KTH ROYAL INSTITUTE OF TECHNOLOGY

Effects of gas phase K and H_2S on catalytic tar reforming using commercial Ni catalysts downstream a biomass gasifier

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It is teamwork…

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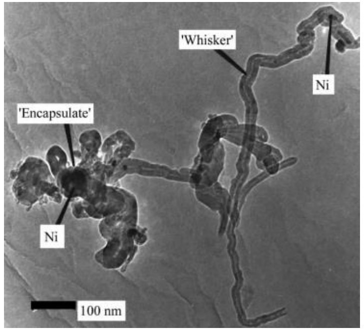
Coking of tar reforming catalysts

Coking can be controlled by controlling:

- Increased steam/carbon ratios in the feed.
- Ensemble size control on available nickel surfaces (e.g. doping with traces of sulfur or with small amounts of metals that concentrate on the nickel surface)

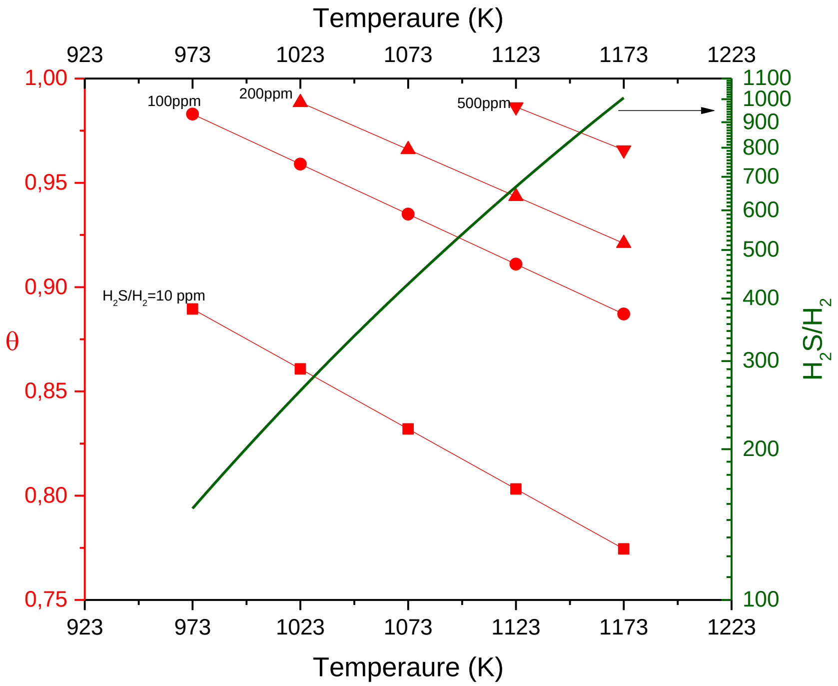


Catalysis Reviews 49(4):511-560

Research Question(s)

- How could we control carbon formation and catalyst deactivation by utilizing biomass gasification impurities (H_2S & K) ?

