# Valorisation of Greenhouse and Acid Gas by Low-Silica Zeolite Catalyst


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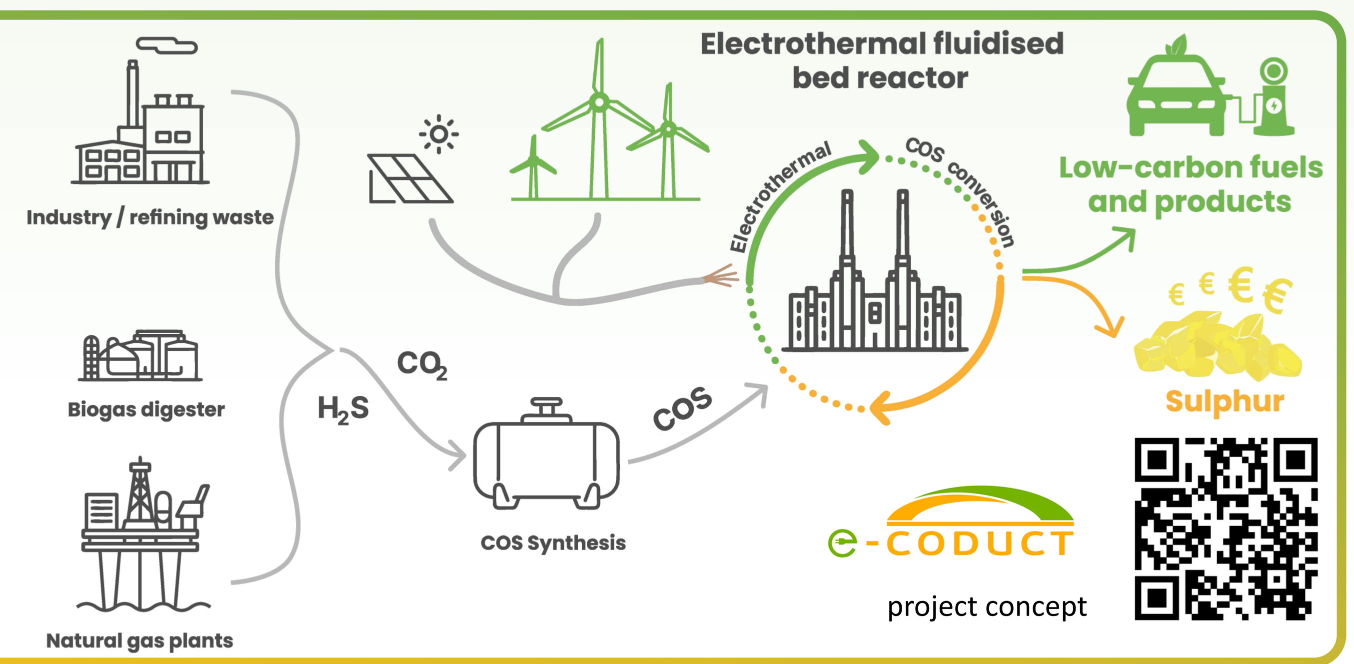
Current industrial treatment of acid gas is industrially treated mainly by the Claus process, which has limitations and require additional fuel, whereas $CO_2$ reduction techniques need high-purity $CO_2$, necessitating effective separation from acid gas. Hence, no existing technologies allow simultaneous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

