Microkinetic study of acid gas valorization on Na zeolites

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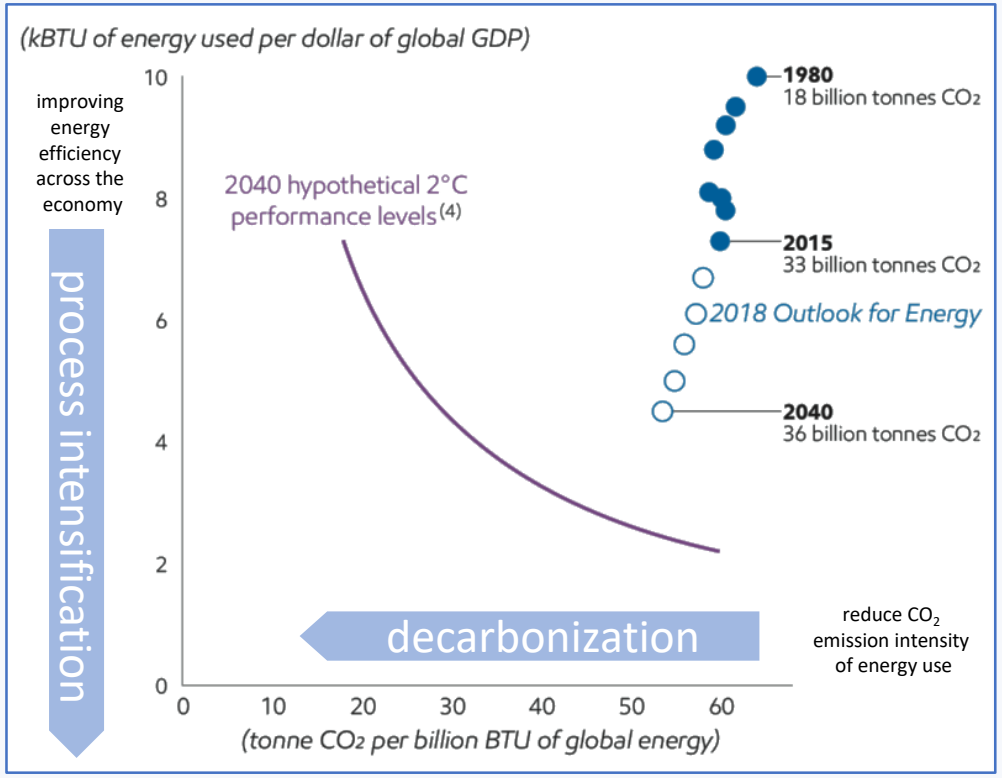
FCCat 4 2025

May 19th-23rd, 2025 - Ronce-les-Bains (France)

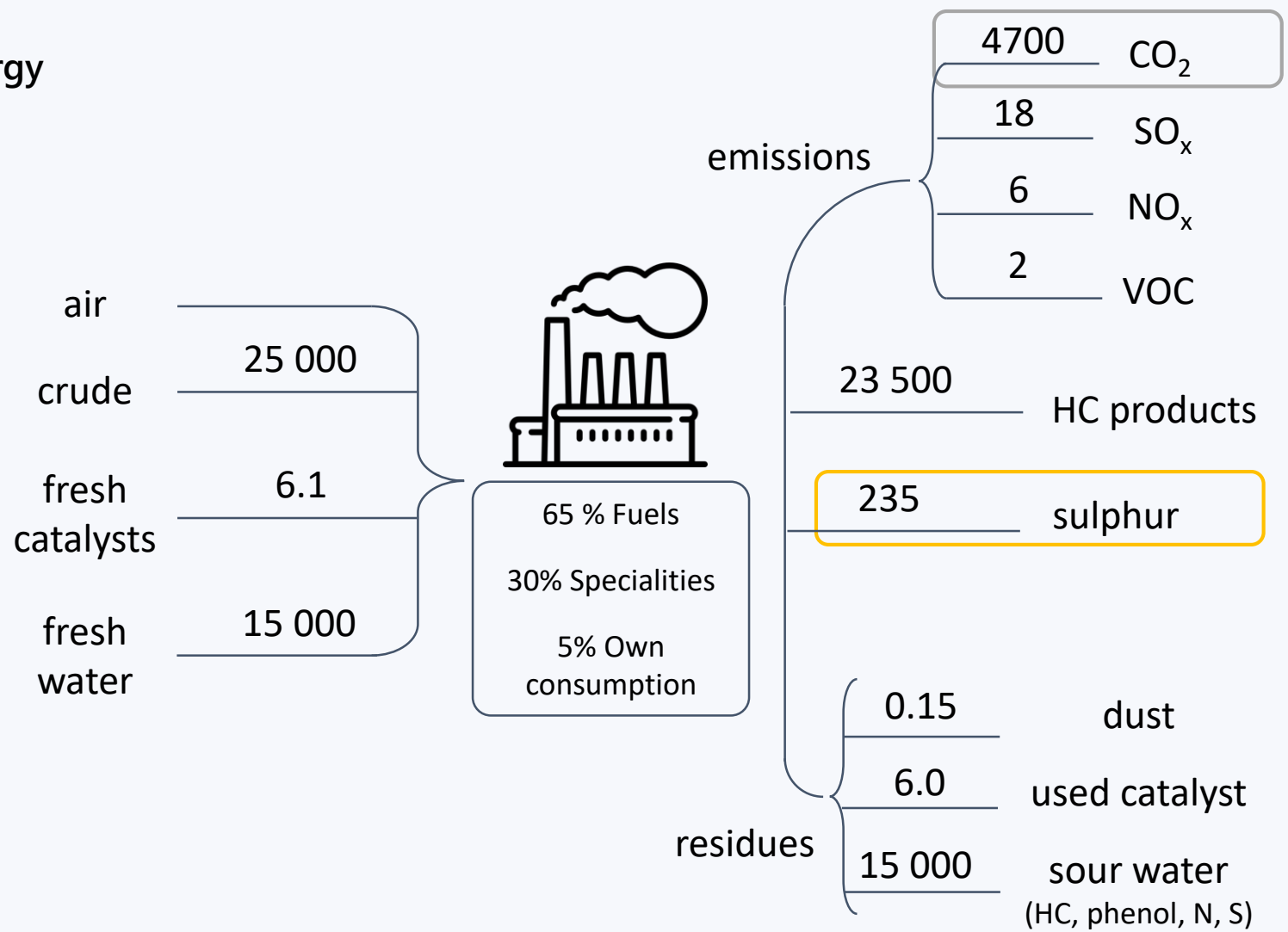
FCCat 2025 : French Conference on Catalysis

Context : energy outlook

World energy-related CO_2 emissions related to energy intensity vs CO_2 emission intensity



(4) Based on average Stanford EMF27 full technology / 450ppm scenarios' CO_2 emissions (~20 billion tonnes including energy and industrial processes), ExxonMobil GDP assumptions consistent with 2018 *Outlook*

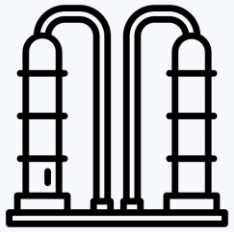


figures are in tonnes per day

Claus vs COS intermediate

Natural Gas

acid gas
$H_2S + CO_2$



separate H_2S and CO_2 streams

mixed CO_2

H_2S (mix)

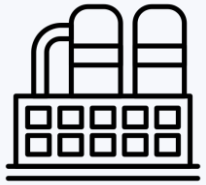
CO_2 purification

pure CO_2

emission

conversion

sequestration



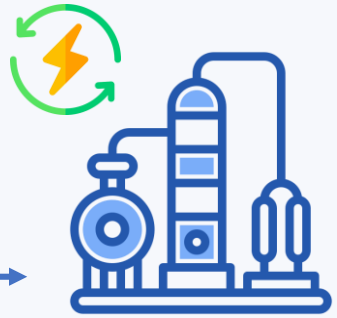
Claus unit

1000°C

$2\ H_2S + 3\ O_2 \rightarrow 2\ SO_2 + 2\ H_2O$
$2\ H_2S + SO_2 \rightarrow 3/2\ S_2 + 2\ H_2O$

recovered sulphur

various stream compositions



e-CODUCT (ETFB)

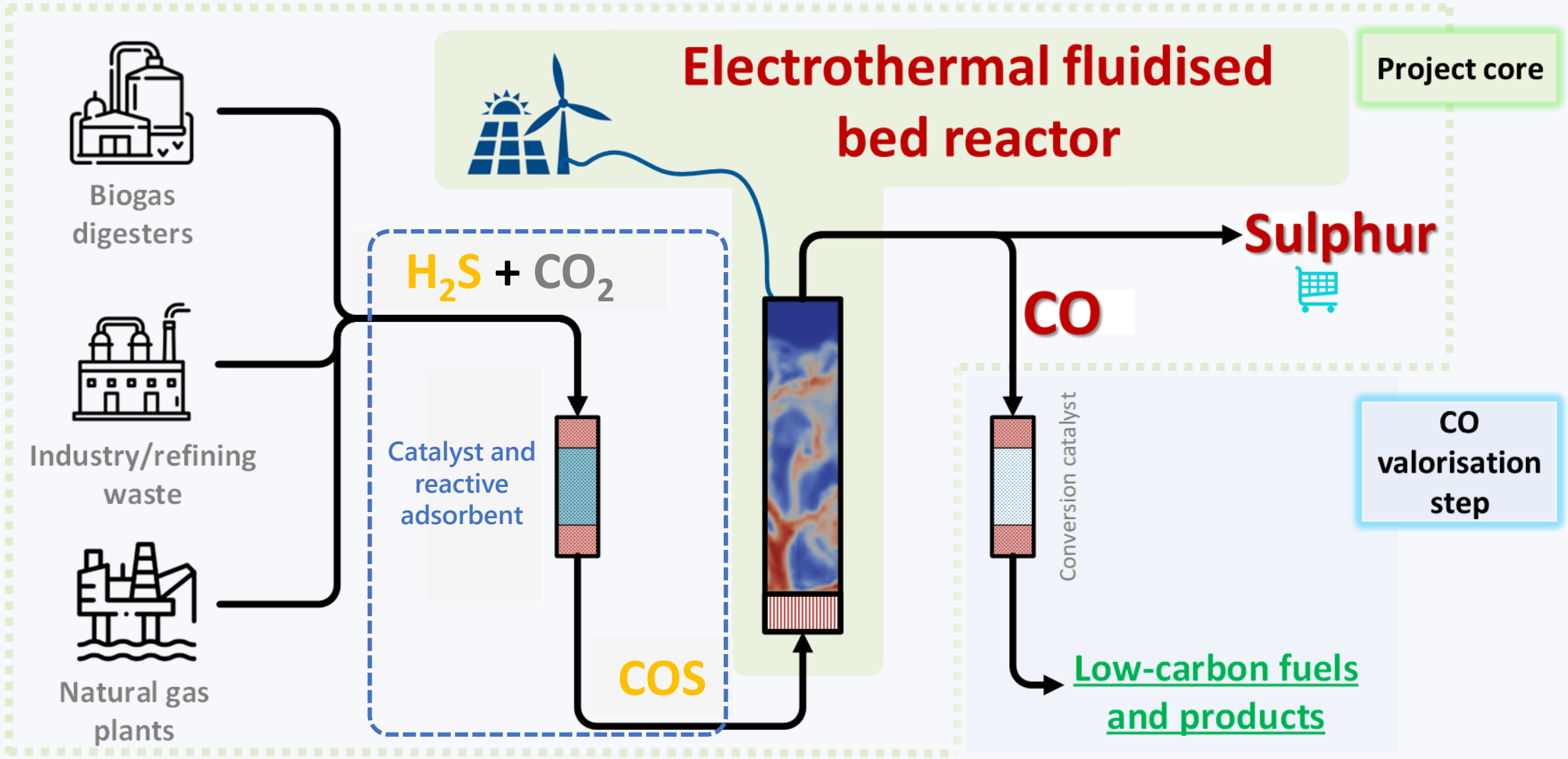
CO_2 → reduced emissions (50%)