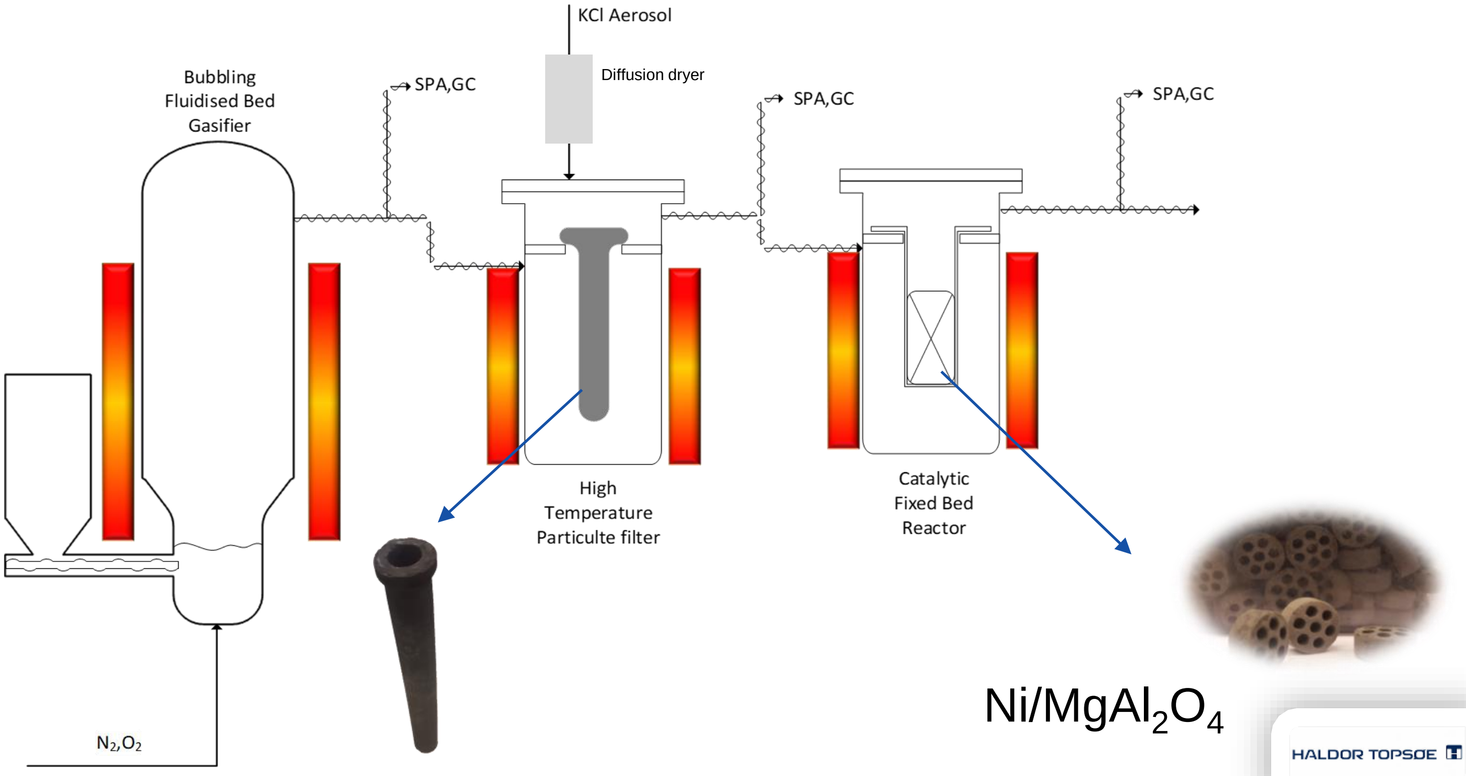
H_2S sorption on Ni



Potassium effects

- Contradictory literature results of gas phase K effects on methane and tar reforming activity
- Deposition mechanisms(impregnation) not realistic, not similar and sometimes not reproducible
- Transient phenomena have not been screened out

Experimental Setup



$Ni/MgAl_2O_4$

HALDOR TOPSOE

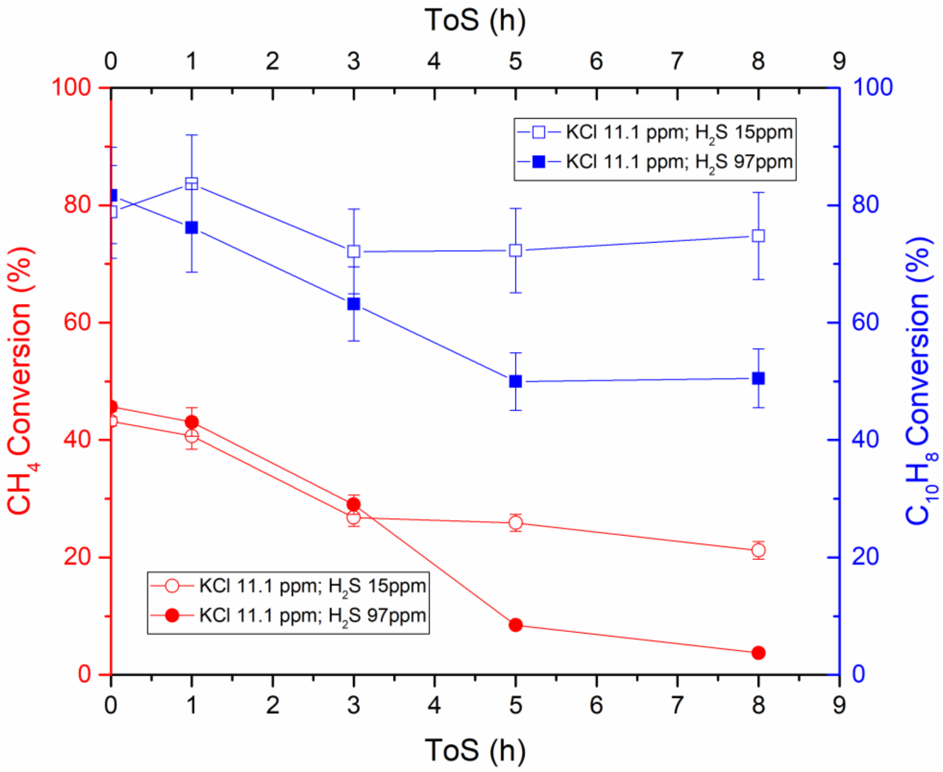
Experimental conditions and materials

Pine Pellets 3mm	
Ash(wt% db)	0.5
VM(wt% db)	76.5
C (wt% db)	47.7
H (wt% db)	6.3
N (wt% db)	0.16
O (wt% db)	45.3
S(wt% db)	<0.012
Cl(wt% db)	0.03
K (mg/kg db)	639
Na (mg/kg db)	57.3

