Synthesis of mixed alcohols over K-Ni-MoS_2 catalysts

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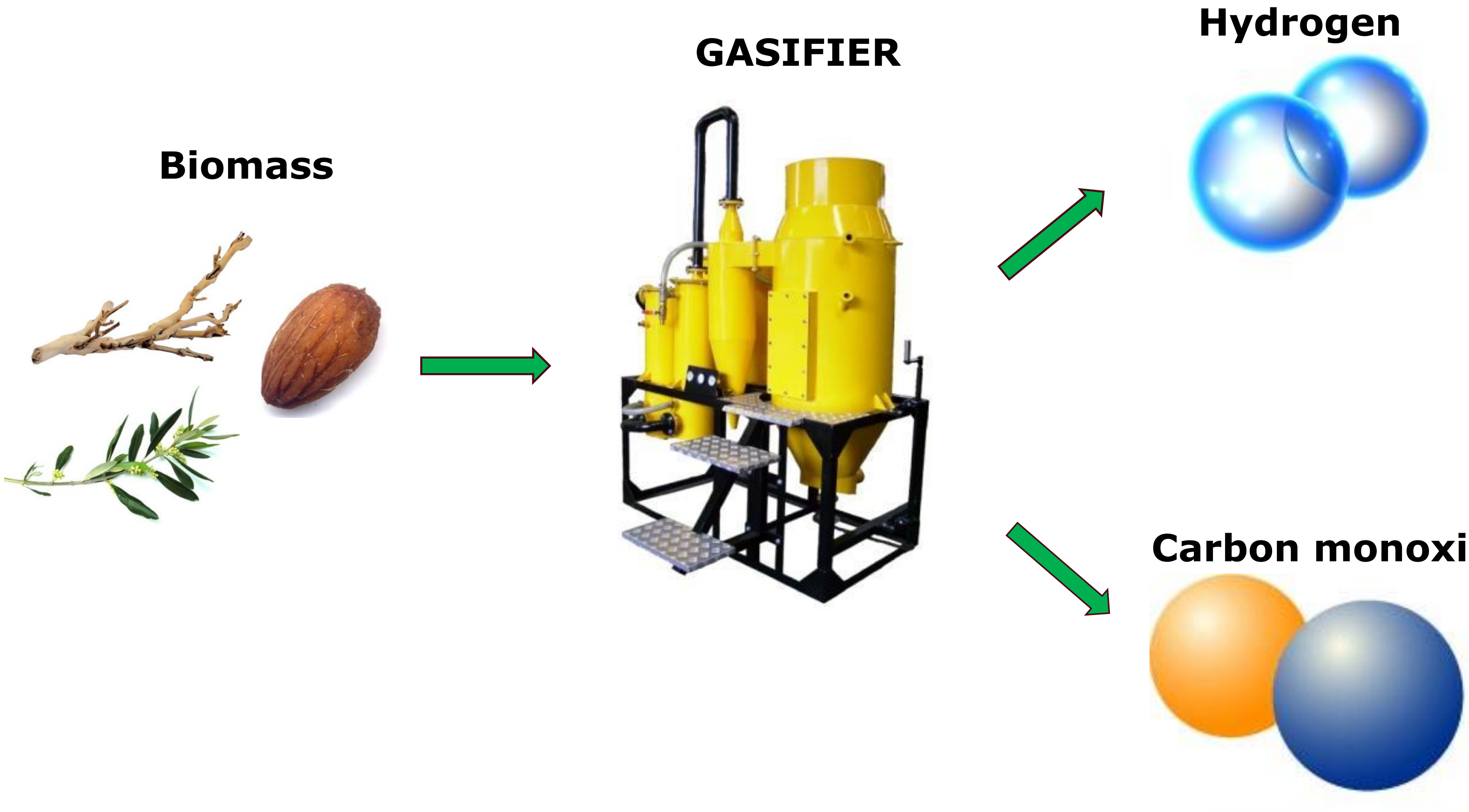
OUTLINE

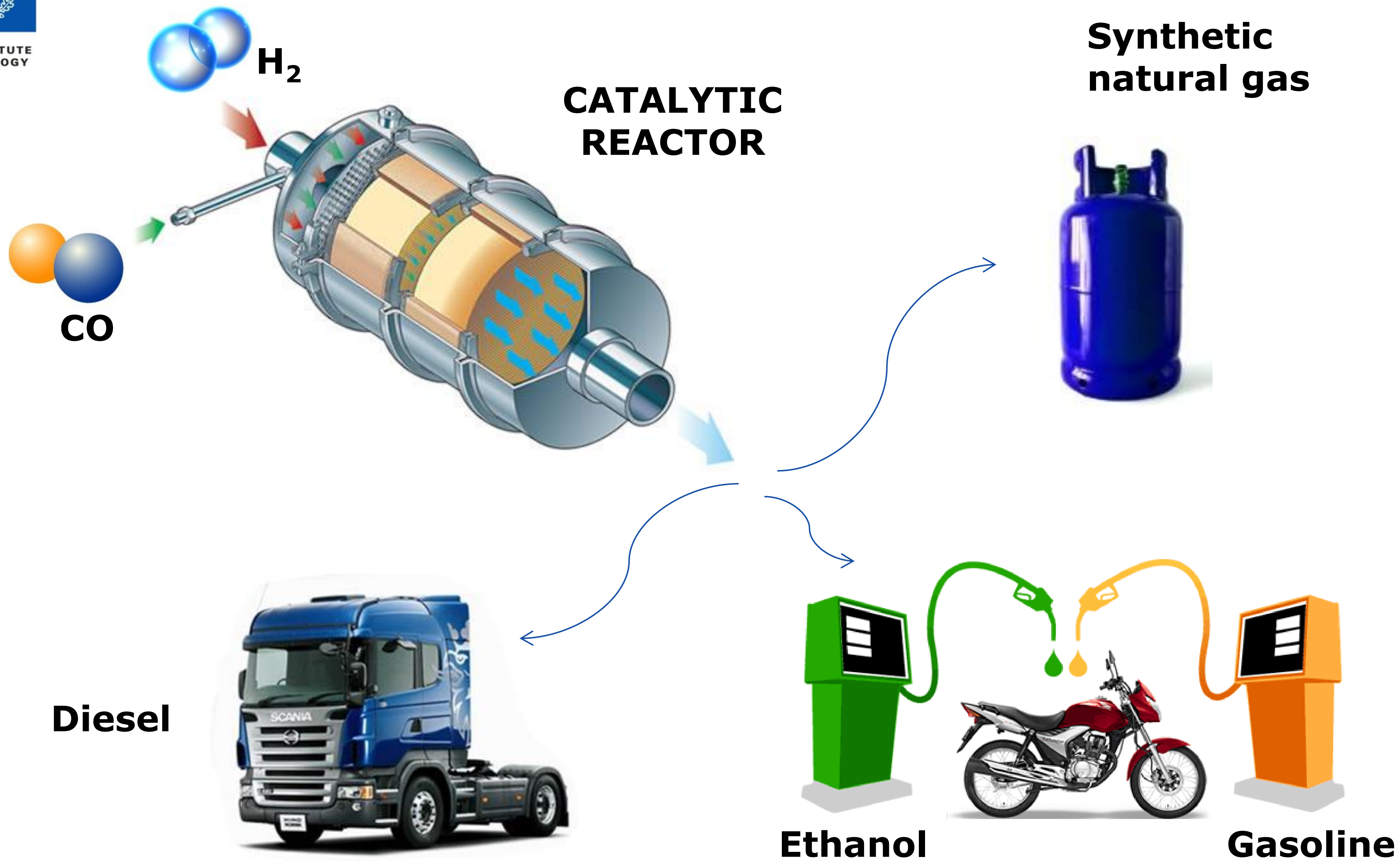
- Introduction and objective
- Experimental
- Results and discussion
- Ongoing work: methanol co-feeding
- Conclusions

INTRODUCTION AND OBJECTIVE

WHAT are we doing at Chemical technology?



WHAT are we doing at Chemical technology?

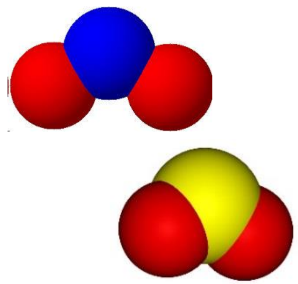


WHY research on biofuels?

Depletion of fossil energy sources

CO_2 emission reduction

No poisoning emissions
(SO_2, NO_x and particulates)



WHY research on biofuels?

