Valorisation Of Greenhouse And Acid Gas By Low-silica Zeolite Catalyst

S.R. Batool[1], M. Fabbiani[1], L. Pinard[1], A. Novikov[2], H. Retot[2], Valentin Valtchev[1]*

[1] LCS, CNRS-ENSICaen-UniCaen, 14050 Caen, France

[2] Saint Gobain Research Provence and NORPRO, Cavaillon, France

*valentin.valtchev@ensicaen.fr

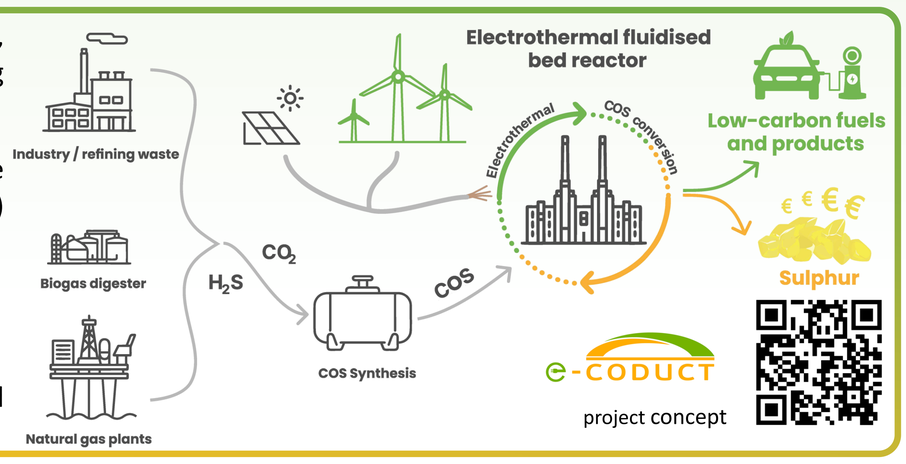
The e-CODUCT project is funded under Horizon Europe Grant Agreement n°101058100

Currently, industrial treatment of acid gas is mainly done by the Claus process, which has limitations and require additional fuel, whereas CO_2 reduction techniques need high-purity CO_2, necessitating effective separation from acid gas. Hence, no existing technologies allow simultaneous reduction of acid gas components i.e., CO_2 and H_2S.

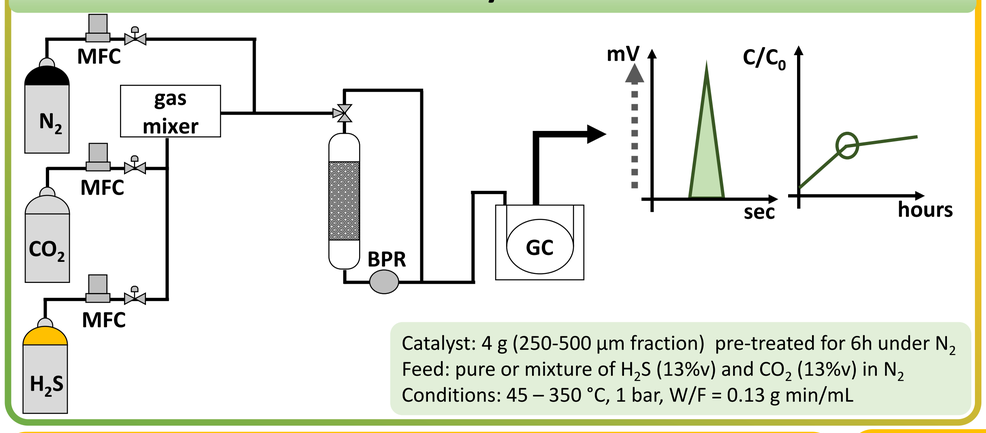
The project **e-CODUCT** aims to electrify simultaneous conversion of acid gas components into platform molecule carbonyl sulfide COS in a fixed bed reactor, which is further converted into CO and marketable Sulphur in a electrothermal fluidized bed (ETFB) reactor. The COS formation in continuous mode from CO_2 and H_2S is the first and most important stage of this process, as follows.

$$H_2S_{(g)} + CO_{2\,(g)} \rightleftharpoons COS_{(g)} + H_2O_{(ads.)}$$

In this work, we explore zeolites 13X and 4A for COS formation, aiming to develop a catalyst that gives high COS yields per pass and low energy demand for regeneration.



