Microkinetic study of acid gas valorization on Na faujasite

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Introduction

In 2022, the production of electricity and heat remained the largest contributor to global CO_2 emissions, accounting for approximately 38% of the total, with emissions reaching a record high of 14.9 Giga tons (Gt)[1]. In industrial applications, fossil fuel combustion is a primary method for generating the heat required for chemical reactions, with about half of the chemical industry's CO_2 emissions attributed to fuel combustion for heat supply. Refineries and petrochemical industries alone are responsible for approximately 1.24 Gt of CO_2 emissions annually[2]. Additionally, this sector manages over 3.6 million tons (Mt) of hydrogen sulfide (H_2S) each year, often mixed with CO_2 as acid gas, which is encountered in refining, in exploration and production (as components of natural gas reservoirs), and in biogas treatment (as natural components of the gas mixture from a digester), etc. Current acid gas treatment predominantly relies on the Claus process to recover sulfur from H_2S-rich gas streams, a method that requires supplemental fuel for lean H_2S sources (less than 55%). However, existing technologies do not enable the simultaneous reduction of CO_2 and H_2S. As the chemical industry transitions toward a low-carbon economy, there is a pressing need to reduce fossil fuel dependence by decarbonizing processes, particularly through electrification. The project eCODUCT (https://e-coduct.eu, Horizon Europe Grant Agreement n. 101058100) introduces an innovative two-step technology for acid gas valorization:

i) conversion of CO_2 and H_2S into carbonyl sulfide (COS) in a fixed-bed reactor, via the reaction:

$$H_2S(g) + CO_2(g) \rightleftharpoons COS(g) + H_2O(ads)$$

ii) COS conversion into carbon monoxide (CO) and elemental sulfur (S_x) using an electrothermal fluidized bed (ETFB) reactor.

In this work, we address the first step (i) by studying the role of FAU-type basic zeolites on the competitive desorption and reaction of CO2 and H2S supported by the development of a microkinetic model.

Materials and Methods

Adsorption and reaction of CO_2 and H_2S were performed at atmospheric pressure in a fixed-bed quartz reactor (9 mm diameter) at variable temperatures from 45 to 120°C. The reactor was fed with a mixture of H2S (Linde, purity: 95%v in N_2) and CO_2 at different dilutions (3-12%v) using a constant flow of 4.8 L/h (STP). Before testing, catalyst (commercial 13X zeolite) was compacted under 5 tons, crushed, and sieved to obtain homogenous particles (0.2-0.5 mm), then loaded in the reactor. All samples were pre-treated at 350°C under nitrogen flow 1.8 L/H (STP) for 8-10 h before being fed with the acid gas mixture with different flow sequences.

Results and Discussion

At low temperatures, both physisorption and chemisorption must be taken into account. These contributions are experimentally distinguished by saturating the zeolite with a single component followed by a thermal desorption process. For both H_2S and CO_2 adsorbed individually on 13X zeolite, the amount is less than 10%, corresponding to a very low ratio relative to the sodium cation (0.6 mol/g for 13X). The overall interaction strength of H_2S with the adsorption site is greater than CO_2, likely due to a dissociative adsorption mechanism on the sodium cation [4,5]. A series of experiments was conducted on 13X zeolite samples pre-saturated with H_2S to investigate the kinetics of COS formation (Figure 1). Chemisorbed H_2S is completely converted upon reaction with CO_2. COS production profile passes through a maximum and then decreases with the reaction time evidencing the progressive deactivation of the catalyst. Temperature significantly influenced the reaction, with conversion rates increasing from 5% at 45°C to 12% at 120°C. The highest COS yield was observed at 100°C. The experimental data were used to develop a microkinetic model based on the Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic (Table 1). This model incorporates the role of sodium cations within the faujasite super-cages as active adsorption and reaction sites and considers water, a reaction co-product, as the primary factor driving catalyst deactivation over time.

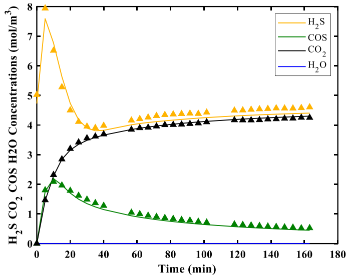

Figure 1. Relative concentrations vs. time of H_2S, CO_2 and COS over 13X zeolite at 100°C. Experimental data (symbols) and simulations (lines).

Table 1. Parameter estimation of coefficient rates.

k^{ads}_{H2S}	7.4 E-4 m^3/(mol.s)	**k^{des}_{H2S}**	7.4 E-3 1/s
k^{ads}_{CO2}	4.6 E-3 m^3/(mol.s)	**k^{des}_{CO2}**	4.1 E-1 1/s
k^{ads}_{COS}	0 m^3/(mol.s)	**k^{des}_{COS}**	3.9 E-3 1/s
k^{f}_{r}	4 E-3 kg/(mol.s)	**k^{r}_{r}**	1.2 E-2 kg/(mol.s)

Significance

This work provides a comprehensive understanding of the conversion of CO_2 and H_2S into the intermediate molecule COS, supported by a detailed microkinetic model. This approach sheds light on the reaction mechanisms and the role of active sites and has significant implications for greenhouse gas mitigation and the reduction of industrial waste impacts.

References

1. The Paris Agreement UNFCCC, May **2023**.
2. https://www.iea.org/data-and-statistics/data-tools/greenhouse-gas-emissions-from-energy-data-explorer
3. Pfeifer S. et al., Microporous Mesoporous Materials, **2025**, 383, 113408.
4. Yum et al., Separations **2022**, 9, 229.
5. Khabazipour et al., Ind. Eng. Chem. Res. **2019**, 58, 22133–22164,