10% renewable energy
in transportation
(EU, 2020)

Mixed alcohol synthesis

- Ethanol can be used as: fuel / fuel additive / H_2 carrier for fuel cells
- Sweden is one of the leading countries in using ethanol as fuel (E5, E85)

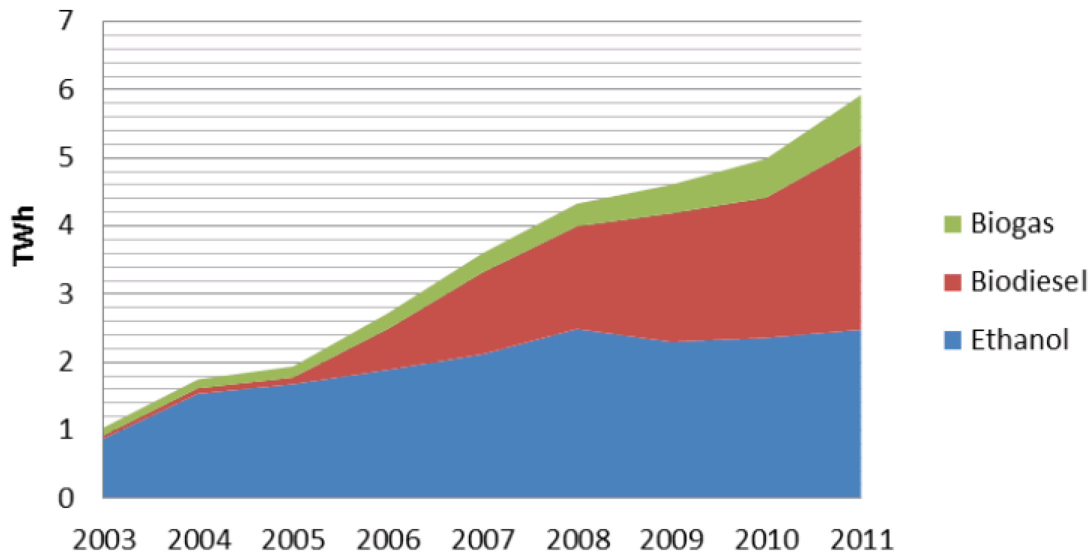
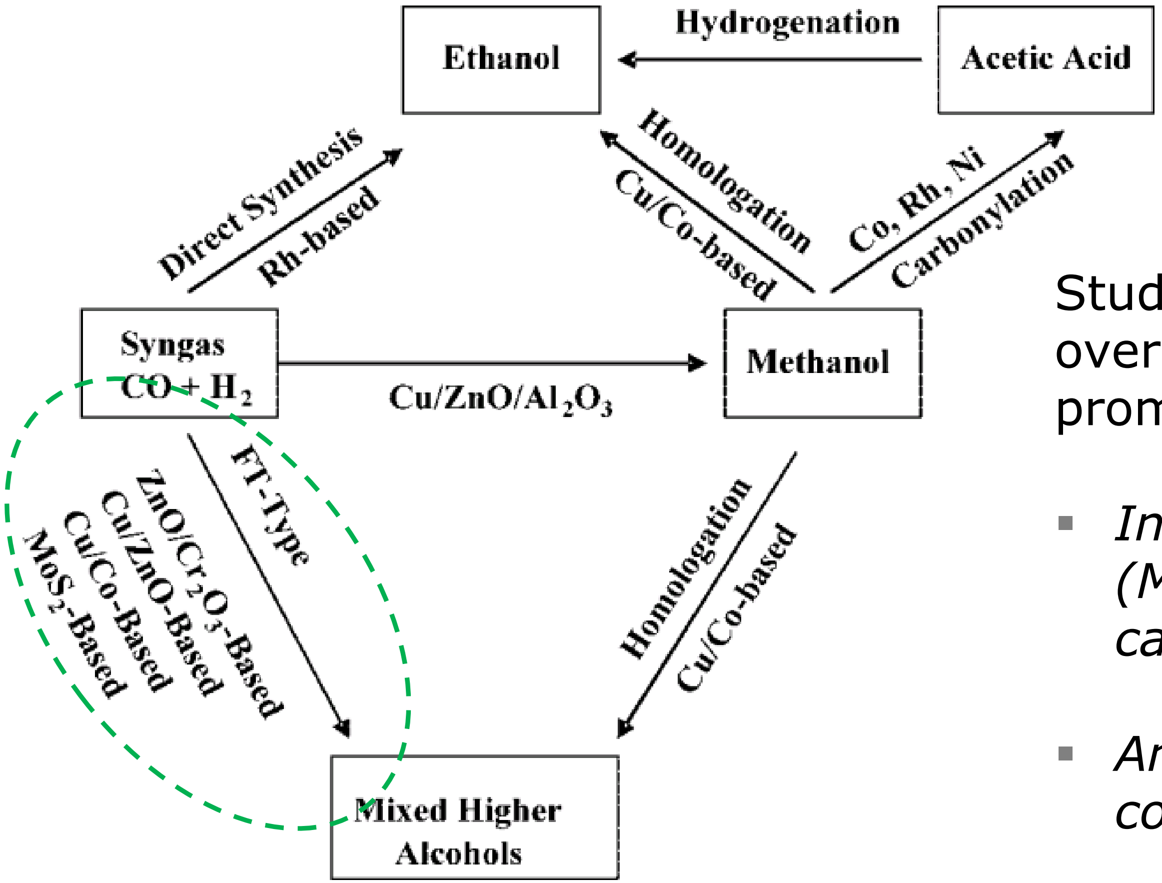


Figure 1. Use of biofuels in the transportation sector (Sweden). [Source: Swedish Energy Agency]

Objective



Study the conversion of syngas over molybdenum sulfide catalysts promoted with Ni and K

- *Introduce the microemulsion (ME) technique for preparing the catalysts*
- *Analyze the effect of methanol co-feeding (ongoing work)*

Figure 2. Pathways for conversion of syngas to ethanol and higher alcohols.
[Source: V. Subramani and S. K. Gangwal, Energy & Fuels, 2008, 22, 814-839]

EXPERIMENTAL

Catalyst preparation

<u>Preparation of Ni-modified K-doped molybdenum sulfide catalysts</u>

(targeted molar ratios: Ni/Mo=0.5; K/Mo=1.5)

Coprecipitation of $(NH_4)_2MoS_4$ and $Ni(CH_3COO)_2\cdot 4H_20$ → Precipitate aging (24 h) → Precipitate recovery and washing → Precipitate drying (50 °C) → Doping with K_2CO_3 → H_2 treatment (90 min, 450 °C)

The difference between the conventional and the novel ME catalyst is the medium where the coprecipitation takes place

Conventional catalyst → aqueous solution
Novel catalyst → microemulsion

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The microemulsion technique

- Optically transparent and thermodynamically stable solution
- Composed of spherical aqueous nanodroplets stabilized by a surfactant
- Metal salts can be solubilized inside the nanodroplets and then precipitated

Figure 3. ME systems, containing Mo and Ni salts.

Table 1. Composition of the ME system.

Phase	Compound (s)	Composition (wt%)
Oil	Iso-octane	53
Surfactant	CTAB	15
Co-surfactant	1-butanol	12
Water	ME1: water, $(NH_4)_2MoS_4$ ME2: water, $Ni(CH_3COO)_2 \cdot 4H_20$, acetic acid	20

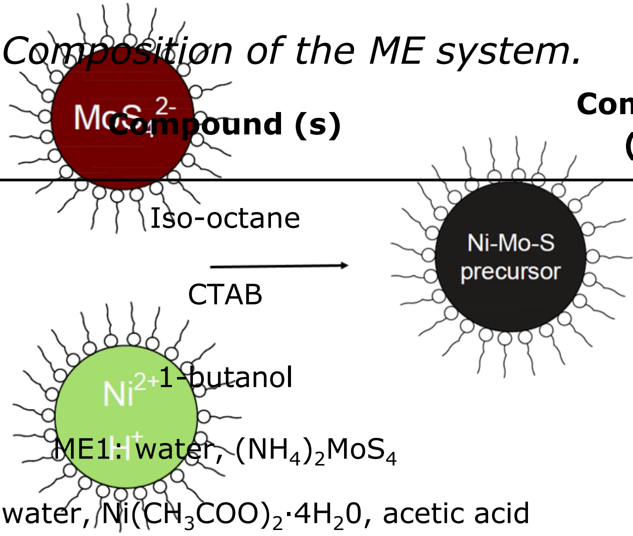

Figure 4. Coprecipitation in ME.