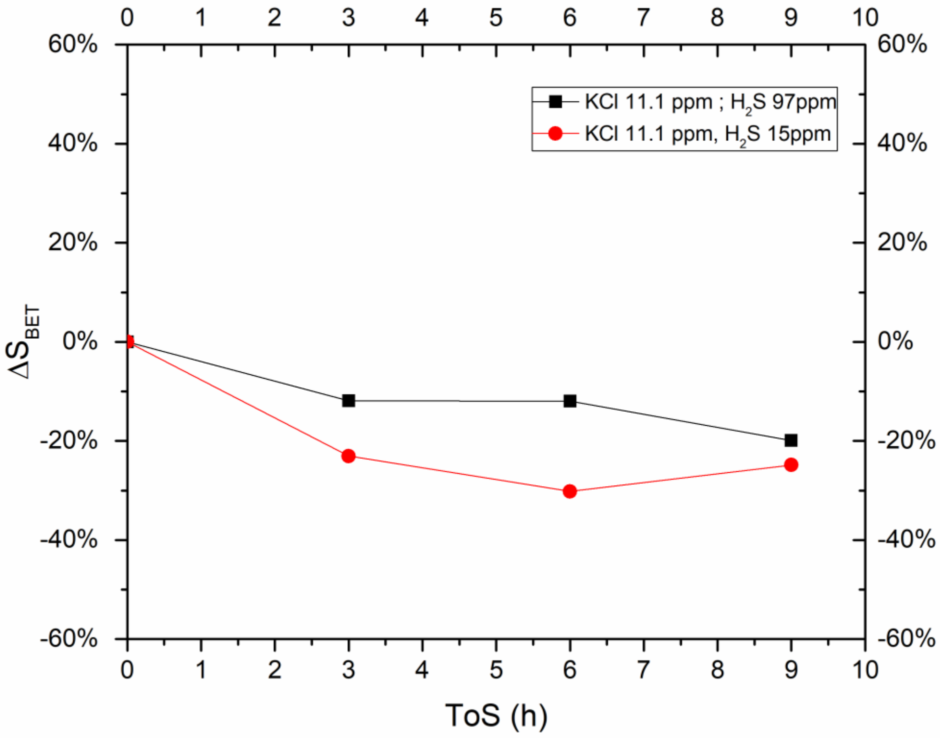
Operating Conditions	
Biomass Feed rate(g/h)	210-225
Gasification Temperature (^oC)	825-850
λ	0.23-0.25
Catalytic Bed Temperature [^oC]	800-850

Results- 850^{o}C Reduced Ni-catalyst

Gradual sulfur coverage affects the rate limiting step of conversion of different molecules