pure CO → platform molecule (CH_3OH)

S → marketable

The e-CODUCT process

Horizon Europe
Grant Agreement
N° 101058100



Acid gas conversion on Na-Zeolites

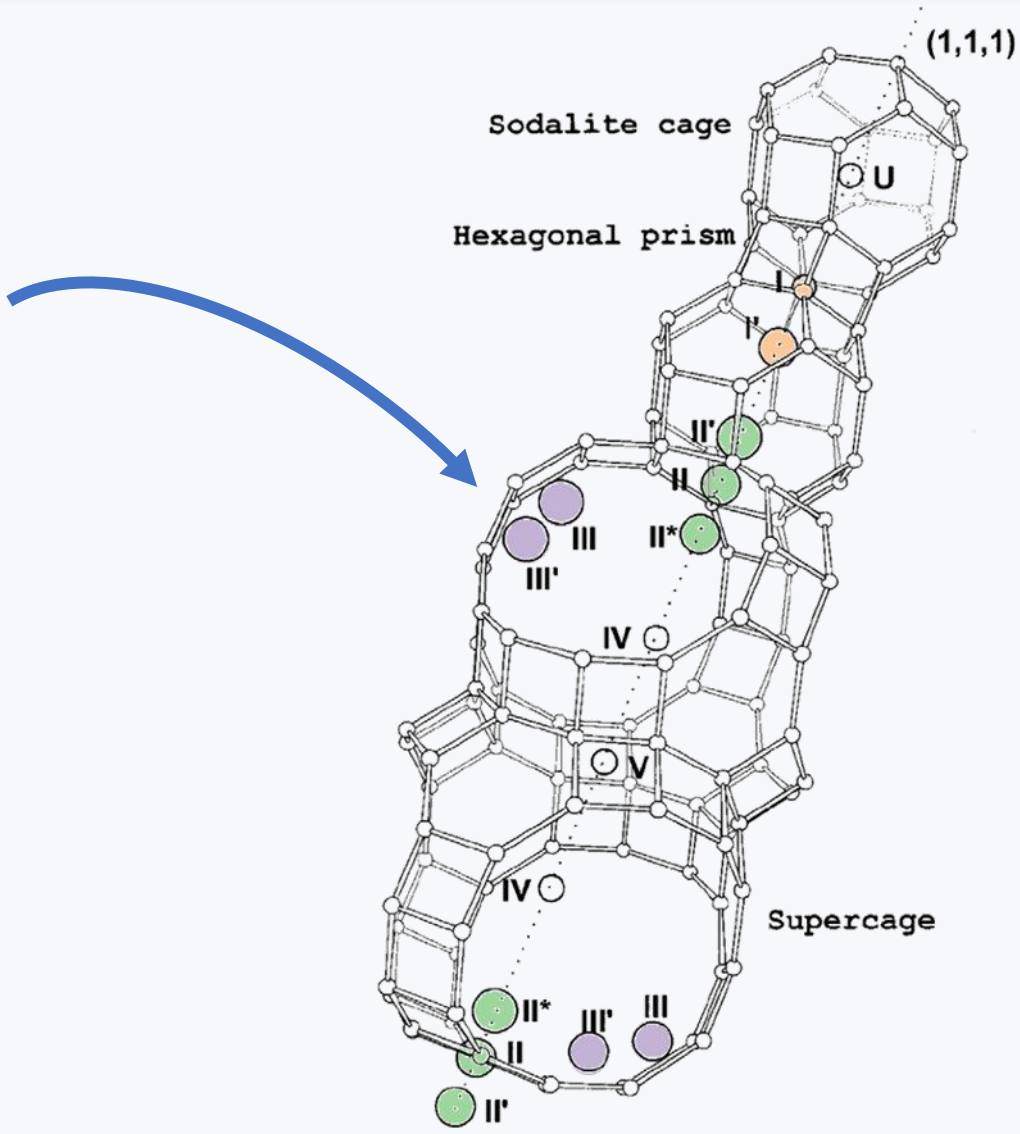
ZEOLITE

$$H_2S_{(g)} + CO_{2\,(g)} \rightleftarrows COS_{(g)} + H_2O_{(x}$$

Low temperature

Water state (x)	gas	adsorbed
$\Delta_r H^0_{298}$ (kJmol^{-1})	31.0	-11.4
$\Delta_r S^0_{298}$ (JK^{-1}mol^{-1})	0	-118
$\Delta_r G^0_{298}$ (kJmol^{-1})	33.4	23.5
Inversion T (K)	∞	199
K eq. (298K)	1.3E-6	7.5E-5
Pressure impact	0	++

M. Bülow, *Stud. Surf. Sci. Catal.* 1998

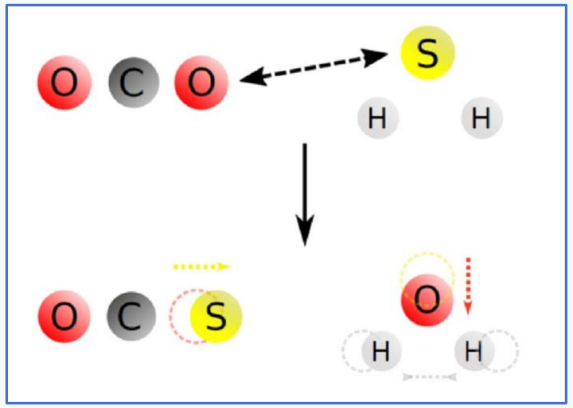


T. Frising, *Microporous Mesoporous Mater.* 2008

The nature of 13X active site

- Reaction happens on **weakly coordinated Na^+** in the *α cage*
  Fellmuth *Zeolites* 1987

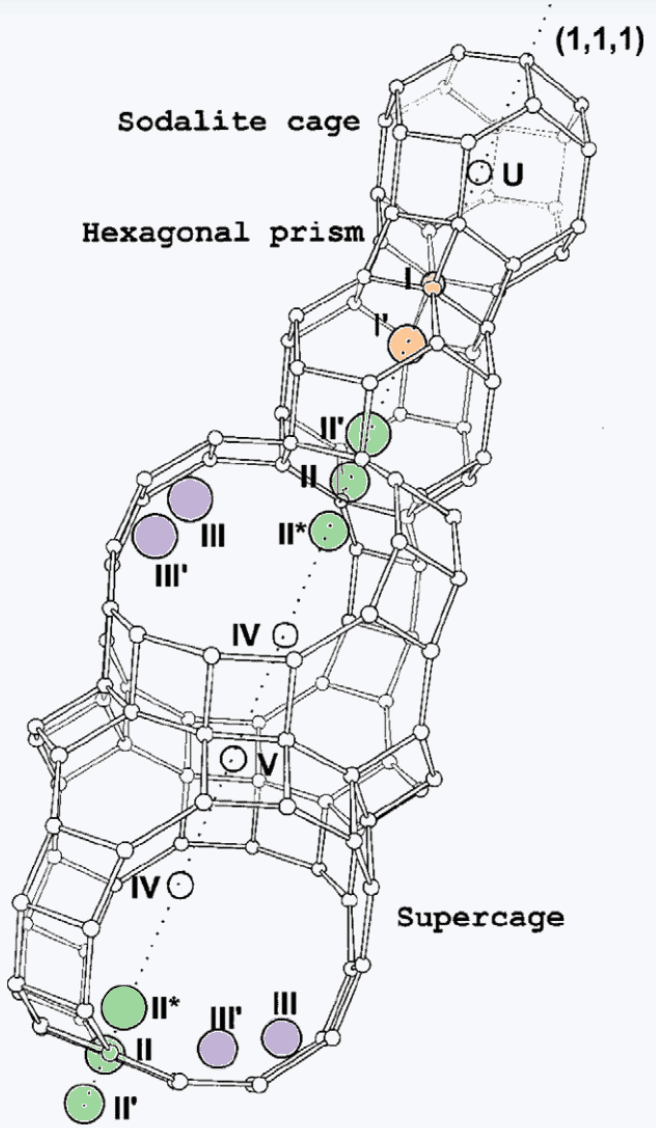
- *β cages* act as **water sinks** (diffusion controlled, slow kinetics)
  W. Lutz *Adsorpt. Sci. Technol.* 1998



E. Fetisov, *ChemPhysChem* 2018

- In NaCaX/A (67-70%) **two sites with different strength** for H_2S dissociative adsorption
  A. Starke *ACSomega* 2022

