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## Modeling of microreactors for ethylene epoxidation and total oxidation

V. Russo<sup>a,b</sup>, T. Kilpiö<sup>a</sup>, J. Hernandez Carucci<sup>a</sup>, M. Di Serio<sup>b</sup>, T.O. Salmi<sup>a,\*</sup><sup>a</sup> Åbo Akademi University, Department of Chemical Engineering, Laboratory of Industrial Chemistry and Reaction Engineering, FI-20500 Turku/Åbo, Finland<sup>b</sup> University of Naples "Federico II". Chemical Sciences Department, IT-80126 Naples, Italy

## HIGHLIGHTS

- Ethylene oxide kinetics was studied.
- A kinetic model was developed.
- A good description of data was obtained.

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## ABSTRACT

Microreactors are especially well-suited for laboratory-scale studies of rapid exothermic reactions, because they have excellent mass and heat transfer characteristics. Two novel reactor models were used for plate microreactors, one for a washcoated reactor and the other one for a silver plate microreactor. The aim of this modeling study was to precisely explain both the concentration and the temperature dependencies of the reaction rates of ethylene oxide (EO) synthesis over a wide range of operating conditions ( $p$ ,  $T$ , flows) by using all the extensive data generated with our microreactors. Microreactors are especially well suited for producing accurate kinetic data because of the uniformity of reaction conditions in the reactor system.

Modeling took into account the reaction and mass transfer effects. The axial and radial concentration profiles and for the washcoated case also the concentration profiles along the coating direction were solved numerically. The models were based on dynamic mass balances for the gas phase, with convection, axial and radial dispersion terms included. From the modeling viewpoint, an interesting phenomenon, the interaction between intrinsic kinetics and diffusion in the porous catalyst layer, was tackled with the aid of mathematical modeling for the washcoated reactor case. The reactor models were solved numerically by using gPROMS software. Ethylene oxidation on silver catalyst was the selected example reaction system, because the main product, ethylene oxide, is a key compound and an important intermediate for chemical industry. The reactor and kinetic models were able to describe all the experimental data with a very satisfactory agreement. The microreactor models developed are generic and applicable to various kinds of heterogeneously catalyzed gas-phase reaction systems.

The industrial breakthrough of flow chemistry and catalyzed single phase microreactor technology is expected to take place first in the production of fine and specialty chemicals. For some bulk products (e.g. EO), flow chemistry has already arisen interest. The benefits that microreactors can offer are the exact control of process conditions, the compact reactor size and the ease of scalability by simply "numbering up". For a new product, ease of scalability shortens the time to market, whereas for a bulk product like EO, millireactors (structurally similar to microreactors, just having larger flow channels) may be more potential candidates for on-site production applications.

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## 1. Introduction

Microreactors are strong tools in the investigation of the intrinsic kinetics of rapid gas-phase reactions. Two main properties of microreactors make them particularly attractive for this

purpose: the catalyst layers in microreactor channels are very thin, typically 20–30  $\mu\text{m}$  or even less and the heat transfer characteristics of microreactors are excellent. Thin catalyst layers suppress the internal mass transfer resistance in the catalyst pores thus guaranteeing the operation within the regime of intrinsic kinetics, which simplifies the interpretation of experimental data. Mathematical modeling of microreactors is discussed in detail in some monographies (Hessel et al., 2004; Keil, 2007).

\* Corresponding author.

The use of simplified description of fluid dynamics (dispersion models and semi-empirical equations for pressure drop) is widely accepted and used way to replace the momentum balances (Navier-Stokes equations, PDEs) in chemical engineering. The accurate solution of momentum balances demands a tight grid especially in places of high velocity gradients. By avoiding the evaluation of velocity profiles with momentum balances PDEs, one reduces the size of the problem essentially and can use also a less tight grid. The merit then is that calculation times shorten an order of magnitude (e.g. from hours to minutes). Parameter estimation task typically demands a multitude of simulations and the benefit of having shorter calculation times cumulates. The disadvantage of the simplification is that local velocities are not evaluated and only the net effect of backmixing is taken into account. On the hand, these systems have been sometimes treated with rough approaches, such as plug flow conditions, in terms of fluid dynamics. In this paper, an attempt in sufficiently describing the fluid dynamics of two types of microreactors for the ethylene oxide synthesis reaction was made.

The differences in total calculation times depend on how much more complicated the other modeling options are. Computational Fluid Dynamics (CFD) is a popular modeling tool nowadays. Single-phase CFD models for this kind of simple geometry (when calculating only the local flows) are converging well perhaps within an hour (without reactions). However, it is hard to predict how much more time is consumed when non-linear Langmuir-Hinshelwood-Hougen-Watson (LHHW) reaction kinetic equations are incorporated. They may retard the calculation progress a lot. Another issue to keep in mind is that although CFD models are strong in calculating vector variables, with scalar variables, numerical diffusion is often faced. When multiple parameter estimations are carried out, one executes the program code tens, even 100 of times, which multiplies the run time difference. When doing model development with rapidly running program codes, a multitude of test runs can be performed each and every day and abundant amount of feedback is received. With CFD, the number of trials becomes limited.