Results- 850^{o}C Reduced Ni-catalyst

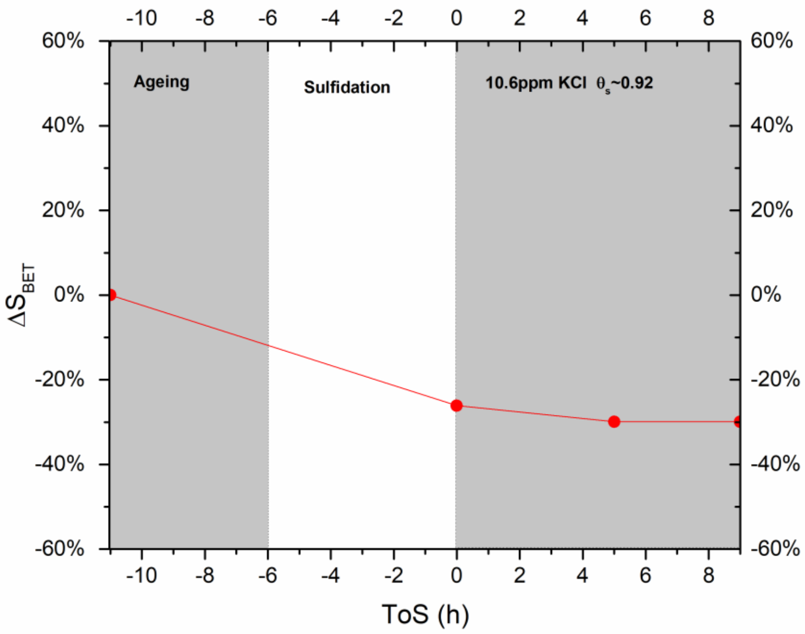


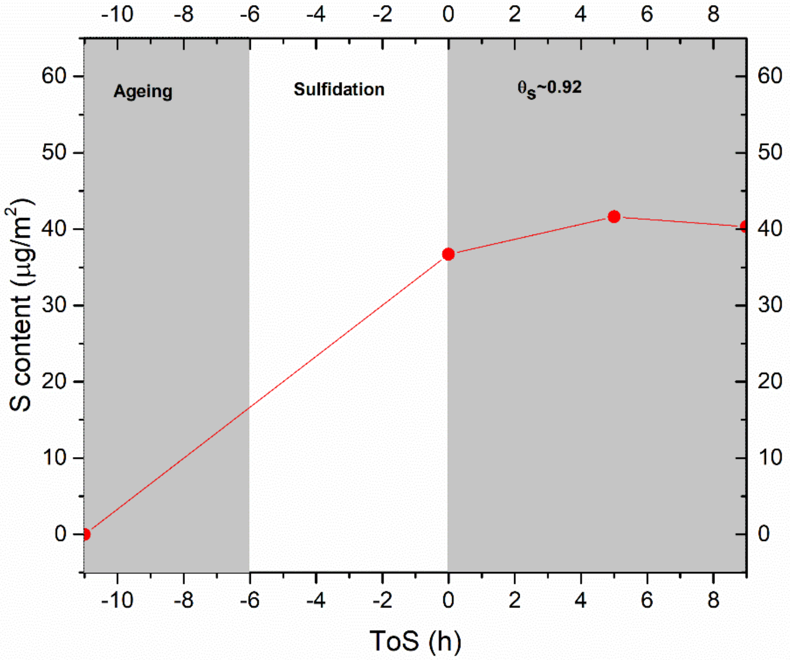
Sintering affects observed conversion changes

Methodology development- Stabilized & S passivated catalyst

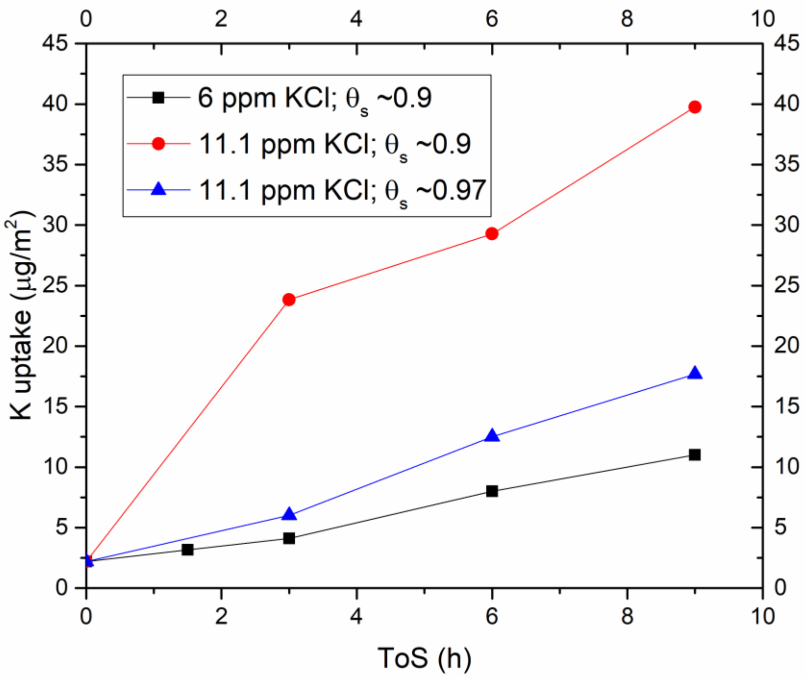
- Ageing @900+ ^oC in steam (H_2O:H_2 =10) for 5hrs - minimization of activity changes due to sintering
- Pre-sulfidation (passivation) at certain θ_s at relevant operating conditions- elimination of activity changes due to transient phenomena related to sulfur adsorption and equilibration on the surface.