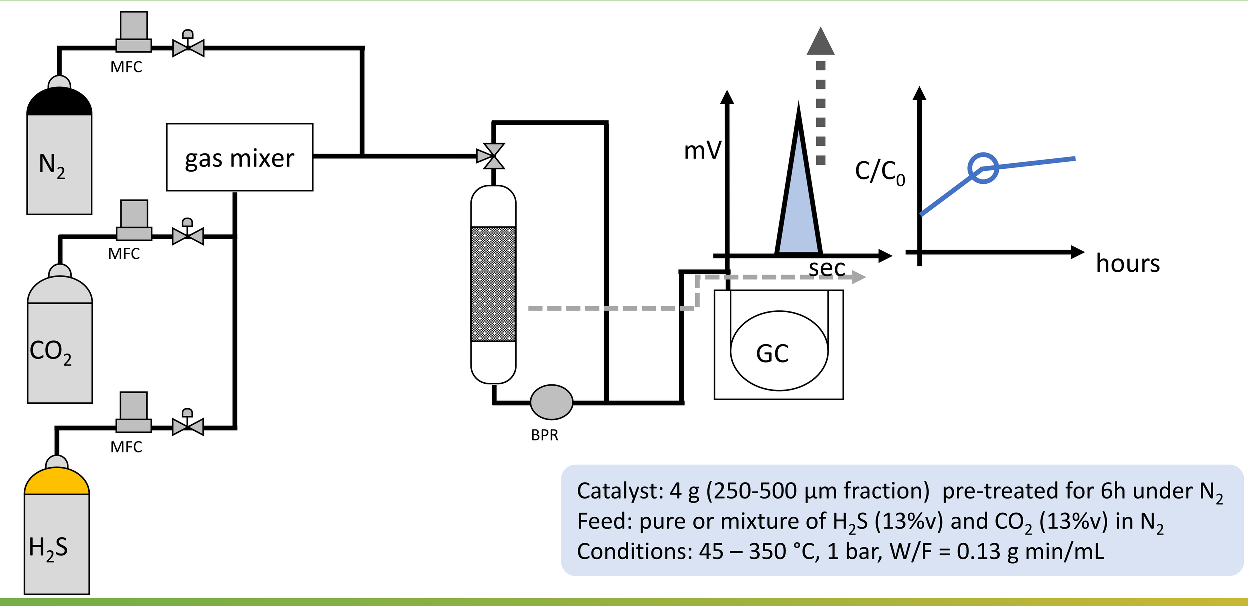
The project e-CODUCT aims to electrify simultaneous conversion of acid gas components into platform molecule carbonyl sulfide COS in a fixed bed reactor, which is further converted into CO and marketable Sulphur in a electrothermal fluidized bed (ETFB) reactor. The COS formation in continuous mode from $CO_2$ 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 two 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

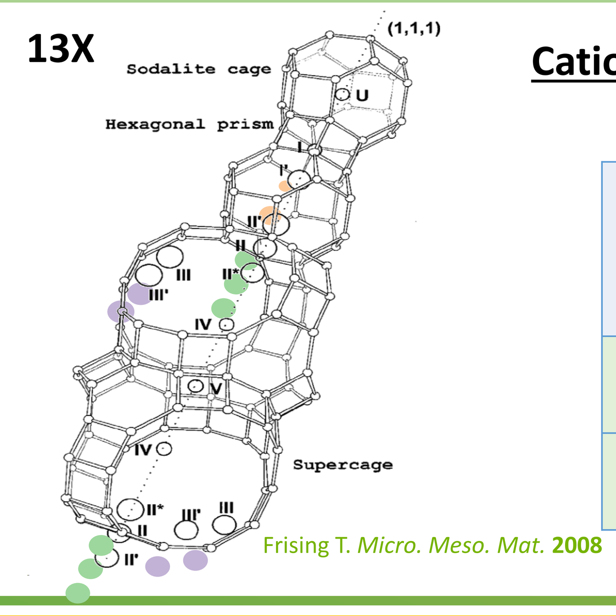



Catalyst: 4 g (250-500 µm fraction) pre-treated for 6h under $N_2$
Feed: pure or mixture of $H_2S$ (13%v) and $CO_2$ (13%v) in $N_2$
Conditions: 45 – 350 °C, 1 bar, W/F = 0.13 g min/mL