Activity and selectivity tests

Cat. 1:	*conventional*	*K-Ni-MoS_2*
Cat. 2:	*ME*	*K-Ni-MoS_2*
Cat. 3:	*conventional*	*Ni-MoS_2*
Cat. 4:	*conventional*	*K-MoS_2*

- ~ 0.7 g catalyst, diluted with SiC
- H_2/CO ratio: 1/1, 4% N_2 as internal standard
- P=91 bar
- T=340 / 370 °C
- WHSV = 2 000 – 14 000 NmL / h·$g_{catalyst}$
- Stabilization period > 100 h on stream

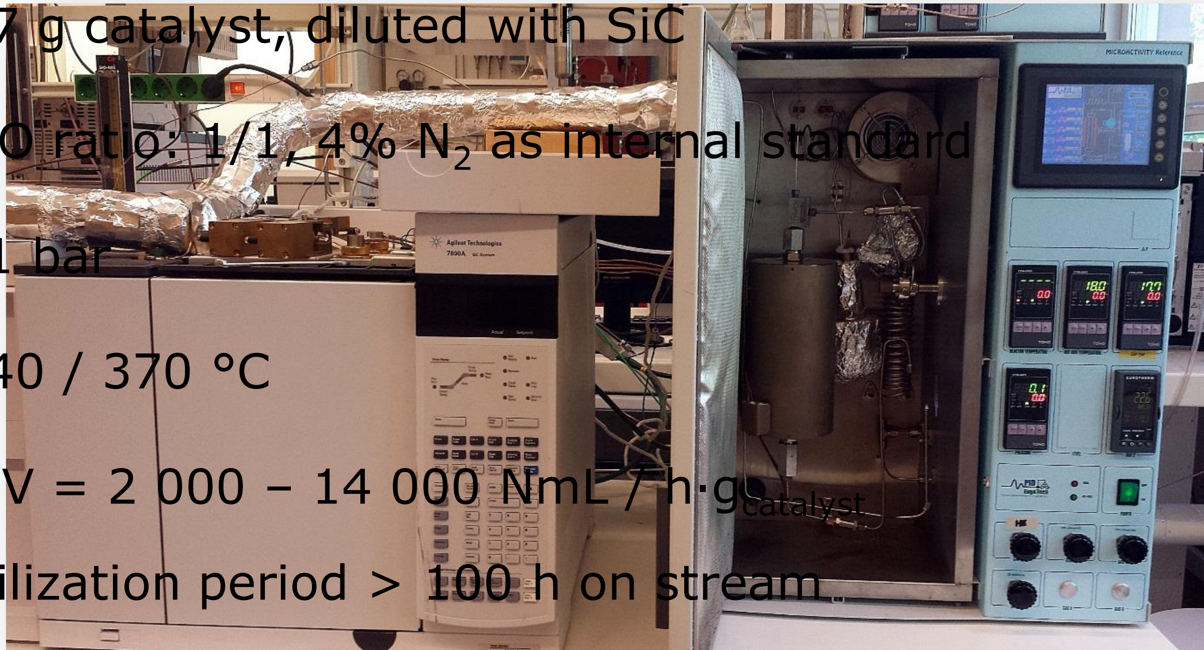

Figure 5. Experimental rig.

RESULTS AND DISCUSSION

Fresh catalyst composition: ICP, EDX, XPS

Table 2. Catalyst composition (fresh catalysts).

Catalyst	**Targeted ratio (mol/mol)**		**Measured ratio by ICP (mol/mol)**		**EDX analysis (atom/atom)**		**XPS analysis (atom/atom)**	
	Ni/Mo	K/Mo	Ni/Mo	K/Mo	Ni/Mo	K/Mo	Ni/Mo	K/Mo
1 (K-Ni-MoS_2)	0.50	1.50	0.45	1.19	0.61	1.42	0.05	1.50
2 (ME K-Ni-MoS_2)	0.50	1.50	0.40	1.51	0.55	1.21	**0.18**	**3.49**
3 (Ni-MoS_2)	0.50	0	0.50	0	0.70	0	0.14	0
4 (K-MoS_2)	0	1.50	0	1.50	0	1.15	0	5.16

- ICP (and EDX) analyses show that the bulk Ni/Mo and K/Mo ratios are approximately the targeted ones
- XPS analyses evidence a higher amount of Ni and K on the surface of the ME catalyst

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Fresh catalysts: SEM

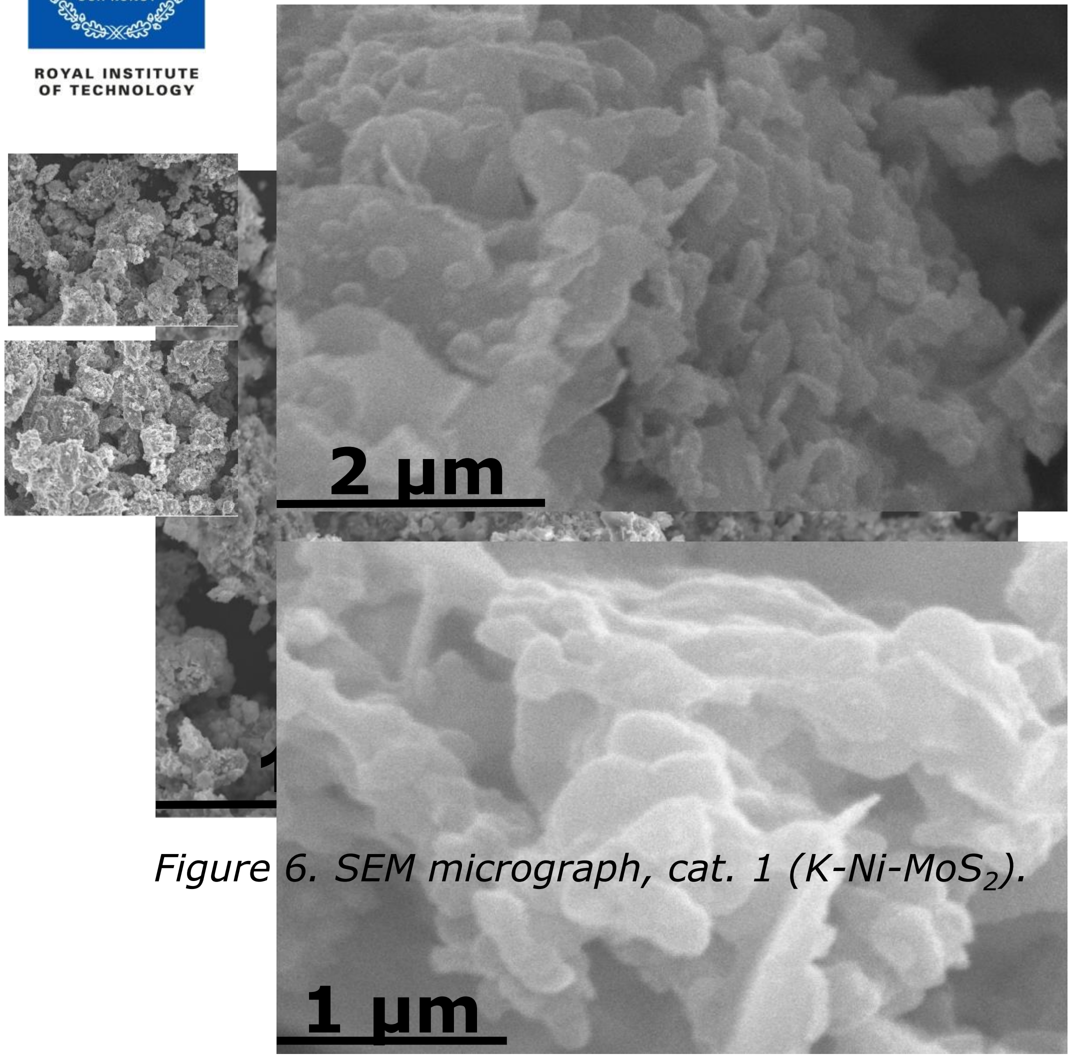

Figure 6. SEM micrograph, cat. 1 (K-Ni-MoS_2).

Figure 8. SEM micrographs, cat. 1 (K-Ni-MoS_2).