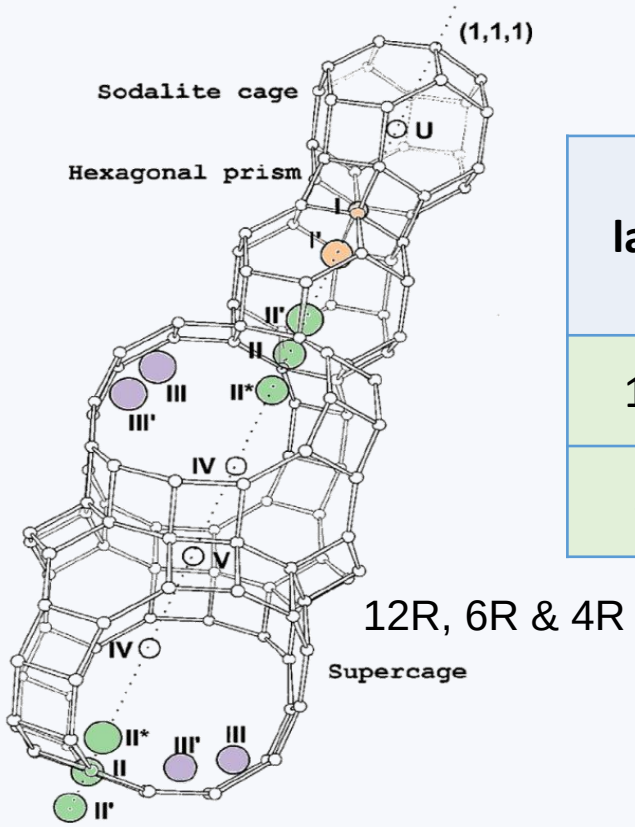
- H_2S conversion up to 75%
  (batch experiment, equimolar to Z capacity)
  M. Bülow *Stud. Surf. Sci. Catal.* 1998



T. Frising, *Microporous Mesoporous Mater.* 2008

13X and 4A; Cationic distribution and physical chemical characterization

13X (FAU)

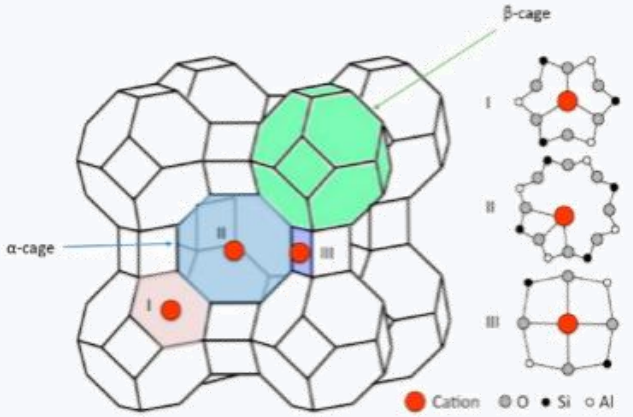


12R, 6R & 4R

Frising T, Micro. Meso. Mat. 2008

label	Si/Al	Na/Al	SSA (m^2/g)	Pore Diameter (Å)
13X	1.2	0.94	800	7.3
4A	0.97	0.88	560	4

4A (LTA)



8R, 6R & 4R

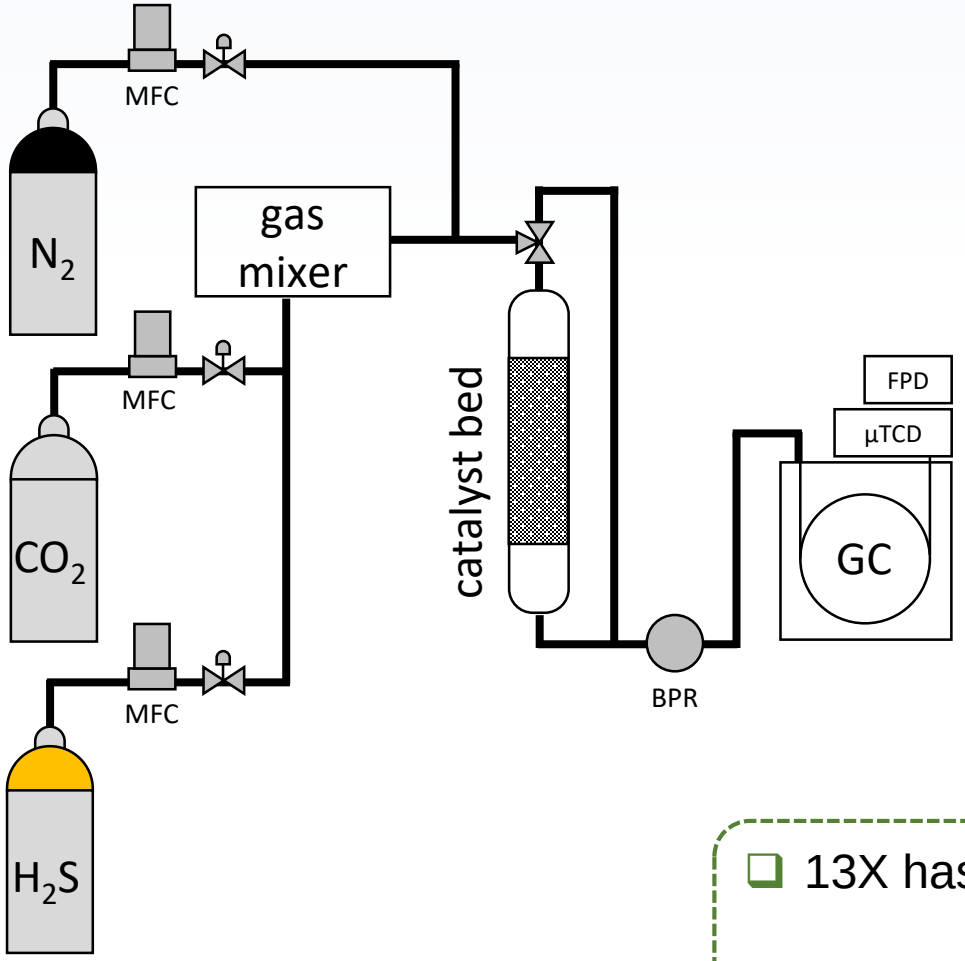
Ronghong Lin, *I & EC Research.* **2015**

- Both zeolites have Na cations in the structure
- 13X has a wider pore diameter than 4A

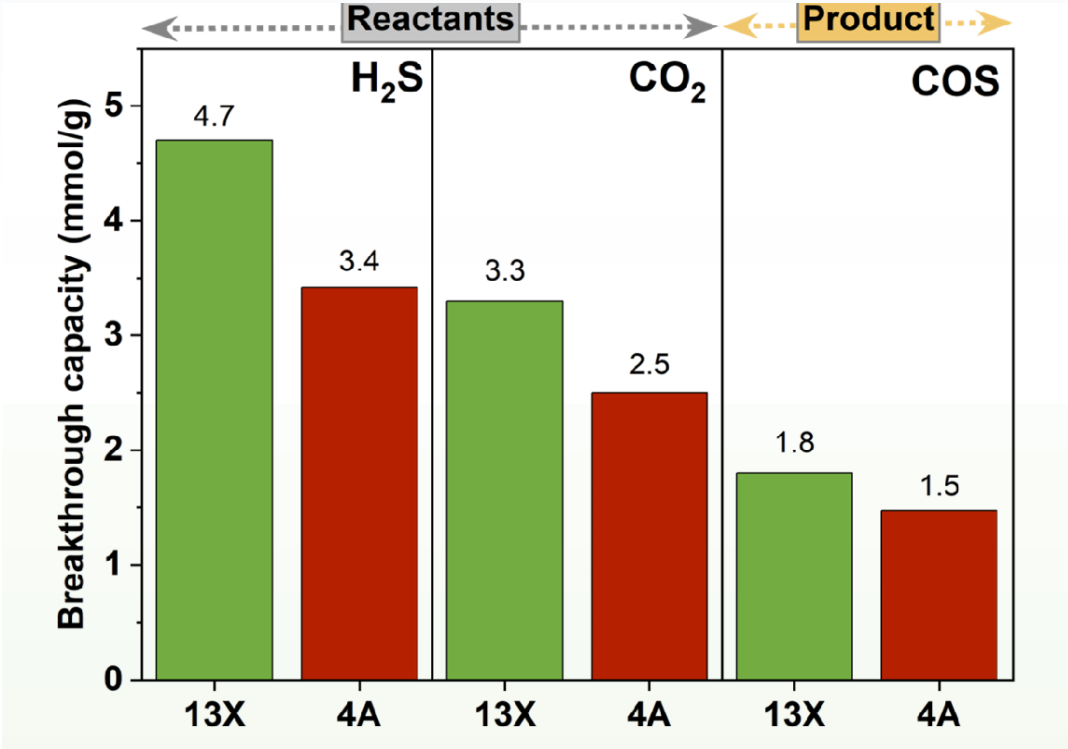
Dynamic capacities of reactants & COS at 45°C

Catalyst: pre-treated 350°C
Feed: H_2S (13%v) in N_2
Conditions: 45°C, 1 bar, W/F = 0.13 g min/mL

Micro Catalytic Bed reactor with in-line Gas Chromatography



Breakthrough experiments



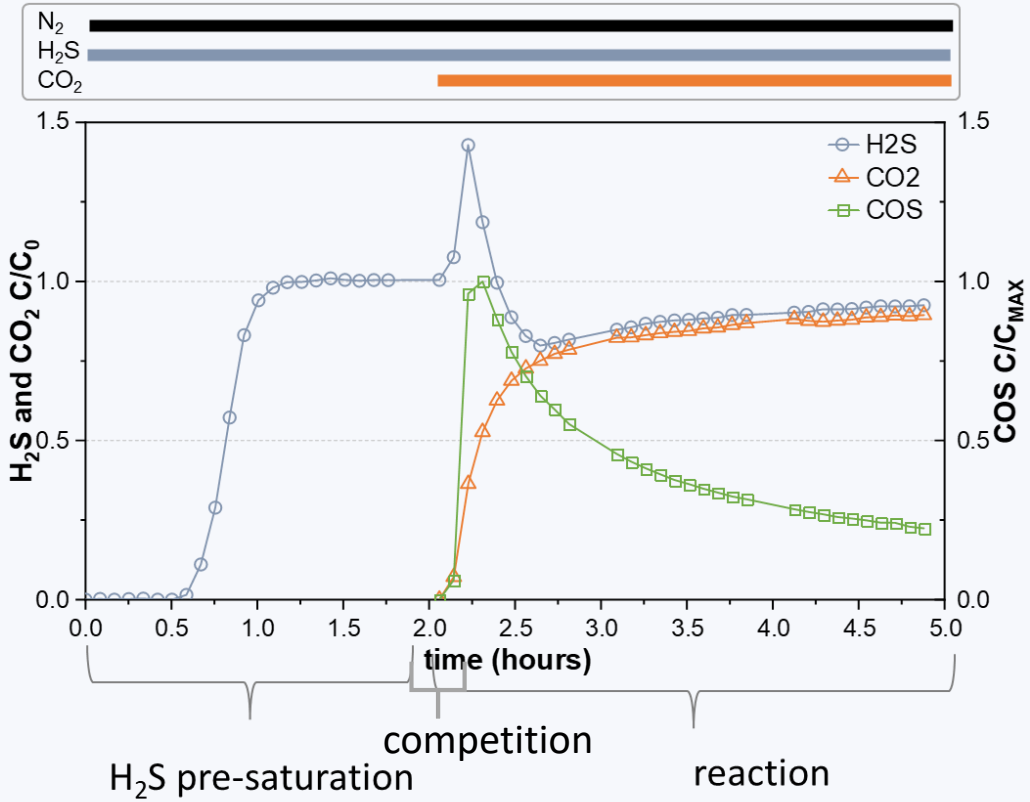
- 13X has greater dynamic capacity for H_2S and CO_2 as compared to 4A
- Both materials have comparable dynamic capacity for COS