Results- 850ºC Aged & passivated Ni-catalyst

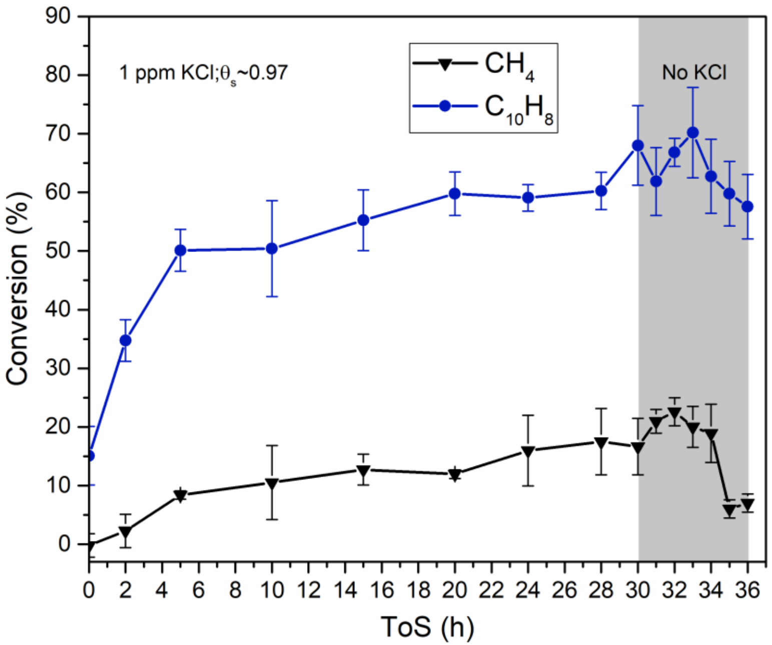


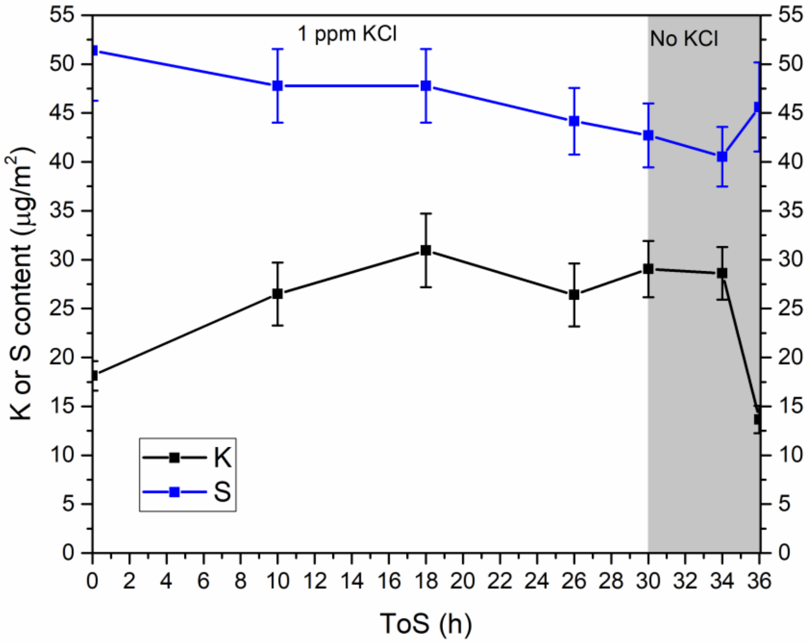


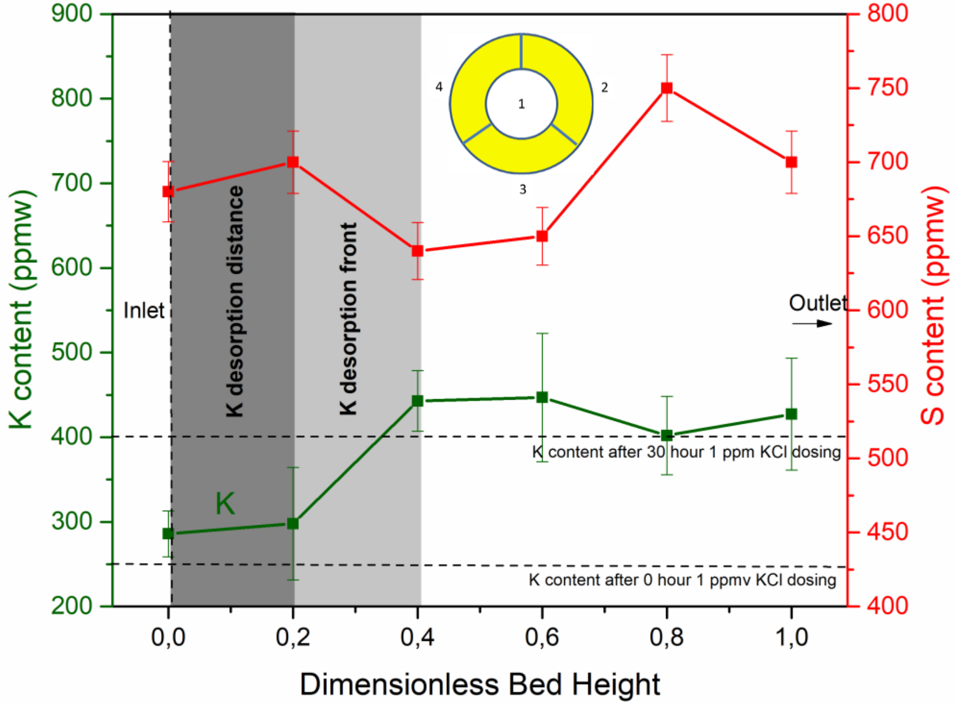
Results- 850ºC Aged & passivated Ni-catalyst