SA=3 m^2 / g

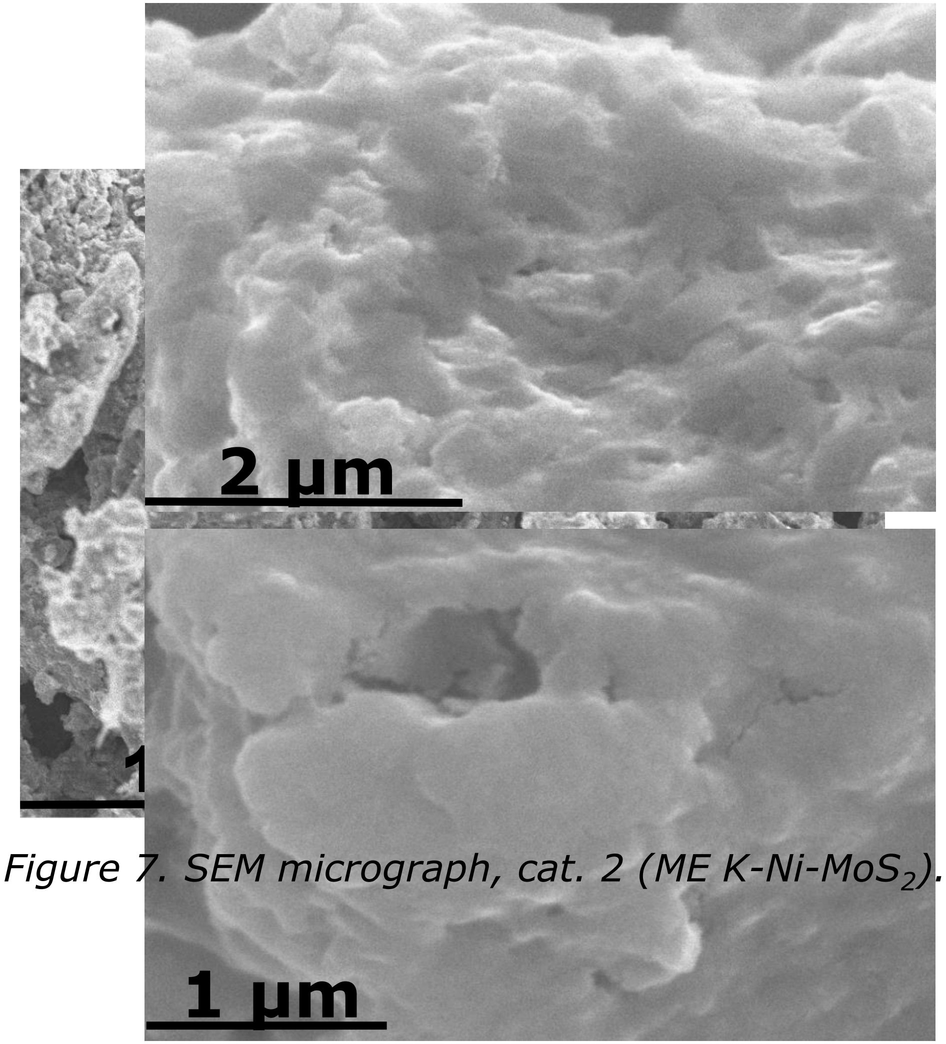

Figure 7. SEM micrograph, cat. 2 (ME K-Ni-MoS_2).

Figure 9. SEM micrographs, cat. 2 (ME K-Ni-MoS_2).

SA=1 m^2 / g

Fresh catalysts: TEM

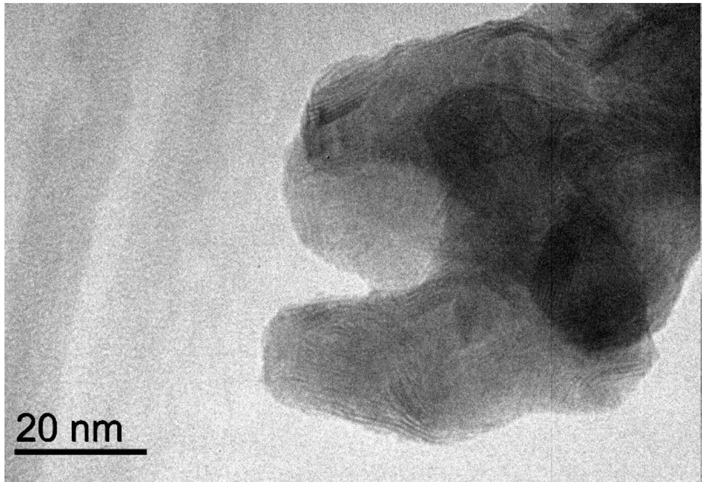

Figure 10. TEM micrograph, cat. 1 (K-Ni-MoS_2).

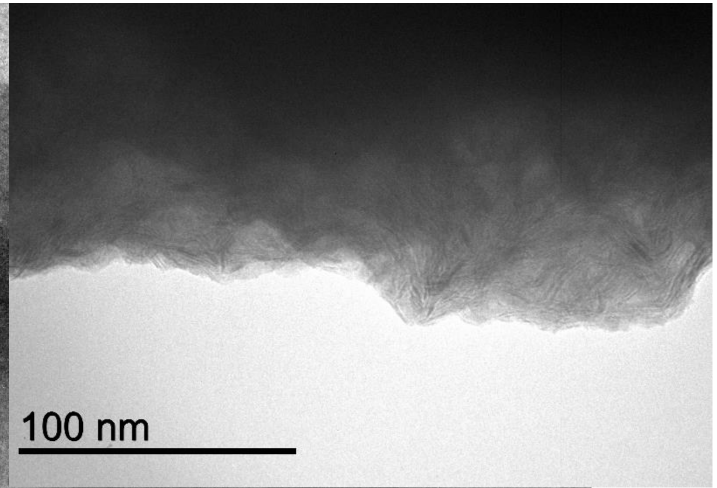

Figure 11. TEM micrograph, cat. 2 (ME K-Ni-MoS_2).

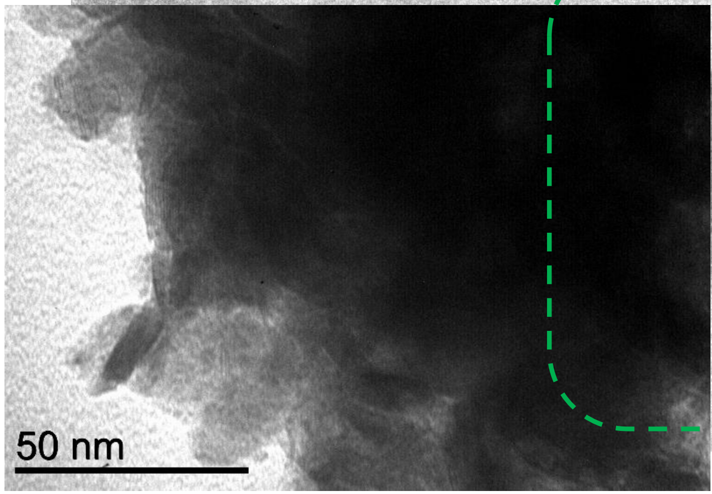

Figure 12. TEM micrograph, cat.3 (Ni-MoS_2).

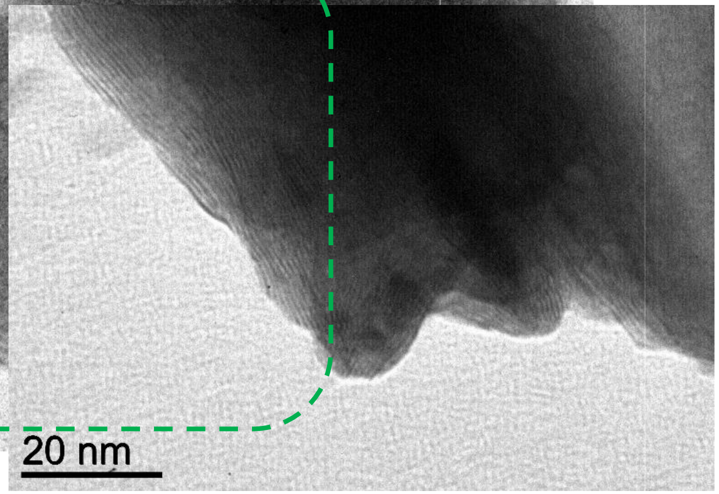

Figure 13. TEM micrograph, cat. 4 (K-MoS_2).

Figure 10. TEM micrograph, cat. 1 (K-Ni-MoS_2).

Activity

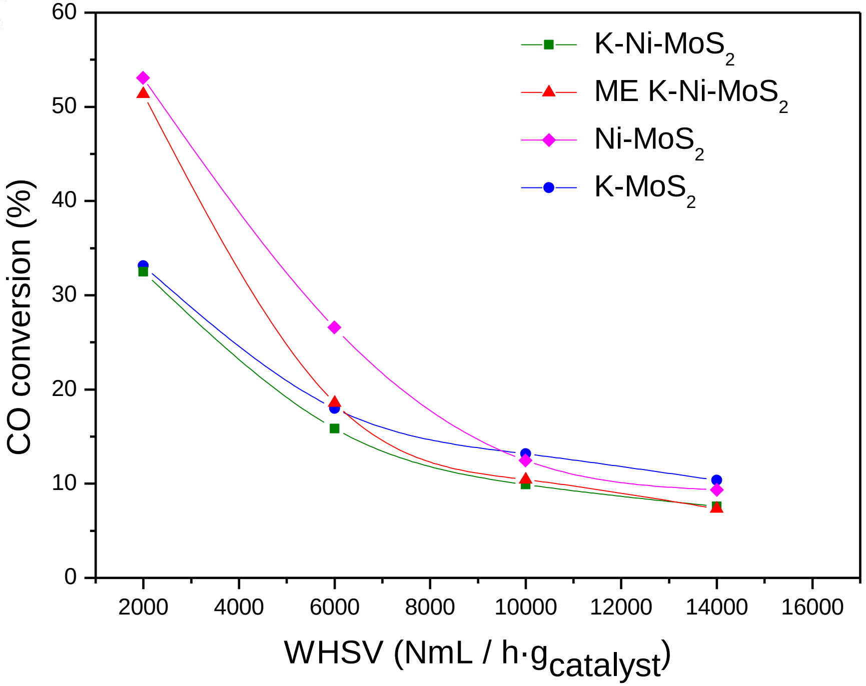

Figure 14. Catalytic activity as a function of space velocity (T=340 ºC).

