Alternative to Claus process through COS as intermediate. Part 1: CO_2 and H_2S competitive adsorption on zeolite 13X

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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 CO_2 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 CO_2 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 CO_2 emissions. At the same time, this sector handles more than 3.6 Mt/y of H_2S, which in admixture with CO_2 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 H_2S and demands additional use of fuel gas for lean H_2S sources (<55%). In contrast, thermo-catalytic or electrocatalytic CO_2 reduction and sequestration demand high purity of CO_2, requiring a proper separation from the acid gas. Moreover, to this date, no existing technologies allow simultaneous reduction of CO_2 and H_2S.

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 CO_2 and H_2S into COS in a fixed bed reactor, following the reaction:

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

and ii) COS conversion into CO and SX 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 CO_2 and H_2S.

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 45°C. The reactor was fed with a diluted mixture of H_2S (Linde, purity: 95%v in N_2) and CO_2 in nitrogen at different ratios (3-12%v) using a constant flow of 4.8 L/h (STP). Before testing, catalysts (13X and 4A zeolites from SGCREE, 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 4g were loaded in the reactor. Firstly, all samples were pre-treated at 350°C under nitrogen flow 1.8 L/h (STP) for 8-10 h.

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, H_2S and CO_2 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 strength of the adsorption of H_2S is higher than the CO_2, 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_2S	2.95	0.21	6.7	330
CO_2	1.44	0.14	9.0	125

The injection of CO_2 on the catalyst with previously chemisorbed H_2S produces COS and H_2O, the latter remaining adsorbed in the zeolite. The almost complete conversion of the chemisorbed H_2S suggests the importance of these species towards the COS formation. The same experiments are carried out with the reverse order of reagents. The co-adsorption and reactivity of H_2S and CO_2 are further characterized by *operando* infrared spectroscopy.

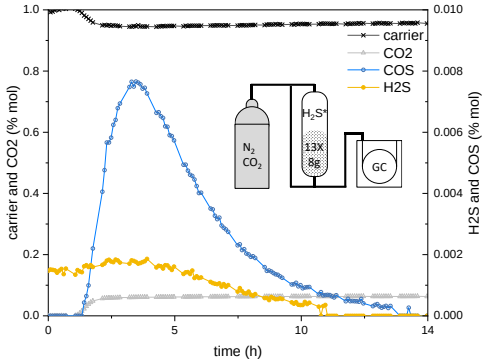

Figure 1. Reaction products from a continuous flow of CO_2 on previously chemisorbed H_2S.

Significance

We report a new route for Clauss process defossilization with potential for industrial implementation.

References

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