Evaluation of catalytic activity

Sequence: pre-saturation of the stronger feed molecule (H_2S) followed by H_2S + CO_2 reaction

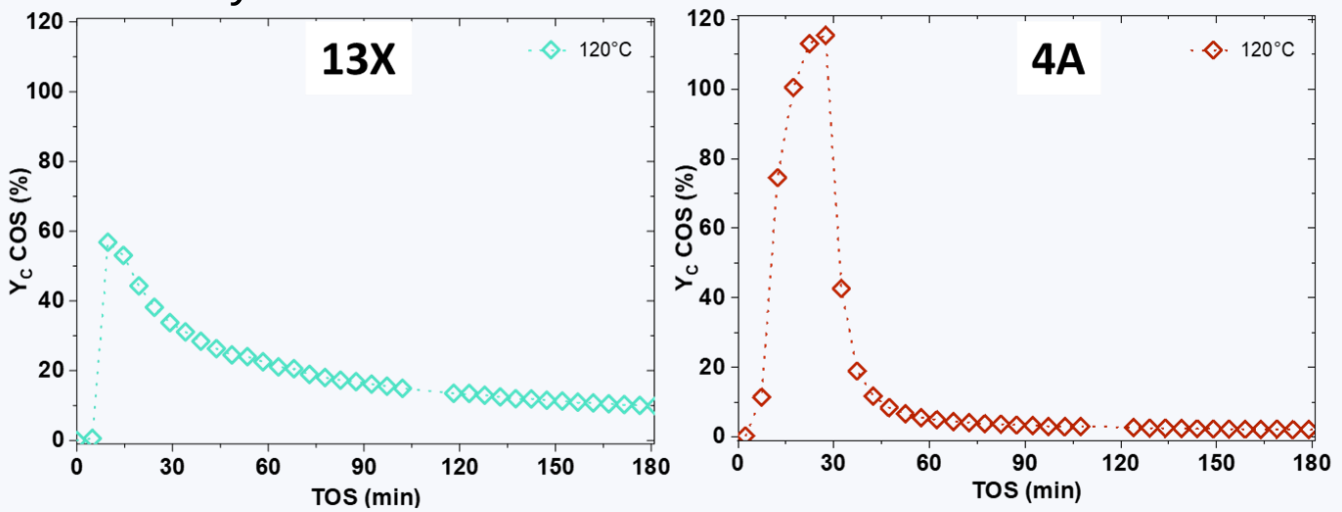
Catalyst	13X pre-treated for 6h under N_2
Bed	4 g (250-500 µm fraction)
Feed	pre-saturation in H_2S (13%v) then mix of H_2S (13%v) and CO_2 (13%v) in N_2
Conditions	45 – 350 °C, 1 bar, W/F = 0.13 g min/mL

H_2S + CO_2 on pre-adsorbed H_2S on 13X at 100°C



- CO_2 and COS adsorption avoided

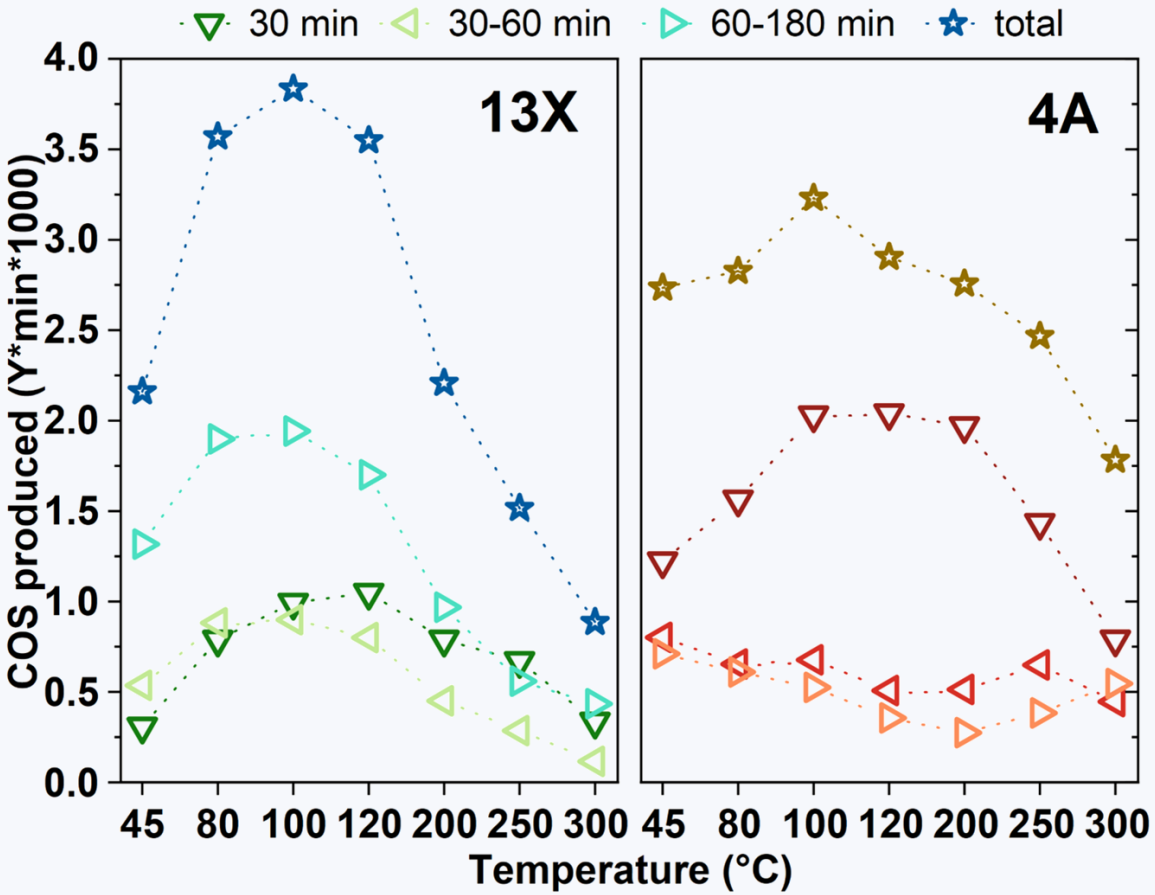
COS yields vs. time curves for 13X and 4A at 120 °C



- 13X deactivates slowly
- 4A undergoes faster deactivation

Catalyst activity at varying temperatures

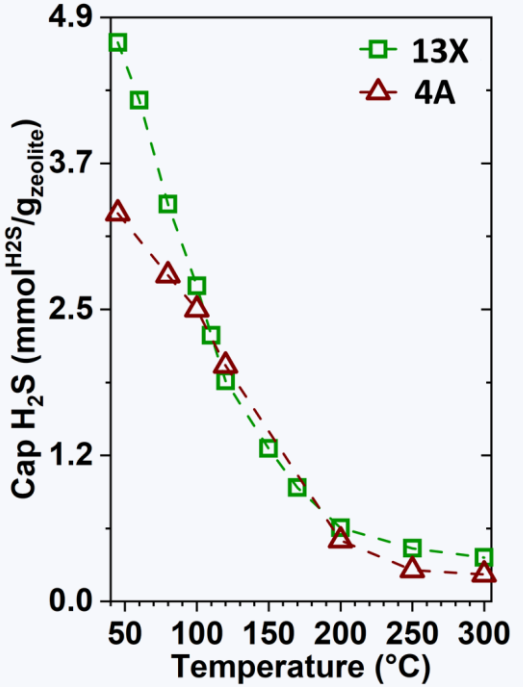
$H_2S + CO_2$ reaction on pre-adsorbed H_2S on 13X at variable T



Catalyst: pre-treated 350°C
Feed: pre-saturation in H_2S (13%v), then mix of H_2S (13%v) and CO_2 (13%v) in N_2
Conditions: variable T (45 – 300 °C)

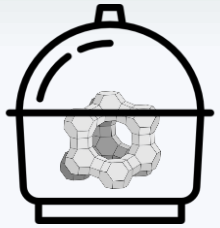
Lower COS yields at high T

Absolute H_2S capacities

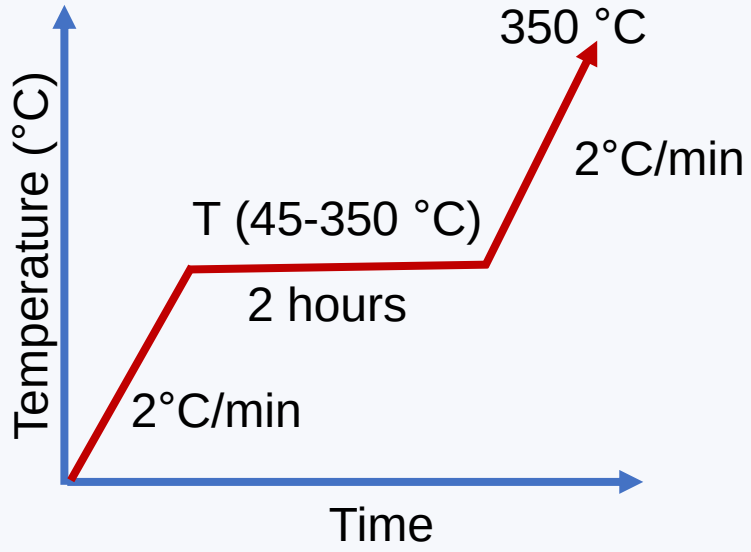


- COS yields during 1st half hour of reaction → 13X < 4A
- Total COS yields after 3 hours → 13X > 4A