From the modeling viewpoint, microchannels and monolith reactor channels resemble each other a lot and both are, thus, shortly addressed. Models for monolith reactors both with and without a washcoat have been developed (Stutz and Poulikakos, 2008; Deutchmann et al., 2001; Pattegar and Kothare, 2004; Carucci et al., 2010; Hayes et al., 1999). All the above-mentioned studies were conducted for various different gas-only reaction systems.

Plug flow, axial dispersion and backmixing models for microreactors are discussed in a recent review article of our group (Carucci et al., 2012). An illustrative parameter estimation study for ethylene oxide using a combined radial molecular diffusion and laminar velocity profiles in the model was included. Parameters for ethylene oxidation were estimated for a single temperature (Carucci et al., 2010). The current work is a summary of experimental and modeling activities carried out in our laboratory-scale microreactors for ethylene oxidation. This effort is a logical continuation of the previous work using the entire data sets together with this far the most detailed model for ethylene oxidation.

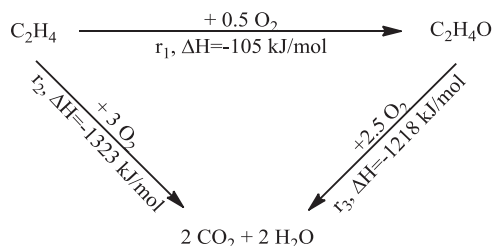


Fig. 1. Reaction scheme of direct ethylene oxide synthesis from ethylene and oxygen.

The reaction scheme for ethylene oxide synthesis is presented in Fig. 1. The exothermic nature of the reactions is clearly demonstrated there. The generally accepted view on the reaction mechanism is that ethylene epoxidation and total oxidation are essentially parallel processes; thus the role of reaction 3 in the scheme is minor compared to reactions 1 and 2.

The high values of the reaction enthalpies imply typically non-isothermal conditions in standard reactors. Typical adiabatic temperature rise curves have been presented for the industrial ethylene oxidation. The point of how much the surface-to-volume ratio improves when scaling down from industrial pipes to micro-reactor channels has been highlighted (Kursawe, 2009). Selectivity/productivity results obtained by a simplified plug flow model have also been presented.

The kinetic investigations pursued for revealing the exact kinetic expression of partial oxidation of ethylene into ethylene oxide using a silver based catalyst are summarized and rate equations for partial and total oxidation of ethylene are presented in a previous paper of our group (Salmi et al., 2013). Through the years, several hypotheses have been proposed for the molecular reaction mechanism of ethylene oxidation on silver surface (Carucci et al., 2010; Kursawe, 2009; Salmi et al., 2013; Borman and Westerterp, 1995; Ghazali et al., 1983; Lafarga et al., 2000; Petrov et al., 1988). In a recent molecular modeling study based on Density Functional Theory (DFT) calculations, a common surface intermediate was proposed for the formation of ethylene oxide and carbon dioxide (Özbek and van Santen, 2013).

## 2. Modeling approach and methods

### 2.1. General principles of the microreactor models

The level of sophistication in the modeling of microreactors is a challenge. The key issues are the interaction of chemical kinetics, mass and heat transfer effects as well as the flow related phenomena in micro-channels. Rate equations describing the intrinsic kinetics of a particular chemical system can be found in literature or derived from plausible reaction mechanisms. An important issue is to reveal the role of the internal mass transfer resistance in the pores of the washcoat layer. Even though the catalyst layer is thin in microreactor channels, the reaction rate can be retarded by diffusion limitations, if the kinetic process itself is rapid. This has recently been illustrated (Schmidt et al., 2013). The role of flow modeling is somewhat contradictory: on one hand, the most sophisticated approach based on CFD should be used, but on the other hand, particularly if kinetic parameters should be estimated from experimental data, a simplified approach is attractive, based on the concepts of plug flow, laminar flow or dispersion effects. In general it can be stated that the model should not be too heavy from the computational point of view, if it is used for the estimation of kinetic parameters from experimental data. Here we present a parameter estimation approach based on reaction kinetics, internal diffusion and dispersion. The approach allows to describe all the important phenomena in the microreactor channels, still keeping the computational effort within very reasonable limits. The models presented in this work are dynamic, based on radial and axial dispersion and reaction was assumed to take place only where it practically proceeds, within the washcoat or on the silver wall.

Two kinds of micro-reactor elements were used, wash-coated elements and silver plates in the experiments reported previously.

Two separate models for heterogeneously catalyzed oxidation of ethylene to ethylene oxide were generated in this work. One model was developed for the washcoated reactor and the other one for the silver plate reactor. In the washcoated reactor model,

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