Catalytic COS formation on Na-Faujasite for acid gas valorization

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Introduction

In 2022, electricity and heat production 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 sulphide (H_2S) each year, often mixed with CO_2 as acid gas, which is encountered in refining, 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 sulphur 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 valorisation:

i)   conversion of CO_2 and H_2S into carbonyl sulphide (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 sulphur (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 CO_2 and H_2S 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, the 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. The amount of H_2S and CO_2 adsorbed individually on 13X zeolite 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.
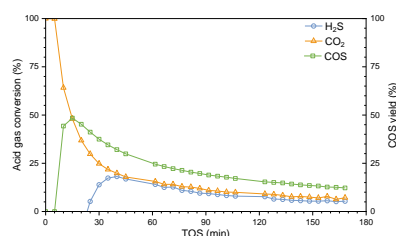

Figure 1 - Conversion of H2S, CO2 (left axis) and yield of COS (right axis) vs. time on 13X zeolite at 100°C.

This model successfully describes the concentration variation of both reagents and products during the reaction on pre-saturated samples, and considers water, co-product, as the primary factor driving catalyst deactivation over time.

References

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Aknowledgment