Tar reforming at 800^oC θ_s~0.97



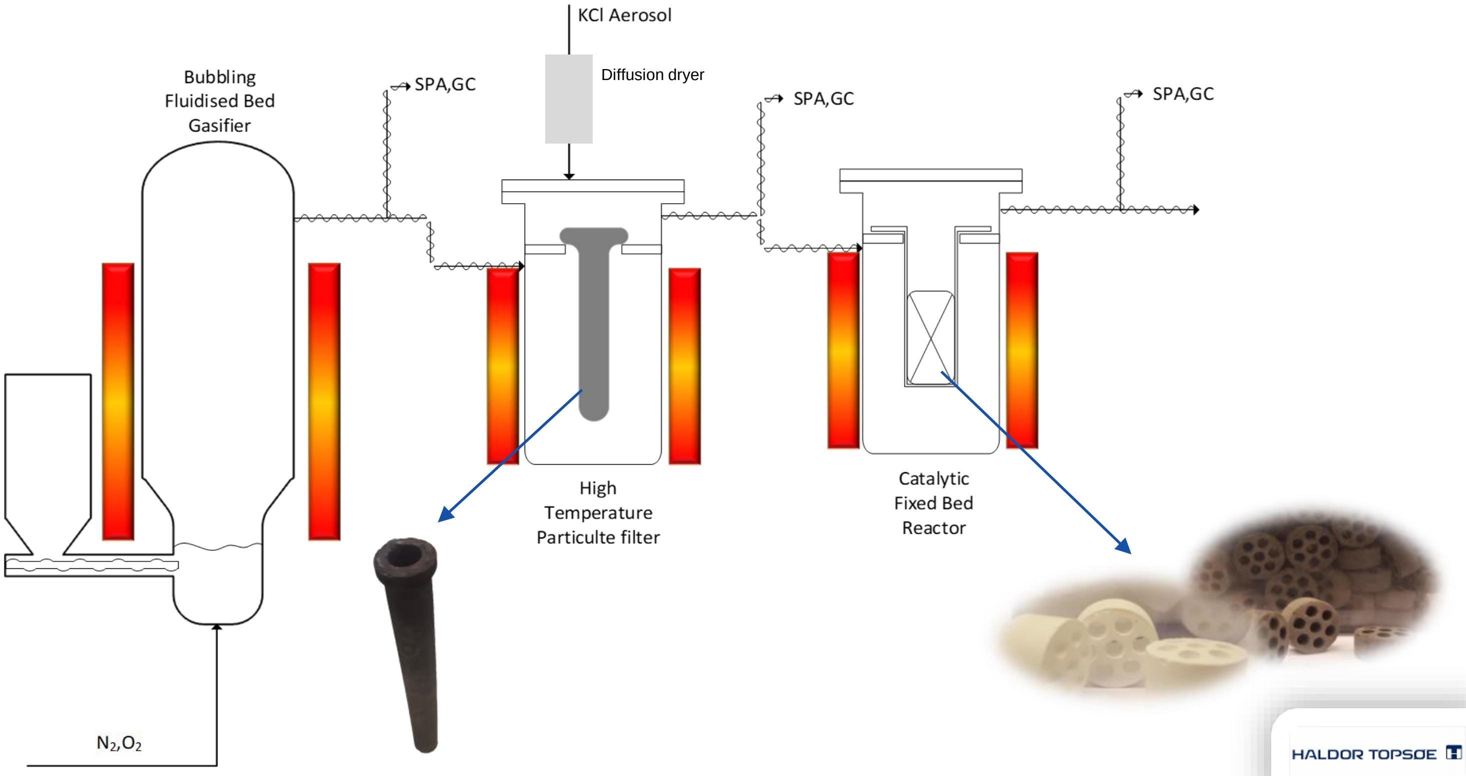



900
800
700
600
500
400
300
200
K content (ppmw)
800
750
700
650
600
550
500
450
400
S content (ppmw)
0,0
0,2
0,4
0,6
0,8
1,0
Dimensionless Bed Height
Inlet
K desorption distance
K desorption front
Outlet
K
K content after 30 hour 1 ppm KCl dosing
K content after 0 hour 1 ppmv KCl dosing
1
2
3
4

Question

- What is the role of the support ?

