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Kinetic investigation of the selective n-Butane oxidation to Maleic Anhydride in an isothermal milli-structured fixed-bed reactor

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Highlights
- Selective oxidation of n-Butane to Maleic Anhydride under isothermal conditions
- Milli-structured fixed-bed reactor
- Kinetic investigation under industrially relevant conditions

1. Introduction

Selective oxidation reactions like the synthesis of Maleic Anhydride (MA) from n-Butane are highly exothermic processes. Industrially, this reaction is typically carried out in multi-tubular fixed-bed reactors. Due to the limited heat removal, the process is accompanied by the occurrence of hot spots as high as 70 K above the temperature of the cooling medium [1]. In previous work, it could be demonstrated that it is possible to carry out this process under nearly isothermal conditions using a milli-structured fixed-bed reactor [2]. During modeling it was found, that despite of intensive investigations in the last decades, none of the published kinetics can satisfactorily describe the results obtained in the considered milli-structured reactor. Therefore, the aim of this work is to determine the reaction kinetics under well-defined isothermal conditions.

2. Methods

In order to determine the kinetics of the selective n-Butane oxidation to MA, the previously described [2] nearly isothermal salt-bath cooled milli-structured fixed-bed reactor (44x72x1.5 mm) was used. To minimize the effects of mass transfer resistances, the experiments were performed at high flow rates and with fine catalyst particles obtained from milling the pellets of a commercial catalyst. The experiments were carried out under industry-related conditions, namely 380 to 420 °C, 1.2 to 1.5 bar and 1.2 to 2.1% n-Butane in air. In order to take account for the conditions in the region of the hot spot of industrial reactors, additional experiments were performed at temperatures of up to 450 °C. For a better characterization of the often described influence of water on the kinetics, some experiments were operated while dosing up to 2% water(vapor) to the feed. The effluent gases were analyzed using an infrared analyzer for n-Butane, CO, CO_2 and O_2 (paramagnetic cell) and a gas chromatograph for MA and side products like Acetic Acid. A detailed two-dimensional heterogeneous reactor model was created and used for determination of kinetic equations and adjusting the kinetic parameters by fitting the experimental data with the parameter estimation tool of gPROMS.

3. Results and discussion

In the experiments, no differences between catalysts of different particle sizes could be observed, so that the mass transfer can be regarded as sufficiently good for reliable kinetic experiments. As described in the

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literature (e.g. [1]), the performed experiments show, that only minor amounts of side products like Acetic Acid and Acrylic Acid are formed and can be neglected for determination of the kinetics. Besides the oxidation of MA, only the undesired oxidation of n-Butane and formed MA to CO and CO_2 must be considered as shown in the reaction scheme in Figure 1.

In literature, one can find several different approaches (e.g. Eley-Rideal, Hougen-Watson, and Mars van Krevelen models) to describe the kinetics of the process, which are compared with each other. For every model, the kinetic parameters were fitted to the experimental data. The best fit could be obtained with a Hougen-Watson type kinetic model as described by Lesser et al [3]. According to this kinetic model, the reaction is inhibited by n-Butane and water. In contrast to the literature, it was found, that CO is further oxidized to CO_2 and this reaction must be added to the reaction network. An example of the obtained values with the fitted kinetic model is depicted in Figure 2. As one can see, the calculated values (lines) fit the measured values (symbols) very well over a broad conversion range.
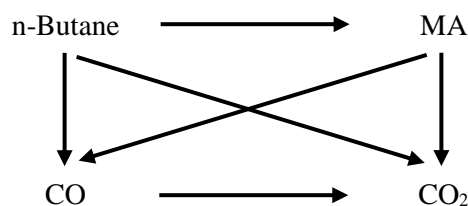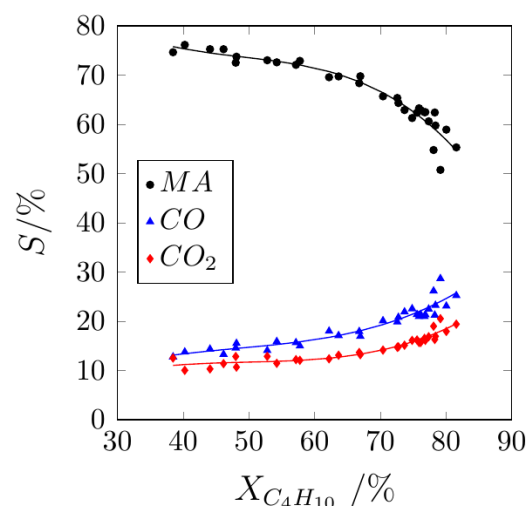

Figure 1. Reaction network

Figure 2. Selectivity to MA, CO and CO_2 as a function of the conversion (symbols: measured values, lines: calculated values)

4. Conclusions

In order to determine the kinetics of the selective oxidation of n-Butane to MA experiments were carried out in a milli-structured fixed bed reactor. The reactor was found to be ideally suited for kinetic measurements, because it allows an almost isothermal operation and the influence of mass transfer resistances are minimal. With the obtained reaction data it was possible to determine a kinetic model to describe the reaction rates, involving the inhibition through formed and added water and the often neglected oxidation of CO to CO_2.

References

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