Microkinetic analysis of acid gas conversion to COS by zeolite 13X

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Highlights

- Transient modelling of acid gas conversion to COS.
- Microkinetic model can describe the breakthrough times of compounds.
- Kinetic parameters for LHHW model are estimated.

1. Introduction

Carbon dioxide emissions are a major contributor to climate change due to their role in the greenhouse effect. In 2018, global CO_2 emissions had risen to 37.1 Gt, mostly originating from fossil fuel combustion during transportation and industrial production [1]. Hence, the development of CO_2 utilization strategies is crucial to mitigate climate change. Various approaches for CO_2 conversion have been explored such as thermochemical and electrocatalytic technologies. However, currently available technologies for CO_2 conversion require highly pure CO_2 streams while many CO_2 streams contain impurities such as sulphur. Thus, transformation of H_2S containing CO_2 streams while avoiding additional separation steps remains a challenge. The e-CODUCT project aims at promoting an integrated treatment of acid gas streams (CO_2 + H_2S) through a two-step procedure. The first challenge in this respect represents the maximization of COS production from mixed CO_2 and H_2S streams by using zeolites as reactive adsorbents. Second, COS is decomposed into CO as a platform molecule and marketable sulphur in an electrothermal fluidized bed. This work focuses on the first stage of the process by developing a microkinetic model for the reaction of CO_2 and H_2S to produce water and COS on zeolite 13X catalyst. The microkinetic model provides the necessary insight into mechanistic understanding of the reaction which can provide a basis for future reactor and process design.

2. Methods

An experimental investigation of acid gas conversion to COS using zeolite 13X is carried out in a fixed-bed reactor. An equimolar flow of H_2S and CO_2, diluted by nitrogen, is fed to the reactor at 45°C and 1.13 bar. The bed is loaded with 4 g of zeolite 13X, which has been pre-treated at 350° C under nitrogen flow.

Elementary-step modeling is conducted using a Langmuir-Hinshelwood-Hougen-Watson (LHHW) reaction mechanism and transient mass balances for gas phase and surface species. The model contains 10 adjustable parameters, i.e., the forward and reverse rate coefficients of the 5 considered steps. The system of equations is numerically solved using the method of lines.

3. Results and discussion

Simulation results exhibit a good agreement with the experimental data, see Figure 1a. The model based on the LHHW mechanism can reproduce the breakthrough times of the various components involved. CO_2 is the first component to breakthrough, closely followed by COS. In addition, model adequately describes the CO_2 and COS rollup. The model nicely reproduces the experimentally observed higher retention capacity of the 13X for H_2S. Figures 2b,c,d, and e represent the evolution of active site coverages throughout the reactor length during the time on stream. In the apparent 'steady-state', i.e., after the CO_2 and COS breakthrough and roll-up, most of the active sites are occupied by H_2S and water coverage is slowly increasing, which can lead to the decrease in COS production. Additionally, the plots exhibit a spatial variation in surface coverages along the length of the reactor after pseudo-steady state is reached. At the end of experiment, near the packed-bed inlet, higher water coverages and lower H_2S coverages in comparison to the points closer to the reactor outlet could be observed, which reflects the changing distribution of surface coverages.

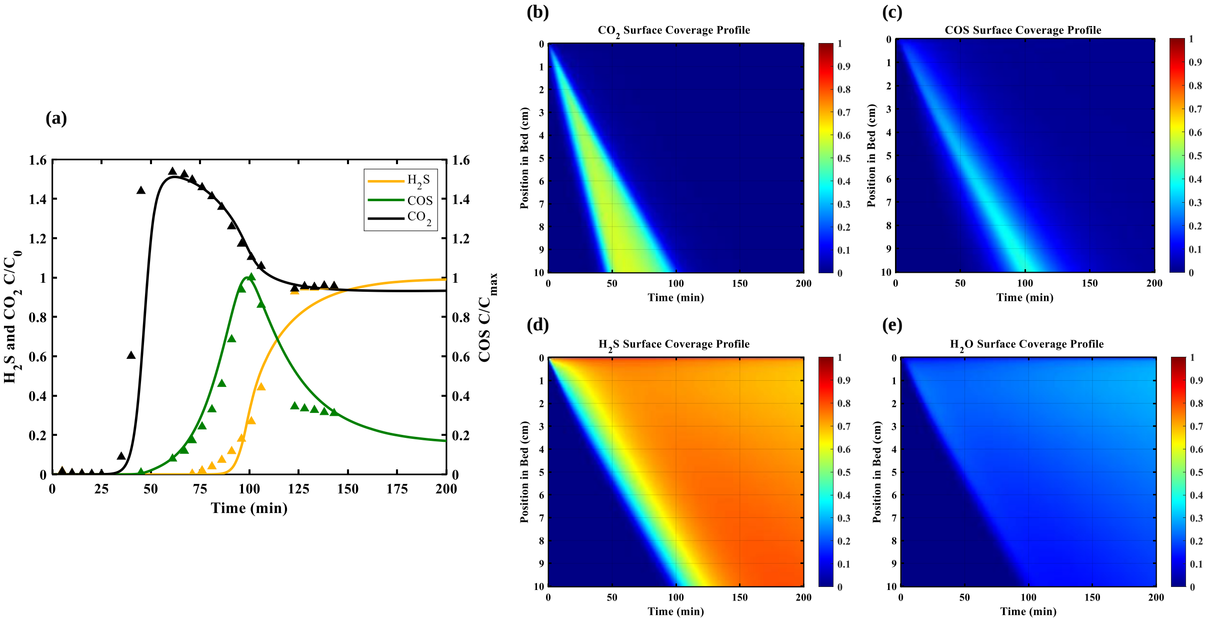

Figure 1. Results for the transient LHHW microkinetic model for acid gas conversion over zeolite 13X at 45°C, (a) comparing simulated results (lines) and experimentally obtained values (symbols) for the relative concentrations of H_2S, CO_2, and COS. (b) Surface coverage profile of CO_2, (c) COS, (d) H_2S, and (e) H_2O.

4. Conclusions

Kinetic parameters estimated for the LHHW mechanism properly predict the experimental data from the transient fixed-bed reactor, accounting for breakthrough, rollup and pseudo-steady state of the components. The developed microkinetic model contributes to understanding acid gas conversion at a fundamental level and allows process optimization in future development.

References

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Keywords

Microkinetic modelling; Acid gas conversion; Zeolite 13X