Experimental Setup



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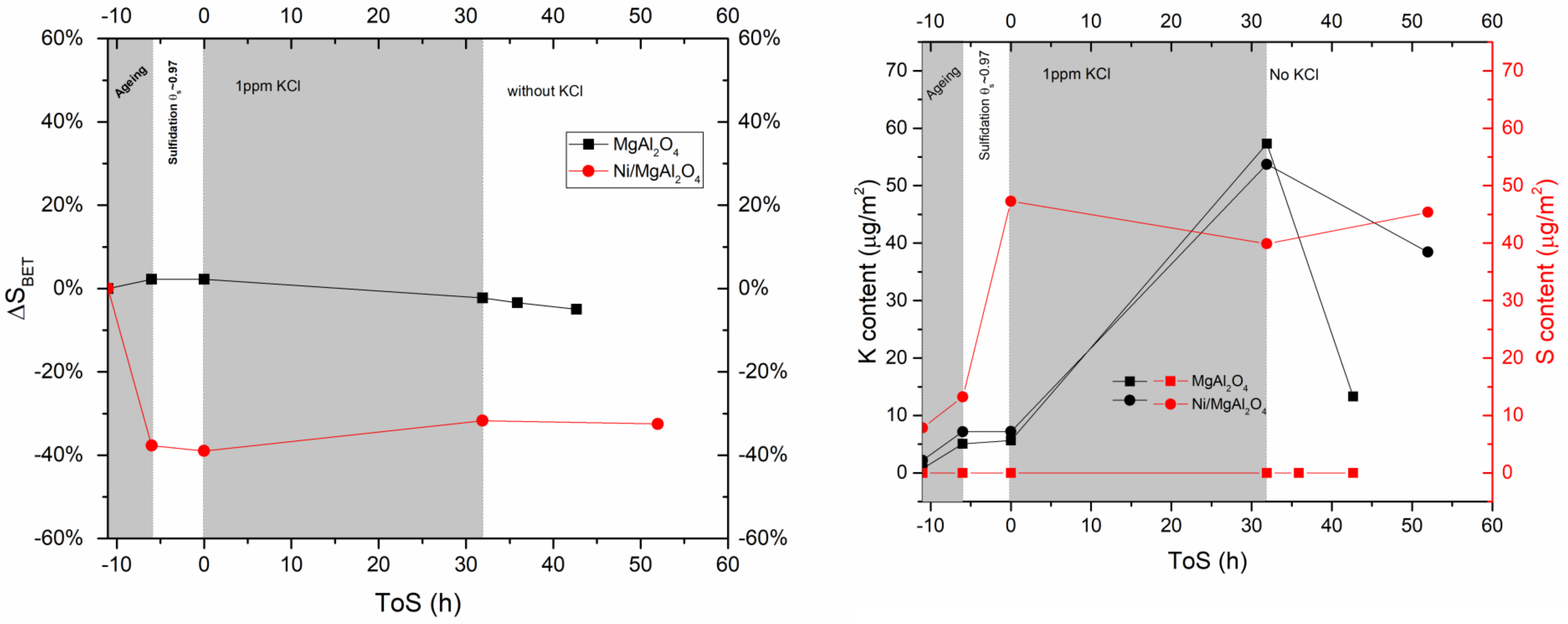
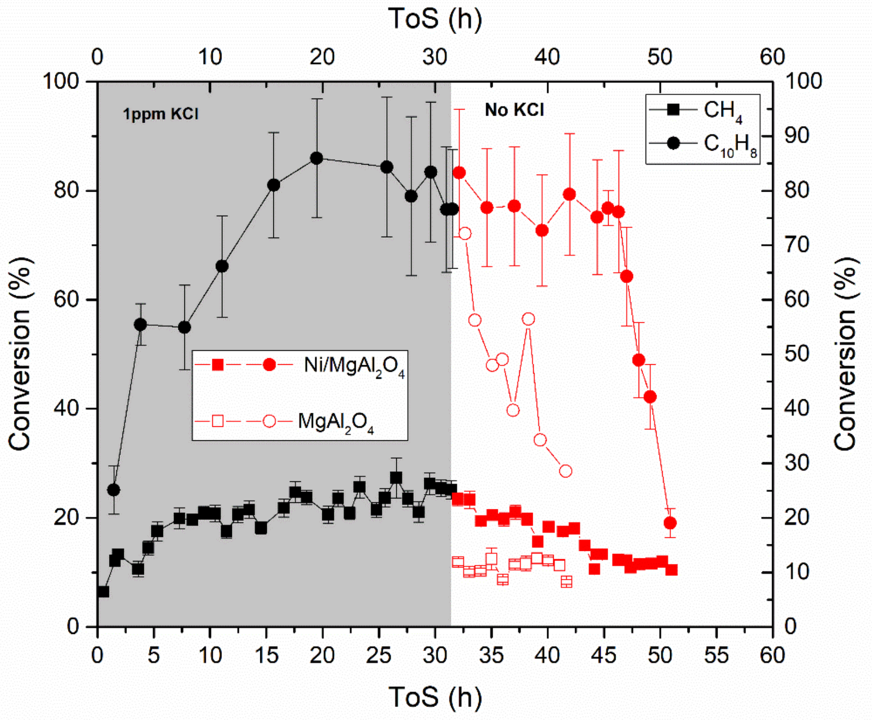


