ETHYLENE OXIDE FORMATION IN A MICROREACTOR: FROM QUALITATIVE KINETICS TO DETAILED MODELLING

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Summary

Silver/alpha-alumina-coated microchannels were tested for the ethylene oxidation reaction. Pure silver microplates were also investigated giving the highest activities and selectivities towards ethylene oxide (EO) formation. Pre-treatment conditions for the pure silver catalyst were studied and optimised. A very precise kinetic model for the ethylene oxide formation in pure silver microchannels was developed. The model was based on the competitive adsorption of ethylene and molecular oxygen over the silver surface. The model was confronted with experimental data obtained in the microchannels, resulting in a very high degree of explanation (99%).

Keywords

Microreactor, kinetic modelling, silver, epoxidation.

Introduction

Ethylene oxide (EO) is one of the most important organic intermediates with an annual global production of ca. 19 million metric tons. EO is industrially produced by the selective partial oxidation of ethylene, with a total heat of reaction between -350 and -550 kJ/mol, causing hot spots and heat removal problems inside conventional reactors. Microreactors, on the other hand, offer a solution to this problem.

Due to the small dimensions of the microreactors and its high surface-to-volume ratio, very fast heat removal capabilities are attained, permitting chemical transformations that are highly exothermic to be carried out almost at isothermal conditions. Moreover, the intrinsic safety provided by these reactors allows the operation under the explosive regime, e.g. ethylene in pure oxygen, conditions not possible to obtain in standard laboratory vessels. A lot of research is done on catalytic gas-phase processes in microdevices, but kinetic modelling is often missing. In this work, we present a systematic approach to a very precise kinetic modelling of data obtained from the microreactor.

Experimental

A gas-phase microreactor purchased from Institut für Mikrotechnik Mainz GmbH (IMM) was used for the synthesis of EO. Three silver/α-alumina catalysts were prepared by thermally decomposing γ-alumina and further silver impregnation by the incipient wetness method. The catalyst was washcoated on the microplates as described in[1]. Pure silver plates were also used for the chemical synthesis.

The temperature of the microreactor was regulated by external heating cartridges controlled by a CAL9500 temperature controller. K-type thermocouples (chromel-alumel) were used for temperature measurements/control. After the microreactor, the effluent gases were analysed by an Agilent 3000A Micro GC with four independent columns and TC detectors. The gases used in the preparation of ethylene oxide were scientific ethylene (99.95%, Linde Gas) and instrument oxygen (99.999%, AGA). Helium (99.996%) was used as the carrier gas. For the kinetic experiments, the temperature was kept at 260°C and the total flow was set to 6 ml/min with concentrations of oxygen and ethylene varying from 5 vol.% to 25 vol.%.

Results and Discussion

Activity tests

A series of experiments were conducted with all four catalysts. The conversion of ethylene remained low for all experiments and was usually between 0.03-0.30%. The selectivity towards ethylene oxide for silver/α-alumina catalysts remained low (<29%). Pure silver plates resulted

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in the highest catalytic activity and selectivity towards EO formation. With pure silver, selectivities up to 51% could be achieved, which are comparable to values found in the literature[2]. Fig. 1 shows the EO conversion and selectivity over pure silver microplates at different temperatures. The catalyst behaviour was sensitive to changes in the feed concentrations; especially high oxygen concentrations were found to decrease the catalyst activity over time.

A good stability of the catalyst was achieved by a two-step pre-treatment, where the catalyst was initially treated under an ethylene flow in helium, followed by a flow of oxygen in helium before each kinetic experiment. Increasing the reaction temperature was found to linearly decrease the selectivity towards ethylene oxide. However, the increase of temperature enhanced the conversion of ethylene into EO. Increasing the total flow decreased the conversion of ethylene, while the selectivity towards ethylene oxide remained almost constant.

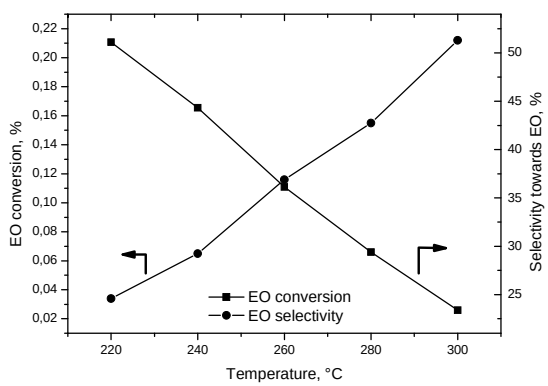

Fig. 1. Conversion and selectivity towards ethylene oxide over pure silver plates; 20 vol.% ethylene, 10 vol.% oxygen, total flow 6.0 ml/min.

It was found that both increasing ethylene and oxygen concentrations had a positive effect on both the rates of ethylene oxide formation and carbon dioxide formation.

Kinetic studies

Kinetic studies were investigated over the pure silver microplates. A differential reactor model was assumed with a steady-state plug-flow model. The influence of the reaction products and internal diffusion limitations were assumed to be negligible. Two models of competitive Langmuir-Hinshelwood type were developed for the partial oxidation of ethylene. The surface reaction between adsorbed ethylene and either molecular or dissociatively adsorbed oxygen was considered the rate-limiting step. A model based on the competitive adsorption of ethylene and molecular oxygen on the surface fitted the experimental data best. The rate expression obtained for the rate of ethylene conversion to ethylene oxide is given by Eq. 1

$$r_1 = \frac{kK_E K_O c_E c_O}{(1 + K_E c_E + K_O c_O)^2} \qquad (1)$$

The results of the kinetic model fit are presented in Fig. 2. The model explains the kinetic features recorded experimentally as shown in the parity plot on Fig. 3.

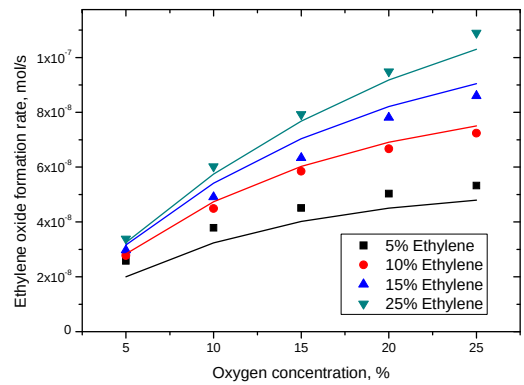

Fig. 2. Kinetic modelling results of the ethylene oxidation. Fitted model. Experimental (symbols), Model (solid lines).

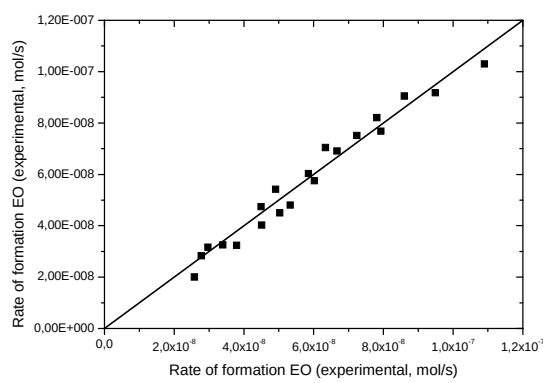

Fig. 3. Kinetic modelling results of the ethylene oxidation. Parity plot.

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