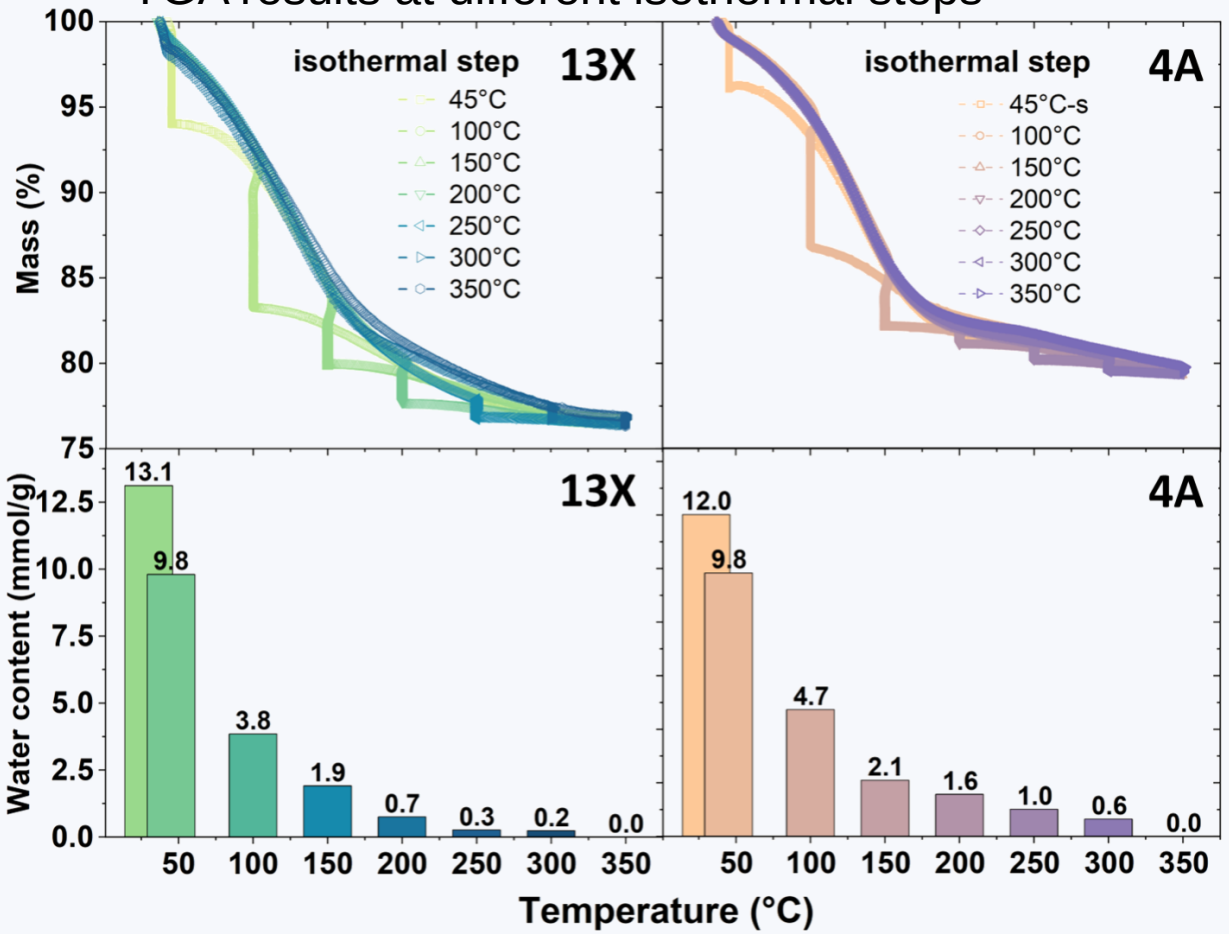
Hydration & progressive dehydration



saturated
NaCl solution(75% RH at 20°C)



TGA results at different isothermal steps



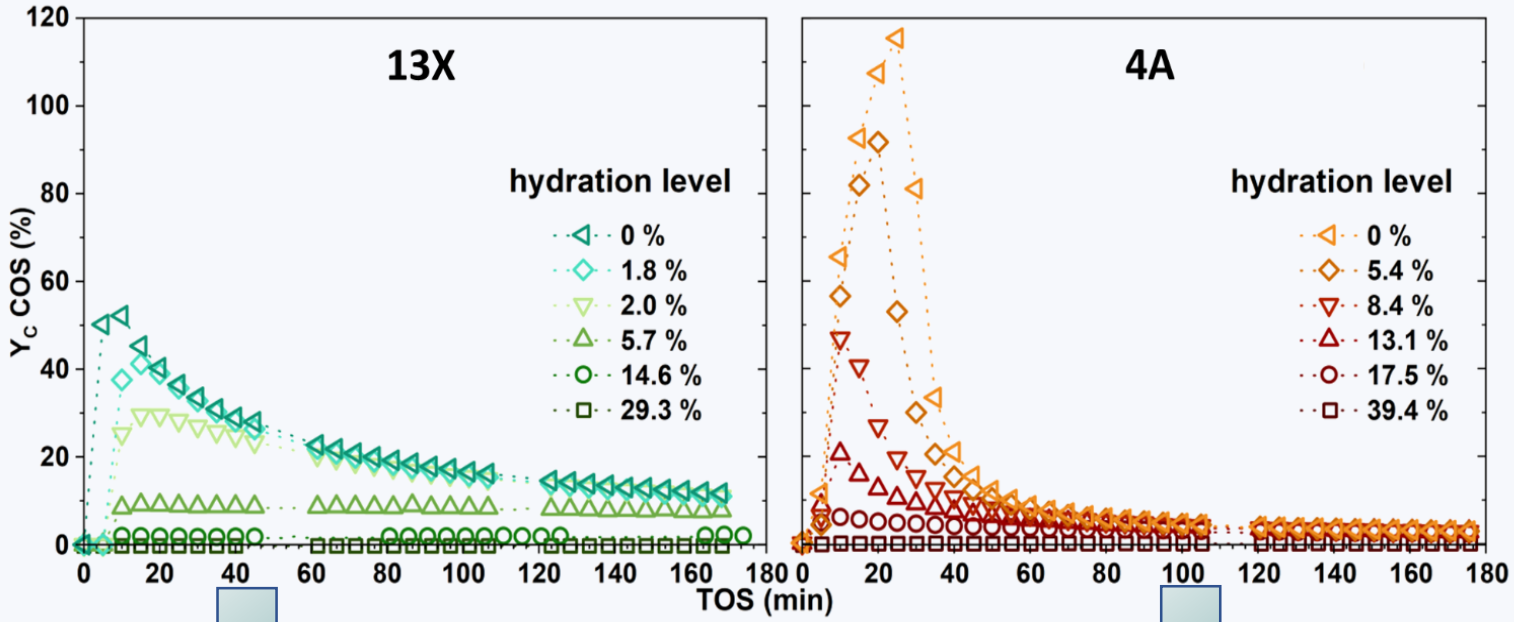
- Total water content of 13X is higher than 4A
- at T > 100 °C, 13X retains less water than 4A
- Both zeolites dehydrate completely at 350 °C

$$Hydration\ level(\%) = 100 - \frac{water\ loss\ at\ isothermal\ step}{total\ water\ loss\ (45\ to\ 350\ °C)}$$

COS production at different hydration levels

Reaction at different hydration levels (from fully hydrated to completely dehydrated zeolite)

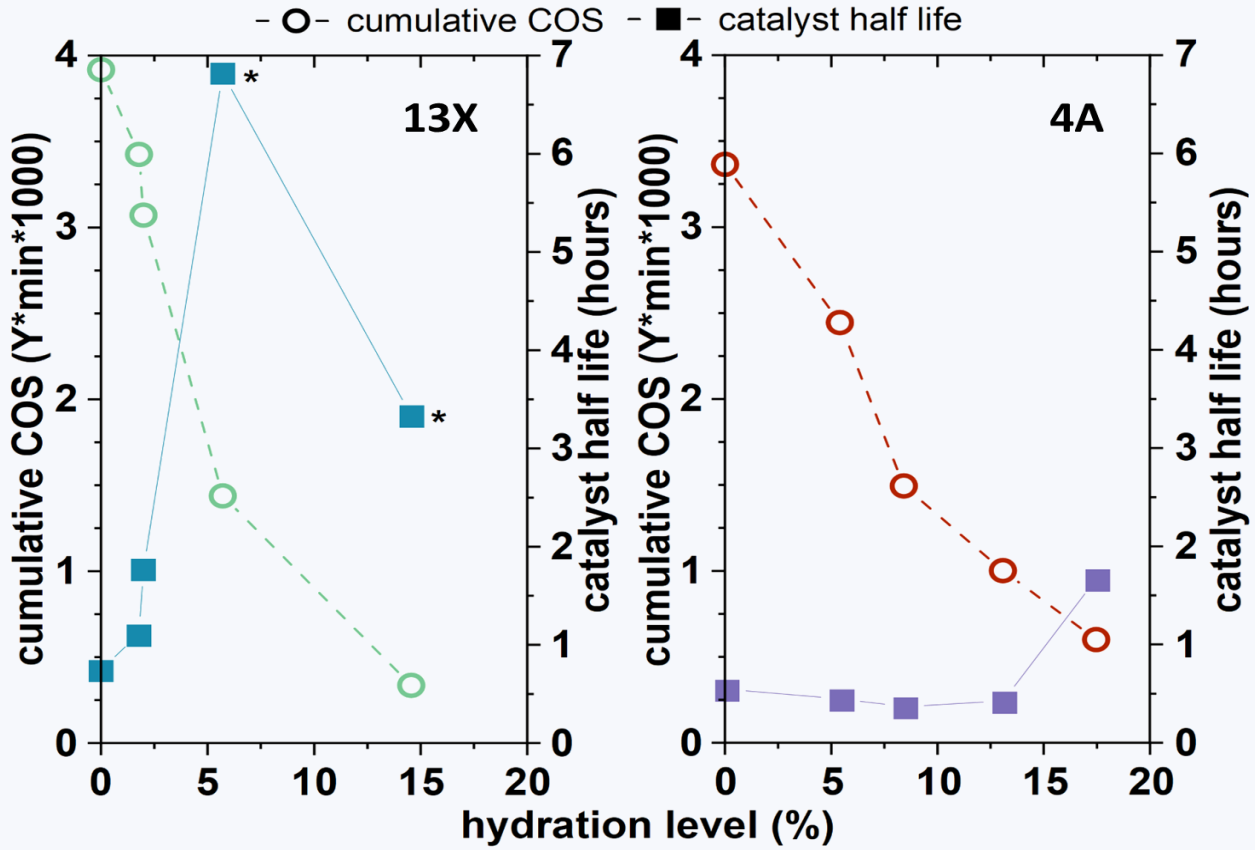
Catalyst: pre-treated at variable T (100-350 °C)
Feed: pre-saturation in H_2S (13%v), then mix of H_2S and CO_2 (13%v) in N_2
Conditions: 100°C, 1 bar, W/F = 0.13 g min/mL