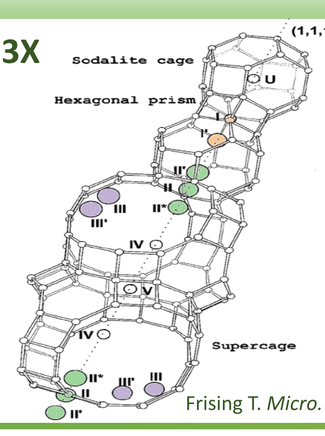
Micro Catalytic Bed unit



Catalyst: 4 g (250-500 µm fraction) pre-treated for 6h under N_2
Feed: pure or mixture 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

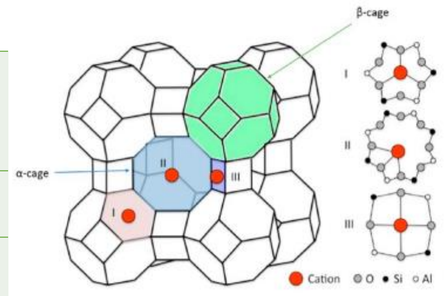
13X vs 4A

13X — Cationic distribution and physical chemical characterization — **4A**



Frising T. *Micro. Meso. Mat.* **2008**

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

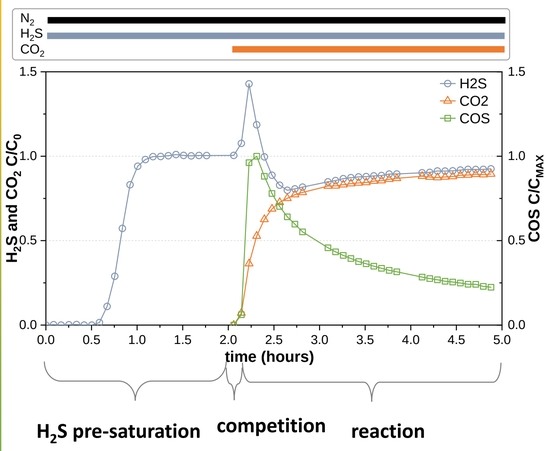


Ronghong Lin, *I & EC Research.* **2015**

Feed sequence

Catalyst: pre-treated 350°C
Conditions: 45°C, 1 bar, W/F = 0.13 g min/mL

Pre-saturation of the stronger feed molecule (H_2S) followed by H_2S and CO_2 reaction



- CO_2 and COS adsorption avoided
- Decoupling of adsorption and reactivity
- Some H_2S is displaced as soon as CO_2 is added

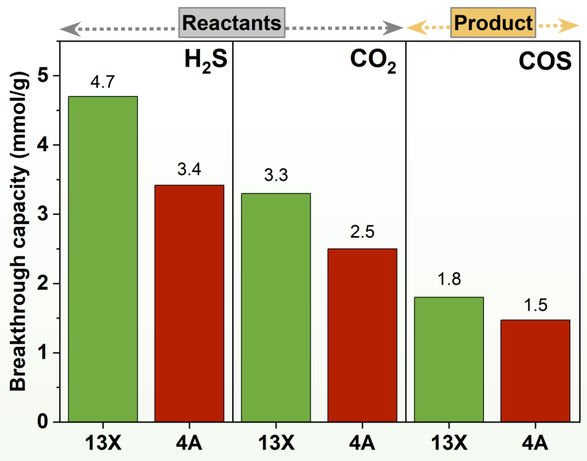
Complex reactivity

Fast catalyst deactivation leading to exponential decay of COS

Dynamic capacities of reactants & COS at 45°C

Material dependence of dynamic capacity 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



13X has greater dynamic capacity for H_2S and CO_2 as compared to 4A

Pre-saturation of H_2S & material dependent dynamic capacity

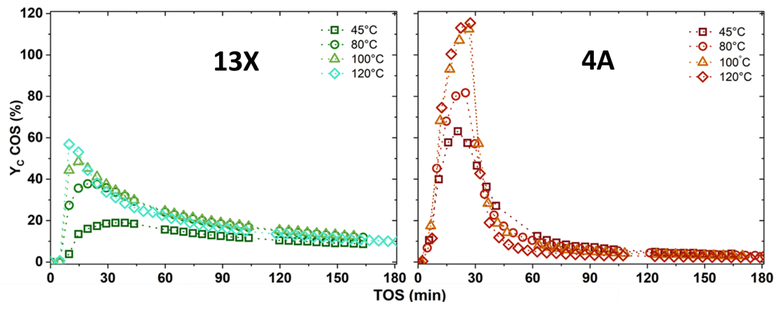
- H_2S pre-saturation allows understanding of concentration evolution
- 13X has higher capacity for reactants than 4A

Effect of temperature on COS formation

COS yield at lower temperatures

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°C ≤ T ≤ 120 °C

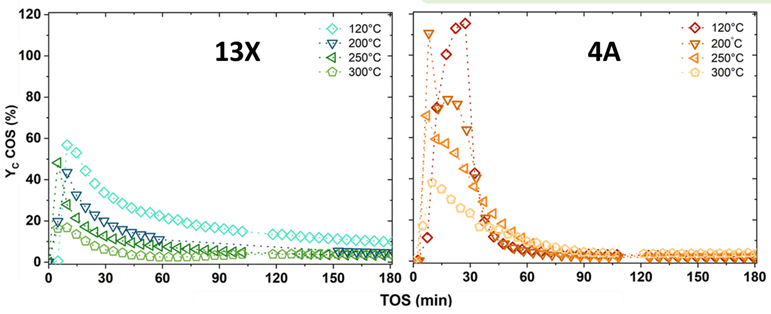


COS yields increase with temperature up to 120 °C for both materials
13X deactivates slowly whereas 4A undergoes faster deactivation