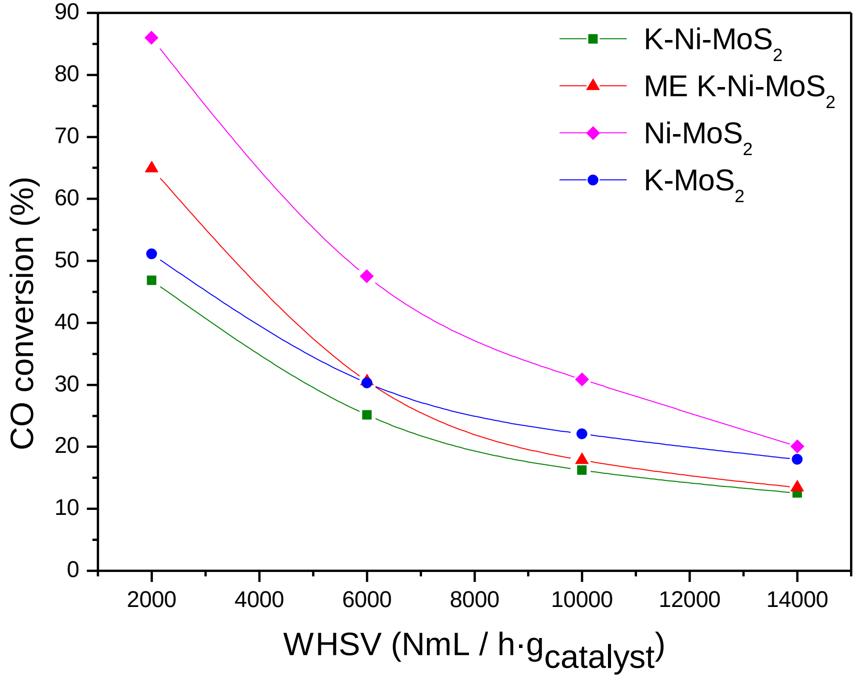

Figure 15. Catalytic activity as a function of space velocity (T=370 ºC).

- Bigger differences at low WHSV
- The most active catalyst is ”Ni-MoS_2”
- Among both K-Ni-MoS_2 catalysts, the ME catalyst results in higher conversions

Selectivity

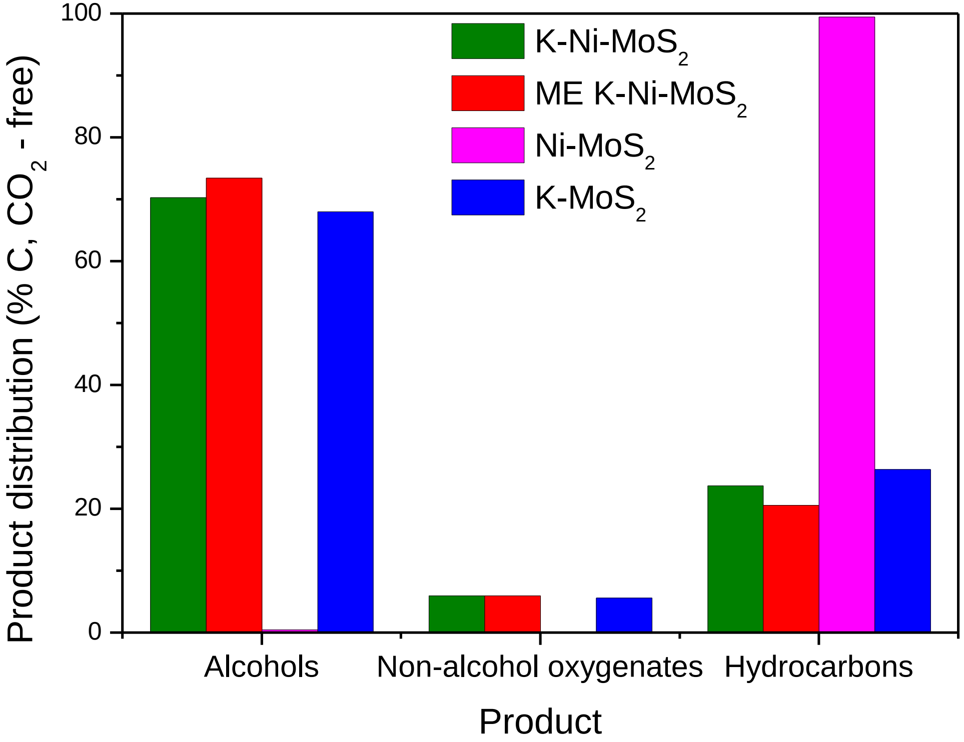

Figure 16. Product distribution (T=340 ºC, WHSV=6 000 NmL / h·$g_{catalyst}$)

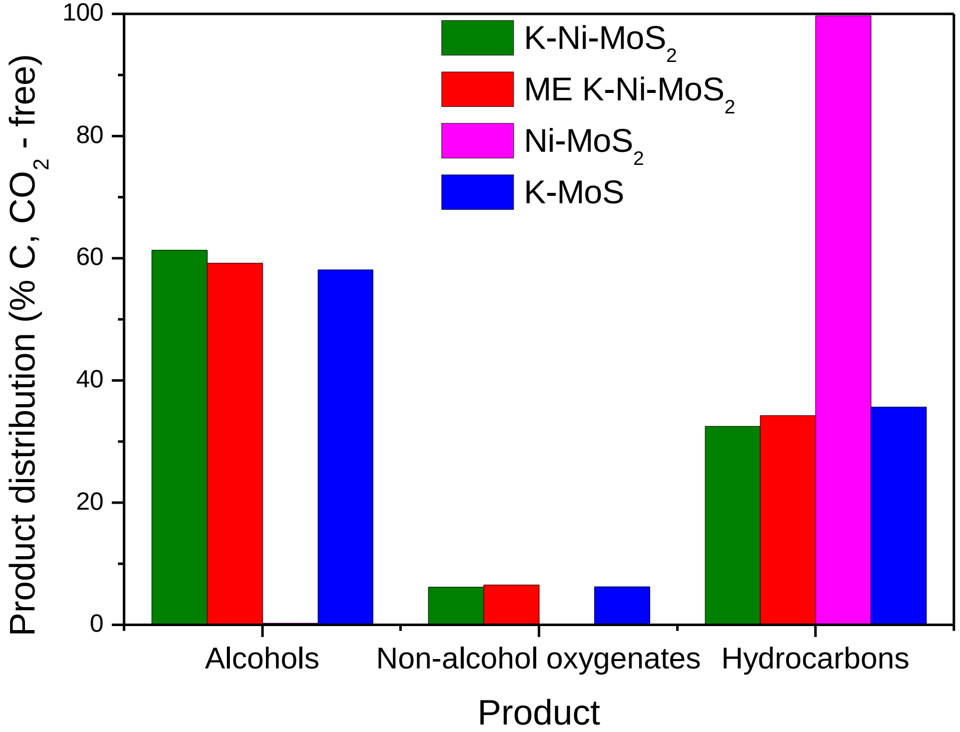

Figure 17. Product distribution (T=370 ºC, WHSV=6 000 NmL / h·$g_{catalyst}$)

