

Alternative to Claus process through COS as intermediate: CO₂ and H₂S competitive adsorption and reaction on sodium zeolites

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The project e-CODUCT provides a new technology for two-step acid gas valorization via the conversion of CO₂ and H₂S into COS and the subsequent COS conversion into CO and S_x. The project relies on the development of electrothermal fluidized bed technology for process intensification. In this work, the reaction between H₂S and CO₂ is carried out on different catalysts. The results allow identifying the fraction of chemisorbed H₂S involved in the reactivity.

Introduction

According to recent data, the largest share of carbon emissions per sector in 2021 came from producing electricity and heat, accounting for 40% of global CO₂ emissions, reaching a historic high of 14.6 Gt [1]. In industrial-scale applications, fossil fuel combustion is commonly used to generate the heat required for chemical reactions. It is estimated that approximately half of the CO₂ emissions in the chemical industry are attributed to fuel combustion for heat supply purposes, where refineries and petrochemical industries are responsible for 1.24 Pty of CO₂ emissions. At the same time, this sector handles more than 3.6 Mt/y of H₂S, which in admixture with CO₂ is called acid gas and is handled not only in refining but also in exploration and production (as components of natural gas reservoirs), in biogas treatment (as natural components of the gas mixture from a digester), etc. The existing acid gas treatment approach relies on the Claus process to recover sulfur from gas streams rich in H₂S and demands additional use of fuel gas for lean H₂S sources (<55%). Moreover, to this date, no existing technologies allow simultaneous reduction of CO₂ and H₂S.

To address the transition to a low-carbon economy, the chemical industry needs to reduce its fossil fuel consumption by decarbonizing its processes, in particular through electrification. The project e-CODUCT provides a new technology for two-step acid gas valorization via i) conversion of CO₂ and H₂S into COS in a fixed bed reactor, following the reaction:



and ii) COS conversion into CO and S_x using an electrothermal fluidized bed (ETFB) reactor. In this work, we address the first step (i) by studying the role of FAU- and LTA-type basic zeolites on the competitive adsorption and reaction of CO₂ and H₂S.

Experimental

Adsorption and reaction of CO₂ and H₂S were performed at atmospheric pressure in a fixed-bed quartz reactor (9 mm diameter) at 45°C. The reactor was fed with a mixture of H₂S (Linde, purity: 95% v in N₂) and CO₂ at different dilutions (3-12% v) using a constant flow of 4.8 L/h (STP). Before testing, catalysts (commercial and lab-made nanosized 13X and 4A zeolites, SAR=1.5 and 1.2, respectively) were compacted under 5 tons, crushed, and sieved to obtain homogenous particles (0.2-0.5 mm), then 4 g were loaded in the reactor. All samples were pre-treated at 350°C under nitrogen flow 1.8 L/h (STP) for 8-10 h prior to being fed with the acid gas mixture, with different flow sequences.

Results and discussion

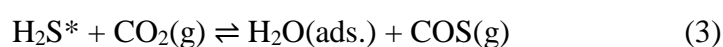
Because of the low temperature, physisorption and chemisorption are discriminated through the saturation of the zeolite followed by a thermal desorption procedure. For both molecules, H₂S and CO₂ adsorbed separately on 13X, the amount is less than 10%, corresponding to an extremely low

ratio with respect to the sodium cation (0.6 mol/g for 13X). Moreover, the adsorption strength of H₂S is higher than CO₂, as witnessed by the higher desorption temperature, typically attributed to a dissociative adsorption mechanism on the sodium cation [2,3].

Table 1. Summary of adsorption results on 13X at 45°C (p=0.13).

molecule	Physisorbed (mmol/g)	Chemisorbed (mmol/g)	% chem.	T desorption (°C)
H ₂ S	2.95	0.21	6.7	> 350
CO ₂	1.44	0.14	9.0	125

A series of experiments using alternated, mixed and pulsed flows allows to separate components adsorption and reaction. Chemisorbed H₂S* is completely converted upon reaction with CO₂. Moreover, a conversion of about 3% when chemisorbed and physisorbed H₂S are both present.



The reaction proceeds towards a slow deactivation of the catalyst, possibly by polluting Na ions with strongly adsorbed water.

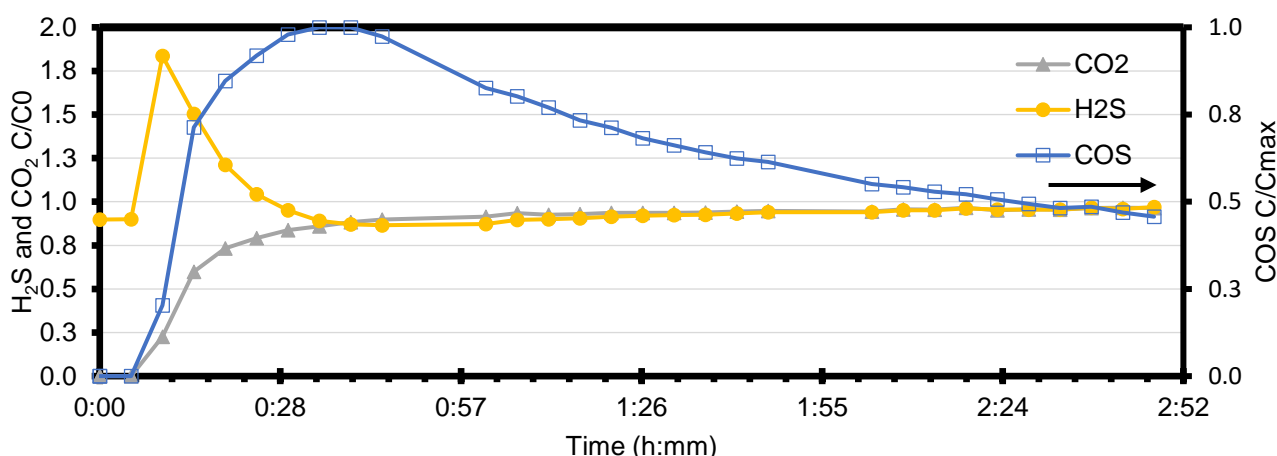


Figure 1. H₂S, CO₂, and COS relative concentrations on 13X.

The same experiments are carried out with the reverse order of reagents, leading to low reactivity. The co-adsorption and reactivity of H₂S and CO₂ are further characterized by operando infrared spectroscopy. The reaction is then tested on different zeolites.

Conclusions

The reactivity of H₂S and CO₂ is studied on 13X, showing a slow deactivation of the catalyst. The contribution of chemisorbed H₂S is evidenced by its complete conversion.

Acknowledgment

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References

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