Most of the activity recovered on decreasing hydration from 5.7 to 2%

Progressive recovery of activity from hydrated to fully dry zeolite

Hydration level dependence of COS production & catalyst half-life



Drop in 13X half-life after 5% hydration

Increase in 4A half-life after 13% hydration

Decrease in COS yields with increase in zeolite hydration level

Microkinetic Modeling (MKM) of acid gas conversion on 13X

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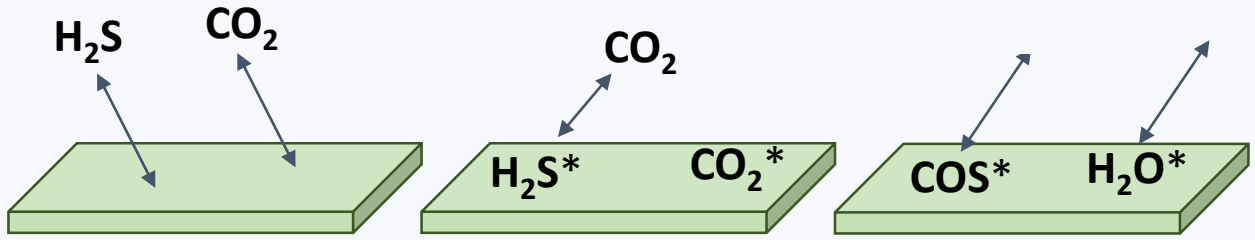
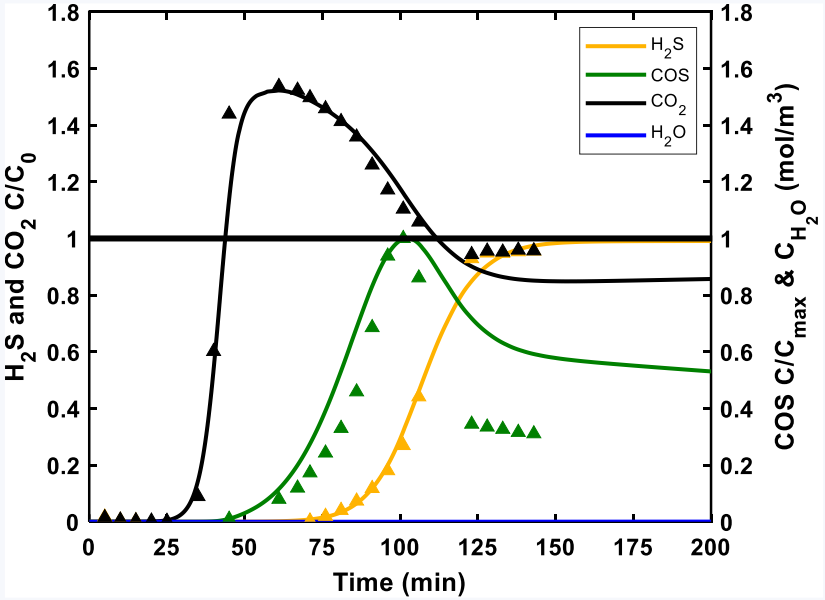
Eley-Rideal (modified) reaction mechanism

$H_2S + * \leftrightarrows H_2S*$	$r_1 = k_1^+ C_{H_2S}\theta_* - k_1^- \theta_{H_2S}$
$H_2S* + CO_2 \leftrightarrows COS + H_2O*$	$r_2 = k_2^+ C_{CO_2}\theta_{H_2S} - k_2^- C_{COS}\theta_{H_2O}$
$H_2O* \leftrightarrows H_2O + *$	$r_3 = k_3^+ \theta_{H_2O} - k_3^- C_{H_2O}\theta_*$
$CO_2 + * \leftrightarrows CO_2*$	$r_4 = k_4^+ C_{CO_2}\theta_* - k_4^- \theta_{CO_2}$
$COS* \leftrightarrows COS + *$	$r_5 = k_5^+ \theta_{COS} - k_5^- C_{COS}\theta_*$



continuous mixed feed
H_2S:CO_2=1:1 on 13X at 45°C



competitive adsorption ☑
pseudo-stationary state ☒

MKM of acid gas conversion on 13X

R. Ghassemi
UNIVERSITEIT GENT

Langmuir-Hinshelwood-Hougen-Watson reaction mechanism

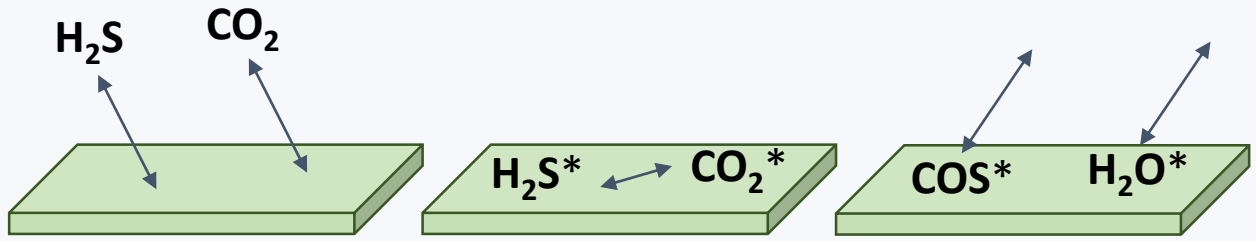
$H_2S + * \leftrightarrows H_2S*$ $\quad r_1 = k_1^+ C_{H_2S}\theta_* - k_1^- \theta_{H_2S}$

$CO_2 + * \leftrightarrows CO_2*$ $\quad r_2 = k_2^+ C_{CO_2}\theta_* - k_2^- \theta_{CO_2}$

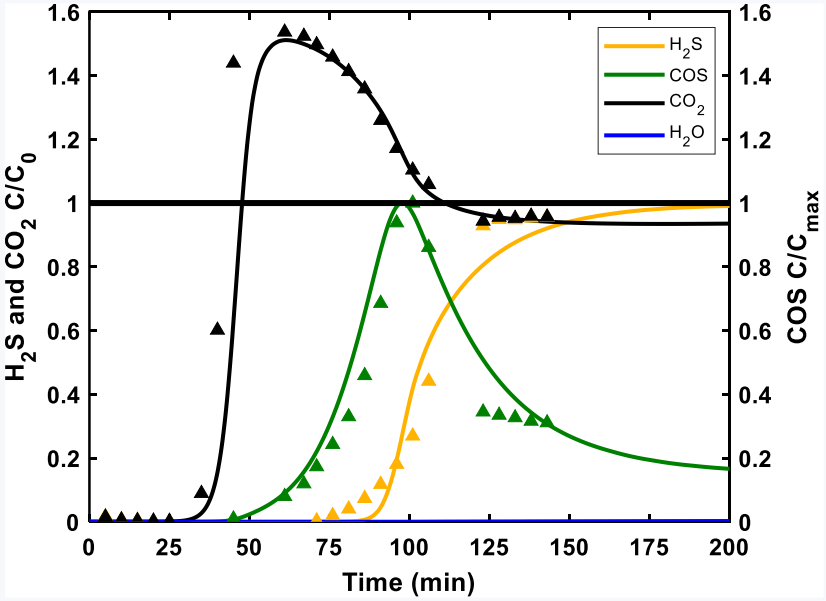
$H_2S* + CO_2* \leftrightarrows COS* + H_2O*$ $\quad r_3 = k_3^+ \theta_{CO_2}\theta_{H_2S} - k_3^- \theta_{H_2O}\theta_{COS}$

$COS* \leftrightarrows COS + *$ $\quad r_4 = k_4^+ \theta_{COS} - k_4^- C_{COS}\theta_*$

$H_2O* \leftrightarrows H_2O + *$ $\quad r_5 = k_5^+ \theta_{H_2O} - k_5^- C_{H_2O}\theta_*$



continuous mixed feed
H_2S:CO_2=1:1 on 13X at 45°C



$k_{H_2S}^{ads}$	$k_{H_2S}^{des}$	k_r^f	k_r^r	$k_{H_2O}^{des}$	$k_{H_2O}^{ads}$	$k_{CO_2}^{ads}$	$k_{CO_2}^{des}$	k_{COS}^{des}	k_{COS}^{ads}
3.5E-3	1.8E-4	2E-3	1E-3	2E-4	2	7E-4	4E-3	7E-4	7E-4