## 13X vs 4A

**Cationic distribution and physical chemical characterization**

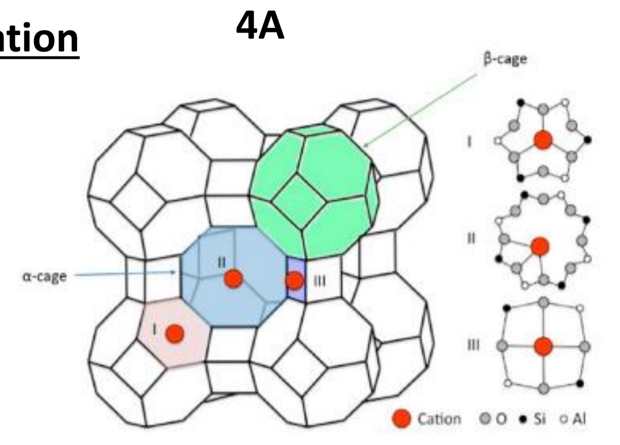
13X




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

| label | Si/Al | Na/Al | SSA (m²/g) |
|---|---|---|---|
| 13X | 1.2 | 0.94 | 800 |
| 4A | 0.97 | 0.88 | 560 |

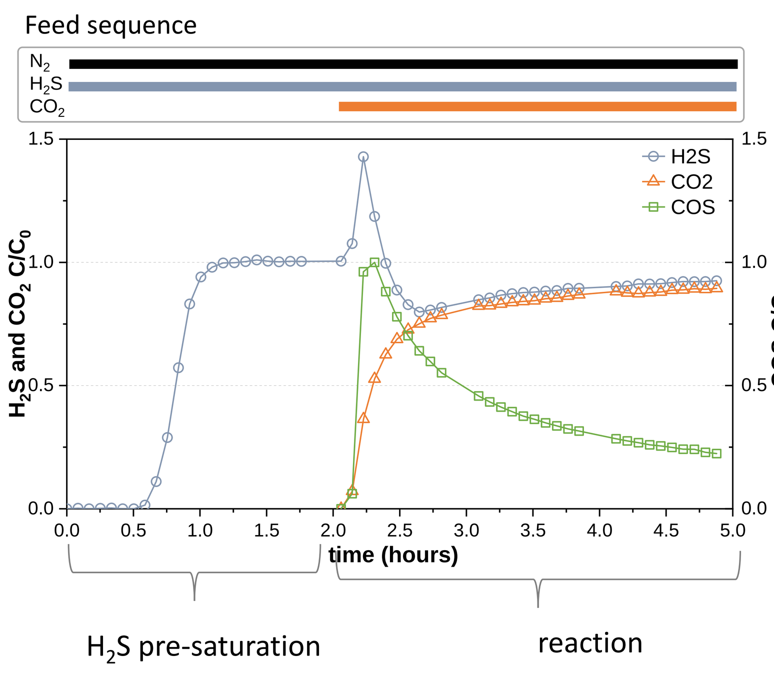
4A




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 $CO_2$ reaction**

- $CO_2$ and COS adsorption avoided.
- Some $H_2S$ is displaced as soon as $CO_2$ is added.