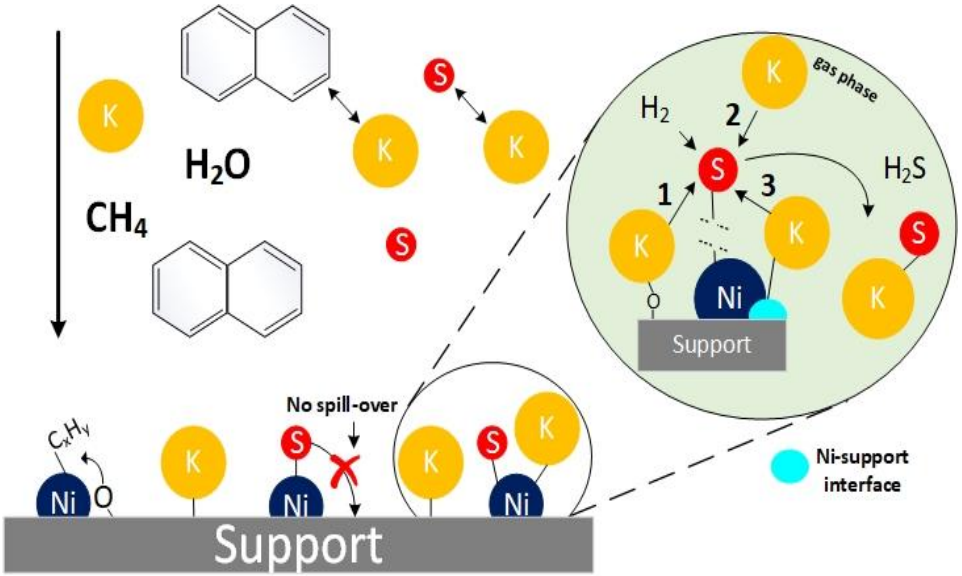
Ageing
Sulfidation θs~0.97
1ppm KCl
without KCl
MgAl2O4
Ni/MgAl2O4
ΔSBET
ToS (h)
Ageing
Sulfidation θs~0.97
1ppm KCl
No KCl
MgAl2O4
Ni/MgAl2O4
K content (μg/m2)
S content (μg/m2)
ToS (h)

Effects of support-sorbed K

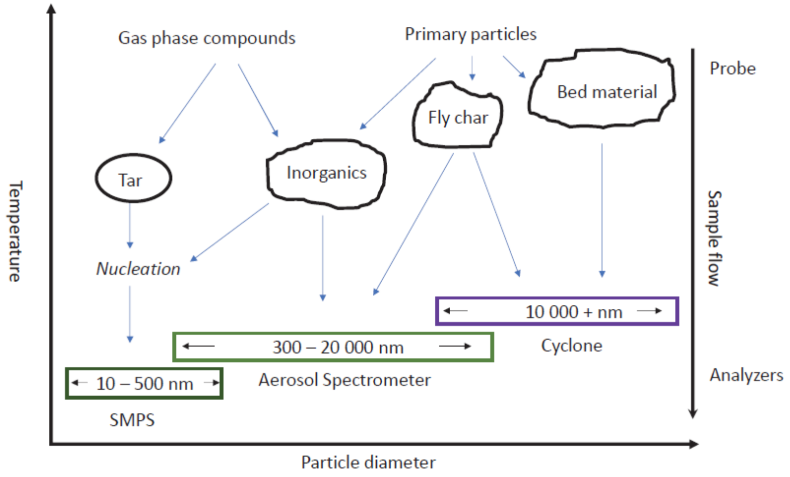


C on catalyst at the end of saturation: 0,56 mg/g_{cat}

C on catalyst after decay: 0,67 mg/g_{cat}

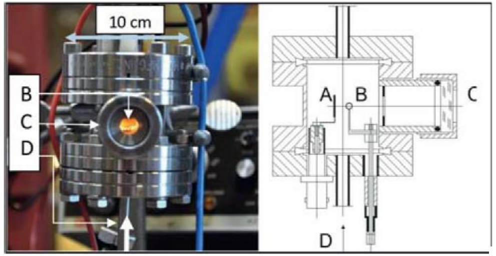

K
H2O
CH4
S
K
K
S
gas phase
H2
2
S
1
3
H2S
K
K
K
S
O
Ni
K
Support
No spill-over
CxHy
Ni
O
K
S
Ni
K
S
K
Ni
Ni-support
interface
Support

On-going



Correlate tar particle size distribution to its content

On Line K measurement using Surface Ionization Detector



H_2S trace detection (0-1ppm) using colorimetric analyzer

Conclusions

- Reproducible dosing of gas-phase K and elimination of transient effects catalyst sintering and sulfur passivation allow for investigation of K/S effects using real gasification gas
- K uptakes of <100 μg/m^2 catalyst under reforming conditions
- As θ_K increase on the catalyst the θ_S on Ni sites decreases improving conversions (Plausible K-induced Ni-S bond weakening)
- Suppport-sorbed K has some effect on conversion of bigger tar molecules and almost no effect on CH_4
- Tailoring K and H_2S concentrations in the gas allows for virtually carbon-free operation

Acknowledgements