Not assuming a rate-determining step
Water assumed to be adsorbed

competitive adsorption ☑
pseudo-stationary state ☑

MKM of acid gas conversion on 13X

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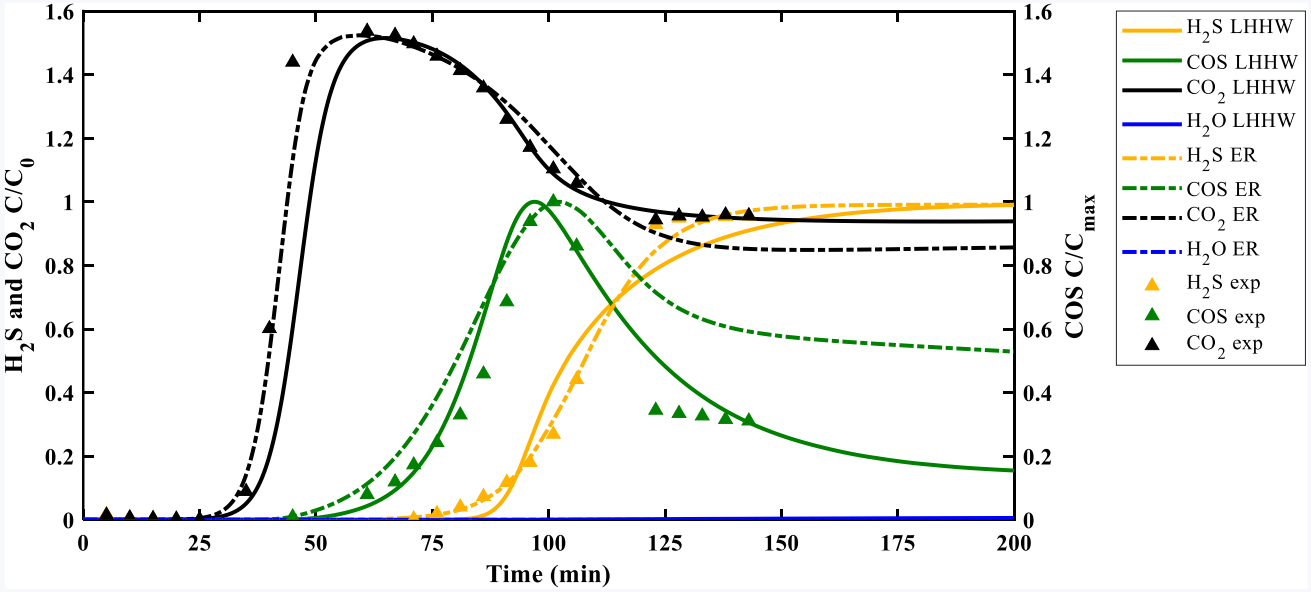
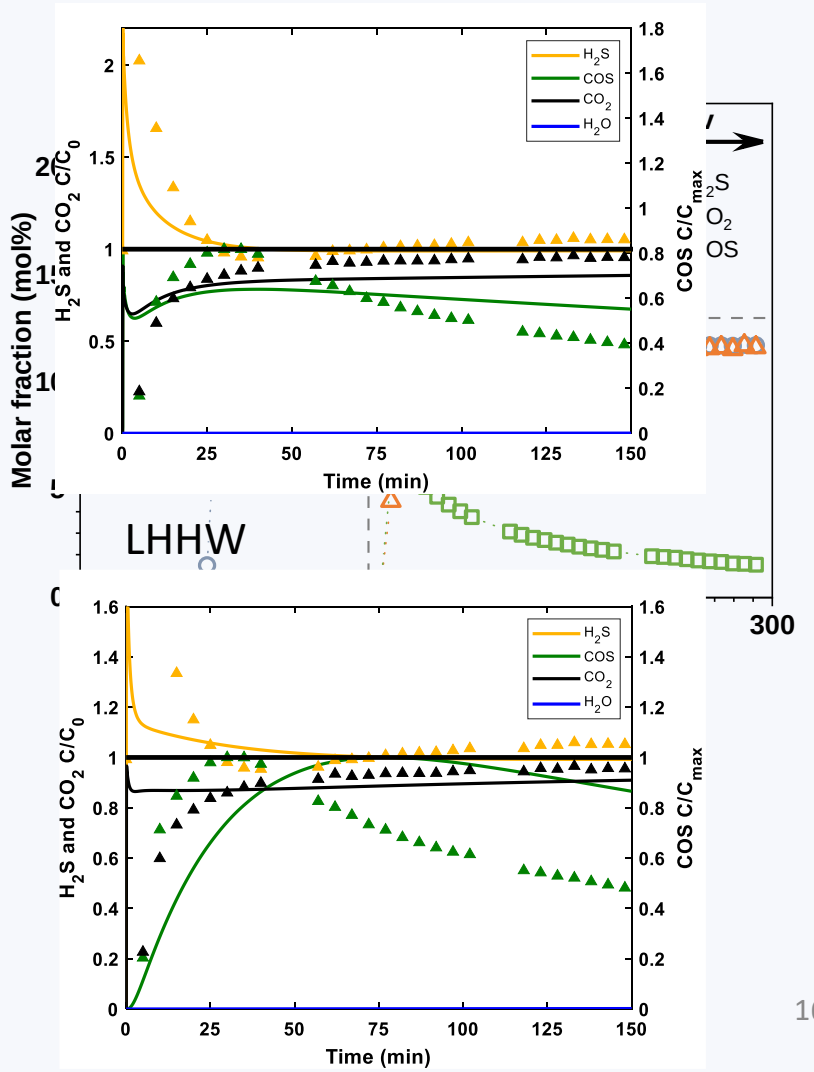
continuous mixed flow of AG=1:1



H2S pre-saturation +continuous mixed feed

$H_2S:CO_2$=1:1 on 13X at 45°C

Modified ER



can be applied to **pre-saturated + mixed flow** sequence ?

MKM of acid gas conversion on 13X

LHHW adapted for pre-saturation

$H_2S + \# \leftrightarrows H_2S^{\#}$ $\quad r_1 = k_1^+ C_{H_2S} \theta_{\#} - k_1^- \theta^{\#}_{H_2S}$

$H_2S^{\#} + * \leftrightarrows H_2S*$ $\quad r_{1'} = k_{1'}^+ \theta_{H2S_{\#}} \theta_* - k_{1'}^- \theta_{H_2S*}$

$CO_2 + * \leftrightarrows CO_2*$ $\quad r_2 = k_2^+ C_{CO_2} \theta_* - k_2^- \theta_{CO_2}$

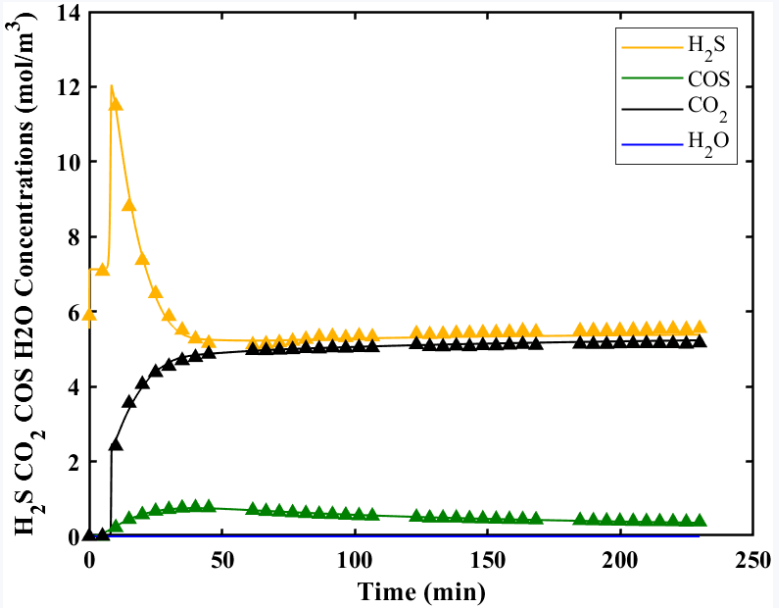
$H_2S* + CO_2* \leftrightarrows COS* + H_2O*$ $\quad r_3 = k_3^+ \theta_{CO_2} \theta_{H_2S} - k_3^- \theta_{H_2O} \theta_{COS}$

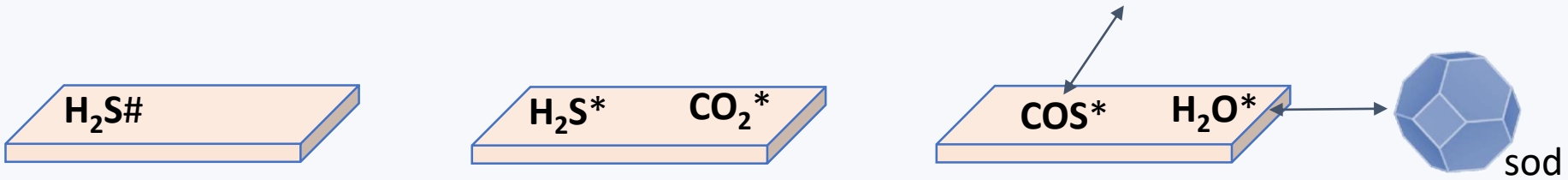
$COS* \leftrightarrows COS + *$ $\quad r_4 = k_4^+ \theta_{COS} - k_4^- C_{COS} \theta_*$

$H_2O* \leftrightarrows H_2O^{\#} + *$ $\quad r_5 = k_5^+ \theta_{H_2O*} - k_5^- C_{H_2O\#} \theta_*$

$H_2O* + sodalite \leftrightarrows H_2O_{sod}$ $\quad r_{5'} = k_{5'}^+ \theta_{H_2O} \theta_{sodalite} - k_{5'}^- \theta_{H_2O_{sod}}$

H_2S pre-saturated + mixed feed
$H_2S:CO_2$=1:1 on 13X at 45°C





Conclusions

- **13X** has **higher capacity** for H_2S and CO_2 than 4A and gives **higher total COS yields**
- Highest COS yields at **100°C** after which the activity decrease with increase in temperature
- Catalyst **deactivation** due to **water poisoning** active sites, 13X deactivates slowly whereas faster deactivation profile of 4A
- **Re-gain** in activity of **4A** after 1st hour at **T > 120°C**
- **COS production** is proportional to **H_2S capacity** as well as to the **hydration level** of zeolite
- **LHHW MKM** works better on 13X

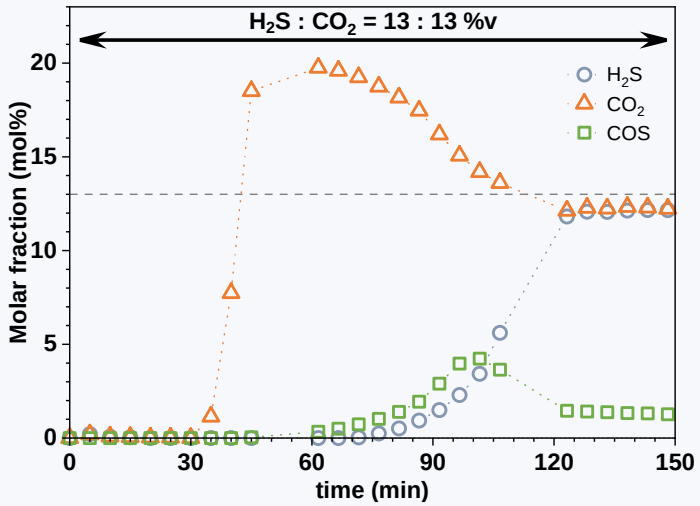
The e-CODUCT project
is funded under Horizon Europe
Grant Agreement n°101058100

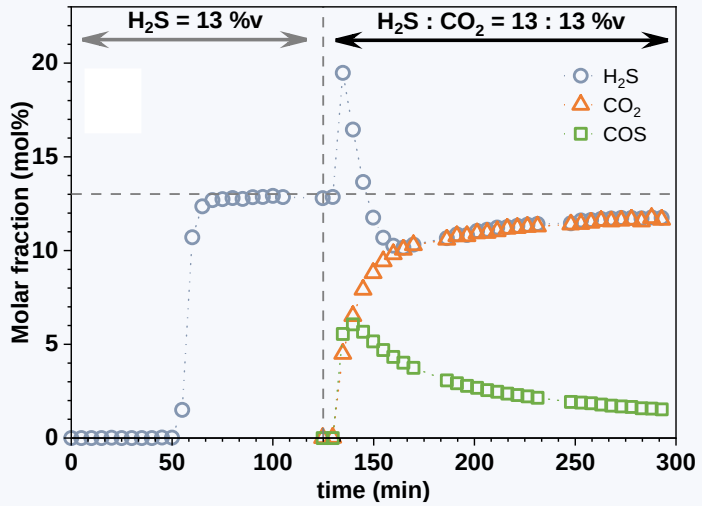
Thank you all for the attention!