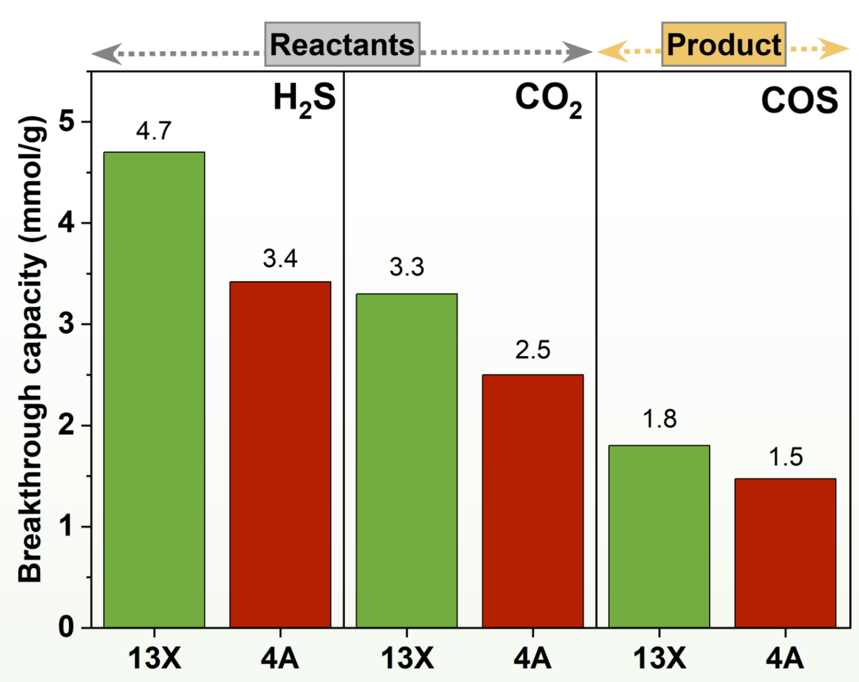
Complex reactivity

Fast catalyst deactivation leading to exponential decay of COS.

