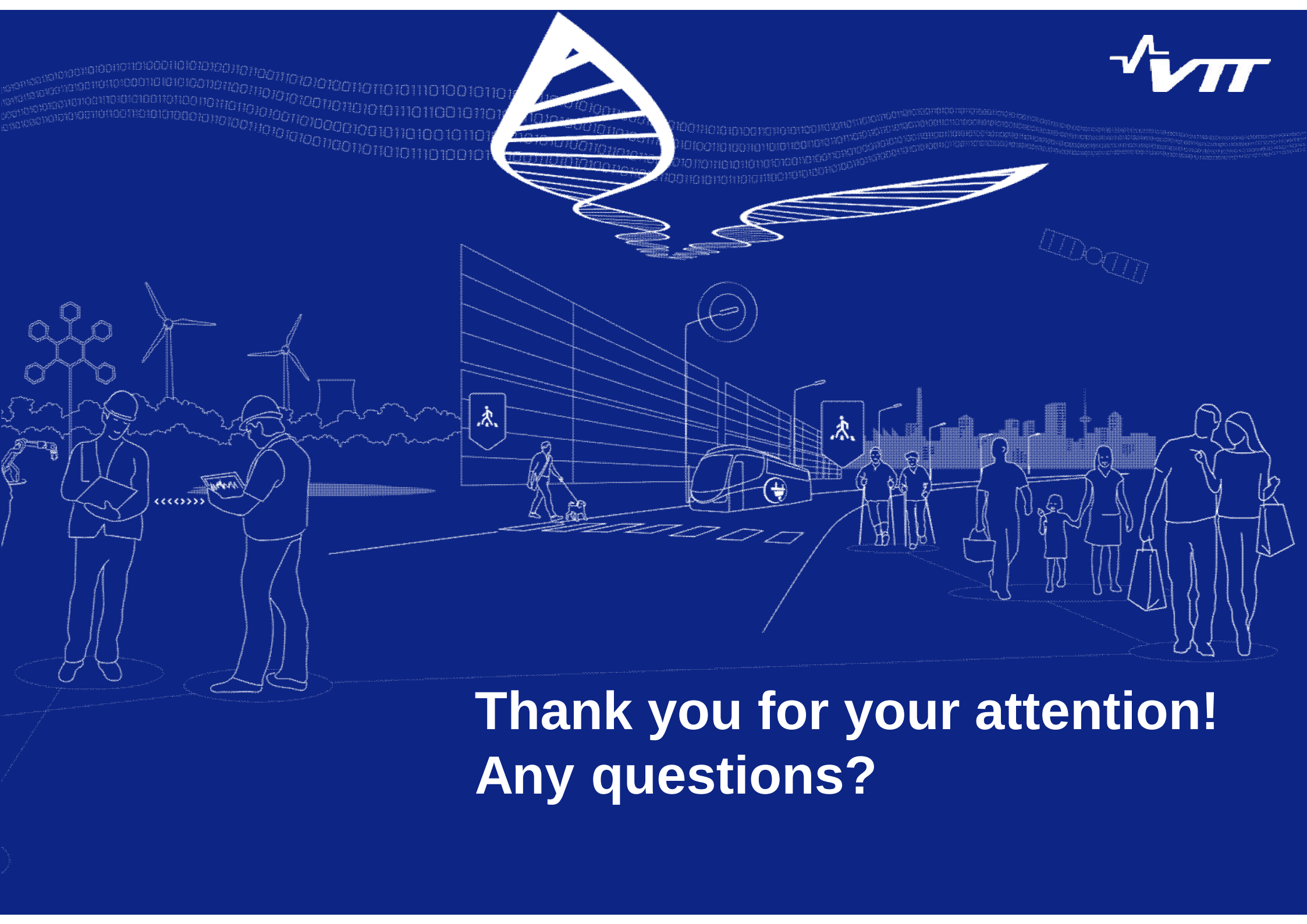

Thank you for your attention!
Any questions?