Potassium is essential to shift selectivity from hydrocarbons to alcohols

Space Time Yields: methanol

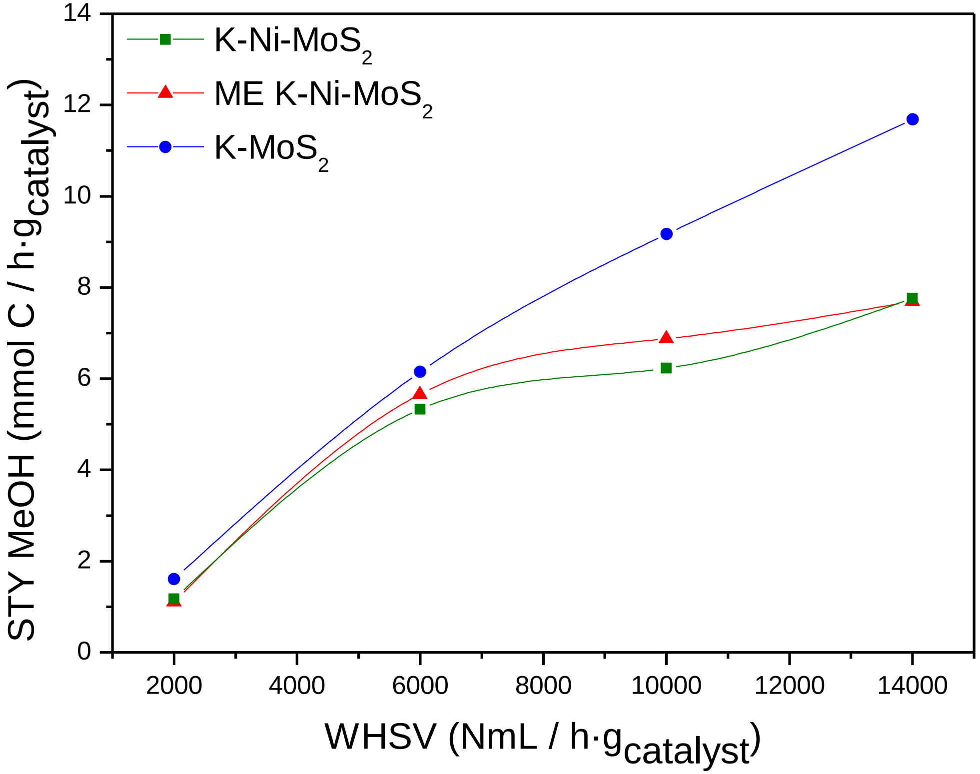

Figure 18. Methanol Space Time Yield (T=340 ºC)

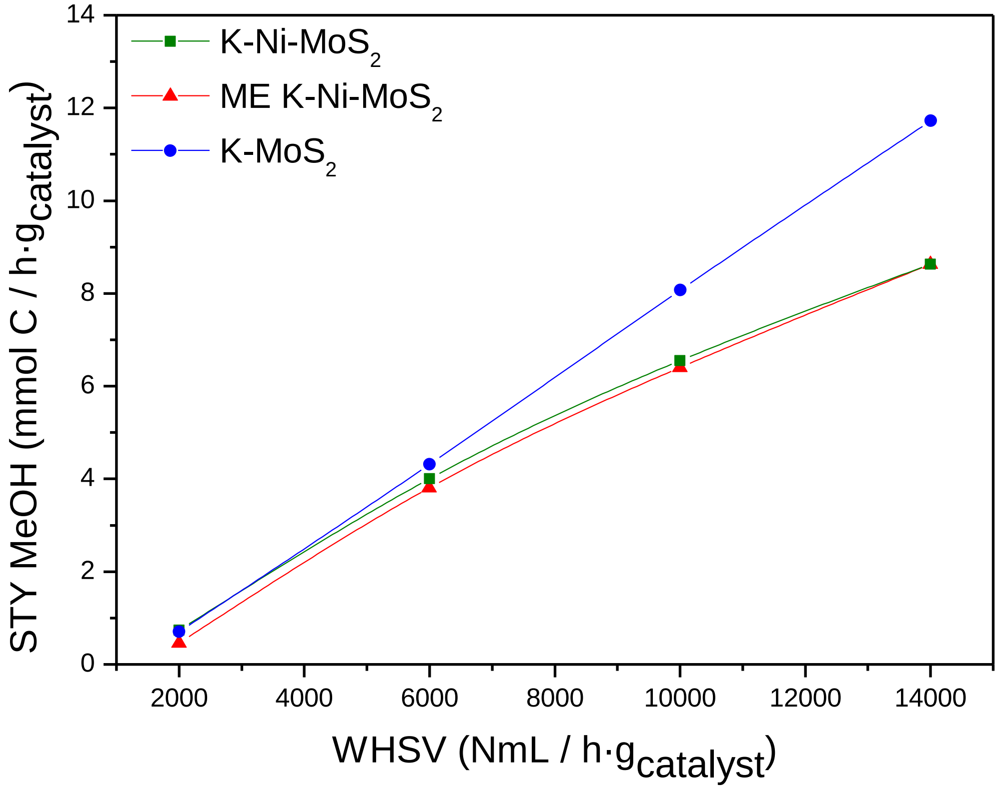

Figure 19. Methanol Space Time Yield (T=370 ºC)

Nickel is essential to shift selectivity from MeOH to higher alcohols

Space Time Yields: ethanol

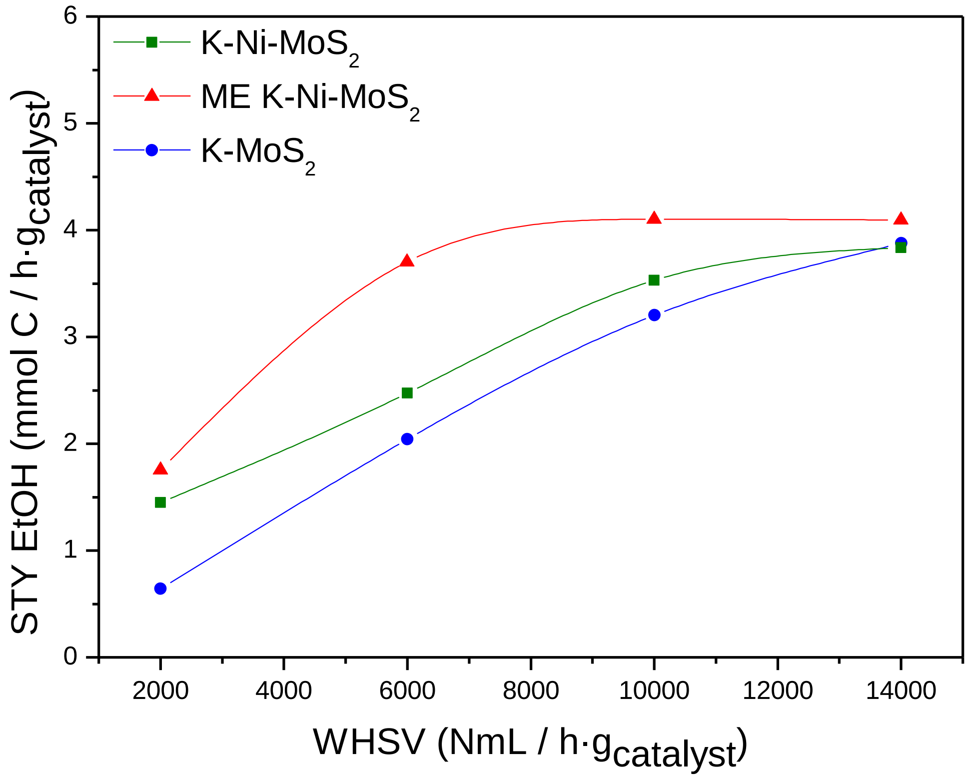

Figure 20. Ethanol Space Time Yield (T=340 ºC)

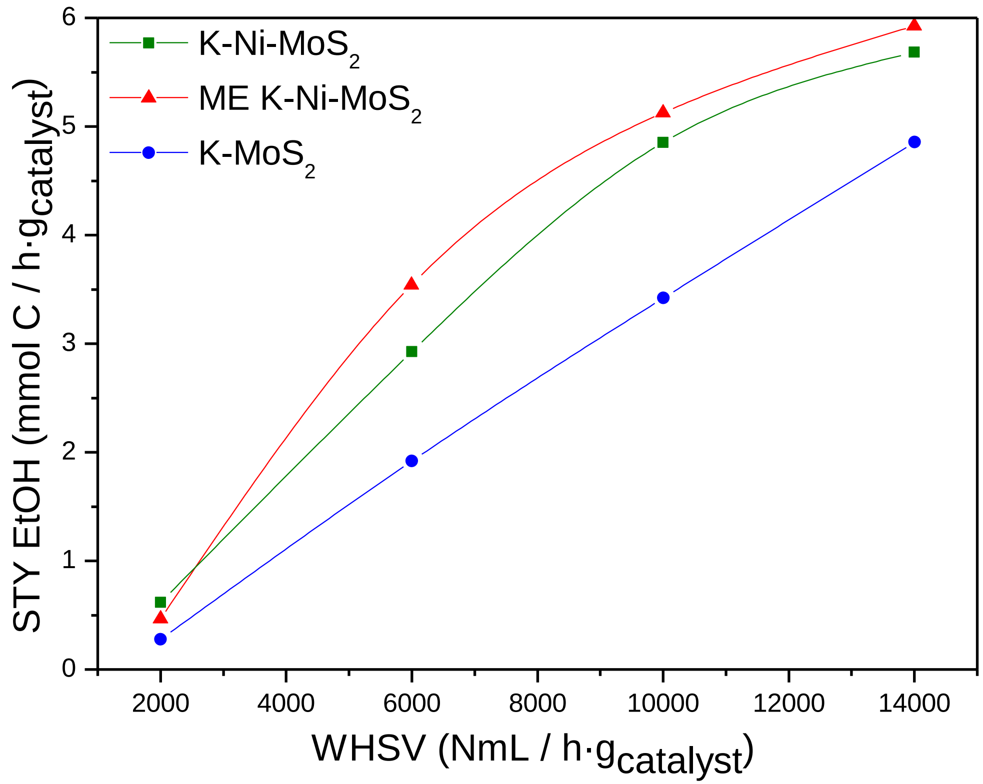

Figure 21. Ethanol Space Time Yield (T=370 ºC)

Ethanol production is clearly enhanced over the ME catalyst

Spent catalyst composition: EDX, XPS

Table 3. Catalyst composition (spent catalysts).