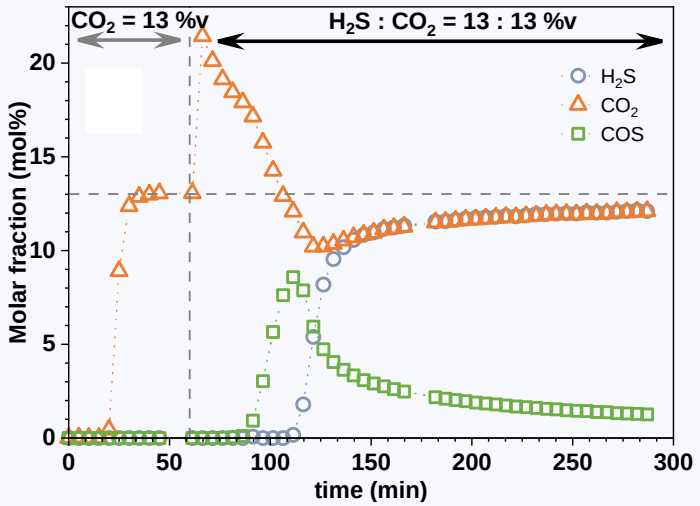
Testing catalytic activity: Na-FAU

mixed feed
continuous or pulsed flow

pre-saturation + mixed feed
continuous flow







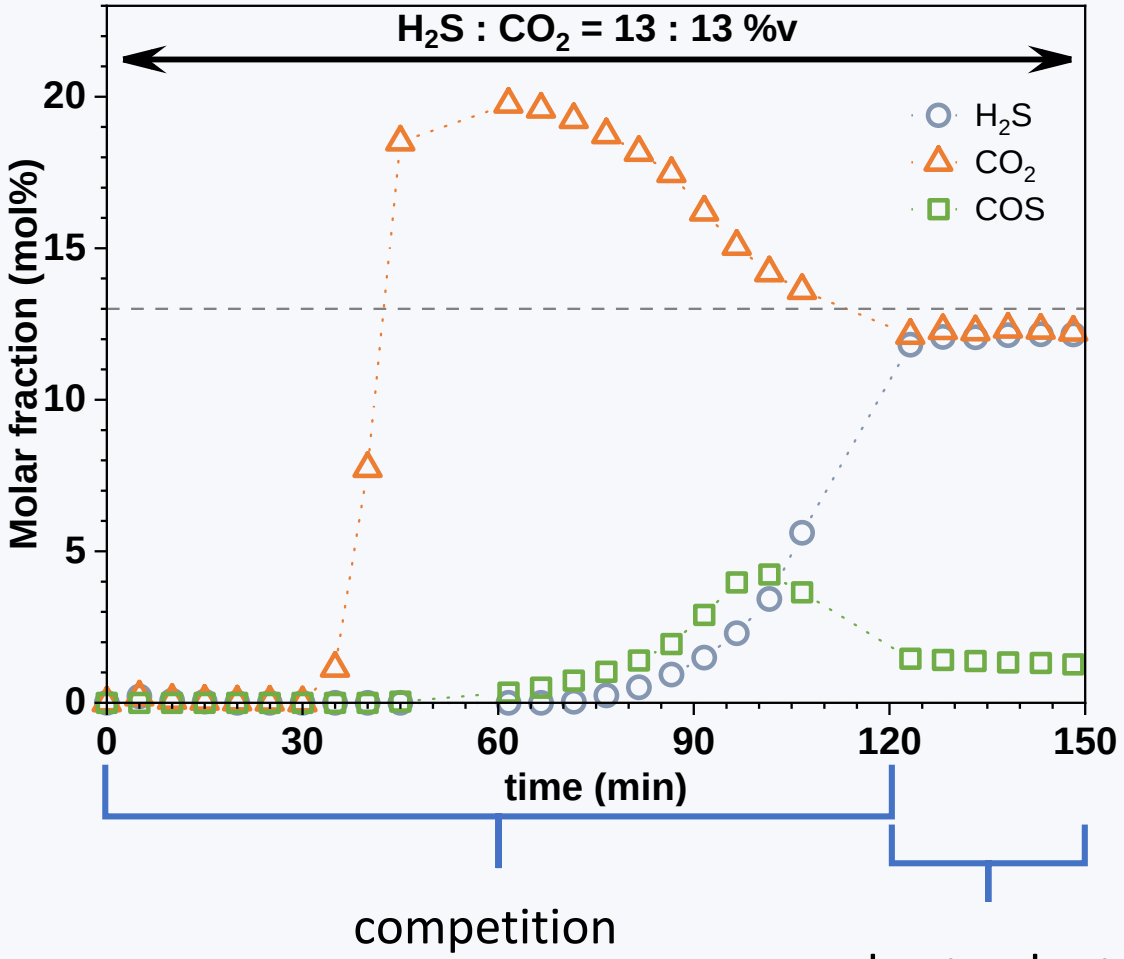
Catalyst	13X pre-treated for 6h under N_2
Bed	up to 4 g (250-500 µm fraction)
Feed	H_2S (13%v) and CO_2 (13%v) in N_2
Conditions	45°C, 1 bar, W/F = 0.13 g min/mL

adsorption strength on 13X

$$H_2O > H_2S >> COS \geq CO_2$$

Continuous mixed feed

$H_2S + CO_2$ on 13X at 45°C



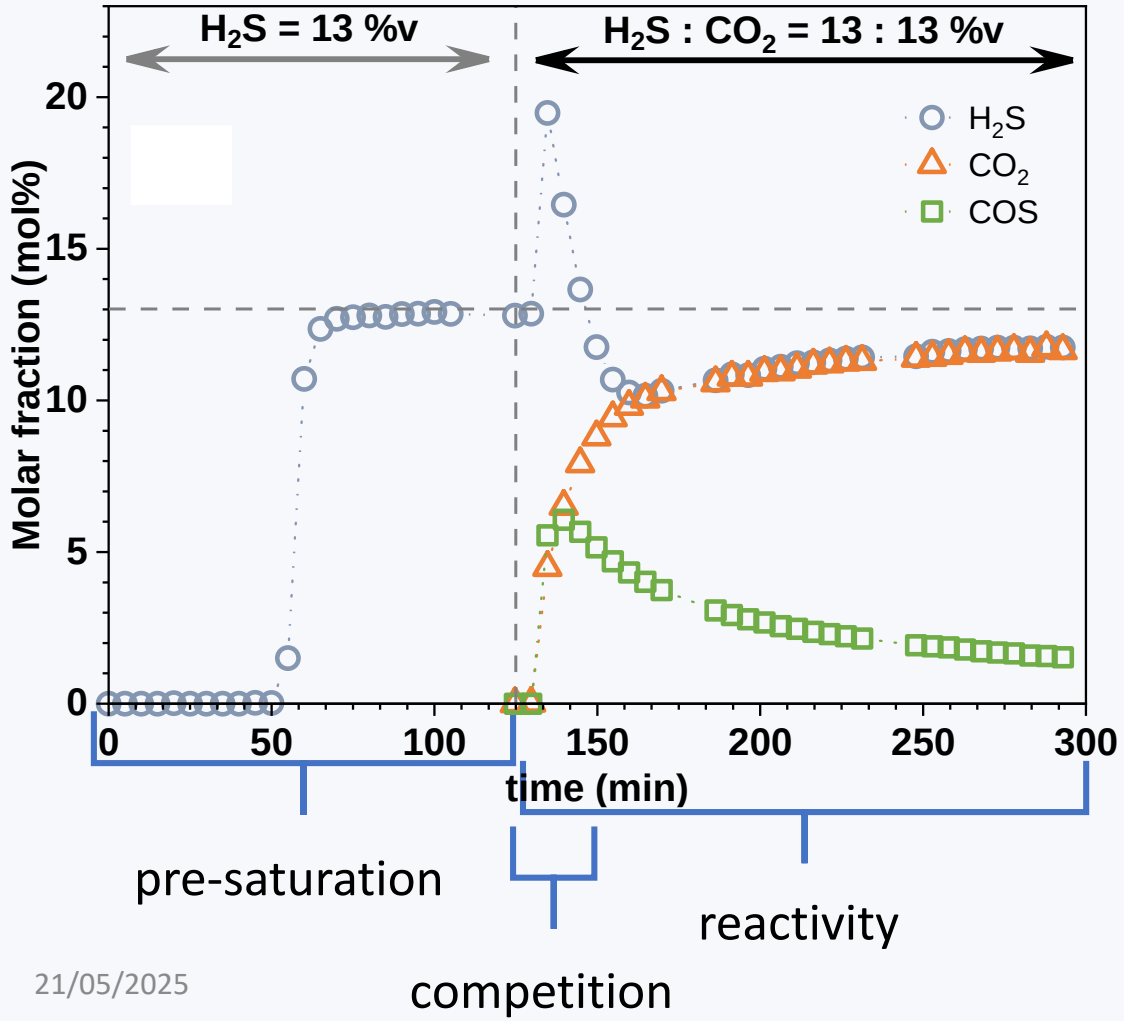
Preferably avoidable phenomena

- Breakthrough of all molecules
- CO_2 rollup effect
- COS (formed instantaneously) can adsorb

decouple adsorption and reactivity

Pre-adsorption + mixed feed

H_2S + CO_2 on pre-adsorbed H_2S on 13X at 45°C



Pre-saturation sequence

- CO_2 and COS adsorption avoided
- Some competition effects with H_2S
- COS decreases over time

Key points

Mechanism and kinetic modelling

- Catalytic acid gas conversion to COS at mild temperature tested in **mixed feed and with pre-saturation**
- MKM of both sequences, each one requiring a **dedicated set** of parameters
- The amount of **Na cations accessible to H_2S** is used as the total amount of active sites
- Catalyst **deactivation due to water poisoning** active sites, where *sod* do not participate in water placement even for long reaction times
- Optimization: effect of **temperature**, pressure, etc.