## Dynamic capacities of reactants & COS at 45°C

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

Material dependence of dynamic capacity at 45°C



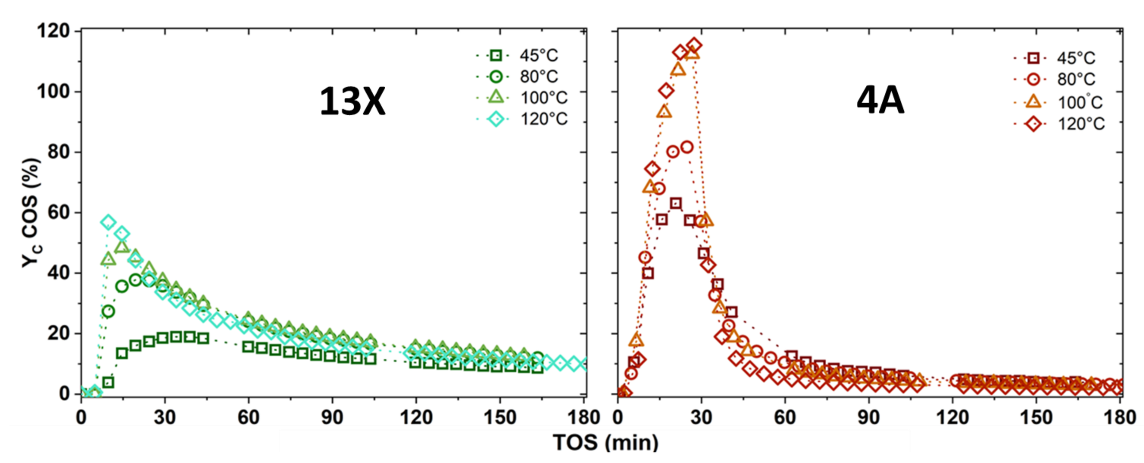

13X has greater dynamic capacity for $H_2S$ and $CO_2$ as compared to 4A

## 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

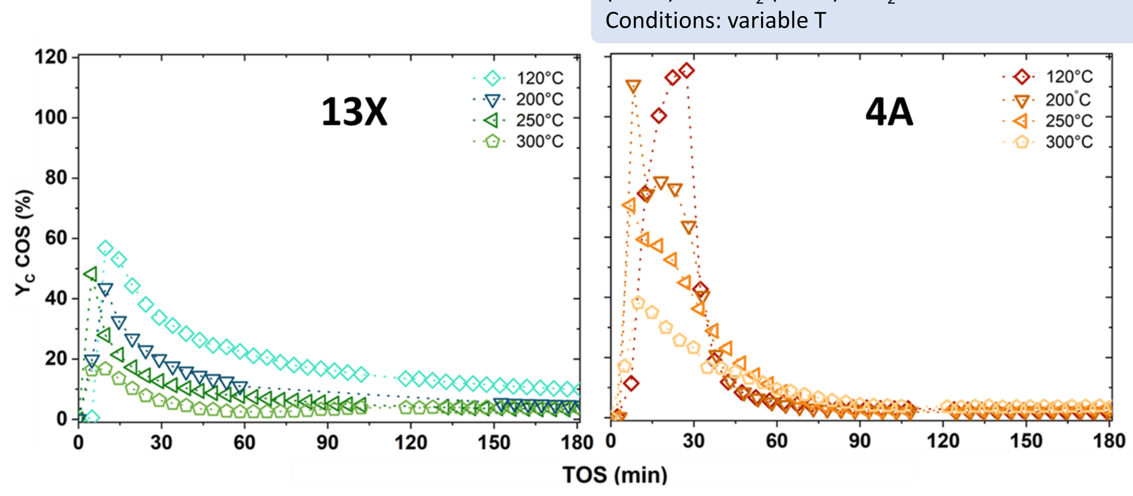



COS yields increase with temperature up to 120 °C for both materials
13X deactivates slowly whereas 4A undergoes faster deactivation

COS yield at higher temperatures

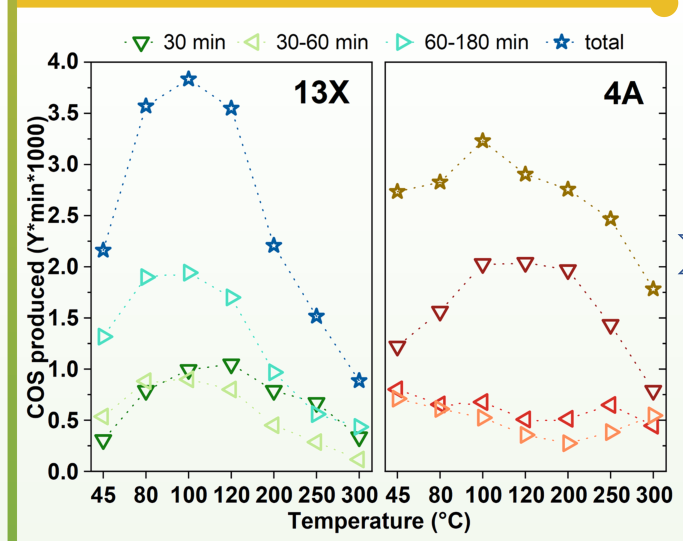
Catalyst: pre-treated 350°C
Feed: pre-saturation in $H_2S$ (13%v), then mix of $H_2S$ (13%v) and $CO_2$ (13%v) in $N_2$
Conditions: variable T

350°C ≥ T ≥ 120 °C



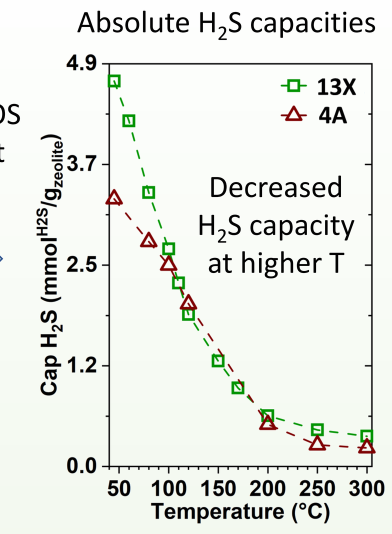

Decrease in COS yields with rise in temperature at T > 120°C
COS peaks move to short reaction times ⟶ faster gas & lower capacity
Re-gain in activity of **4A** after 1st hour at T > 120°C