COS yield at higher temperatures

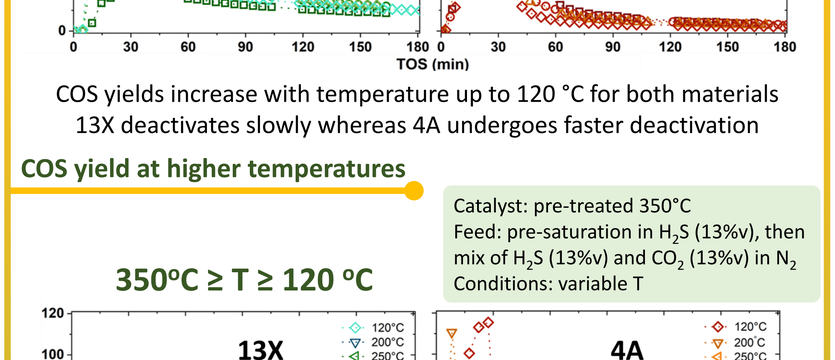
Catalyst: pre-treated 350°C
Feed: pre-saturation in H_2S (13%v), then mix of H_2S (13%v) and CO_2 (13%v) in N_2
Conditions: variable T

350°C ≥ T ≥ 120 °C



Decrease in COS yields with rise in temperature at T > 120°C
COS peaks move to short reaction times → faster gas & lower capacity
Re-gain in activity of 4A after 1st hour at T > 120°C

Catalyst activity at varying reaction times



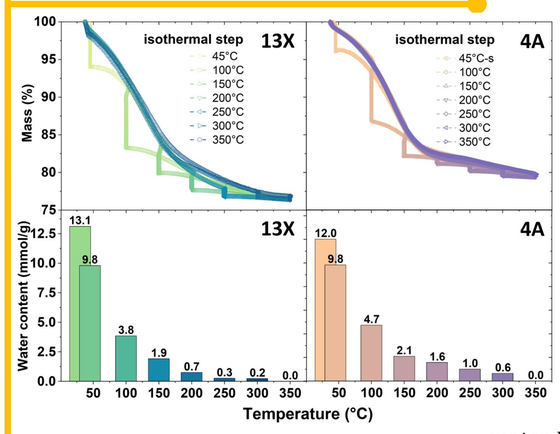
COS yields during 1st of reaction → 13X < 4A
Total COS yields after 3 hours → 13X > 4A

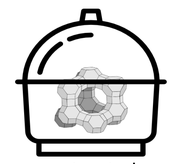
Temperature dependent variation of reactivity of 13X and 4A

- Highest conversion at 100 – 120 °C, 13X gives higher total COS yields than 4A
- Slow poisoning of 13X by water and faster deactivation profile of 4A
- 4A regains some activity at high T due to H_2O removal from some sites

Effect of zeolite hydration level on catalyst activity

Hydration & progressive dehydration





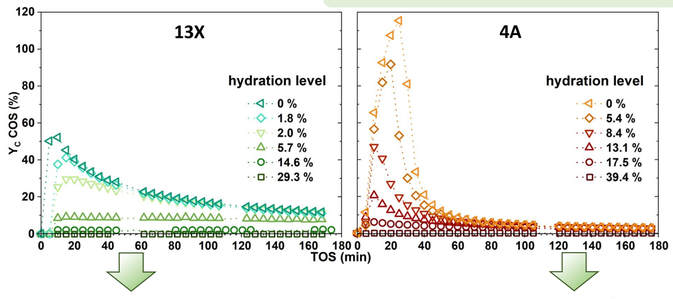
Despite higher initial water content, at T > 100 °C, 13X retains less water than 4A

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

COS production on available sites

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

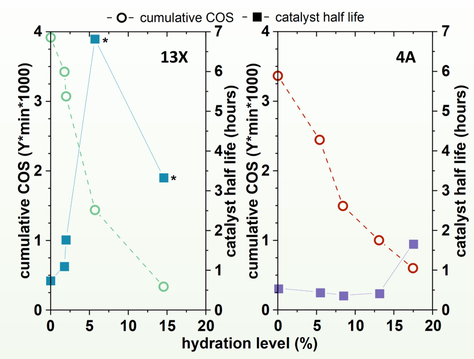
Catalyst: pre-treated at variable T
Feed: pre-saturation in H_2S (13%v), then mix of H_2S and CO_2 (13%v) in N_2
Conditions: 100°C, 1 bar, W/F = 0.13 g min/mL



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

Influence of hydration state towards reactivity

- More pronounced change in half-life of 13X than 4A with varying hydration level
- COS yields proportional to both water sites occupancy and H_2S capacity