Catalyst	**Targeted ratio (mol/mol)**		**EDX analysis (atom/atom)**		**XPS analysis (atom/atom)**	
	Ni/Mo	K/Mo	Ni/Mo	K/Mo	Ni/Mo	K/Mo
1 (K-Ni-MoS_2)	0.50	1.50	0.61	1.42	0.05	1.50
Spent 1 (K-Ni-MoS_2)	-	-	0.02	1.23	0.06	2.90
2 (ME K-Ni-MoS_2)	0.50	1.50	0.55	1.21	0.18	3.49
Spent 2 (ME K-Ni-MoS_2)	-	-	0.18	1.42	0.26	5.27

- Nickel is partially removed during reaction, remaining mainly on the surface

- Potassium migrates to the surface during reaction → previously reported on K-Co-MoS_2 *[Source: J. Iranmahboob, H. Toghiani and D. O. Hill, Applied Catalysis A: General, 2003, 247, 207-218]*

The ME catalyst shows a higher concentracion of Ni and K on the surface after reaction, which could explain the improved ethanol yields

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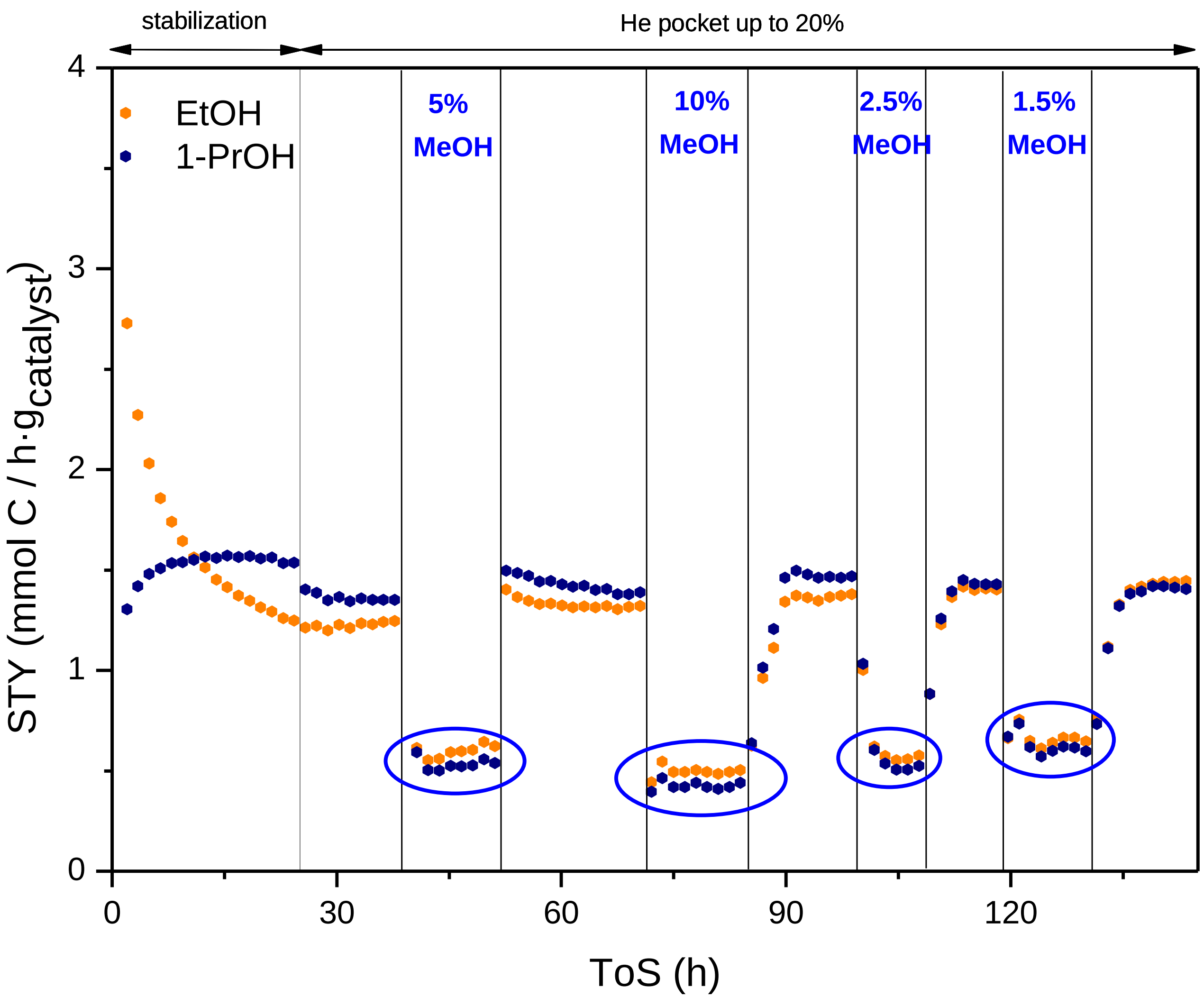
ONGOING WORK

Ongoing work: methanol co-feeding

- The C-C bond formation to **transform C_1 to C_2 species is the rate-determining step** in ethanol and higher alcohol synthesis from syngas
- To enhance the reactivity of the C_1 intermediate that is formed from syngas, lower alcohols such as methanol and ethanol have been added to the feed
- The carbon chain growth enhanced by co-feeding methanol is known as **methanol homologation**
- Reported on catalysts based on cobalt, bimetallic Rh-Fe or copper
- **Molybdenum-based catalysts?** Few published results, contradictory

K-MoS_2



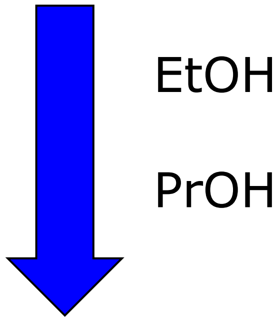


Figure 22. Effect of methanol co-feeding on ethanol and 1-propanol Space Time Yields (K-MoS_2, P=71bar, T=340ºC, WHSV = 6000 NmL / h·g$_{catalyst}$*).*