Catalyst activity at varying reaction times




Lower COS yields at high T

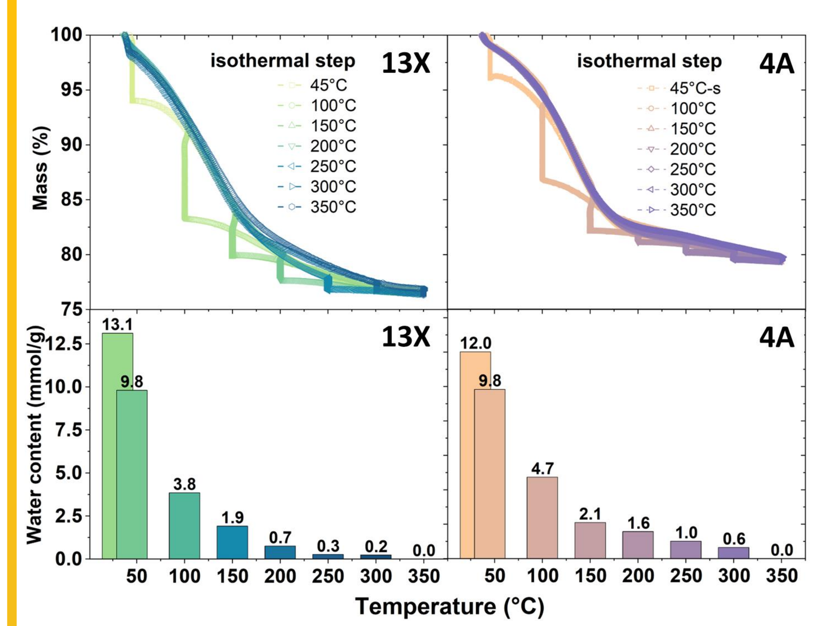
Absolute $H_2S$ capacities

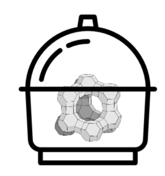



COS yields during 1st of reaction ⟶ 13X < 4A
Total COS yields after 3 hours ⟶ 13X > 4A

## Effect of zeolite hydration level on catalyst activity

Hydration & progressive dehydration



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

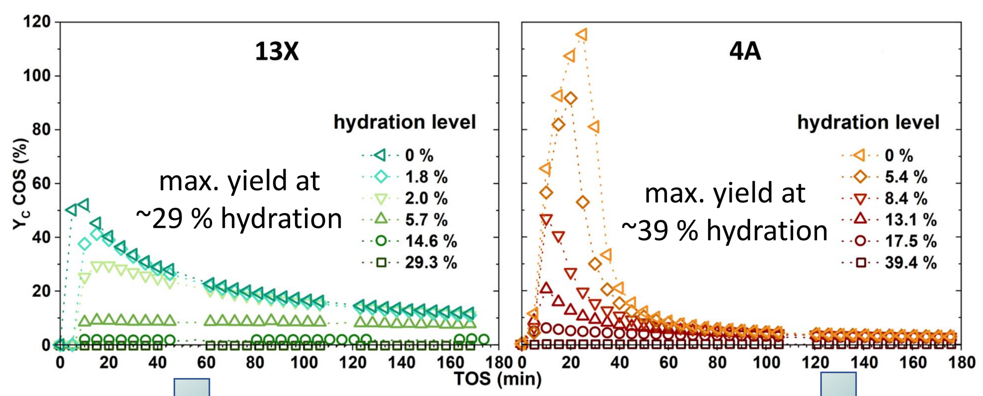
Despite higher initial water content, at T > 100 °C, 13X retains less water than 4A

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

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

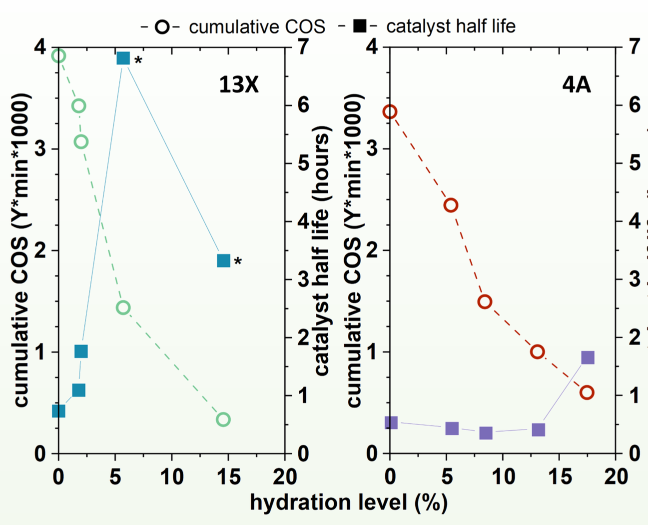



Most of the activity recovered on decreasing hydration from 5.7 to 2%

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

### 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

### 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 whereas faster deactivation profile of 4A
- 4A regains some activity at higher T due to removal of water from some sites

### 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.