

Alternative to Claus process through COS as intermediate:

CO₂ and H₂S competitive adsorption and reaction on sodium zeolites

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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], where it is estimated that refineries and petrochemical industries are responsible for 1.24 Ptp 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, in biogas treatment, etc. The existing acid gas treatment approach relies on the Claus process to recover sulphur from gas streams rich in H₂S and demands additional use of fuel gas for lean H₂S sources (<55%). To this date, no existing technologies allow simultaneous reduction of CO₂ and H₂S. The project e-CODUCT provides a new technology for two-step acid gas valorisation via i) conversion of CO₂ and H₂S into COS in a fixed bed reactor, following the reaction $H_2S(g) + CO_2(g) \rightleftharpoons COS(g) + H_2O$, 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 zeolites on the competitive adsorption and reaction of H₂S and CO₂. Adsorption and reaction of CO₂ and H₂S were performed at atmospheric pressure in a fixed-bed quartz reactor at 45°C. The reactor was fed with a mixture of H₂S and CO₂ at different dilutions (3-12%v) using a constant flow. Catalysts (commercial and lab-made nanosized 13X and 4A zeolites, SAR=1.5 and 1.2, respectively) were pre-treated at 350°C under nitrogen flow for 8-10 h prior to being fed with the acid gas mixture, with different flow sequences. Because of the low temperature, physisorption and chemisorption are discriminated through the saturation of the zeolite followed by a thermal desorption procedure. A series of experiments using alternated, mixed and pulsed flows allows to separate components adsorption and reaction. 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]. 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. The reaction is then tested on different zeolites.

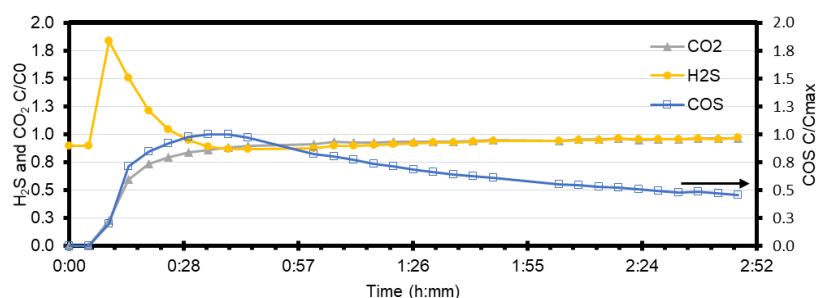


Figure 1. H₂S, CO₂, and COS relative concentrations on 13X.

[1] The Paris Agreement UNFCCC, (May 2023), unfccc.int/process-and-meetings/the-paris-agreement

[2] Yum et al., Separations (2022) 9, 229.

[3] Khabazipour et al., Ind. Eng. Chem. Res. (2019) 58, 22133–22164.