K-MoS_2

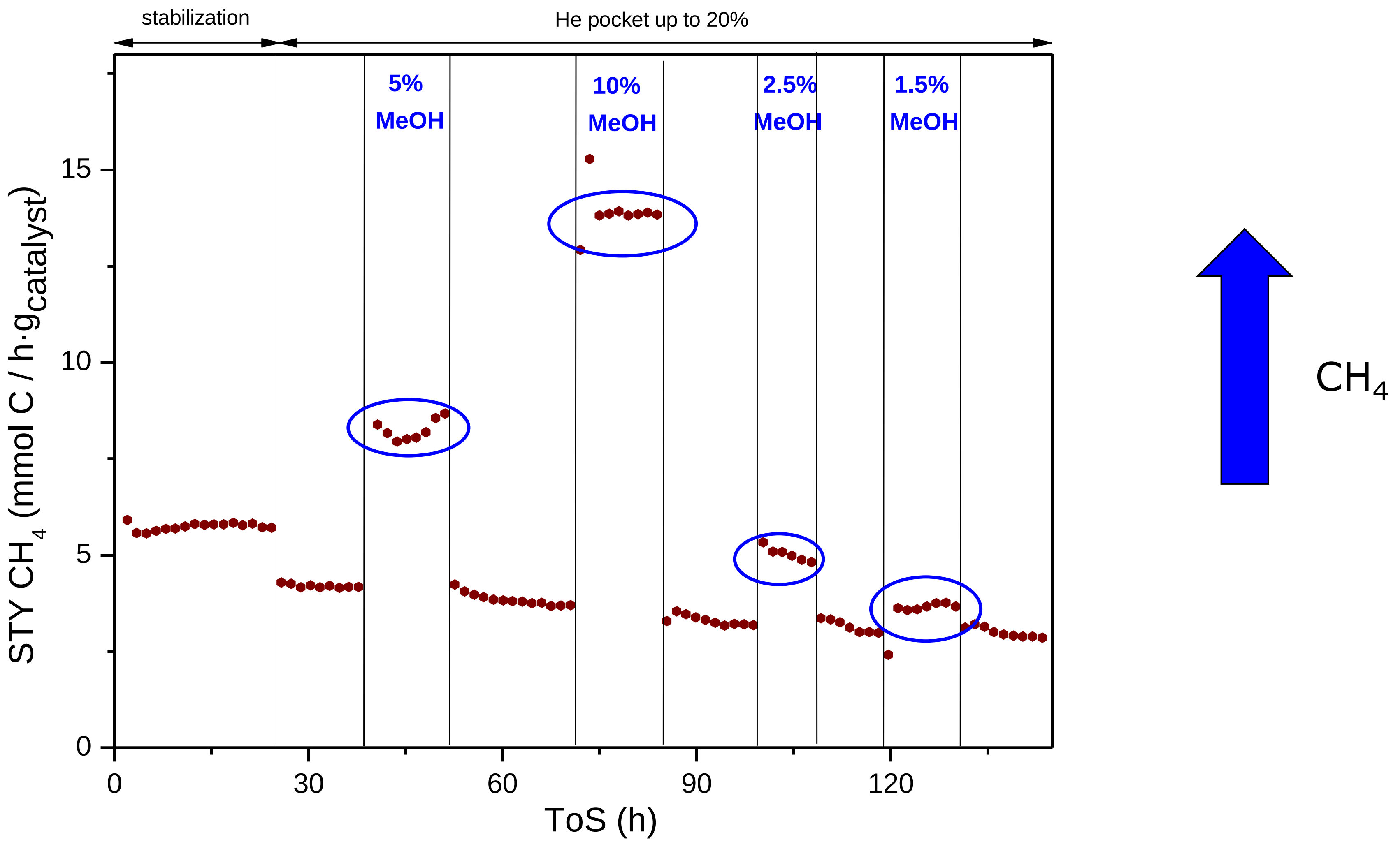


Figure 23. Effect of methanol co-feeding on methane Space Time Yield (K-MoS_2, P=71bar, T=340ºC, WHSV = 6000 NmL / h·$g_{catalyst}$*).*

Comparison between K-MoS$_2$ and K-Ni-MoS$_2$

K-MoS$_2$

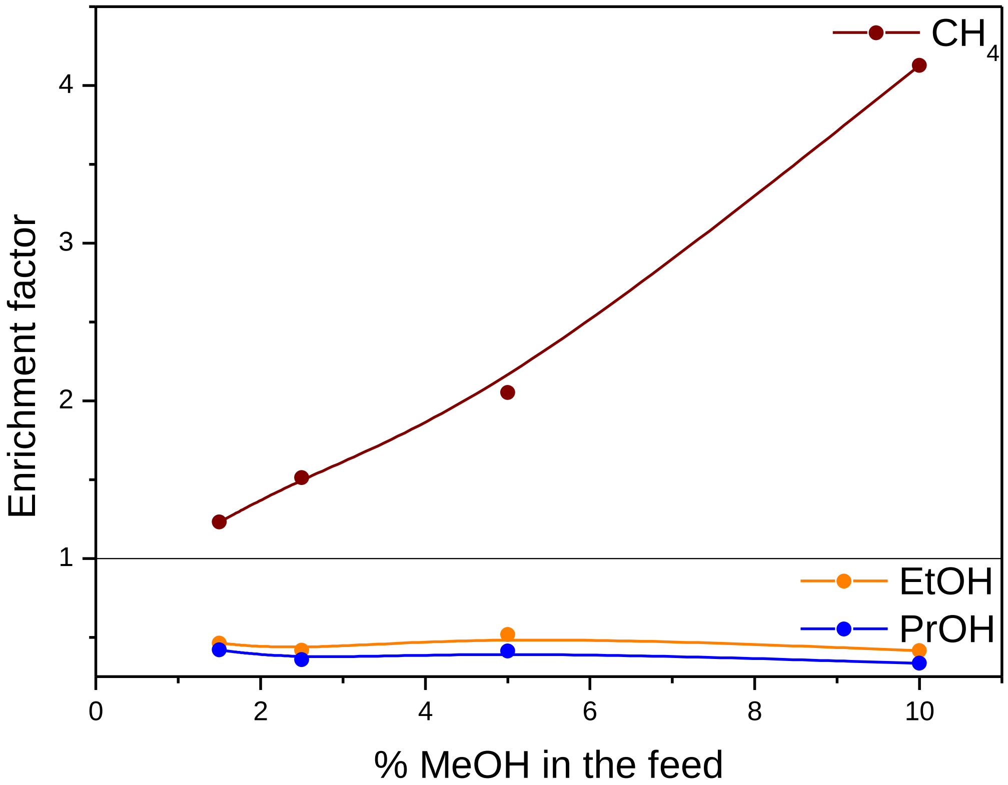


Figure 24. Effect of methanol co-feeding on STY (K-MoS$_2$, P=71bar, T=340ºC, WHSV = 6000 NmL / h·g$_{catalyst}$*).*

K-Ni-MoS$_2$

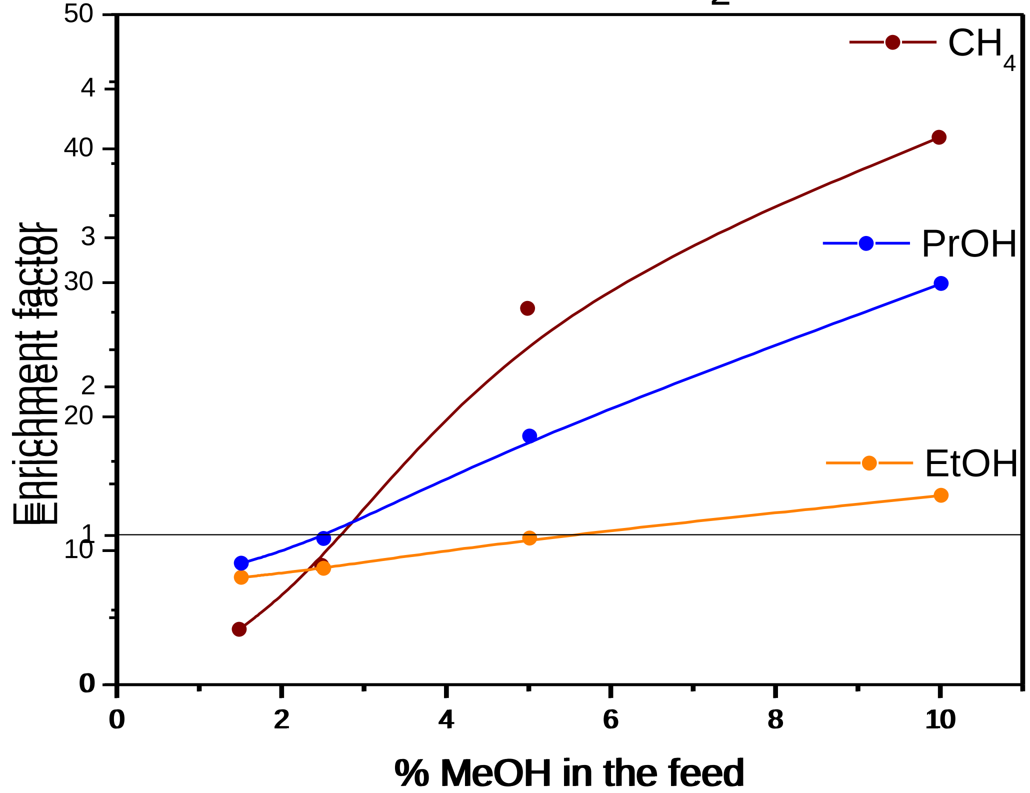


Figure 26. Effect of methanol co-feeding on alcohols STY (K-Ni-MoS$_2$, P=71bar, T=340ºC,* WHSV = 6000 NmL / h·g$_{catalyst}$*).

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CONCLUSIONS

Conclusions

- The novel catalyst, prepared through coprecipitation in ME solutions, is a **good candidate** for ethanol and higher alcohol synthesis

- **Activity** and **ethanol yield** are specially enhanced using the novel ME catalyst

- The novel ME catalyst shows larger agglomerates and lower surface area

- The new preparation method leads to a greater **enrichment** of **promoters** (Ni, K) on the catalyst **surface**, both before and after reaction. This could explain the better catalytic properties.

- On-going experiments, where **methanol is added to the feed** together with syngas, show a great **increase** in **methane** formation, while the effect in ethanol and higher alcohol yield is negative (K-MoS_2) or not significant (K-Ni-MoS_2)

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Thank you for your attention!

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